SOLUTIONS MANUAL

Elements of Chemical Reaction Engineering

THIRD EDITION

by Timothy Hubbard, Jessica Hamman, and
David Johnson

with Kylas Subramanian, Sumate Charoenchaidet, Probjot
Singh, John Santini, H. Scott Fogler, Lisa Ingalls, Abe
Sendijarevic, and Nicholas Abu-Absi

Chapter 1

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 might encourage students to get in the habit of writing down what they learned from each chapter.

P1-2. Small open-ended question from which one could choose one or two parts. Parts **(a)**, **(b)** or **(e)** are recommended.

P1-3. This problem use Example 1-3 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 **P1-11** and **P1-12**.

P1-4. Alternative to **P1-3**, **P1-11**, and **P1-12**. See P1-3 above.

Problems **P1-5**, **P1-6**, and **P1-7** review the definitions given in the chapter.

P1-8. This problem 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.

P1-9. This problem 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**.

P1-10. 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 and part **(g)** is usually omitted.

Problems **P1-11** and **P1-12** show a bit of things to come in terms of reactor sizing. Can be rotated from year to year with **P1-3** and **P1-4**. See P1-3 above.

P1-13. Asks for details of operation of an industrial reactor.

P1-14. Encourages and requires the student to go outside the text for information related to CRE. May be a bit early in the text to assign this problem.

P1-15. Encourages and requires using other sources to obtain information.

P1-16. Encourages using other sources to obtain information.

P1-17. I strongly recommend this problem be assigned. It can be used in conjunction with Problem P1-9. **Professor Susan Montgomery** has done a great job pulling together the material on real reactors in her equipment module on the CD-ROM.

P1-18. I always assign this problem so that the students will learn how to use POLYMATH/MatLab before needing it for chemical reaction engineering problems.

P1-19. As the WWW becomes more developed, it may be more and more important to assign this problem.

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	Solution Given
P1-1	O				No
● P1-2(b)	AA	2(a),2(d), 2(e)	SF	15	c&d Yes
● P1-3	AA	3,4,11,12,A	FSF	30	Yes
P1-4	AA	3,4,11,12,A	FSF	30	Yes
P1-5	I				Yes
P1-6	I				Yes
P1-7	I				Yes
● P1-8		– Read Only	SF	5	Yes
P1-9	O				Yes
P1-10	O		FSF	60	Yes
P1-11	AA	3,4,11,12,A	FSF	30	Yes
P1-12	AA	3,4,11,12,A	FSF	30	Yes
P1-13	I				Yes
P1-14	S/G				No
P1-15	S/G				Partial
P1-16	S/G				Partial
● P1-17			SF	45	No
● P1-18			SF	60	Yes
P1-19	I				No
CDP1-A	AA	3,4,11,12,A	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.

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

Summary Table Ch-1

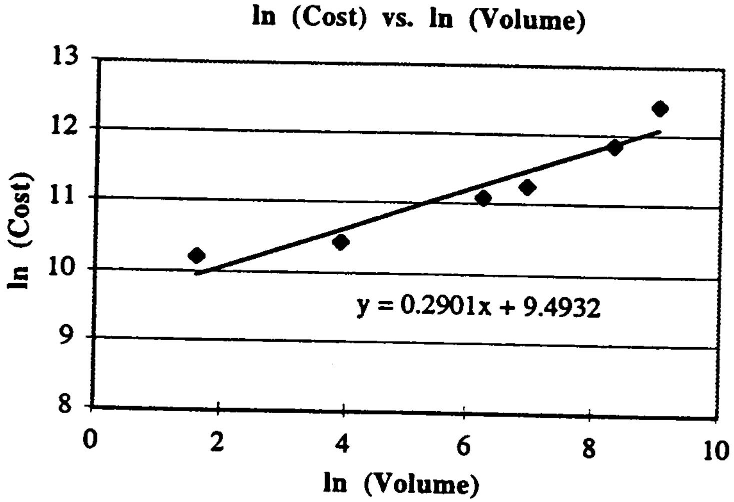
Review of Definitions and Assumptions	1,5,6,7,8,9
Introduction to the CD-ROM	17,18,A
Make a calculation	10,11,12,13
Open-ended	14,15,16
Straight forward	2(b),3,13
Fairly straight forward	4,11,12,B
More difficult	10

P1-1 No solution will be given.

P1-2

(a) Reactants might not be hot enough to react.

(b) Plot Cost vs. Volume on log-log paper. Use this graph to generate an equation for cost as a function of volume.



From this we generate the equation: $\text{Cost} = 13{,}270(V)^{0.29}$

We can use this equation to find the desired prices:

For a 6000 gallon reactor: $\text{Cost} = 13{,}270(6000)^{0.29} = \$165{,}400$

For a 15,000 gallon reactor: $\text{Cost} = 13{,}270(15{,}000)^{0.29} = \$215{,}740$

(c) $$V = \frac{10\ \text{dm}^3/\text{min}}{0.23\ \text{min}} \ln\frac{C_{Ao}}{0.001C_{Ao}} = 300.3\text{dm}^3$$

(d) For Constant Pressure:

$$r_A = \frac{1}{V}\frac{dN_A}{dt} = \frac{1}{V}\frac{d(C_AV)}{dt} = \frac{dC_A}{dt} + \frac{C_A}{V}\frac{dV}{dt}$$

$$r_A = \frac{dC_A}{dt} + \frac{C_A}{V_o + V_1\sin(wt)} wtV_1\cos(wt)$$

(e) He/She might not be able to respond to a malfunction if he/she became injured, and no one would be there to come to his/her aid.

P1-3. For a CSTR, equation (S1-3) is

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

where $-r_A = kC_A$

$F_A = C_A v$

So the first equation becomes

$$V = \frac{C_{A0}v - C_A v}{kC_A}$$

given that $C_A = 0.1\ C_{A0}$, $v = 10\ \text{dm}^3/\text{min}$ and $k = 0.23/\text{min}$.

$$V = \frac{C_{A0}\ v - 0.1\ C_{A0}v}{k(0.1)C_{A0}} = \frac{0.9v}{0.1k} = \frac{9(10\ \text{dm}^3/\text{min})}{0.23/\text{min}} = 391.3 \text{ liters}$$

The CSTR is 4 times larger than the plug flow reactor for these conditions.

Solution

P1-4 Reaction: $A \longrightarrow B$

Problem: Determine time to reduce the number of moles of A to 1% of its initial value.

Mole Balance: (constant volume, batch reactor)

$$\frac{dN_A}{dt} = r_A V$$

Rate Law: (first order)

$$-r_A = kC_A, \text{ where } k = .23/\text{min and } C_A = \frac{N_A}{V}$$

Therefore, $-r_A = k\dfrac{N_A}{V}$

Combine:

$$\frac{dN_A}{dt} = -kN_A$$

$$\int_0^t dt = -\frac{1}{k}\int_{N_{A0}}^{N_A} \frac{dN_A}{N_A}$$

$$t = -\frac{1}{k}\left[\ln\frac{N_A}{N_{A0}}\right] = -\frac{1}{k}\left[\ln\frac{0.01\,N_{A0}}{N_{A0}}\right]$$

$$t = -\frac{1}{(0.23/\text{min})}[\ln 0.01]$$

$$t = 20.0 \text{ min.}$$

(Solution by J.T. Santini, Jr.)

P1-5.

a) The assumptions made in deriving the design equation for a batch reactor are:
- closed system: no streams carrying mass enter or leave the reactor
- no spatial variation in system properties

b) The assumptions made in deriving the design equation for a CSTR, are:
- steady state
- no spatial variation in concentration, temperature, or reaction rate through the vessel.

c) The assumptions made in deriving the design equation for a plug-flow reactor are:
- steady state
- no radial variation in properties of system.

d) The assumptions made in deriving the design equation for a packed-bad reactor are:
- steady state
- no radial variation in properties of system.

e) $-r_A'$ is the rate of disappearance of species A per unit mass (or area) of catalyst [=] moles / (time-mass catalyst). r_A' is the rate of formation of species A per unit mass (or area) of catalyst [=] moles / (time-catalyst). $-r_A$ is an <u>intensive</u> quantity, in that it is a function of the concentration, temperature, pressure, and the type of catalyst (if any), and is defined at any <u>point</u> within the reactor. An extensive quantity is a property which is obtained by summing up the properties of individual subsystems within the <u>total</u> system; in this sense, $-r_A$ is independent of the 'extent' of the system.

P1-6

General Mole Balance:

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

For a CSTR, there is no accumulation. Also, assume well mixed, so that there is no spatial variation in the reactor. The mole balance simplifies to:

$$0 = F_{jo} - F_j + r_j V$$

The rate of reaction based on volume is related to the rate of reaction based on catalyst weight by the bulk catalyst density ρ_b. The reactor volume and catalyst weight are also related by a similar equation.

$$-r_j = \rho_b\left(-r_j'\right)$$

$$W = V\rho_b$$

Combining and rearranging the last three equations gives the equation for a "fluidized" CSTR:

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

(Solution by J.T. Santini, Jr.)

P1-7. Mole balance on species j is:

$$F_{jo} - F_j + \int_o^V r_j dV = \frac{dN_j}{dt} \qquad (1\text{-}4)$$

let M_j = mol. wt. of species j

Then $F_{jo}M_j = w_j \; [=] \; \frac{(\text{moles})}{(\text{time})}\frac{(\text{mass})}{(\text{mole})}$ = mass flow rate of j into the reactor;

$N_jM_j = m_j \; [=] \; (\text{moles}) \frac{(\text{mass})}{(\text{mole})}$ = mass of species j in the reactor

Multiplying Eqn. (1-4) by M_j

$$F_{jo}M_j - F_j M_j + M_j \int^V r_j dV = M_j \frac{dN_j}{dt} \qquad (1\text{-}4a)$$

and noting that M_j is constant:

$$M_j \int^V r_j dV = \int^V r_j M_j dV \quad ; \quad M_j \frac{dN_j}{dt} = \frac{d(M_j n_j)}{dt}$$

Or, upon substitution into Eqn. (1-4a)

$$F_{jo}M_j - F_j M_j + \int^V M_j r_j \, dV = \frac{d}{dt}(M_jN_j) = \frac{d}{dt}(m_j)$$

$$w_{jo} - w_{jF} + \int^V M_j r_j dV = \frac{dm_j}{dt}$$

P1-8. No solution will be given.

		Present			
Simpel Batch	Reactor is charged via two holes in the top of the tank;while reaction is carried out, nothin else is put in or taken out until the reaction is done: tank easily heated or cooled by jacket	1. Gas phase 2. Liquid phase 3. Liquid solid	1. Small scale production 2. Intermediate or one shot production 3. Pharmaceutical 4. Fermantation	1. High conversion per unit volume for one pass 2. Flexibility of operation- sam reactor can produce one product one time and a different product the next 3. Easy to clean	1. High operating cost 2. Product quility more variable than with continous operation
Semi Batch	Either one reactant is charged and the other is fed continously (at small concentrations) or else one of the product can be removed continously (ie. avoid side reactions)	1. Two phase rxns 2. Gas-liquid 3. Liquid-solid	1. Small scale production 2. Competing reactions	1. High conversion per unit volume for one run 2. Good selectivity; feed can be contolled as to minimize side runs 3. Flexibility of operation; can be used with a reflux condenser for solvent recovery, or in bubble type runs	1. High operating labor cost 2. Product quility more variable than with continous operation
Continously Stirred Tank Reactor (CSTR)	Run at steady state with continous flow of reactants and products; the feed assumes a uniform composition throughout the reactor, exit stream has the same composition as in the tank	1. Liquid phase 2. Gas-liquid rxns 3. Solid-liquid rxns	1. When agitation is required 2. Series configurations for diffenent concentration streams	1. Continous operation 2. Good temperature control 3. Easily adapts to two phase runs 4. Good control 5. Simplicity of construction 6. Low operating (labor) cost 7. Easy to clean	1. Lowest conversion per unit volume 2. By-passing and channeling possible with poor agitation
Plug Flow Reactor (PFR)	Arranged as one long long reactor or many short reactors in a tube bank; no radial variation in reaction rate (concentration); concentration chnges with length down the reactor	1. Primarily gas phase	1. Large scale 2. Fast reactions 3. Homogeneous rxns 4. Heterogeneous rxns 5. Continous production 6. High temperature	1. High conversion per unit volume 2. Low operating (labor) cost 3. Continous operation 4. Good heat transfer	1. Undesired thermal gradiants may exist 2. Poor temperature control 3. Shutdown and cleaning may be expensive
Tubular fixed bed Reactor	Tubular reactor that is packed with solid catalyst particles	1. Gas phase/solid catalyzed 2. Gas-solid rxns	1. Used primarily in heterogeneous has phase reactions with a catalyst	1. High conversion per unit mass of catalyst 2. Low operating cost 3. Continous operation	1. Undesired thermal gradiants may exist 2. Poor temperature control 3. Chanelling may occur 4. Unit may be difficult to service and clean
Fluidized Bed Reactor	Heterogeneous reactions; like a CSTR in that the reactants are will mexed	1. Gas-solid 2. Gas-solid catalyzed	1. Heterogeneous has phase reactions with a catalyst	1. Good mixing 2. Good uniformity of temperature 3. Catalyst can be continously regenarated with the use of an auxilliary loop	1. Bed-fluid mechanics not well known 2. Severe agitation can result in catalyst destruction and dust formation 3. Uncertain scale-up

P1-9.

Type of Reactor	Characteristics	Kinds of Phases Present	Usage	Advantages	Disadvantages

P1-10

Given: Los Angeles Basin: A = Basin area = 2×10^{10} ft^2, H_i = Inversion height = 2000 ft, V = 4×10^{13} ft^3. Basin may be considered 'well-mixed'.

v_o wind from Mojave Desert T = 75 °F and P_o = 1.0 atm

$F_{CO,A}$ = CO emission from autos $F_{CO,S}$ = CO in Santa Ana wind

$Y_{CO,A} = 0.02$ $C_{CO,S} = 2.04 \times 10^{-10}$ lbmol/ft^3

V_A = 3000ft^3/car at STP C = number of cars = 400,000

1. N_B = no. of lb moles gas in system:

$$\frac{P_oV}{RT} = \frac{(1.0\text{atm})(4\times10^{13})}{(0.7302\,\text{atm}\cdot\text{ft}^3/\text{lbmol}\cdot{}^\circ\text{R})(535^\circ\text{R})} = 1.024\times10^{11}$$

2.

$$F_{CO,A} = y_{CO,A}V_AC = (0.02\,\text{molCO/molgas})(3000\,\text{scf/hr}\cdot\text{car})(400{,}000\text{cars})(\text{lbmol}/390.66\text{scf})$$

$$F_{CO,A} = 6.143\times10^4\,\text{lbmol/hr}$$

3. v = wind speed = 15 mph W = corridor width = 20 miles

$$v_o = vWH_i = (15\text{mph})(20\text{miles})(2000\text{ft})(5280\text{ft/mile})^2$$

$$v_o = 1.67\times10^{13}\,\text{ft}^3/\text{hr}$$

4.

$$F_{CO,S} = v_oC_{CO,S} = (2.04\times10^{-10}\,\text{lbmol/ft}^3)(1.67\times10^{13}\,\text{ft}^3/\text{hr})$$

$$F_{CO,S} = 3.407\times10^3\,\text{lbmol/hr}$$

5. CO Balance: Input to LA Basin from cars = $F_{CO,A}$, from the Santa Ana wind = $F_{CO,S}$; Output = v_oC_{CO}, where C_{CO} = Concentration of CO in Basin.

$$\therefore F_{CO,A} + F_{CO,S} - v_oC_{CO} = V\frac{dC_{CO}}{dt}$$

6. At t = 0, $C_{CO} = C_{CO,0}$; rearranging and integrating above

$$\therefore \int_{C_{CO,0}}^{C_{CO}} \frac{dC_{CO}}{F_{CO,A}+F_{CO,S} - v_oC_{CO}} = \frac{-\ln}{v_o}\left[\frac{F_{CO,A}+F_{CO,S} - v_oC_{CO}}{F_{CO,A}+F_{CO,S} - v_oC_{CO,0}}\right] = \int_0^t \frac{dt}{V} = \frac{t}{V}$$

$$\therefore t = \frac{V}{v_o}\ln\left[\frac{F_{CO,A}+F_{CO,S} - v_oC_{CO,0}}{F_{CO,A}+F_{CO,S} - v_oC_{CO}}\right]$$

P1-10 (cont'd)

7. At 8 ppm, $C_{CO} = 2.04\times10^{-8}$ lb mole/ft^3;

$\therefore$ at 2 ppm, $C_{CO} = \frac{2}{8} \times 2.04\times10^{-8}\ \frac{\text{lbmole}}{\text{ft}^3}$

$C_{CO} = 0.51\times10^{-8}$ lb mole/ft^3

$\therefore\ t = \frac{4\times10^{13}\,\text{ft}^3}{1.67\times10^{13}\ \frac{\text{ft}^3}{\text{hr}}}\ \ln(A)$ where

$$A = \left[\frac{6.685\times10^{4}\ \frac{\text{lbmole}}{\text{hr}} + 3.407\times10^{3}\ \frac{\text{lbmole}}{\text{hr}} - 2.04\times10^{-8}\ \frac{\text{lbmole}}{\text{ft}^3} \times 1.67\times10^{13}\ \frac{\text{ft}^3}{\text{hr}}}{6.685\times10^{4}\ \frac{\text{lbmole}}{\text{hr}} + 3.407\times10^{3}\ \frac{\text{lbmole}}{\text{hr}} - 0.51\times10^{-8}\ \frac{\text{lbmole}}{\text{ft}^3} \times 1.67\times10^{13}\ \frac{\text{ft}^3}{\text{hr}}}\right]$$

$$t = \frac{4\ (\text{hr})}{1.67}\ \ln\left[\frac{6.685\times10^{4}+3.407\times10^{3}-3.407\times10^{5}}{6.685\times10^{4}+3.407\times10^{3}-.8517\times10^{5}}\right] = \frac{4}{1.67}\ \ln\left[\frac{2.705}{1.492}\right]\ \text{hr.}$$

$$= 1.42\ \text{hr.}$$

For NO:

2. $C_{NO,A} = 3.84\times10^{-6}$ lb mole/ft^3 $\therefore\ F_{NO,A} = C_{NO,A}\, v_A\, C$

$F_{NO,A} = 3.84\times10^{-6}$ lb mole/ft^3 $\times$ 3000 ft^3/hr.car

$\times$ 400,000 cars $= 4.608\times10^{3}$ lb mole/hr

3. $v_o = 1.67\times10^{13}$ ft^3/hr (same as for CO)

4. $F_{AO,S} = 0$ (given)

5. NO material balance becomes, with $F_{NO,S} = 0$

$F_{NO,A} - v_o C_{NO} = V \frac{dC_{NO}}{dt}$ $\quad C_{NO,O} = 0.5\ \text{ppm} = \frac{0.5\text{ppm}}{8\text{ppm}} \times 2.04\times10^{-8}\ \frac{\text{lbmole}}{\text{ft}^3}$

$C_{NO,O} = .1275\times10^{-8}$ lb mole/ft^3

6. Solution to D.E. is now

$$t = \frac{V}{v_o}\ \ln\left[\frac{F_{NO,A} - v_o C_{NO,O}}{F_{NO,A} - v_o C_{NO}}\right]$$

P1-10 (cont'd)

7. The lowest concentration of NO occurs when that taken away by the wind is just balanced by that produced by the autos, i.e. when

$$\frac{dC_{NO}}{dt} = 0 \quad \therefore \quad C_{NO,SS} = \frac{F_{NO,A}}{v_o} = \frac{4.608\text{x}10^{3}\ \frac{\text{lbmole}}{\text{hr}}}{1.67\text{x}10^{13}\ \text{ft}^3/\text{hr}} = 2.759\text{x}10^{-10}\ \frac{\text{lbmole}}{\text{ft}^3}$$

$$\text{with } C_{NO} = 0.1\ \text{ppm} = \frac{0.1\ \text{ppm}}{8\ \text{ppm}} \text{ x } 2.04\text{x}10^{-8}\ \text{lbmole/ft}^3 = 2.55\text{x}10^{-10}\ \frac{\text{lbmole}}{\text{ft}^3}$$

It is seen that this is less than $C_{NO,SS}$. ∴ The concentration of NO will never reach 0.1 ppm unless L.A.'s driving habits are altered.

P1-11. **Solution**

Reaction: $A \longrightarrow B$

constant volumetric flowrate; isothermal; continuous flow reactor

F_{Ao}=5.0 mol/hr, v_o=10 dm³/hr ——> C_{Ao}=0.5 mol/dm³

(a) $-r_A = k$, with $k = 0.05 \frac{\text{mol}}{\text{hr dm}^3}$

CSTR

Mole Balance: $V = \frac{F_{Ao} - F_A}{-r_A}$

Rate Law: $-r_A = k = 0.05 \frac{\text{mol}}{\text{hr dm}^3}$

Combine: $V = \frac{F_{Ao} - 0.01F_{Ao}}{-r_A} = \frac{\left(5\frac{\text{mol}}{\text{hr}}\right)(0.99)}{\left(0.05\frac{\text{mol}}{\text{hr dm}^3}\right)} = 99.0\ \text{dm}^3$

Volume of the CSTR=99.0 dm³

P1-11 (cont'd)

PFR

Mole Balance: $\frac{dF_A}{dV} = r_A$

Rate Law: $-r_A = k = 0.05 \frac{mol}{hr\ dm^3}$

Combine: $\frac{dF_A}{dV} = -k$

$$-\frac{1}{k}\int_{F_{Ao}}^{F_A} dF_A = \int_0^V dV$$

$$V = -\frac{1}{k}[0.01\,F_{Ao} - F_{Ao}] = -\frac{\left(5\frac{mol}{hr}\right)}{\left(0.05\frac{mol}{hr\ dm^3}\right)}(-0.99)$$

Volume of PFR=99.0 dm^3

(b) $-r_A = kC_A$ with $k = 0.0001\ s^{-1}$

CSTR

Mole Balance in terms of concentration: $V = \frac{v_o(C_{Ao} - C_A)}{-r_A}$

Rate Law: $-r_A = kC_A$

Combine: $V = \frac{v_o(C_{Ao} - 0.01C_{Ao})}{k(0.01)(C_{Ao})} = \frac{\left(10\frac{dm^3}{hr}\right)(0.99)}{\left(\frac{0.0001}{s}\right)(0.01)\left(\frac{3600\ s}{hr}\right)}$

$V = 2750\ dm^3$

PFR

Mole Balance in terms of concentration: $\frac{dC_A}{dV} = \frac{r_A}{v_o}$

Rate Law: $-r_A = kC_A$

Combine: $\int_0^V dV = -\frac{v_o}{k}\int_{C_{Ao}}^{0.01C_{Ao}} \frac{dC_A}{C_A}$

$$V = -\frac{v_o}{k}\left[\ln\frac{0.01\,C_{Ao}}{C_{Ao}}\right] = \frac{-\left(\frac{10\,dm^3}{hr}\right)}{\left(\frac{0.0001}{s}\right)\left(\frac{3600\,s}{hr}\right)}\ln(0.01)$$

Volume of PFR=128.0 dm^3

(c) $-r_A=kC_A^2$, with $k=3.0\frac{dm^3}{mol\ hr}$

CSTR

Mole Balance in terms of concentration: $V=\frac{v_o(C_{Ao}-C_A)}{-r_A}$

Rate Law: $-r_A=kC_A^2$

Combine: $$V=\frac{v_o(C_{Ao}-0.01C_{Ao})}{k(0.01C_{Ao})^2}=\frac{(0.99)\left(10\frac{dm^3}{hr}\right)}{\left(3.0\frac{dm^3}{mol\ hr}\right)(0.0001)\left(0.5\frac{mol}{dm^3}\right)}$$

Volume of CSTR=66,000 dm^3

PFR

Mole Balance in terms of concentration: $\frac{dC_A}{dV}=\frac{r_A}{v_o}$

Rate Law: $-r_A=kC_A^2$

Combine: $$\int_0^V dV=-\frac{v_o}{k}\int_{C_{Ao}}^{0.01C_{Ao}}\frac{dC_A}{C_A^2}=-\frac{v_o}{kC_{Ao}}\left[-\frac{1}{0.01}+1\right]$$

$$V=-\frac{\left(10\frac{dm^3}{hr}\right)}{\left(3.0\frac{dm^3}{mol\ hr}\right)\left(0.5\frac{mol}{dm^3}\right)}[-99.0]$$

Volume of PFR=660 dm^3

(Solution by J.T. Santini, Jr.)

P1-12. **Solution**

Reaction: $A \longrightarrow B + C$

isothermal; well-mixed; constant volume batch reactor

$V=20\ dm^3$, $N_{Ao}=20$ moles

(a) $-r_A=kC_A$, with $k=0.865\ min^{-1}$

Mole Balance: (constant volume batch reactor)

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

Rate Law: $-r_A=kC_A$

Combine: $$\frac{dC_A}{dt}=-kC_A$$

$$\int_0^t dt=-\frac{1}{k}\int_{C_{Ao}}^{C_A}\frac{dC_A}{C_A}$$

$$t=-\frac{1}{k}\ln\left[\frac{N_A}{N_{Ao}}\right]=-\frac{1}{0.865\ min^{-1}}\ln\left[\frac{0.2}{20}\right]$$

$t=$ <u>5.3 min.</u>

(b) $-r_A=kC_A^2$, with $k=\dfrac{2\ dm^3}{mol\bullet min}$

Mole Balance: $$\frac{dC_A}{dt}=r_A$$

Rate Law: $-r_A=kC_A^2$

Combine: $$\frac{dC_A}{dt}=-kC_A^2$$

$$\int_0^t dt=-\frac{1}{k}\int_{C_{Ao}}^{C_A}\frac{dC_A}{C_A^2}$$

$$t=-\frac{1}{k}\left[-\frac{1}{C_A}+\frac{1}{C_{Ao}}\right]=-\left(\frac{2\ dm^3}{mol\bullet min}\right)^{-1}\left[-\left(\frac{0.05\ mol}{dm^3}\right)^{-1}+\left(\frac{1\ mol}{dm^3}\right)^{-1}\right]$$

$t=$ <u>9.5 min.</u>

(c) Assume Ideal Gas Equation Holds

Temperature = 127°C = 400K (constant because isothermal)

Volume = 20 dm^3 (constant)

Initial Total Moles = 20

Final Total Moles = 40 (reaction goes to completion)

Gas Constant $= 0.082\dfrac{dm^3\bullet atm}{mol\bullet K}$

Initial Pressure:

$$P_o=\frac{nRT}{V}=\frac{(20\ moles)(0.082)(400\ K)}{(20\ dm^3)}$$

$P_o=$ <u>32.8 atm</u>

Final Pressure:

$$P_f=\frac{nRT}{V}=\frac{(40\ moles)(0.082)(400\ K)}{(20\ dm^3)}$$

$P_f=$ <u>65.6 atm</u>

P1-13. PBR

The volumetric flow rate is given as υ_{01} =30,000 m3/hr at T1=513K and P1 = 27 atm. The ideal gas law is used to determine the volumetric flow rate, υ_{02} , at STP.

$$\frac{\upsilon_{01} P_1}{T_1} = \frac{\upsilon_{02} P_2}{T_2}$$

Solving for υ_{02} yields:

$$\upsilon_{02} = \frac{\upsilon_{01} P_1 T_2}{T_1 P_2} = \frac{30{,}000\frac{m^3}{hr} * 298K * 27atm}{513K * 1atm} * \left(\frac{1ft}{.3048m}\right)^3 * \frac{1hr}{3600\sec} = 4616\frac{ft^3}{\sec}$$

In order to find the residence time of each molecule, we will first calculate the gas velocity, u, in each tube (where N is the total number of tubes and AC is the cross sectional area of each tube).

$$u = \frac{\upsilon_{01}}{NA_C} = \frac{30{,}000\frac{m^3}{hr}}{2050 * 5.89 * 10^{-4} m^2} = 24{,}846\frac{m}{hr} = 6.90\frac{m}{\sec}$$

The residence time can now be calculated using the gas velocity and the length, L, of each tube.

$$\tau = \frac{L}{u} = \frac{12m}{6.90\frac{m}{\sec}} = 1.75\sec$$

STTR

$$u = \frac{\upsilon_{01}}{A_C} = \frac{300{,}000\frac{m^3}{hr}}{9.62m^2} = 31{,}191.4\frac{m}{hr} = 8.66\frac{m}{\sec}$$

$$\tau = \frac{L}{u} = \frac{38m}{8.66\frac{m}{\sec}} = 4.4\sec$$

$$\rho_{catalyst} = \frac{m}{V} = \frac{150{,}000kg}{38m * 9.62m^2} = 410.3\frac{kg}{m^3}$$

P1-14. No solution will be given.

P1-15. a) Chemical Marketing Report, Chemical Week

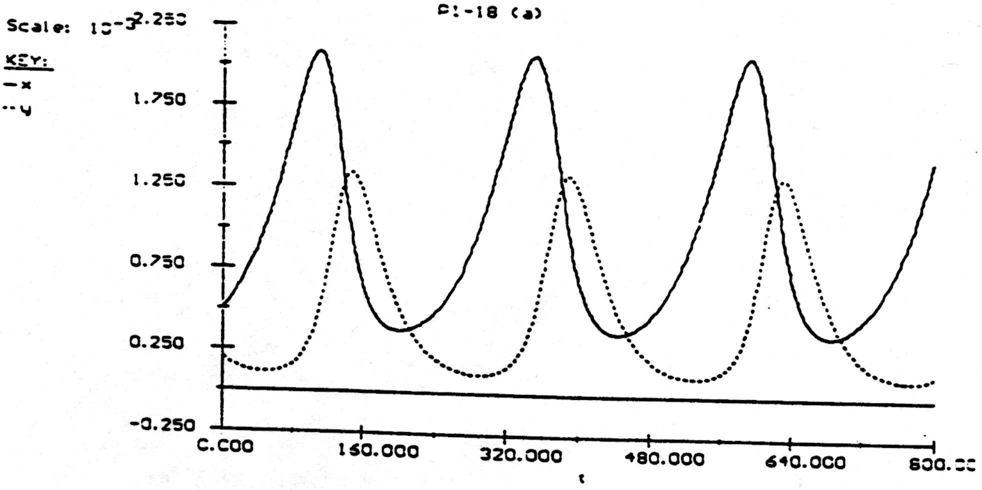
b) Chemical Process Industries (R.N. Shreve, J.A. Brink, Jr., 4th ed., New York - McGraw - Hill Book Co., Inc., 1977), Industrial and Engineering Chemistry.

P1-16. A typical catalytic cracking reactor used in petroleum refining operates at 885-1020°F and 10-30 psig. Chemical Process Industries, R.C. Shreve and J.A. Brink, Jr., 4th ed., New York - McGraw - Hill Book Co., Inc., 1977, p. 675.

P1-17. No solution will be given

P1-18.

```
P1-18 (a)
Equations:                                         Initial value
d(x)/d(t)=k1*x-k2*x*y                              500
d(y)/d(t)=k3*x*y-k4*y                              200
k1=.02
k2=.00004
k3=.00004
k4=.04
t0 = 0,    tf = 800
```



```
P1-18 (b)
Equations:                                         Initial value
f(x)=x**3*y-4*y**2+3*x-1                           2
f(y)=6*y**2-9*x*y-5                                2
```

```
                    P1-18 (b)
                    Solution
Variable            Value             f()
x                   2.38504           2.292e-14
y                   3.79703           -2.554e-15
```

P1-19. No solution will be given

CDP1-A a) Find number of moles and concentration

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

$$molesA=.75*97.5=73.1\,molesA$$

$$C_A=\frac{moles}{volume}=\frac{73.1\,moles}{200\,dm^3}=0.37\,molesA$$

b) Determine reaction time

$$\frac{dN_A}{dt}=r_AV$$

$$\frac{dN_A}{dt}=-kN_A$$

$$\int_{73.1}^{.731}\frac{dN_A}{N_A}=-k\int_0^t dt$$

$$\ln .731-\ln 73.1=-.1t$$

$$t=23\text{ min}$$

c) Determine reaction time

$$\frac{dN_A}{dt}=r_AV$$

$$C_A=\frac{N_A}{V}$$

$$\frac{dC_A}{dt}=-kC_A^2$$

$$\int_{.37}^{.074}\frac{dC_A}{C_A^2}=-k\int_0^t dt$$

$$-10.8=-0.7t$$

$$t=15\text{ min}$$

CDP1-B Given: Liquid phase reaction A —> B in a foam reactor:

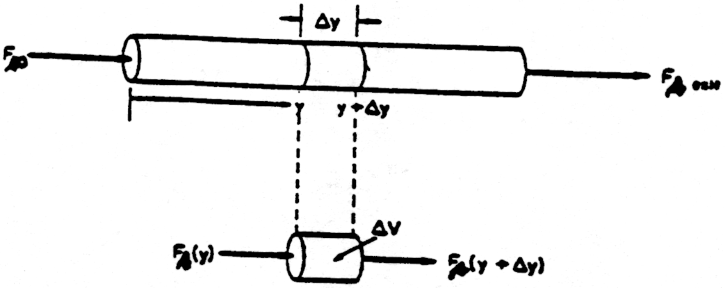


Figure P1-10.

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:

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

$\therefore \frac{dF_A}{dV} = r_A\ (1-e)$ 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 (gmoles A per cu cm of liquid per sec)

e = volume fraction of gas

F_A = molar flow rate of A (gmoles/sec)

V = volume of reactor

Chapter 2

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. Part (a) is open-ended and encourages the student to do little "OUT OF THE BOX" thinking.

P2-3. Straight forward rehash of Example 2-7 to calculate reactor volumes.

P2-4. Uses definition of space time to calculate V. Can be done in 30 seconds.

P2-5. No calculations necessary for this problem, but does require some thinking.

P2-6. This problem encompasses most all the key points of Chapter 2. That is, if we are given $-r_A=f(X)$ then we can size any number of reactor systems. Some parts plug and chug, others require more thinking.

P2-7. Good troubleshooting problem. Could ask the students to brainstorm in groups what could have happened.

Problems **P2-8, P2-9,** and **P2-12** are alternative problems to **P2-6** and can be assigned in different years.

P2-10. The point is to estimate the sizes of these real reactors. The students can use the door as a point of reference to estimate the reactor volumes. Could be used with the ethical dilemma problems. CDP2-B.

P2-11. Open-ended in that student is faced with decision on how to relax.

P2-13. In recent years, a number of students have on their own fit a polynomial to the curves in **P2-6, P2-8, P2-9,** and **P2-12** and then used POLYMATH to solve the problems.

Problems **P2-14** and **P2-15** encourage outside reading and help to develop life-long learning skills by obtaining information on their own.

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	Solution Given
	P2-1	O			5	No
	P2-2	O		OE	30	No
	P2-3	I			15	Yes
	P2-4	O			10	Yes
	P2-5	O		M	40	Yes
●	P2-6		8,12	SF	20	Yes
●	P2-7		6,8,12	M	45	Yes
	P2-8	AA	6,7,12	FSF	50	Yes
	P2-9	O	A,B,D	SF	60	Yes
	P2-10	S		SF	20	No
●	P2-11			SF		Yes
	P2-12	AA	6,7,8	SF	60	Yes
	P2-13	S		M	30	No
	P2-14	S			60	No
	P2-15	S			30	No
	CDP2-A	O	9,B,C,D	FSF	45	Yes
	CDP2-B	O	9,B,C,D	FSF	15	No
	CDP2-C	O	9,B,C,D		10	Yes
	CDP2-D	O	9,B,C,D		10	Yes

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.

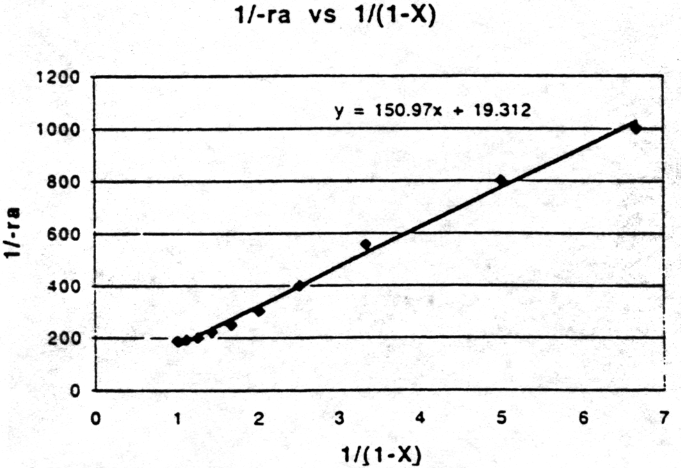
Summary Table Ch-2

Straight forward	3,4,6
Fairly straight forward	8,11
More difficult	5,7,13
Open-ended	2(a),2(b),7,10,11,14,15, B
Comprehensive	2,3,4,5,6
Parameter sensitivity	---
Critical thinking	5(d),9(a)

P2-1 No solution will be given.

P2-2

(a) Plotting the given data as $1/-r_A$ vs. $1/(1-X)$ produces a linear graph. This can be used to extrapolate values for $-r_A$ for all of the conversion values up to the desired 0.98. These values can be used to calculate the desired volume.



The following equation was found to fit the data:

$$\frac{1}{-r_A} = 19.312 + \frac{150.97}{(1-X)}$$

Graphing $1/-r_A$ vs. $1/(1-X)^2$ proved to be non-linear.

(b) One cannot extrapolate to a higher temperature unless the activation energy is given.

P2-3

a) Scheme A

$$V_1 = F_{A0}\int_0^{0.3} \frac{dX}{-r_A} = F_{A0}\left[\frac{h}{2}\left(\frac{1}{-r_A(X=0)} + \frac{1}{-r_A(X=0.3)}\right)\right]$$

$$= 52\,\frac{mol}{min} \times \frac{1 min}{60 s}\left[\frac{0.3}{2}(200 + 250)\right]\frac{dm^3 \cdot s}{mol}$$

$$= 58.5\ dm^3$$

$$V_2 = F_{A0}\frac{X_2 - X_1}{-r_A(X_2)} = \frac{52}{60}\,(.8 - .3)\,(800)$$

$$V_{Total} = 58.5 + 346.7 = 405.0\ dm^3$$

Scheme B

$$V_1 = \frac{F_{A0} X_1}{-r_A} = \frac{52}{60}(0.3)(300) = 78 \text{ dm}^3$$

$$V_2 = F_{A0}\int_{.3}^{.8}\frac{dX}{-r_A} = F_{A0}\frac{h}{3}\left[\frac{1}{-r_A(.3)}+\frac{4}{-r_A(.425)}+\frac{2}{-r_A(.55)}+\frac{4}{-r_A(.675)}+\frac{1}{-r_A(.8)}\right]$$

$$V_2 = \frac{52}{60}\left(\frac{.125}{3}\right)[250 + 4(275) + 2(325) + 4(500) + 800]$$

$$V_2 = 173 \text{ dm}^3$$

$$V_{Total} = 78 \text{ dm}^3 + 173 \text{ dm}^3 = 251 \text{ dm}^3$$

b) Scheme A

$$V_1 = F_{A0}\frac{h}{3}\left[\frac{1}{-r_A(0)}+\frac{4}{-r_A(.35)}+\frac{1}{-r_A(.7)}\right]$$

$$= \frac{52}{60}\,\frac{(.35)}{3}[200 + 4(265) + 550] = 183 \text{ dm}^3$$

$$V_2 = \frac{52}{60}(.8 - .7)(800) = 69.3 \text{ dm}^3$$

$$V_{Total} = 252 \text{ dm}^3$$

Scheme B

$$V_1 = \frac{52}{60}(.7)(550) = 333.7 \text{ dm}^3$$

$$V_2 = \frac{52}{60}\,\frac{0.10}{2}[550 + 800] = 58.5 \text{ dm}^3$$

$$V_{Total} = 392 \text{ dm}^3$$

P2-3 cont'd

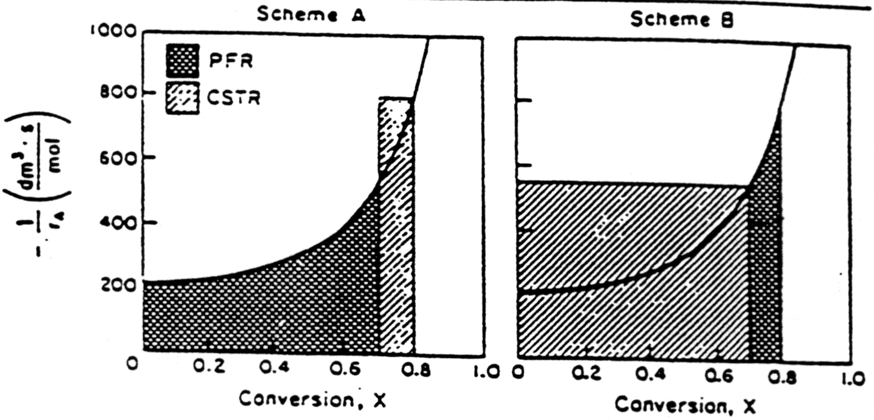


Figure E2-6.2

P2-4. Given: t = 5 hrs. to achieve X = 0.8 in a CSTR;

$v_o = 2 ft^3/min.$

$$V = t\,v_o = (5\ hrs)\left[\frac{2 ft^3}{min}\right]\left[\frac{60\ min}{hr}\right] = 600\ ft^3$$ ans.

$$SV = \frac{1}{t} = \frac{1}{5\ hr.} = 0.2\ hr^{-1}$$

P2-5

$$-r_A = kC_A^2 = kC_{Ao}^2(1-X)^2$$

System 1:

CSTR

$$V = \frac{F_{Ao}X_{exit}}{-r_A} = \frac{F_{Ao}X_{exit}}{kC_{Ao}^2(1-X_{exit})^2}$$

$$(1-X_{exit})^2 = \frac{F_{Ao}}{VkC_{Ao}^2}X_{exit} = aX_{exit}$$

P2-5 cont'd

$$\text{where} \qquad a = \frac{F_{Ao}}{VkC_{Ao}^2}$$

$$X_{exit}^2 - (2+a)X_{exit} + 1 = 0$$

$$X_{exit} = \frac{(2+a)-\sqrt{(2+a)^2-4}}{2} \qquad \frac{(2+a)+\sqrt{(2+a)^2-4}}{2}$$

For the second root $X_{exit} \geq 1$, which is impossible. Hence,

$$X_{exit} = \frac{(2+a)-\sqrt{(2+a)^2-4}}{2} \qquad (1)$$

PFR

$$V = \int_{X_{exit}}^{X_{OA}} \frac{dX}{kC_{Ao}^2(1-X)^2} \qquad \Rightarrow \qquad 1 = a\left[\frac{1}{1-X}\right]_{X_{exit}}^{X_{OA}}$$

$$\frac{1}{1-X_{OA}} - \frac{1}{1-X_{exit}} = \frac{1}{a}$$

$$\frac{1}{1-X_{OA}} = \frac{1}{a} + \frac{1}{1-\dfrac{(2+a)-\sqrt{a^2+4a}}{2}} = \frac{1}{a} + \frac{2}{\sqrt{a^2+4a}-a}$$

$$1-X_{OA} = \frac{a(\sqrt{a^2+4a}-a)}{\sqrt{a^2+4a}+a} \qquad \Rightarrow \qquad X_{OA} = 1-\frac{a(\sqrt{a^2+4a}-a)}{\sqrt{a^2+4a}+a}$$

$$\text{For } a = 1, \quad X_{OA} = 0.618$$

System 2:

PFR

$$V = \int_0^{X_{exit}} \frac{dX}{kC_{Ao}^2(1-X)^2} = \frac{F_{Ao}}{kC_{Ao}^2}\left[\frac{1}{1-X}\right]_0^{X_{exit}}$$

$$\frac{1}{1-X_{exit}} - 1 = \frac{1}{a} \qquad \Rightarrow \qquad 1-X_{exit} = \frac{a}{a+1}$$

$$X_{exit} = \frac{1}{1+a} \qquad (2)$$

CSTR

$$V = \frac{F_{Ao}(X_{OA}-X_{exit})}{kC_{Ao}^2(1-X_{OA})^2} \qquad \Rightarrow \qquad (1-X_{OA})^2 = a(X_{OA}-X_{exit})$$

P2-5 cont'd

$$X_{OA}^2 - (2+a)X_{OA} + \left(1+\frac{a}{1+a}\right) = 0$$

$$X_{OA} = \frac{(2+a) - \sqrt{(2+a)^2 - 4\left(1+\frac{a}{1+a}\right)}}{2}$$

$$X_{OA} = \frac{(2+a) - \sqrt{a^2 + 4a - \frac{4a}{1+a}}}{2}$$

For $a = 1$, $X_{OA} = 0.634$

System 3:

CSTR

From Equation (1)

$$X_1 = \frac{(2+a/2) - \sqrt{a^2/4 + 2a}}{2}$$

PFR

From Equation (2)

$$X_2 = \frac{1}{1+a/2}$$

$$X_{OA} = \frac{X_1 + X_2}{2} = \frac{1}{2}\left(\frac{(2+a/2) - \sqrt{a^2/4+2a}}{2} + \frac{1}{1+a/2}\right)$$

For $a = 1$, $X_{OA} = 0.583$

(a) System 2 will give the highest conversion.

(b) System 3 will give the lowest conversion.

P2-6

Solution

X	0	0.2	0.4	0.6	0.8	0.9
$-r_A$	10	16.67	50	50	12.5	9.09
$1/-r_A$	0.1	0.06	0.02	0.02	0.8	0.11

(a) To solve this problem, first plot $1/-r_A$ vs. X from the chart above (see attached plot). Second, use mole balances as given below.

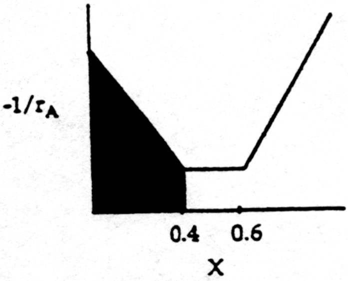
CSTR:

$$\text{Mole Balance: } V_{CSTR} = \frac{F_{A0}X}{-r_A} = \frac{\left(300\,\frac{\text{mol}}{\text{min}}\right)(0.4)}{\left(50\,\frac{\text{mol}}{\text{dm}^3 \bullet \text{min}}\right)}$$

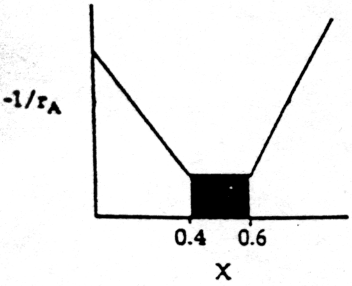
$$V_{CSTR} = \underline{2.4\ \text{dm}^3}$$

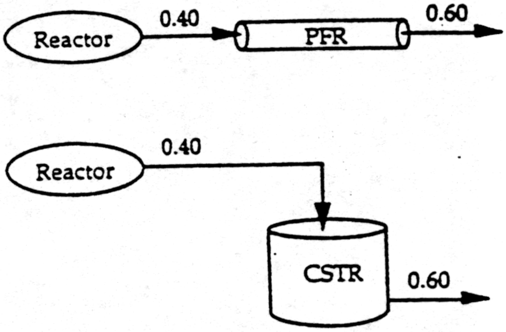
PFR:

$$\text{Mole Balance: } V_{PFR} = F_{A0}\int_0^X \frac{dX}{-r_A} = 300\,[\text{area under the curve}] = \underline{7.2\ \text{dm}^3}$$



(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 the rate is constant over this conversion range. (see below)





(Note: The reactor(s) before and up to achieving a conversion of 0.40 must be in series with no side streams.)

P2-6 **cont'd**

(c) $V_{CSTR} = 10.5\ \text{dm}^3$

Mole Balance: $V_{CSTR} = \dfrac{F_{A0}X}{-r_A}$

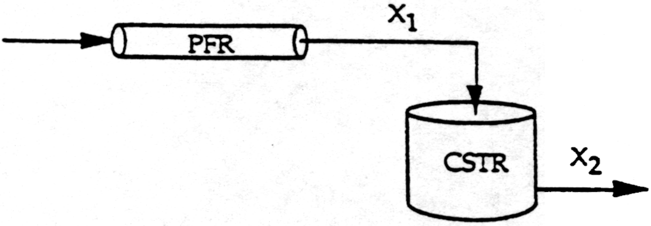
$$\frac{X}{-r_A} = \frac{V}{F_{A0}} = \frac{10.5\ \text{dm}^3}{300\dfrac{\text{mol}}{\text{min}}} = 0.035\frac{\text{dm}^3\ \text{min}}{\text{mol}}$$

Use trial and error to find the maximum conversion. First, pick a conversion. Second, find $1/-r_A$ from the plot. Third check to see if $X/-r_A$ is equal to 0.035. If it is, then the correct conversion has been chosen.

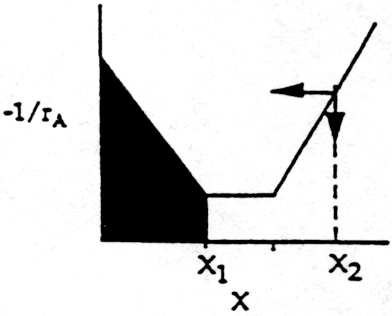
At $X = 0.70, \dfrac{1}{-r_A} = 0.05$, and $\dfrac{X}{-r_A} = 0.035\dfrac{\text{dm}^3\ \text{min}}{\text{mol}}$

Maximum conversion = 0.70

(d)



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



P2-6 cont'd

Mole Balance: $V = \frac{F_{A0}(X_2 - X_1)}{-r_A)_{X_2}}$

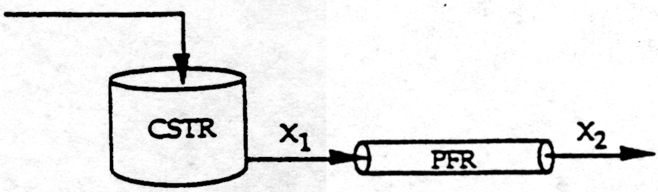
rearranging, we get

$$\frac{X_2 - 0.40}{-r_A)_{X_2}} = \frac{V}{F_{A0}} = \frac{2.4}{300} = 0.008$$

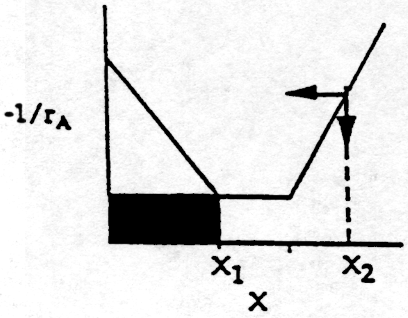
At $X_2 = 0.64$, $\frac{X_2 - 0.40}{-r_A)_{X_2}} = 0.008$

Conversion = 0.64

(e)



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



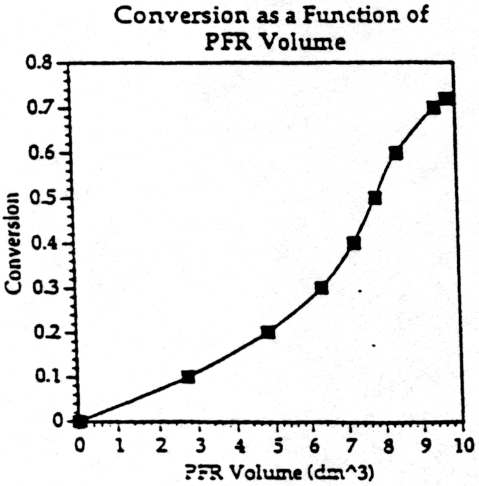
Mole Balance: $V = 7.2 = F_{A0}\left[\int_{0.40}^{X_2}\frac{dX}{-r_A}\right] = 300\left[\int_{0.40}^{X_2}\frac{dX}{-r_A}\right]$

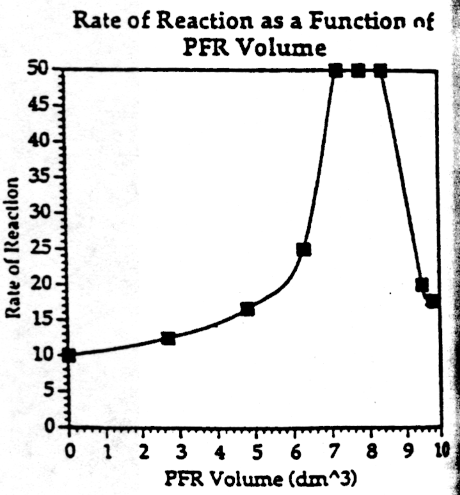
At $X_2 = 0.908$, V = 300 [Area Under the curve] = 300 [0.024] = 7.2 dm³

Conversion = .908

P2-6 cont'd

(f) See plots below.


Conversion as a Function of PFR Volume


Rate of Reaction as a Function of PFR Volume

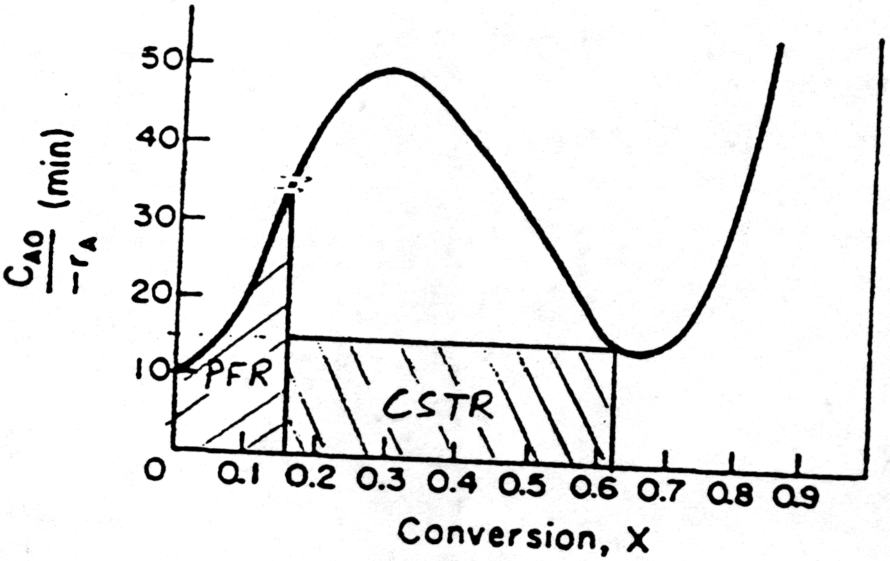
P2-7

Questions from Sgt. Ambercromby:

1. Could a dent cause the stirring blade not to turn?
2. Is the temperature the same?
3. What causes the whoosh sound?
4. How much does the dent reduce the volume?

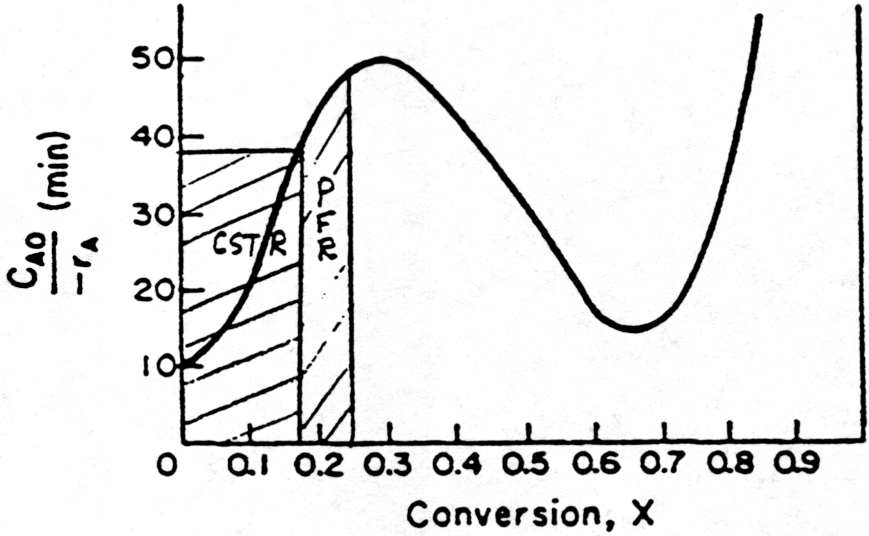
Possible reasons for the drop:

1. Temperature of the feed.
   The rate of reaction depends on temperature.
2. Flow rate
   Residence time depends on the flow rate. If flow rate ↑, residence time ↓, hence conversion ↓.
3. Level of liquid in the CSTR
   If liquid level ↓, effective volume of CSTR ↓, hence conversion ↓.
4. Concentration of A in feed
   Rate of reaction depends on the concentration of A in the feed.
5. Performance of the stirrer in the CSTR
   If there is some malfunctioning in the stirrer, the CSTR will no longer be well-stirred and there will be some 'dead volume'. This decrease in the effective volume would cause a decrease in conversion.



Initial Operating Conditions:

$X_o = 0$, $X_1 = 0.64$, $X_2 = 0.82$



Final Operating Conditions:

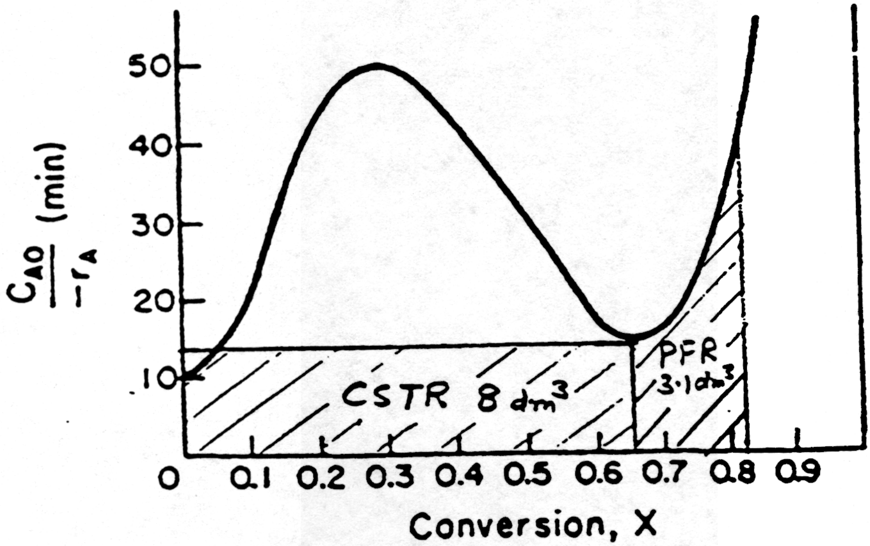
$V_{effective} = 38*0.17 = 6.5\ dm^3$
Decrease in volume = $1.5\ dm^3$

P2-7 cont'd

This 20% decrease in volume could not have been caused by a small dent. The most likely explanation is that the stirrer fell off, which caused 'dead zones' and a decrease in the effective volume.

To increase the conversion to above 0.50, switch the order of reactors. By placing the PFR before the CSTR, the necessary conversion can be achieved.

$X_1 = 0.16$
$V_{eff(CSTR)} = 6.5\ dm^3 \Rightarrow X_2 = 0.62$



P2-8.

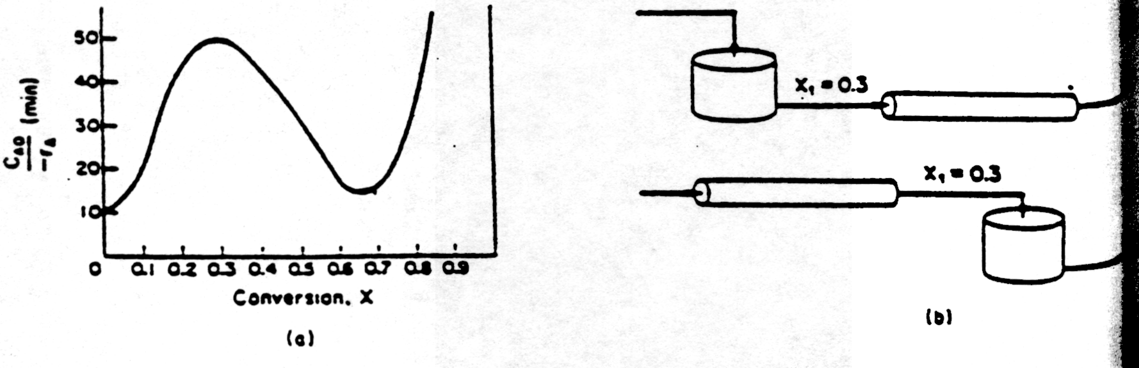


Figure P2-8.

a) For an intermediate conversion of 0.3, Figure P2-8a 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.

b) $v_o = 50\ 1/\text{min}$

$V = v_o\ I$, where

I = area considered in part a.

$$I = \int_0^{0.3} \frac{C_{A0}}{-r_A}\, dX + (0.7-0.3)\left.\frac{C_{A0}}{-r_A}\right|_{X=0.7}$$

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

$$= 15 \text{ min}$$

So $V = v_o\ I = (50\ 1/\text{min})\ (15\ \text{min}) = 750\ 1 = 750\ \text{dm}^3$.

c) The smallest area can be achieved by using only one CSTR with this system,

$$I = (0.7-0.0)\left.\frac{C_{A0}}{-r_A}\right|_{X=0.7} = (0.7-0)(15) = 10.5 \text{ min}$$

So $V = v_o\ I = (50)\ 1/\text{min}\ (10.5)\ \text{min} = 525\ 1$

We would further reduce the total volume by using a PFR at first up to the conversion that gives the same $C_{A0}/-r_A$ as X=0.7.

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,

$$I = (0.45-0)\left.\frac{C_{A0}}{-r_A}\right|_{X=0.7} = (0.45-0)(37) = 16.65 \text{ min}$$

So $V = v_o\ I = (50\ 1/\text{min})(16.65\ \text{min}) = 832.5\ 1$

P2-8 **cont'd**

For the PFR

$$I = \int_0^{0.45} \frac{C_{A0}}{-r_A}\,dX$$

Using Simpson's rule

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

$$= \frac{0.05}{3}\,(10 + 4(15 + 35 + 48 + 48) + 2(20 + 43 + 50 + 43) + 37) = 15.7$$

So $V = v_0 I = (50\ \text{l/min})(15.72\ \text{min}) = 786\ \text{l}$ 6% difference, pretty

There is also a solution at an $X > 0.7$

Try $X = 0.8$

For the CSTR

$I = (0.8-0)(33) = 26.4$ min

For the PFR

$$I = \int_0^{0.8} \frac{C_{A0}}{-r_A}\,dX$$

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

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

Try $X=0.79$

For the CSTR

$I = (0.79)(30) = 23.7$ min

So $V = v_0 I = (50\ \text{l/min})(23.7\ \text{min}) = 1185\ \text{l}$ (dm^3)

P2-8 cont'd

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

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
$C_{AO}/-r_A$(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

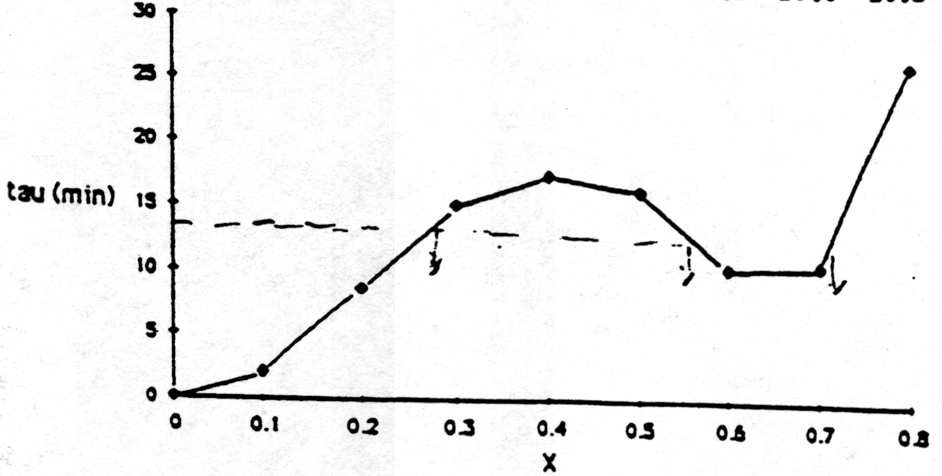


Figure P2-8E.

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.

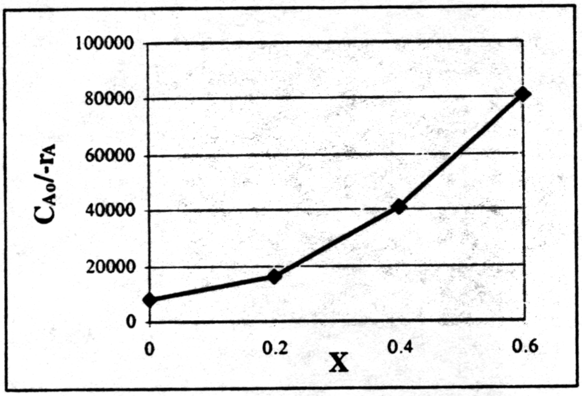
P2-9

$$A + 2B \rightarrow C$$

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



(a) 30% conversion in PFR:

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

(b) 30 to 50% conversion in CSTR:

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

(c) Total Volume:

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

(d) 60% conversion in PFR:

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

80% conversion in PFR:

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

(e) 50 % in CSTR:

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

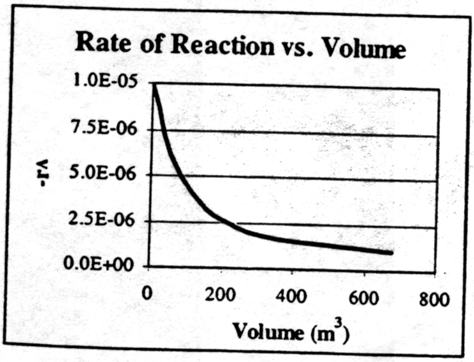
$$V = v_o\tau = (30{,}422.9\,\text{s})\left(\frac{1\,\text{min}}{60\,\text{s}}\right)(2\,\text{m}^3/\text{min}) = 1014.1\,\text{m}^3$$

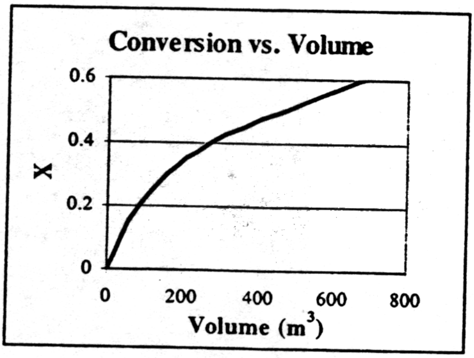
(f) 50 to 60% conversion in CSTR:

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

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

(g)





(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?

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

$h = 56$ ft $\qquad d = 9$ ft
$V = \pi r^2 = \pi(4.5\text{ ft})^2(56\text{ ft}) = 3562\text{ ft}^3 = 100{,}865\text{ L}$

PFR

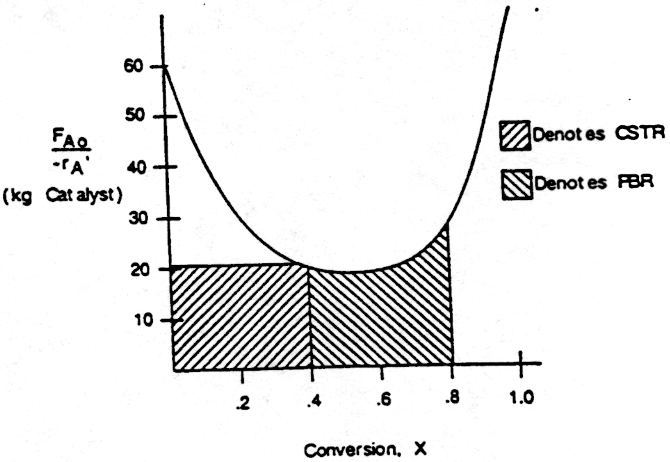
Length of one segment = 23 ft
Length of entire reactor = (23 ft) (12) (11) = 3036 ft
D = 1 ft
$V = \pi r^2 = \pi(0.5\text{ ft})^2(3036\text{ ft}) = 2384\text{ ft}^3 = 67{,}507\text{ L}$

Answers will vary for each individual.

P2-11 No solution necessary.

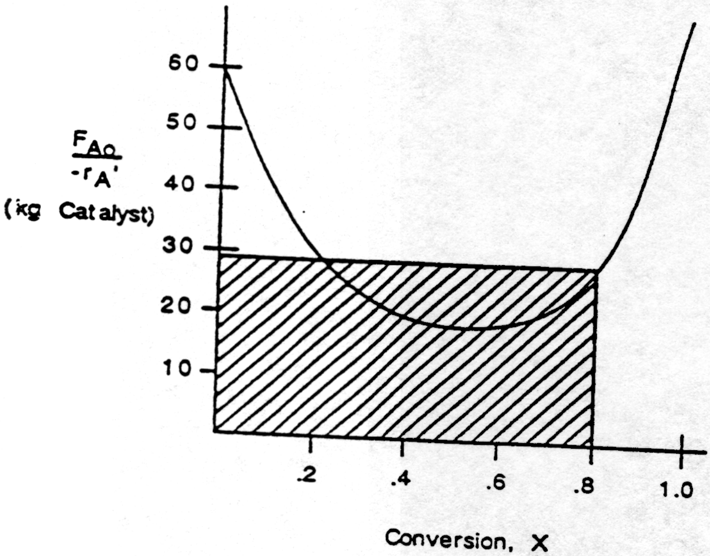
P2-12

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



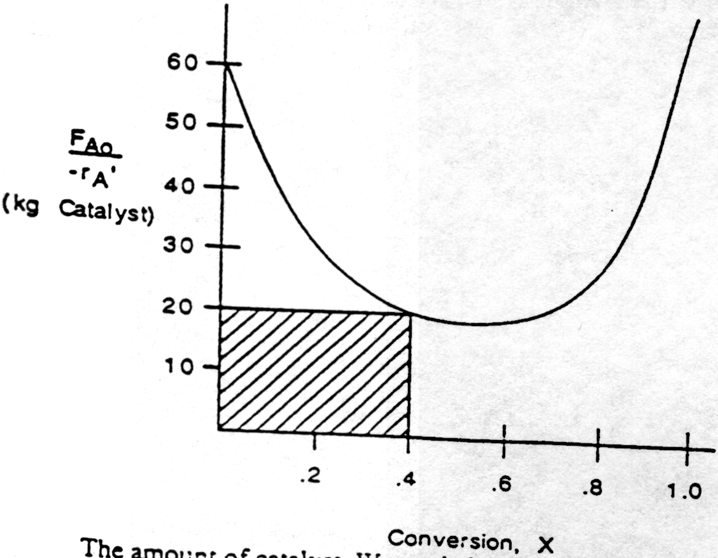
The first shaded area with the lines going up from the right to the left denotes the CSTR while the area with the lines going up from right to left denotes the PBR. This figure shows that the smallest amount of catalyst used is obtained when the CSTR is used before the PBR.

(b) One can calculate the amount of catalyst needed to carry out the same reaction to 80% conversion using a single CSTR by determinning the area of the shaded rectangle below.



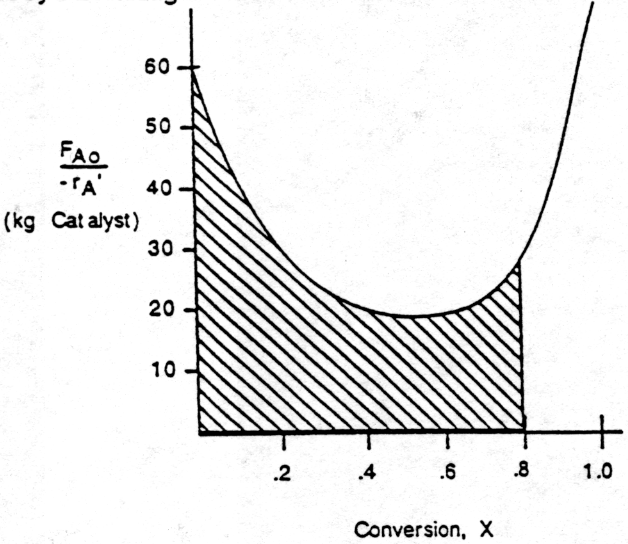
The area of rectangle can be found to equal approximately 22.4 kg catalyst.

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



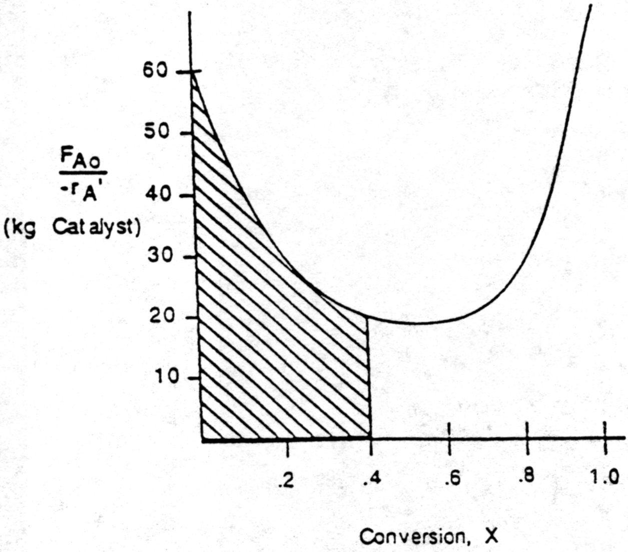
The amount of catalyst, W, needed can be found to be about 8 kg.

(d) The catalyst weight necessary to achieve 80% conversion for a PBR can be determined by calculating the shaded area underneath the curve in the figure below



The necessary catalyst weight can be found to be approximately 30 kg.

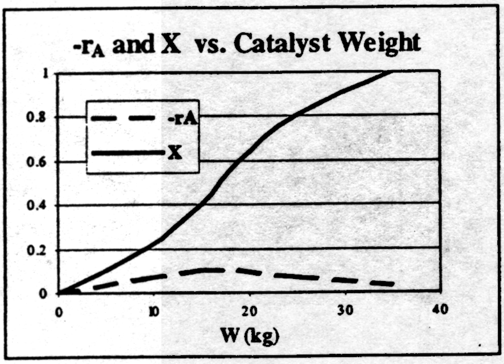
(e) The amount of catalyst necessary for a single PBR to obtain 40% conversion can be calculated by finding the area of the shaded region below.



The area of this region can be found to equal approximately 15 kg catalyst.

P2-12 (cont'd)

(f)


$-r_A$ and X vs. Catalyst Weight

(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. This can be done by minimizing the area that is occupied by a given reactor.

One useful heuristic is that for curves with a negative slope, it is generally better to use a CSTR. Similarly, when the curve has a positive slope, it is generally better to use a PBR.

P2-13 No solution will be given.

P2-14 No solution will be given.

P2-15 No solution will be given.

CDP2-A The reaction $A \longrightarrow 2B$

$C_{AO} = 0.2$ gmol/l

$v_o = 5.0\ m^3/s$

a) Until the point where $-1/r_A$ is independent of X_A, i.e.

$X = .5$. (Both have same area until $X_A = .5$)

$$\frac{10^{-8}}{-r_A} = 3.0\ \frac{m^3.s}{mol}, \quad : \quad \frac{1}{-r_A} = 3x10^8\ \frac{m^3.s}{mol}$$

b) $$V_{CSTR} = \frac{F_{AO}\ X_A}{-r_A}$$

$$= \frac{C_{AO}\ v_o\ X_A}{-r_A} = \frac{0.2 \times 5.0 \times 10^3}{-r_A}\ X_A = \frac{10^3\ X_A}{-r_A}$$

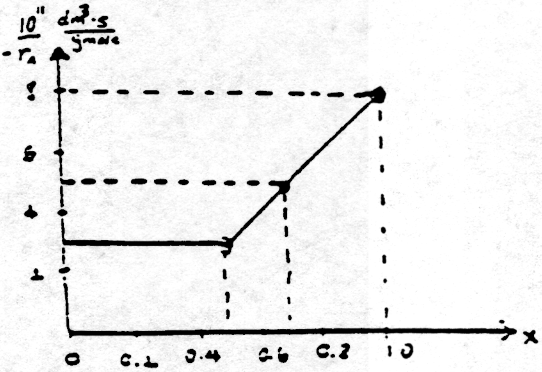
$V_{CSTR} = 90\ dm^3$

assume $X_A < 0.5$. Hence $-1/r_A = 3x10^8\ \frac{m^3.s}{mol} = 3x10^{11}\ \frac{dm^3.s}{mol}$

so $90 = 3x10^{14}\ X_A$

and hence conversion $= X = 3x10^{-13}$

Note - our assumption was correct.



c) $$V_{PFR} = F_{AO} \int_0^{X_A} \frac{dX}{-r_A}$$

CDP2-A cont'd

$$F_{AO} = \frac{0.2\ \text{gmol}}{\text{dm}^3} \times \frac{5 \times 10^3\ \text{dm}^3}{\text{s}} = 1000\ \frac{\text{gmol}}{\text{s}}$$

$$\text{so}\quad V_{PFR} = F_A \int_0^{X_A} \frac{dX}{-r_A} = F_{AO} = 1000\ \frac{\text{gmol}}{\text{S}} \int_0^{0.7} \frac{dX}{-r_A}$$

The integral on the R.H.S. using the graph is

$$= (3\text{x}10^{11} \times 0.5) + \left(\frac{3\text{x}10^{11} + 5\text{x}10^{11}}{2}\right) \text{X}\ (0.7 - 0.5) = 2.3 \times 10^{11}\ \frac{\text{dm}^3 \cdot \text{s}}{\text{gmole}}$$

So the plug flow reactor volume = $2.3 \times 10^{11}\ \text{m}^3$ (<u>Size of L.A. Basin</u>).

d) $$V_{CSTR} = \frac{F_{AO}(X_2 - X_1)}{-r_A}$$

$F_{AO} = 1000$ mole/min

$X_1 = 0.70$

$X_2 = 0.90$

$-1/r_A$ = (reaction rate)$^{-1}$ at $X = X_2$ = $7\text{x}10^{11}\ \frac{\text{dm}^3}{\text{gmole}}$

so $V_{CSTR} = 1 \times (0.9 - 0.7) \times 7\text{x}10^{11}$

$= 1.4\text{x}10^{11}\ \text{m}^3$ (<u>Size of L.A. Basin</u>).

e) For a batch reactor

$$t = N_{AO} \int_0^{X} \frac{dX}{(-r_A)V}$$

For constant pressure $V = V_o(1 + \varepsilon X)$

$\varepsilon = y_{AO}\delta$

$y_{AO} = 1$ (pure A feed)

$\delta = \frac{2-1}{1} = 1$

so $\varepsilon = 1$

$N_{AO} = V_o\ C_{AO}$

$$\text{so } t = C_{AO} \int_0^{0.4} dX \left(\frac{3\text{x}10^{11}}{1+X}\right)$$

CDP2-A cont'd

$$= 0.2 \int_0^{0.4} dX \left(\frac{3x10^{11}}{1+X}\right)$$

Since for X between 0 and .4, $-1/r_A$ is constant with a value

$= 3x10^{11}$ l/gmole

So $t = 0.2(3x10^{11}) \int_0^{0.4} \frac{dX}{1+X} = 6.10^{10} \ln (1+X)\Big]_0^{0.4} = 6x10^{10}\ [\ln(1.4) - \ln 1]$

$= \underline{2.02x10^{10} s}$

$=$ <u>640 yrs</u> A reaction whose progress can be followed by generations!

Citique: This is a ridiculously small rate of reaction.

CDP2-B

No solution will be given.

CDP2-C

For the CSTR:

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

$$\text{Area} = \frac{V_1}{F_{A0}} = \frac{1200\ \text{ft}^3}{5\ \text{lbmol/hr}} = 240$$

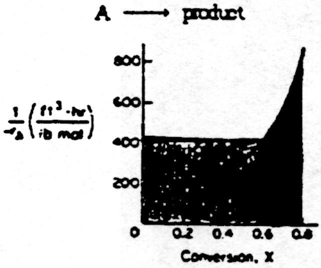
From the graph we can see that $X_1 = 0.60$

For the PFR:

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

$$\text{Area under curve} = \frac{V_2}{F_{A0}} = \frac{600}{5} = 120$$

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



CDP2-D

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

$P = 10$ atm $T = 227°C = 500$ K

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

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

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

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

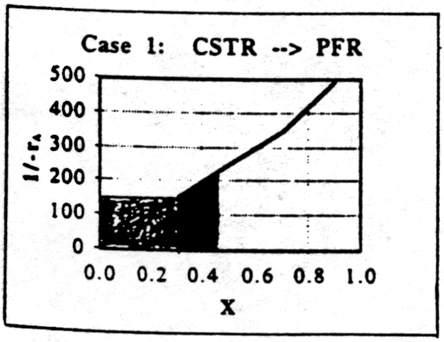
$$\text{Area} = \frac{V_1}{F_{Ao}} = \frac{400}{6} = 66.67$$

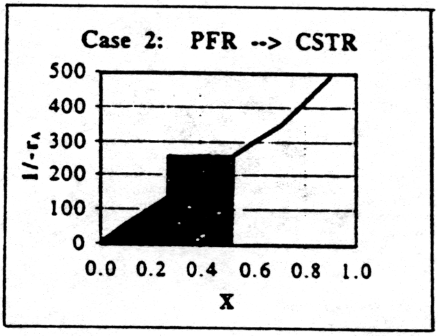
From the graph - $X_1 = 0.36$

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 - $X_2 = 0.515$

(b) Two 400 L CSTR's in series.

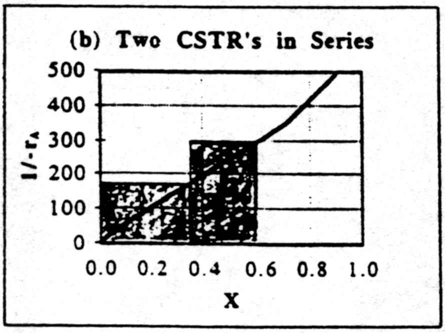
CSTR1: $V = F_{Ao}(\text{Area})$

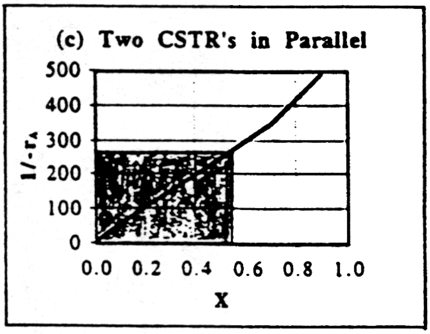
$\text{Area} = 66.67$

From the graph - $X_1 = 0.36$

CSTR2: $\text{Area} = 66.67$

From the graph - $X_2 = 0.595$





(c) Two 400 L CSTR's in parallel.

To each CSTR goes half of the feed.

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

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

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

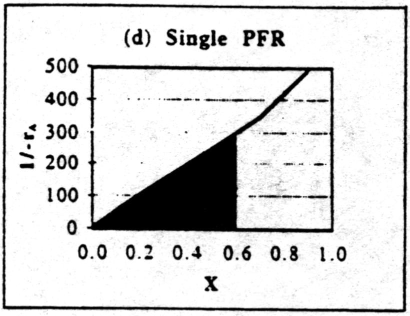
From the graph: $X = 0.52$

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

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

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

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



(e) Pressure reduced by a factor of 10.

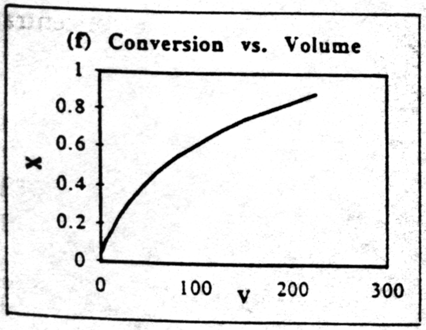
A decrease in pressure would cause a decrease in the overall concentration which would in turn cause a decrease in C_{Ao} and F_{Ao}. By looking at the design equation:

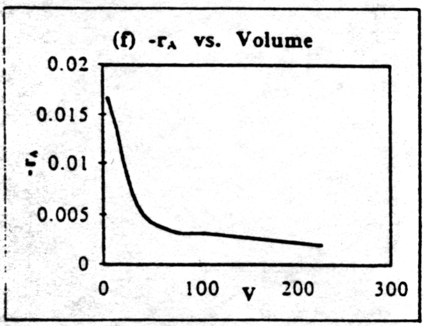
$$V = \frac{F_{Ao}X}{-r_A}$$

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

(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





Chapter 3

P3-1. See **P4-1**, page 205 of the text for guidelines.

P3-2. (c), the point is that the rate law (Eqn. E3-2.1) is not valid at very low concentrations of NaOH (i.e. the rate law predicts a rate of reaction even if $C_{NaOH} \equiv 0$).

P3-3. This problem motivates the students as they see applications of CRE outside examples found in chemical plants. Surprisingly, the activation energies are essentially the same.

P3-4. Short problem from DuPont about competing effects corrosion rate as a function of concentration and temperature that involves reasoning, no calculations.

P3-5. Challenges the rule of thumb, the rate doubles for every 10°C increase in temperature, that the students learned in chemistry. Part (b) is a dull version of **P3-3**.

P3-6. Short problem that reinforces the specific reaction rate, k_i, must be defined w.r.t. a particular species *i*. This problem, which helps lay the foundation for multiple reactions in chapter 6, can be given at the same time as **P3-10**.

Problems **P3-7**, **P3-8**, **P3-9**, **P3-11**, **P3-12**, and **P3-13** all give practice at setting up stoichiometric tables. The industrial flow sheets are given for **P3-8** and **P3-11**. These problems can be alternately assigned from year to year. My favorite is **P3-7**.

P3-9. This problem begins to prepare the students for those situations (e.g membrane reactors, multiple reactions) where they <u>cannot</u> use conversion as a variable.

P3-10 This problem reinforces the concept that at or near equilibrium, the rate law must reduce to give the equilibrium conversion (and the concentrations that are derived from thermodynamics.

P3-11 See above.

P3-12 See above.

P3-13 See above.

P3-14. Reinforces the point that the equilibrium conversion will be different for a flow system and a constant volume batch system.

P3-15. Uses the rate law and stoichiometric table to give practice at expressing $-r_A=f(X)$. In Chapter 2 the student saw that once one has $-r_A=f(X)$ a number of reaction systems can be designed.

P3-16. Straight forward problem to set up a stoichiometic table and then substitute numbers to calculate various parameters.

P3-17. Alternate to P3-14.

P3-18. This problem to express $-r_A=f(X)$ requires thinking and is not particularly straight forward. Reinforces the fact that concentration must be known as a function of pressure. Prepares the student for pressure drop problems in chapter 4.

P3-19. Requires the student to go outside of the textbook for information and practice life-long learning skills.

P3-20. Usually assigned at graduate level in conjunction with Appendices I and J.

Problems **P3-21**, **P3-22**, and **P3-23** all involve setting up stoichiometric tables for reactions with phase changes.

CDP3-A Similar to the honey bee, firefly, and cricket problem where the activation energy must be calculated.

CDP3-B Similar to problem P3-23.

CDP3-C Points out that the concentration of B in the gas phase can be a constant.

CDP3-D Alternative to problem P3-22.

CDP3-E Alternative to problem P3-12.

Summary

	Assigned	Alternates	Difficulty	Time	Solution Given
P3-1	S				No
P3-2	O				(b&c) Yes
P3-3	O	A^{*}	FSF	40	Yes
● **P3-4**			SF	15	Yes
P3-5	I		SF	30	Yes
● **P3-6**		7,8,11,12,B,E		20	Yes
● **P3-7**		7,8,11,12,13,E		65	Yes
P3-8	AA	7,11,12,13,E		35	No
● **P3-9**	A(a&b)			20&20	Yes
● **P3-10**				20	Yes

	P3-11	A A	7,8,11,12,13,E	45	Yes
	P3-12	A A	7,8,11,1213,E	35	Yes
	P3-13	A A	7,8,11,12,13,E	35	Yes
●	P3-14	A A	17	45	Yes
	P3-15	O	13	35	Yes
	P3-16	O		45	Yes
●	P3-17	A A	14	30	Yes
●	P3-18	A		50	Yes
	P3-19	G		60	No
	P3-20	G		45	No
	P3-21	G	22,C,D	50	Yes
	P3-22	G	21,C,D	50	Yes
	P3-23	G	B	50	Yes
	CDP3-A	A A	3	15	Yes
	CDP3-B	A A	23	30	Yes
	CDP3-C	A A		45	Yes
	CDP3-D	A A	C,21,22	30	Yes
	CDP3-E	A A	7,8,11,12,13	25	Yes

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.

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

Summary Table Ch-3

	Arrhenius Equation	Rate Law	Equilibrium	Stoichiometry	Rate Law & Stoichiometry	Phase Change
	3,5,19,A	6,10	14,17	Gas 7(b)&(c),11, 12,13,E Liquid 7(a)	9(b)&(c), 13(d),16(c), 9(a)	21,22,23, B,C
Straight Forward		6,10(a)		7,12	16(c),E	21
Fairly Straight Forward	3(a)		14,17	11,13	9,13(d)	22,D,C
More Difficult	3(b)	10(b),10(c)				23,B
Open-ended	3(c)			11(e)		
Critical Thinking	3(d)					

P3-1 No solution will be given

P3-2

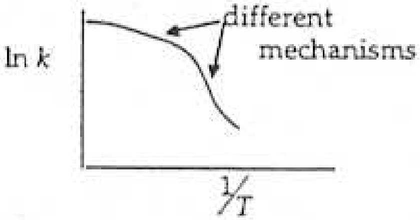
a) Cooking food (effect of temperature), removing a stain with bleach (effect of bleach concentration), dissolution of sugar in tea or coffee.

b) Parts a and b will stay the same while the reaction rates will increase by a factor of ten.

c) Rate law should always be determined from an experimental observtion

$-r_A = kC_{TBB}$ the reaction rate is zero-order with respect to NaOH.

d)



$A \xrightarrow{k_1} C$ (low temp)

$A \xrightarrow{k_2} D$ (high temp)

$$-r_A = \underbrace{(k_1 + k_2)}_{k} C_A$$

e) Cake will burn on the outside because the cake dough offers a resistance to heat transfer so reaction temperature will be lower in the center of the cake than on the outside.

P3-3. Given: Frequency of flashing of fireflies and the frequency of chirping of crickets as a function of temperature:

A. Fireflies				B. Crickets			
T°C	21.0	25.0	30.0	T°C	14.2	20.3	27.0
Flashes/min.	9.0	12.16	16.2	Chirps/min.	80	126	200
T°K	294	298	303	T°K	287.2	293.3	300°K
1/T°Kx1000	3.401	3.356	3.300	1/T°Kx1000	3.452	3.409	3.333

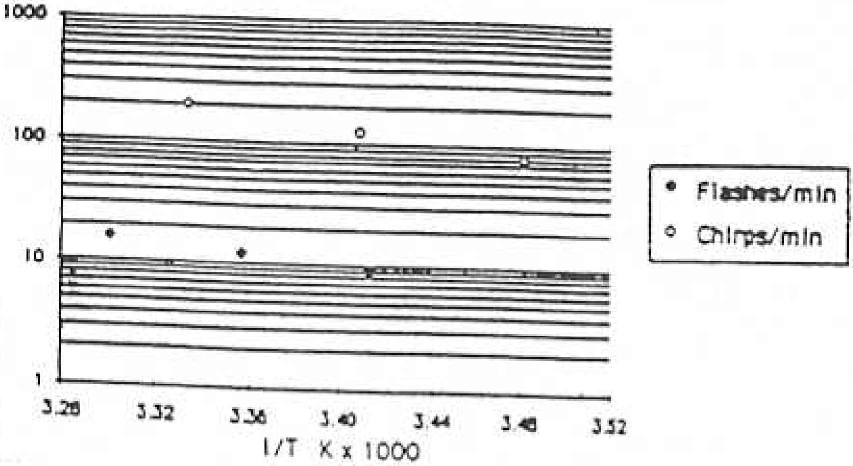


Figure P3-2.

Assume an Arrhenius dependence for both the flashing rate and the chirp rate, i.e.

$r_F = A_F e^{-E_F/RT}$ = flashing rate

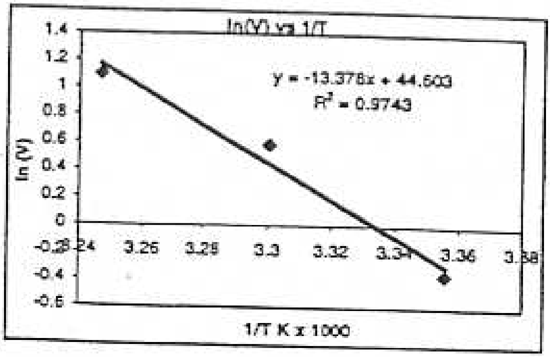
$r_c = A_c e^{-E_c/RT}$ = chirping rate

Then:

$\ln r_F = \ln A_F - E_T/RT$ and

b) Flight Speed of the Honey bee

T(C)	1/T(K)	V(cm/s)	ln(V)
25	3.3557	0.7	-0.356675
30	3.30033	1.8	0.587787
35	3.24675	3	1.098612



From the graph:

E=13.4 kcal/mole

Therefore at 40°C,

$\ln(V) = -13.378(3.73) + 44.603 = 1.86$

V = 6.44cm/s

At -5°C,

$\ln(V) = -13.378(3.73)+44.603 = -5.31$

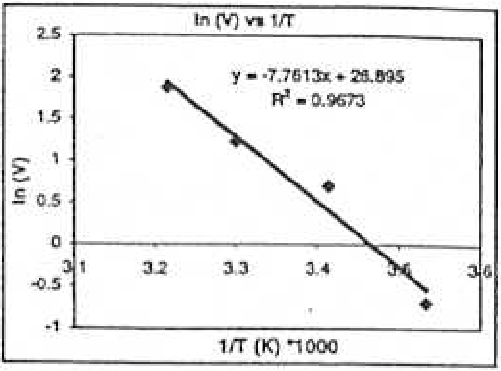
V= 0.005 cm/s

Unfortunately for the bee, it would not be alive at this temperature.

P3-3 cont'd

Running Speed of Ants

T	1/T (K)	V	ln (V)
10	3.53357	0.2	-0.693147
20	3.41297	2	0.693147
30	3.30033	3.4	1.223775
40	3.21543	6.5	1.871802



From the graph:
E = -7.7613 kcal/mole

c) The activity of bees, ants, crickets, and fireflies increases with an increase in temperature. The activation energy of fireflies and crickets is the same while ants and bees have a different frequency that is dependent on temperature.

d) There is a limit to the temperature for which the data for any one of the insects can be extrapolated. Data which wolud be helpfull is the maximum and the minimum temperature that these insects can indure before death. Therefore, even if extrapolation gives us a value that looks reasonable, at certain temperatures it could be useless.

P3-4. There are two competing effects that bring about the maximum in the corrosion rate: temperature and HCN-H2SO4 complex concentration. The corrosion rate increases with increasing temperature and increasing concentration of the HCN-H2SO4 complex. The temperature increases as we go from the top to bottom of the column, and consequently the rate of corrosion should increase. However, the HCN concentration (and the HCN-H_2SO_4 complex) decreases as we go from the top to the bottom of the column. There is virtually no HCN in the bottom of the column. These two opposing factors result in a maximum in the corrosion rate somewhere around the middle of the column.

P3-5. 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

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

P3-5 cont'd

$$\therefore E = R\,\frac{\ln(k_2/k_1)(T_1(T_1 + 10))}{(T_2-T_1)} = \frac{R\ \ln 2(T_1(T_1+10))}{10°K}$$

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

which can be approximated by $T = (\frac{(10)°K\ E}{R\ \ln\ 2})^{1/2}$

(b) Given the following data

	k min^{-1}	.001	0.050
	T°C	0	100
Then	T°K	273	373

Eqn. 3-2 is $k = A\ e^{-E/RT}$

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

Dividing $\frac{k_2}{k_1} = e^{-E/R\ (\frac{1}{T_2} - \frac{1}{T_1})}$

or $$E = -\frac{R\ \ln(k_2/k_1)}{(1/T_2 - 1/T_1)} = \frac{R\ T_1T_2}{(T_2- T_1)}\ \ln(k_2/k_1)$$

$$\therefore E = \frac{[1.99\text{cal/mole°K}][273°K][373°K]}{100°K}\ \ln(\frac{.050}{.001}) = 7{,}960\ \text{cal/mol}$$ ans

$$\therefore A = k_1\ e^{+E/RT_1} = 10^{-3}\ \exp\ [\frac{7960\text{cal/mol}}{1.99\text{cal/mol°K} \times 273°K}]\text{min}^{-1} = 2.1\text{x}10^3\text{min}^{-1}$$ ans

P3-6. **Solution**

For this problem, recall that for any reaction

$$A + B \longrightarrow C + D$$

the rate laws are related to the stoichiometric coefficients by the following equation.

P3-6 cont'd

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

$$\text{(a)}\quad -r_B = \frac{b}{a}(-r_A) = \frac{1}{2}\left(k_A C_A^2 C_B\right)$$

$$-r_B = k_B C_A^2 C_B \quad \text{where} \quad k_B = 12.5\left(\frac{\text{dm}^3}{\text{mol}}\right)^2\left(\frac{1}{\text{sec}}\right)$$

$$r_C = \frac{c}{a}(-r_A) = \frac{1}{2}\left(k_A C_A^2 C_B\right)$$

$$r_C = k_C C_A^2 C_B \quad \text{where} \quad k_C = 12.5\left(\frac{\text{dm}^3}{\text{mol}}\right)^2\left(\frac{1}{\text{sec}}\right)$$

$$\text{(b)}\quad -r_B = \frac{b}{a}(-r_A) = 3\left(k_A C_A C_B\right)$$

$$-r_B = k_B C_A C_B \quad \text{where} \quad k_B = 75.0\left(\frac{\text{dm}^3}{\text{mol sec}}\right)$$

$$r_C = \frac{c}{a}(-r_A) = 2\left(k_A C_A C_B\right)$$

$$r_C = k_C C_A C_B \quad \text{where} \quad k_C = 50.0\left(\frac{\text{dm}^3}{\text{mol sec}}\right)$$

$$\text{(c)}\quad r_B = \frac{b}{a}(-r_A) = 3\left[k_A\left(C_A^2 - \frac{C_B^6}{K_C}\right)\right]$$

$$r_B = k_B\left[C_A^2 - \frac{C_B^6}{K_C}\right] \quad \text{where} \quad k_B = 75.0\left(\frac{\text{dm}^3}{\text{mol sec}}\right)$$

$$\text{(d)}\quad -r_B = \frac{b}{a}(-r_A) = \frac{5}{4}\left(k_A C_A^2 C_B\right)$$

$$-r_B = k_B C_A^2 C_B \,. \quad \text{where} \quad k_B = 31.25\left(\frac{\text{dm}^3}{\text{mol}}\right)^2\left(\frac{1}{\text{sec}}\right)$$

$$r_C = \frac{c}{a}(-r_A) = \left(k_A C_A^2 C_B\right)$$

P3-6 cont'd

$$r_C = k_C C_A^2 C_B \quad \text{where} \quad k_C = 25.0\left(\frac{dm^3}{mol}\right)^2\left(\frac{1}{sec}\right)$$

$$r_D = \frac{d}{a}(-r_A) = \frac{3}{2}(k_A C_A^2 C_B)$$

$$r_D = k_D C_A^2 C_B \quad \text{where} \quad k_D = 37.5\left(\frac{dm^3}{mol}\right)^2\left(\frac{1}{sec}\right)$$

Given the reaction $CH_4 + 3/2\ O_2 \rightarrow HCOOH + H_2O$

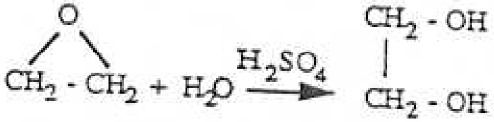
Reactions are related by $\frac{-r_{CH_4}}{1} = -\ 2/3\ r_{O_2} = r_{HCOOH} = r_{H_2O}$

or

$r_{CH_4} = 2/3\ r_{O_2}$ C.

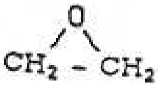
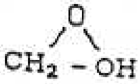
P3-7

a)



$$A + B \xrightarrow{cat} C$$

Because this is a liquid phase reaction, the stoichiometric table will be the he same whether the reaction is carried out in either a batch or flow reactor. $N_A/V = N_A/V_o = C_A$

Species	Symbol	Initial	Change	Remain
	A	$C_{AO} = 1$ lb mol/ft^3	$-\ C_{AO}X$	$C_A = 1\ (1-X)$
H_2O	B	$C_{BO} = 3.47$ lb mol/ft^3 $\theta_B = 3.47$	$-\ C_{AO}X$	$C_B = (3.47-X)$
	C	0	$+\ C_{AO}X$	$C_C = X$

P3-7 cont'd

b) $C_2H_6 \rightarrow C_2H_4 + H_2$

$A \rightarrow B + C$

Species	Symbol	Entering	Change	Leaving
C_2H_6	A	F_{AO}	$-F_{AO}X$	$F_A = F_{AO}(1-X)$
C_2H_4	B	0	$+F_{AO}X$	$F_B = F_{AO}X$
H_2	C	0	$+F_{AO}X$	$F_C = F_{AO}X$
		$F_{TO} = F_{AO}$		$F_T = F_{AO}(1+X)$

Gas Phase, constant temperature, and no pressure drop.

$$\upsilon = \upsilon_o(1+\varepsilon X)$$

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

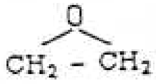
$$\upsilon = \upsilon_o(1+X)$$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{AO}(1-X)}{\upsilon_o(1+X)} = C_{AO}\frac{(1-X)}{(1+X)}$$

$$C_B = C_C\,\frac{F_B}{\upsilon} = \frac{F_{AO}\,X}{\upsilon_o(1+X)} = C_{AO}\frac{X}{1+X}$$

$$C_{A0} = y_{A0}\,C_{TO} = y_{A0}\frac{P_O}{RT_O} = \frac{(1)(6\text{atm})}{\frac{.082\text{m}^3}{{}^\circ\text{K k mol}}\,\text{atm}\,1100^\circ\text{K}} = 0.067\,\frac{\text{kmol}}{\text{m}^3} = 0.067\,\frac{\text{mol}}{\text{dm}^3}$$

c)



$$C_2H_2 + \frac{1}{2}O_2 \rightarrow CH_2 - CH_2$$

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

Species	Symbol	Entering	Change	Leaving
C_2H_2	A	F_{A0}	$-F_{A0}X$	$F_A = -F_{A0}(1-X)$
O_2	B	F_{B0}	$-1/2F_{A0}X$	$F_B = F_{A0}(\theta_B - X/2)$
Ethylene oxide	C	0	$F_{A0}X$	$F_C = F_{A0}X$

P3-7 cont'd

Gas Phase, Isothermal and no pressure drop.

$$\theta_B = \frac{\frac{1}{2}F_{A0}}{F_{A0}} = \frac{1}{2}$$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} + \frac{1}{1+\theta_B} = \frac{1}{1+0.5} = .67$$

$$\varepsilon = y_{A0}\delta = 0.67(1-\frac{1}{2}-1) = -0.34$$

$$C_{A0} = y_{A0}C_{T0} = y_{A0}\frac{P_0}{RT_0} = 0.67\frac{6atm}{\left(\frac{0.082atmdm^3}{molK}\right)(533K)}$$

$$C_{A0} = 0.092\frac{mol}{dm^3}$$

$$C_A = \frac{F_{A0}}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0}\frac{(1-X)}{1+\varepsilon X} = \frac{(0.092)(1-X)}{1-0.34X}$$

$$C_B = C_{A0}\frac{\left(\theta_B - \frac{X}{2}\right)}{1+\varepsilon X} = \frac{0.092(\frac{1}{2}-\frac{1}{2}X)}{1-0.15X} = \frac{0.046(1-X)}{1-0.34X}$$

$$C_C = \frac{C_{A0}X}{1+\varepsilon X} = \frac{0.092X}{1-0.34X}$$

P3-8 An inert, Nitrogen would be added to the stoichiometry table

Species	Symbol	Entering	Change	Leaving
C_2H_4	A	F_{A0}	$-F_{A0}X$	$F_{A0} = -F_{A0}(1-X)$
O_2	B	$F_{B0} = \theta_B$	$-1/2F_{A0}X$	$F_B = F_{A0}(\theta_B-X/2)$
N_2	I	$F_I = \theta_I F_{A0}$	-------	$F_I = F_{A0}\theta_I$
Ethylene oxide	C	0	$F_{A0}X$	$F_C = F_{A0}X$

Gas Phase, Isothermal, and no Pressure drop

$$\theta_B = \frac{\frac{1}{2}F_{A0}}{F_{A0}} = \frac{1}{2}$$

P3-8 cont'd

$$\theta_I = \theta_B \frac{.79}{.21} = \left(\frac{1}{2}\right)\left(\frac{.79}{.21}\right) = 1.88$$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{1}{1+\theta_I+\theta_B} = \frac{1}{1+0.5+1.88} = 0.30$$

$$\varepsilon = y_{A0}\delta = 0.30\left(1-\frac{1}{2}-1\right) = -0.15$$

The inert Nitrogen would also change the values of y_{A0} and ε.

P3-9 a) $A+B \longrightarrow C$

Mole Balance for a CSTR:

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

$F_{B0}-F_B = -r_B V$

$F_{C0}-F_C = -r_C V$

Rate Law:

$-r_A = kC_AC_B$

Stoichiometry:

$-r_A = -r_B = r_C$

Combine with Eq 3-40 and 3-48: Liquid phase

$$F_{A0} - F_A = k\left(\frac{F_{T0}}{v_0}\right)^2\left(\frac{F_A}{F_A+F_B+F_C}\right)\left(\frac{F_B}{F_A+F_B+F_C}\right)V$$

$$F_{B0} - F_B = k\left(\frac{F_{T0}}{v_0}\right)^2\left(\frac{F_A}{F_A+F_B+F_C}\right)\left(\frac{F_B}{F_A+F_B+F_C}\right)V$$

$$F_{C0} - F_C = k\left(\frac{F_{T0}}{v_0}\right)^2\left(\frac{F_A}{F_A+F_B+F_C}\right)\left(\frac{F_B}{F_A+F_B+F_C}\right)V$$

P3-9 cont'd

(b) A+B–>C

Mole balance for a PFR:

$$\frac{dF_A}{dV} = -r_A$$

$$\frac{dF_B}{dV} = -r_B$$

$$\frac{dF_C}{dV} = -r_C$$

Rate Law:

$$-r_A = kC_AC_B$$

Stoichiometry:

$$-r_A = -r_B = r_C$$

Combine with Eq. 3-40 and 3-48:

$$\frac{dF_A}{dV} = k\left(\frac{F_{T0}}{\upsilon_0}\right)^2\left(\frac{F_A}{F_A+F_B+F_C}\right)\left(\frac{F_B}{F_A+F_B+F_C}\right)$$

$$\frac{dF_B}{dV} = k\left(\frac{F_{T0}}{\upsilon_0}\right)^2\left(\frac{F_A}{F_A+F_B+F_C}\right)\left(\frac{F_B}{F_A+F_B+F_C}\right)$$

$$\frac{dF_C}{dV} = -k\left(\frac{F_{T0}}{\upsilon_0}\right)^2\left(\frac{F_A}{F_A+F_B+F_C}\right)\left(\frac{F_B}{F_A+F_B+F_C}\right)$$

This set of differential equations can be solved using POLYMATH or a similar software package.

(c) A –> B+C (gas phase reaction)

Mole Balance for a PFR:

$$\frac{dF_A}{dV} = -r_A$$

$$\frac{dF_B}{dV} = -r_B$$

$$\frac{dF_C}{dV} = -r_C$$

Rate Law:

$$r_A = kC_A$$

Stoichiometry:

$$-r_A = r_B = r_C$$

Combine with Eq. 3-40 and 3-48:

$$\frac{dF_A}{dV} = k\frac{P_{T0}}{RT_0}\left(\frac{F_A}{F_A+F_B+F_C}\right)$$

P3-9 cont'd

$$\frac{dF_B}{dV} = -k\frac{P_{To}}{RT_o}\left(\frac{F_A}{F_A + F_B + F_C}\right)$$

$$\frac{dF_C}{dV} = -k\frac{P_{To}}{RT_o}\left(\frac{F_A}{F_A + F_B + F_C}\right)$$

This set of differential equations can be solved using POLYMATH or a similar software package.

(d) $A + \frac{1}{2}B \rightarrow C$ (gas phase reaction)

Mole balance for a PFR:

$$\frac{dF_A}{dV} = -r_A$$

$$\frac{dF_B}{dV} = -r_B$$

$$\frac{dF_C}{dV} = -r_C$$

Rate Law:

$-r_A = kC_AC_B^{0.5}$

Stoichiometry:

$-r_A = -2r_B = r_C$

Combine with Eq. 3-40 and 3-48:

$$\frac{dF_A}{dV} = k\left(\frac{P_{To}}{RT_o}\right)^{\frac{3}{2}}\left(\frac{F_A}{F_A + F_B + F_C}\right)\left(\frac{F_B}{F_A + F_B + F_C}\right)^{\frac{1}{2}}$$

$$\frac{dF_B}{dV} = \frac{1}{2}k\left(\frac{P_{To}}{RT_o}\right)^{\frac{3}{2}}\left(\frac{F_A}{F_A + F_B + F_C}\right)\left(\frac{F_B}{F_A + F_B + F_C}\right)^{\frac{1}{2}}$$

$$\frac{dF_C}{dV} = -k\left(\frac{P_{To}}{RT_o}\right)^{\frac{3}{2}}\left(\frac{F_A}{F_A + F_B + F_C}\right)\left(\frac{F_B}{F_A + F_B + F_C}\right)^{\frac{1}{2}}$$

This set of differential equations can be solved using POLYMATH or a similar software package.

P3-10.

a) At high temperatures

$$A \rightleftarrows B$$

At equilibrium, we know from thermodynamics

$$K_C = \frac{C_{Be}}{C_{Ae}} \qquad \text{(PS39.1)}$$

Consequently, we know that the rate law most reduced to Equation (PS3-9.1) when $-r_A = 0$

Therefore

$$-r_A = k\left[C_A - \frac{C_B}{K_C}\right] \qquad \text{(PS39.2)}$$

At equilibrium $-r_A = 0$ and equation (PS3-9.2) becomes upon rearrangment

$$K_C = \frac{C_{Be}}{C_{Ae}}$$

b) $A + 2B \longrightarrow 2D$

At low temperatures reaciton is irrversible and the rate law is:

$$-r_A = k\, C_A^{1/2}\, C_B$$

$$-r_{A_{toward}} = k_1\, C_A^{1/2}\, C_B \,, \qquad -r_{A_{reverse}} = -\, k_2\, C_D$$

$$-r_A = k_1\, C_A^{1/2}\, C_B - k_2\, C_D$$

$$= k_1\, (C_A^{1/2} C_B - \frac{k_2}{k_1}\, C_D)$$

$$= k_1\, (C_A^{1/2} C_B - \frac{C_D}{K_c}) \qquad \text{where } K_c = \frac{k_1}{k_2}$$

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

Low temperatures

$$-r_A = \frac{k\, P_A\, P_B}{1 + K_A\, P_A + K_B\, P_B}$$

P3-10 cont'd

High temperatures

$$-r_A = \frac{k\left[P_A P_B - \frac{P_C P_D}{K_P}\right]}{1 + K_A P_A + K_B P_B}$$

P3-11

$$2A + 9B \rightarrow 2C + 4D + 4E$$

Species	Symbol	Initial Moles	Change in Moles	Final Moles	Concentration
Napthaline	A	Fao	-Fao X	Fao(1-x)	$\frac{Fao\,(1-x)}{vao\,(1+\varepsilon X)}\frac{P}{Po}\frac{To}{T}$
Oxygen	B	θ_BFao	-9/2Fao X	Fao(θ_B-9/2X)	$\frac{Fao\,(\theta_B - 9/2X)}{vao\,(1+\varepsilon X)}\frac{P}{Po}\frac{To}{T}$
Phthalic Anhydride	C	0	Fao X	Fao X	$\frac{Fao\,X}{vao\,(1+\varepsilon X)}\frac{P}{Po}\frac{To}{T}$
Carbon Dioxide	D	0	2Fao X	2Fao X	$\frac{2Fao\,X}{vao\,(1+\varepsilon X)}\frac{P}{Po}\frac{To}{T}$
Water	E	0	2Fao X	2Fao X	$\frac{2Fao\,X}{vao(1+\varepsilon X)}\frac{P}{Po}\frac{To}{T}$

$F_{T0}=Fao(1+\theta_B)$ $\quad$ $F_T=Fao(1+\theta_B-.5X)$

$\delta = -1/2$ $\quad y_{A0} = 0.035$ $\quad \theta_B = 20.3/3.5 = 5.8$ $\quad \varepsilon = y_{A0}{*}\delta = 0.035{*}{-1/2} = -0.0175$

$v_{A0} = F_{T0}\,R\,T / P_0$

$C_{T0}=Po / RT = 10\text{ atm} / (.08206\,(L * atm / mol\,K) * 500K) = .24\text{ mol} / L$

$C_{A0} = .035 * .24\text{ mol} / L = .0084\text{ mol} / L$

a)

(1) $P_B = C_B\,R\,T = \frac{Cao\,(\theta_B - 9/2X)}{(1 + \varepsilon X)}\,R\,T$

$= 0.345 * (5.8 - 9/2X) / (1-0.0175X)$

$P_D = C_D\,R\,T = \frac{2Cao\,X}{(1 + \varepsilon X)}\,R\,T$

$= 0.689 * X / (1-0.0175X)$

(2) $C_B = \frac{Cao\,(\theta_B - 9/2X)}{(1 + \varepsilon X)}$

$= \frac{0.0084\,(5.8 - 9/2X)}{(1 - 0.0175X)}$

$C_A = \frac{Cao\,(1 - X)}{(1 + \varepsilon X)}$

$= \frac{0.0084\,(1 - X)}{(1 - 0.0175X)}$

(3) $v = v_{A0}\,(1+ \varepsilon X) = Fao\,(1+\theta_B)\,(1+ \varepsilon X)\,R\,T / P_0$

P3-11 cont'd

b)

(1) $P_B = C_B R T = \frac{C_{ao}(\theta_B - 9/2X)}{(1+\varepsilon X)} \frac{P R T}{P_o}$ $P_D = C_D R T = \frac{2C_{ao} X}{(1+\varepsilon X)} \frac{P R T}{P_o}$

(2) $C_B = \frac{C_{ao}(\theta_B - 9/2X)}{(1+\varepsilon X)} \frac{P}{P_o}$ $C_A = \frac{C_{ao}(1-X)}{(1+\varepsilon X)} \frac{P}{P_o}$

(3) $v = v_{Ao}(1+\varepsilon X)\, P_o/P$

c) $-r_A = k_1 C_A^2 C_B$

from part a P3 $-r_A = k_1 * \frac{C_{ao}^3 (1-X)^2 * (5.8 - 9/2X)}{(1+\varepsilon X)^3}$

from part b $-r_A = k_1 * \frac{C_{ao}^3 (1-X)^2 * (5.8 - 9/2X)}{(1+\varepsilon X)^3} (P/Po)^3$

d) $-r_A = k_1 C_A^2 C_B$

from part a $-r_A = k_1 * \frac{C_{ao}^3 (1-X)^2 * (9/2 - 9/2X)}{(1+\varepsilon X)^3}$

from part b $-r_A = k_1 * \frac{C_{ao}^3 (1-X)^2 * (9/2 - 9/2X)}{(1+\varepsilon X)^3} (P/Po)^3$

By using pure oxygen instead of air, the concentration of the reactant are higher and the reaction rate is therefore faster.

e) No answer will be given

P3-12.

$H_2 + 1/3N_2 \longrightarrow 2/3\ NH_3$

a)

compound	symbol	inlet mole	change	outlet moles
H_2	A	0.5	$-0.5X$	$0.5(1-X)$
N_2	B	0.5	$\frac{-0.5X}{3}$	$0.5(1-1/3X)$
NH_3	C	0	$+2/3(0.5X)$	$1/3\ X$
Total	T	1.0	$-1/3X$	$1-1/3X$

b) $P_o = 16.4$ atm $T_o = 1727°C = 2000$ K $X = 0.60$

P3-12 cont'd

assuming isothermal,-isentropic and ideal gases

$$C_{H_2} = C_{AO}\frac{0.5(1-X)}{1-1/3X}\frac{P}{P_O}\frac{T}{T} = \frac{n_{AO}}{v_o}\frac{0.5(1-X)}{1-1/3X} = \frac{P_{AO}}{RT}\frac{0.5(1-X)}{1-1/3X}$$

$$C_{H_2} = \frac{y_{AO}P_o}{RT}\frac{(1-X)}{(1-1/3\,X)} = \frac{(0.5)(16.4\ \text{atm})}{0.082\ \frac{\text{atm}}{\text{gmol}^\circ\text{K}}\ (2000\text{K})}\ \frac{(1-0.6)}{(1-1/3\ (0.6))}$$

$$C_{H_2} = (0.05\ \frac{\text{gmol}}{\text{liter}})\ (0.5) = 0.025\ \text{gmol/l}$$

$$C_{NH_3} = \frac{(1/3)X}{0.5(1-X)}C_{H_2} = \frac{(1/3)(0.6)}{0.5(1-0.6)}(0.025)\ \frac{\text{gmol}}{\text{l}} = 0.025\ \frac{\text{gmol}}{\text{l}}$$

c) If N_2 were the basis of calculation, the chemical equation would be rewritten as

$$3H_2 + N_2 \longrightarrow 2NH_3$$

The outlet moles of H_2 would then be 0.5(1-3X). Sixty percent conversion of N_2 would yield a negative number of moles of H_2 coming out, which is not possible. H_2 is thus the limiting reagent and the maximum conversion of N_2 possible would be 0.33, giving an outlet number of moles of H_2 equal to zero.

P3-13.

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

$Y_{NH_{3,0}} = 0.15$ P=8.2 atm T = 227°C = 500K

a) Assuming ideal gas law

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

b) $C_{NH_{3,0}} = Y_{NH_{3,0}}\,C_{To} = (0.15)(0.2\ \text{gmol/l}) = 0.03\ \text{gmol/l}$

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

P3-13cont'd

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 $\underline{N_2} = 0.79(1-0.15) = 0.79(0.85) = 0.67$

Initial $\overline{O_2} = 0.85-0.67=0.18$

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

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

i	n_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	$0.18-\frac{5}{4}(0.15X)$	$8.2\left(\frac{0.18-5/4(0.15X)}{1+[0.15/4]X}\right)$	$(0.036-\frac{0.15}{4}X)/(1+\frac{0.15}{4}X)$
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	$5.49\ \frac{1}{1+[0.15/4]X}$	$0.133/(1+\frac{0.15}{4}X)$

P3-13 cont'd

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

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

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

2) Constant volume

$C_i = 0.2\ n_i$

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

i	n_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
		$0.199+0.008X$	$8.2-0.313\ X$
		$=0.2\left(1+\frac{0.15}{4}X\right)$	

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

3) Same as (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):

$$-r_A = kC_A{}^4C_B{}^5$$

P3-13 cont'd

Combine with equation 3-40 and 3-48

$$\frac{dF_A}{dV}=k\left(\frac{P_{T0}}{RT_0}\right)^9\left(\frac{F_A}{F_A+F_B+F_C}\right)^4\left(\frac{F_B}{F_A+F_B+F_C}\right)^5$$

$$\frac{dF_B}{dV}=\frac{5}{4}k\left(\frac{P_{T0}}{RT_0}\right)^9\left(\frac{F_A}{F_A+F_B+F_C}\right)^4\left(\frac{F_B}{F_A+F_B+F_C}\right)^5$$

$$\frac{dF_C}{dV}=-k\left(\frac{P_{T0}}{RT_0}\right)^9\left(\frac{F_A}{F_A+F_B+F_C}\right)^4\left(\frac{F_B}{F_A+F_B+F_C}\right)^5$$

$$\frac{dF_D}{dV}=-k\left(\frac{P_{T0}}{RT_0}\right)^9\left(\frac{F_A}{F_A+F_B+F_C}\right)^4\left(\frac{F_B}{F_A+F_B+F_C}\right)^5$$

P3-14. **Solution**

Thermodynamics predicts the reacting species in a reversible reaction are related by the equation given below.

$$K_C=\frac{C_{B,e}^2}{C_{A,e}}$$

Stoichiometry:

Constant Volume Batch:

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

Plug Flow Reactor (PFR):

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

$$\varepsilon=y_{Ao}\delta=(y_{Ao})(2-1)=y_{Ao}$$

Combine and Rearrange:

Constant Volume Batch:

$$X_e = \sqrt{\frac{K_C(1-X_e)}{4C_{A0}}}$$

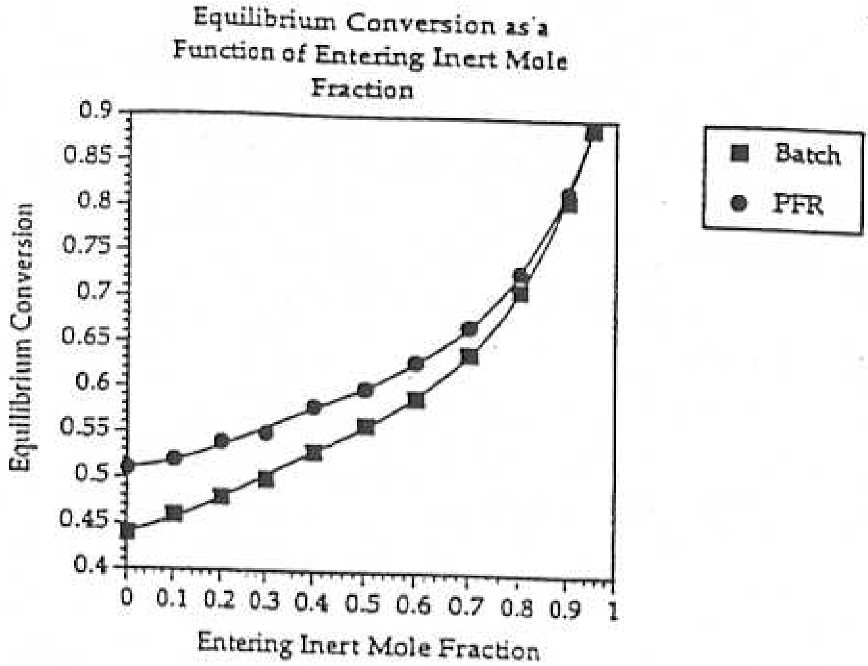
PFR:→

$$X_e = \sqrt{\frac{K_C(1-X_e)(1+\varepsilon X_e)}{4C_{A0}}}$$

The equations above were solved using POLYMATH. The equations in POLYMATH notation are shown below.

```
f(xef) = xef - ((kc * (1 - xef) * (1 + eps * xef)) / (4 * cao)) * *0.5
f(xeb) = xeb - (kc * (1 - xeb) / (4 * cao)) * *0.5
kc = 0.1
p0 = 2
t0 = 340
cao = (ya0 * p0) / (t0 * 0.082)
eps = ya0
yI0 = 1 - ya0
ya0 = (number between 0 and 1.0)
```

P3-14 cont'd



Equilibrium conversion is higher in the PFR because number of moles of gas increases during a reaction, increasing the volume. Since batch is constant volume, change in moles of gas does not influence the system.

If number of moles of gas stays constant PFR and constant volume batch would achieve same equilibrium conversion. If number of moles of gas decreased, constant volume batch would achieve higher equilibrium conversion.

P3-15 $H_2 + Br_2 \rightarrow 2HBr$, Given that $y_{H2} = 0.25$, $y_{Br2} = 0.25$

$Y_I = 0.50$, $P_0 = 10$ atm, $T_0 = 400°C = (400 + 273)K = 673$ K

The kinetic expression for this reaction is

$$r_{HBr} = \frac{k_1 C_{H_2} C_{Br_2}^{\frac{1}{2}}}{k_2 + \frac{C_{HBr}}{C_{Br_2}}}$$ from equation 3-18 of the text

$\delta = 2\text{-}1\text{-}1 = 0$ $\therefore \varepsilon = y_{H2}\delta = 0$ and $v = v_0 f[P_0/P]$

$$C_{H_{2,0}} = \frac{y_{H_2} P_0}{RT_0}$$ (all quantities known)

P3-15 cont'd

$$\theta_{Br_2} = \frac{N_{Br_2,0}}{N_{H_2,0}} = \frac{y_{Br_2,0}}{y_{H_2,0}} = 1 \qquad \theta_{HBR} = 0$$

$$C_{H_2} = \frac{N_{H_2,0}(1-X)}{v} = \frac{N_{H_2,0}}{v_0 f(P/P_0)}(1-X) = \frac{C_{H_2,0}}{f(P/P_0)}(1-X)$$

$$C_{H_2} = \frac{y_{H_2,0}P_0}{RT_0}(1-X)$$

$$C_{Br_2} = \frac{N_{H_2,0}(\theta_B - X)}{v} = \frac{y_{H_2,0}P_0}{RT_0}(1-X)$$

$$C_{HBr} = \frac{N_{H_2,0}}{v}(\theta_B + 2X) = \frac{y_{H_2,0}P_0}{RT_0}(2X)$$

Substituting expressions for C_{H2}, C_{Br2}, C_{HBR} into eqn. 3-18

$$r_{HBr} = \frac{k_1\left(\dfrac{y_{H_2,0}P_0}{RT_0}\right)^{\frac{3}{2}}(1-X)^{\frac{3}{2}}}{k_2 + \dfrac{2X}{1-X}} = \frac{k_1\left(\dfrac{.25 * 10atm}{\dfrac{0.08211atm}{molK} * 673K}\right)^{\frac{3}{2}}(1-X)^{\frac{3}{2}}}{k_2 + \dfrac{2X}{1-X}}$$

$$r_{HBr} = \frac{0.0097k_1(1-X)^{\frac{3}{2}}(mole/1)^{\frac{3}{2}}}{k_2 + 2X/(1-X)}$$

(b) Given: $C_6H_5CH(CH_3) \rightleftarrows C_6H_6 + C_3H_6$, denoted symbollically as:

$C \rightleftarrows B + P$ with $y_{C,0} = .75$ $y_{I,0} = .25$

$$-r'_C = \frac{k[P_C - P_B P_P/K]}{1 + K_C P_C + P_B K_B} \qquad \text{Eqn. 3.19 of text.}$$

P3-15 cont'd

(a) Constant Volume (see next page)

$$C_C = C_{CO}(1-X) \; ; \; C_B = C_P = C_{CO}X$$

$$P_C = C_C RT = C_{CO}RT\,(1-X)$$

$$P_B = C_B RT = C_{CO}RT\,X = P_P$$

$$-r_C' = \frac{k(C_{C0}RT)\left[(1-X) - \dfrac{C_{C0}^2 R^2 T X^2}{K}\right]}{1 + K_C C_{C0} RT(1-X) + K_B C_{C0} RTX}$$

$$= \frac{k(C_{CO}RT)\left[(1-X) - \dfrac{C_{CO}RT\,X^2}{K}\right]}{1 + C_{CO}RT\,(K_C(1-X) + K_B\,X)}$$

Consider the general case in which both P and T are varying

$\delta = 1 + 1 - 1 = 1 \qquad \varepsilon = y_{C,0}\,\delta = .75 \qquad \theta_P = \theta_B = 0$

From Eqn. S3-7 From Eqn. S3-8

$$C_C = \frac{C_{CO}[1-X]}{(P_o/P)(T/T_o)[1+.75X]} \; ; \qquad C_B = C_P = \frac{C_{CO}X}{(P_o/P)(T/T_o)[1+.75X]}$$

From Eqn. 3.30

$$P_C = C_C RT = \frac{C_{CO}RT[1-X]}{(P_o/P)(T/T_o)[1+.75X]} = \left[\frac{C_{CO}RT_oP}{P_o}\right]\left[\frac{1-X}{1+.75X}\right]$$

Similarly for B and P

$$P_B = C_B RT = \frac{C_{CO}RTX}{(P_o/P)(T/T_o)[1+.75X]} = \left[\frac{C_{CO}RT_oP}{P_o}\right]\left[\frac{X}{1+.75X}\right]$$

$$P_P = C_P RT = \frac{C_{CO}RT\,X}{(P_o/P)(T/T_o)[1+.75X]} = \left[\frac{C_{CO}RT_oP}{P_o}\right]\left[\frac{X}{1+.75X}\right]$$

P3-15 cont'd

Substitution of above expressions for P_C, P_B, and P_P into rate expression

$$-r_C' = \frac{k_1 \left[\frac{C_0 RT_o P}{P_o(1 + .75X)}\right] \left[(1-X) - \frac{1}{K}\left[\frac{C_{CO}RT_o P}{P_o}\right]\left[\frac{X^2}{1 + .75X}\right]\right]}{1 + k_c \left[\frac{C_{CO}RT_o P}{P_o}\right]\left[\frac{1-X}{1 + .75X}\right] + K_B \left[\frac{C_{CO}RT_o P}{P_o}\right]\left[\frac{X}{1 + .75X}\right]}$$

The above expression can be simplified further by noting that

$$P_{CO} = y_{C,0} P_o = C_0 RT_o \quad \text{i.e.} \quad y_{C,0} = \frac{C_o RT}{P_o}$$

$$-r_C' = \frac{\left(\frac{k_1 y_{C,0} P}{1+0.75X}\right)\left[(1-X) - \frac{1}{K}\left(y_{C,0}P\right)\left(\frac{X^2}{1+0.75X}\right)\right]}{1 + K_C y_{C,0} P\left(\frac{1-X}{1+0.75X}\right) + K_B y_{C,0} P\left(\frac{X}{1+0.75X}\right)}$$

P3-16.

$$2A + 4B \longrightarrow 2C$$

$$A + 2B \longrightarrow C$$

$$\varepsilon = y_{A0}\delta = 0.5(1-1-2) = 0.5(-2) = -1$$

$$-r_A = kC_AC_B$$

$$k = Ae^{-E/RT} = 4 \text{ dm}^3/\text{gmol min}$$

$$A = 4 \frac{\text{dm}^3}{\text{gmol min}} \exp\left(\frac{15{,}000 \text{ cal/gmol}}{1.987 \text{ cal/gmol°K } (727+273)\text{K}}\right)$$

$$A = 4 \frac{\text{dm}^3}{\text{gmol min}} (1898.97) = 7.60\text{x}10^3 \frac{\text{dm}^3}{\text{gmol min}}$$

If we neglect pressure drop

$$v = v_o \frac{P_O}{P}(1+\varepsilon X)\frac{T}{T_O} = v_o(1+\varepsilon X) = v_o(1-X)$$

P3-16 cont'd

Stoichiometric Table

A	F_{AO}	$-F_{AO}X$	$F_{AO}(1-X)$
B	$F_{BO}=F_{AO}$	$-2F_{AO}X$	$F_{AO}(1-2X)$
C		$+F_{AO}X$	$F_{AO}X$
	$2F_{AO}$	$-2F_{AO}X$	$2F_{AO}(1-X)$

a) at $X=0.25$, $v=v_o(1-X)= 2.5\ \frac{dm^3}{min}(0.75)= 1.88\ dm^3/min$

b) $-r_A = kC_AC_B = kC_{AO}C_{BO}$ at entrance to the reactor

$$-r_A = kC_{AO}C_{BO} = kC_{AO}^2$$

$$C_{AO} = \frac{Y_{AO}P_O}{RT_O} = \frac{0.5(10atm)}{.08205\ atm\ l/gmol°K\ (1000)K} = 6.09x10^{-2} gmol/l$$

$$-r_A = 4\ \frac{dm^3}{gmol\ min}(6.09X10^{-2})^2\ \frac{gmol^2}{dm^6} = 1.49x10^{-2}\ \frac{gmol}{dm^3min}$$

c) $-r_A = kC_AC_B = k\ \frac{F_AF_B}{v^2} = \frac{kF_{AO}(1-X)\ F_{AO}(1-2X)}{v_O{}^2(1-X)^2}$

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

$$-r_A = 4\ \frac{dm^3}{gmol\ min}\ (6.09x10^{-2})^2\ \frac{gmol^2}{dm^6}\ \frac{(1-0.8)}{(1-0.4)}$$

$$-r_A = 4.95X10^{-3}\ \frac{gmole}{dm^3\ min}$$

d) $C_{AO} = 6.09x10^{-2}\ gmol/l$

e) $C_A = \frac{F_A}{v} = \frac{F_{AO}(1-X)}{v_o(1-X)} = C_{AO} = 6.09x10^{-2}\ gmol/l$

f) $k = Ae^{-E/RT} = 7.60x10^3\ \frac{dm^3}{gmol\ min}\ exp\ [\frac{-15,000\ cal/gmol}{1.987\ cal/gmol°K\ 1500\ K}]$

$$k = 49.6\ \frac{dm^3}{gmol\ min}$$

P3-16 cont'd

From Equation (E3.7-4), $C_A = \frac{C_{AO}(1-X)}{(1-X)} = C_{AO}$. The concentration of A in the gas phase does indeed remain constant. For each mole of A reacted, one mole of gas condenses (as product D), and hence C_A remains constant. When considering the reaction as a mixture of both gas and liquid, however, the amount of A in this mixture continually decreases.

P3-17. Solution

(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:

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

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

$$C_A C_B K_C = C_C$$

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

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

$$X_e = 0.80$$

To find the equilibrium concentration, substitute the equilibrium conversion into the stoichiometric relations.

$Ca = Cao\,(1 - X) = 2\ \text{mol}/\text{dm}^3\ (1-.80) = .4\ \text{mol}/\text{dm}^3$

$Cb = Cao\,(1 - X) = 2\ \text{mol}/\text{dm}^3\ (1-.80) = .4\ \text{mol}/\text{dm}^3$

$Cc = Cao\,X = 2\ \text{mol}/\text{dm}^3 \cdot (.80) = 1.60\ \text{mol}/\text{dm}^3$

b) Stoichiometry:

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

P3-17 cont'd

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

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

Combine (and solve for X_e):

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

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

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

$$X_e = 0.58$$

Find equilibrium concentrations:

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

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

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

c) same reaction, rate law, and initial concentration as part (b) gas phase, batch reaction

Stoichiometry:

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

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

Combine and Solve for Xe:

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

$$Xe = 0.39$$

P3-17 cont'd

Find the equilibrium concentrations:

$$C_{Ae} = (0.305)(1 - 0.39) = 0.19$$

$$C_{Ce} = (0.305)(0.39) = 0.36$$

d) gas phase reaction in a constant pressure, batch reactor

Rate law (reversible reaction):

$$-r_A = k[C_A - C_C^3/K_C]$$

Stoichiometry:

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

$$C_A = N_A / V = N_{A0}(1 - X) / [V_O(1 + \varepsilon X)] = C_{A0}(1 - X) / (1 + 2X)$$

$$C_C = N_C / V = 3N_{A0}X / [V_O(1 + \varepsilon X)] = C_{A0}\,3X / (1 + 2X)$$

Combine and solve for Xe:

$$K_C C_{A0}(1 - Xe) / (1 + 2Xe) = [C_{A0}\,3Xe / (1 + 2Xe)]^3$$

$$Xe = .58$$

Find equilibrium concentrations:

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

$$C_c = 3\,(0.305)\,(0.58) / (1 + 2(0.58)) = 0.246 \text{ mol / dm}^3$$

(Solutions by J.T. Santini, Jr.)

P3-18 Given: Gas phase reaction A + B → C in a Batch reactor fitted with a piston such that

$V = 0.1\,P_0$; $k = 1.0\ (\text{ft}^3)^2/\text{lbmole}^2\ \text{sec}$

$-r_A = kC_A^2C_B$ $N_{A0} = N_{B0}$ at t=0

$V_0 = 0.15\ \text{ft}^3$ $T = 140°\text{C} = 600°\text{R} = \text{Constant}$

(a) $y_{AO} = N_{AO} / (N_{AO} + N_{BO}) = 0.5$ $\delta = 8 - 1 - 1 = 6$ $\varepsilon = y_{AO}\,\delta = 3$

Now $V = V_OP_O / P\,(T / T_O)\,(1 + \varepsilon X)$ $T / T_O = 1$ $P = 10V$

therefore $V = 10\,V_O^2 / 10V\,(1 + \varepsilon X)$ or $V^2 = V_O^2\,[1 + \varepsilon X]$ $P_O = 10\,V_O$

P3-18 cont'd

$N_A = N_{AO}[1 - X]$ $\qquad N_B = N_{AO}[\theta_B - X]$ $\qquad \theta_B = N_{BO} / N_{AO} = 1.0$

therefore

$-r_A = k\,C_A^2\,C_B = k\,N_A^2\,N_B / V^3 = k\,N_{AO}^3\,[1 - X]^3 / (V_O^3\,1 + \varepsilon X]^{3/2});$ $\qquad N_{AO} = (y_{AO}P_O/RT)\ V_O$

therefore

$$-r_A = k\left(\frac{y_{A,0}P_0}{RT}\right)^3 \frac{(1-X)^3}{(1+\varepsilon X)^{3/2}}$$

$-r_A = 1.0\ (ft^3)^2 / ((1lbmole)^2 sec)\quad [0.75 / (.730\ atm\ ft^3/lbmol\ {}^\circ R * 600^\circ R)]^3 \quad \dfrac{(1 - X)^3}{(1 + 3X)^{3/2}}$

$-r_A = 5.03 * 10^{-9}\ \dfrac{(1 - X)^3}{(1 + 3X)^{3/2}}\ lbmol / ft^3\ sec.$

(b) $V = V_O\,(1 + \varepsilon X)1/2$

$.2 = 0.15\,(1 + 3X)^{1/2} \qquad X = .259$

$-r_A = 8.63 * 10^{-10}\ lbmol / ft^3\ sec$

P3-19 There will be no solution given.

P3-20 There will be no solution given.

3-21 $4\ Cl_2 + CH_4 \longrightarrow CCl_4 + 4HCl$

T = 75°C = 348 K $\qquad$ P = 950 kPa = 9.39 atm

Cl_4 vapor pressure = 95 kPa = 0.94 atm = P_V

P3-21 cont'd

$$C_i = \frac{F_i}{v} = \frac{F_i}{v_o(1+\varepsilon X)} = \frac{F_i}{v_o}$$

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	$F_{AO}\ X$	$C_{AO}\ X$
	$5\ F_{AO}$	$5\ C_{AO}$

where $C_{AO} = 0.0658$ gmol/l and $F_{AO} = 0.02631$ gmol/s

After condensation

$$v = v_o \frac{F_t}{F_{to}} = v_o \frac{F_{AO}\ (5-X)}{5\ F_{AO}\ (0.90)} = v_o \frac{5-X}{4.5}$$

$$C'_i = \frac{F_i}{v} = \frac{F_i}{v_o}\frac{(4.5)}{(5-X)}$$

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

P3-21 cont'd

$$y_{DE} = \frac{P_V}{P} = \frac{95}{950} = 0.10$$

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_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$	$F_{A0}(1-X)$
Cl_2	B	$4F_{A0}$	$-4F_{A0}X$	$F_B = 4F_{A0}(1-X)$	$4F_{A0}(1-X)$
HCl_4	C	0	$+4F_{A0}X$	$F_C = 4F_{A0}X$	$4F_{A0}X$
CCl_4	D(g)	0	$+F_{A0}X$	$F_D = F_{A0}X$	$0.10F_T'$
	D(l)	0	--	--	--
	$F_{T0} =$	$5F_{A0}$		$F_T = 5\,F_{A0}$	$F_T' = 5F_{A0} - F_{A0}X + 0.10F_T'$
					$F_T' = \frac{F_{A0}\,(5-X)}{0.90}$

When condensation first begins $F_T = F_T'$

$$5\,F_{A0} = F_{A0}\,\frac{(5-X)}{0.90} \dashrightarrow X_c = 0.50$$

Before Condensation

$$\varepsilon = y_{A0}\delta \quad \delta = 0 \quad \longrightarrow \varepsilon = 0$$

$\Delta T = \Delta P = 0$ ---> Total concentration is constant

$$C_T = C_{To} = \frac{P_o}{RT_o} = \frac{9.39 \text{ atm}}{0.08205 \frac{\text{atm lit}}{\text{gmol K}} \times 348 \text{ K}} = 0.329 \frac{\text{gmol}}{\text{lit}}$$

$$C_{A0} = \frac{1}{5}\,C_{To} = \frac{0.329}{5} \text{ gmol/l} = 0.0658 \text{ gmol/l}$$

$$F_{A0} = C_{A0}\,v_o = (0.0658) \text{ gmol/l } (0.4) \text{ l/s} = 0.02631 \text{ gmol/s}$$

P3-22 $C_2H_6(g) + 2Br_2(g) \longrightarrow C_2H_4Br_2\ (g,l) + 2HBr(g)$

$T + 200°C = 473\ K \qquad P = 2500\ kPa = 24.7\ atm; \qquad P_{V,C_2H_4Br_2} = 506.5\ kPa$

$$y_{DE} = \frac{P_v}{P} = \frac{506.5}{2500} = 0.203$$

Stoich table

$$C_2H_6(g) + 2\ Br_2(g) \dashrightarrow 2\ HBr(g) + C_2H_4Br_2(g,l)$$

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	-	-	-
		$F_{T0} = 3F_{A0}$		$F_T = 3F_{A0}$	$F'_T = 3F_{A0}-F_{A0}X+0.203F'_T$

$$F_T' = \frac{F_{A0}(3-X)}{0.797}$$

when condensation first begins $F_T = F_T'$

$$3F_{A0} = \frac{F_{A0}(3-X)}{0.797} \longrightarrow X_C = 0.609$$

Before condensation

$$\varepsilon = y_{A0}\delta \quad \delta = 0 \quad \longrightarrow \varepsilon = 0$$

$\Delta T = \Delta P = 0$ So total concentration is constant

$$C_T = C_{T0} = \frac{P_0}{RT_0} = \frac{24.7\ atm}{0.08205\ \frac{atm\ lit}{gmol\ K} \times 473\ K} = 0.673\ gmol/l$$

$$C_{A0} = \frac{1}{3}C_{T0} = \frac{0.673}{3}\ gmol/l = 0.212\ gmol/l$$

P3-22 cont'd

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	$F_{AO}(1-X)$	$2F_{AO}(1-X)$	$2F_{AO}X$	$F_{AO}\frac{(3-X)}{3.93}$	$F_{AO}\frac{(3-X)}{0.797}$	$C_{AO}\frac{(1-X)(2.39)}{(3-X)}$
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
$2C_{AO}\frac{(1-X)(2.39)}{(3-X)}$	$2C_{AO}X\frac{(2.39)}{(3-X)}$	$C_{AO}(0.609)$
0.166	0.258	0.129
0.078	0.312	0.109
0	0.338	0.090

$F_{AO} = C_{AO}\, v_o = (0.212)$ gmol/l (0.5) l/s $= 0.106$ 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	$3\,F_{AO}$	$3\,C_{AO}$

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) $C_i = C_i'$

P3-22 cont'd

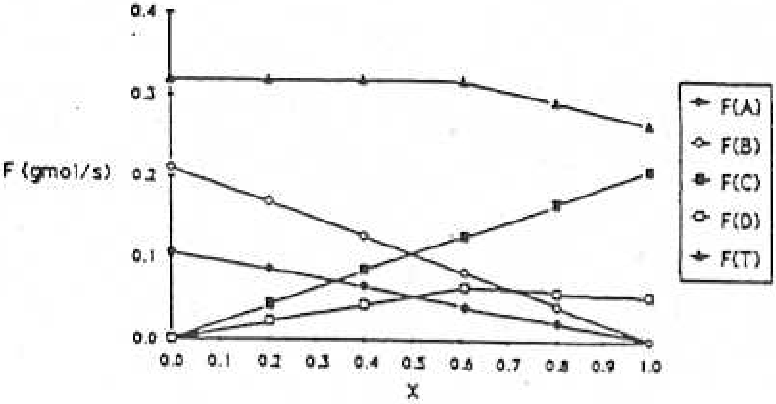


Figure P3-22a

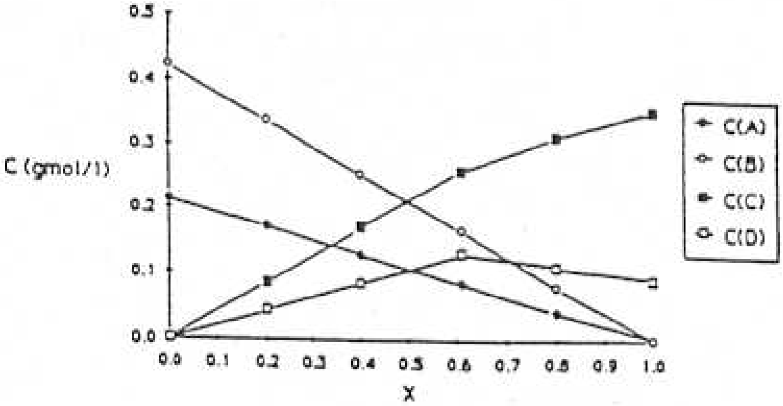


Figure P3-22b

P3-23

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	$12F_{A0}X$	$4F_{A0}X$

$$\theta_B = \frac{F_{B0}}{F_{A0}} = 1$$

$$y_{A0} = 0.5$$

$$\varepsilon = y_{A0}\delta = 0.5(1+12-3-4) = 3$$

P3-23 cont'd

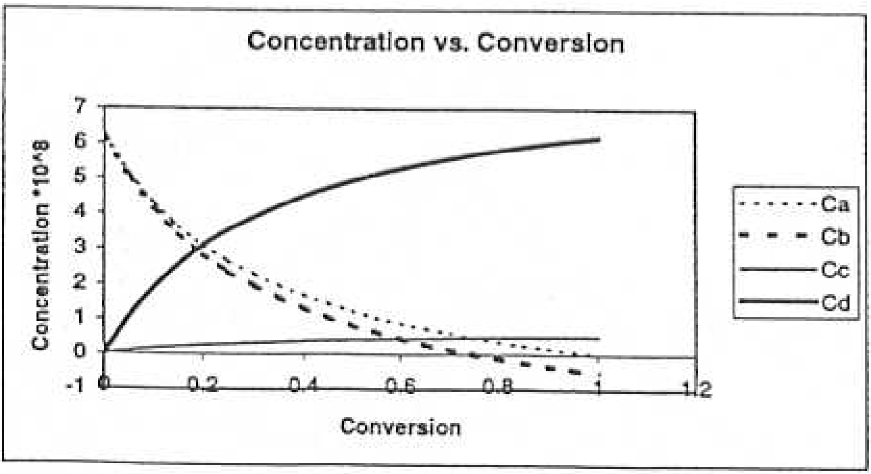
$$C_{A0} = y_{A0}C_{T0} = 0.5\left(\frac{P_0}{RT_0}\right) = 0.5\left(\frac{1Pa}{8314\frac{Pa*dm^3}{mol*k}*973K}\right) = 6.18*10^{-8}$$

$$C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X} = \frac{6.18*10^{-8}(1-X)}{1+3X}$$

$$C_B = \frac{1.68*10^{-8}\left(1-\frac{4X}{3}\right)}{1+3X}$$

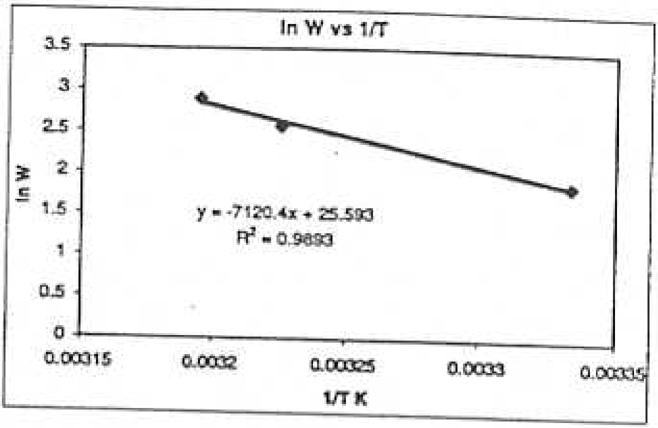
$$C_C = \frac{2.06*10^{-8}X}{1+3X}$$

$$C_D = \frac{2.47*10^{-7}X}{1+3X}$$



CDP3-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
a)

$$3\,Si\,HCl_3 + 3H_2 \rightarrow 2Si\,(S) + 7HCl + Si\,H_2\,Cl_2$$

Take $S_i\,HCl_3$ as basis

$$Si\,HCl_3 + H_2 \rightarrow \frac{2}{3}\,Si\,(s) + \frac{7}{3}\,HCl + \frac{1}{3}\,SiH_2Cl_2$$

CDP3-B cont'd

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

$$\varepsilon = y_{AO}\,\delta = \frac{1}{2}\left(\frac{1}{3} + \frac{7}{3} - 1 - 1\right)$$

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

$$C_{AO} = y_{AO}\frac{P_0}{R\,T_0} = \frac{1}{2}\left(\frac{2.0}{(0.082)(1327)}\right) \qquad C_{AO} = 0.0088\ \text{mol/dm}^3$$

$$C_A = \frac{F_A}{\upsilon} = C_{A0}\frac{(1-X)}{(1+\varepsilon X)} = \frac{0.0088\,(1-X)}{1+X/3}$$

$$C_B = \frac{F_B}{\upsilon} = C_A\frac{(\theta_B - X)}{(1+\varepsilon X)} = \frac{0.0088\,(1-X)}{1+X/3}$$

$$C_C = \frac{F_C}{\upsilon} = \frac{7}{3}\frac{F_{A0}X}{\upsilon_0(1+\varepsilon X)} = \frac{7}{3}C_{A0}\frac{X}{(1+\varepsilon X)} = 0.021\frac{X}{(1+X/3)}$$

$$C_D = \frac{F_D}{v} = \frac{1}{3}\frac{F_{A0}X}{v_0(1+\varepsilon X)} = 0.0031\frac{X}{1+X/3}$$

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-C Given : A + B -> C taking place in a square duct.

P_0 = 1 atm. = constant

$k = 10^6\ ft^3/(lb.mole)(sec.)$

$T = T_0 = 540°F = 1000°R$

$P_B^* = 0.25$ atm.

$F_{A0} = 1.5$ lb mole/sec.

(a) If B is at equilibrium in the gas phase throughout the reactor

$C_B = \frac{P_B^*}{RT}$ = 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, $\delta = 1 - 1 = 0$, $\varepsilon = Y_{A0}\delta$.

$-r_A = k\ C_A\ C_B = k\ C_{B0}\ C_{A0}[1-X]$; Just inside the reactor.

$$C_{A0} = \frac{y_{A0}P_0}{RT} = \frac{(1-y_{B0})P_0}{RT}$$

$$\therefore -r_A = k \hat{}\ \ C_B = k\ y_{B0}[1-y_{B0}]\ [\frac{P_0}{RT}]^2\ \ (1-X)$$

(b) At X = 0.5

$$-r_A = \frac{10^6 ft^3}{(lbmole)(sec)}\ \left[\frac{(.25\ atm)(.75\ atm)}{(\frac{.730\ atm\ ft^3}{lb\ mole\ °R} \times 1000°R)^2}\right]\ [0.5] = .174\ \frac{lbmole}{ft^3 sec.}$$

CDP3-D $CH_4(g) + 2\ Cl_2(g) \xrightarrow{hv} CH_2Cl_2(g,l) + 2HCl(g)$

(a)

Component	Symbol	Initial moles	Change	Out
Cl_2	A	1.0	$-X$	$1-X$
CH_4	B	0.5	$-0.5X$	$0.5(1-X)$
CH_2Cl_2	C	0	$+0.5X$	$0.5X$
HCl	D	0	$+X$	X
Total	T	1.5		1.5

(b) $\delta = 1 + 2 - 1 - 2 = 0$; $y_{A0} = 1.0$

$\varepsilon = y_{A0}\ \delta = 0$

CDP3-D cont'd

(c) System is gas phase until $P_c = 400$ mmHg

$$\frac{0.5X'}{1.5}(760) = 400$$

$\therefore X' = 1.5789 \longrightarrow CH_2\,Cl_2$ 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) $C_{AO} = y_{AO}\,\frac{P}{RT}$

$$C_{AO} = \frac{1}{1.5} = \frac{1}{0.08206}\;\frac{1}{298.2} = 0.02724\,\frac{gmol}{dm^3}$$

$$C_A = C_{AO}\,(1-X_A) = 0.02724\,(1-0.6) = 0.01090\,\frac{gmol}{dm^3}$$

(e) $-r_A = \frac{1}{2}\,k\,C_{AO}^3\,(1-X_A)^3$

$$-r_A = \frac{1}{2}\,(0.2)(0.02724)^3\,(1-0.6)^3$$

$$-r_A = 1.297 \times 10^{-7}\,\frac{gmol}{dm3\ s}$$

(f) $k = A\,\exp\left(-\frac{E}{RT}\right)$

$$A = 2 \times 10^{12}\,\frac{dm^6}{s\ gmol^2}$$

$$0.2 = 2 \times 10^{12}\,\exp\left(\frac{-E}{(8.314)(298.2)}\right) \quad \text{at } 25°C$$

$$E = 74212\,\frac{J}{gmol}$$

(g) At 100°C = 373.2 °K

$$\frac{k_{100}}{k_{25}} = \exp\left[-\frac{E}{R}\left(\frac{1}{373.2} - \frac{1}{298.2}\right)\right] = 409.8$$

$$k_{100°C} = 81.95\left(\frac{dm^3}{gmol}\right)^2 \frac{1}{S}$$

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

$\theta_B = C_{B0}/C_{A0} = 6/2=3$

$$X = \frac{N_{AO} - N_A}{N_{AO}}$$

$\theta_C = \theta_D=0$

$X=0.25$

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.

Chapter 4

General: I feel one of the purposes of the homework problem is to encourage th students to re-read the text and lecture notes. The problems in this chapter reinfor the algorithm that will be used throughout reaction engineering.

P4-1. This problem gives the guidelines for the students to develop origin problems. If you think other guidelines should be added send me an e-ma (sfogler@umich.edu) and I will see if they can be added to the next printing

P4-2. I would suggest assigning (a), perhaps (i) or (k) and then only one or two parts (b) through (i). The ones that are assigned could be alternated fro year to year.

P4-3. Shows a CRE application in the food industry.

P4-4. Many of our students are taking jobs in the food industry and General Mi provided this problem to give an example of reaction kinetics in the fo industry. This is a fairly straight forward problem.

P4-5. Liquid phase reaction in which parts (a-d) are quite straight forward provide a reinforcement of the CRE principles. Applied to a PFR and CST Part (e) is open-ended and requires some judgment. (There is not necessar one exact answer for part (e), it depends on the reactor down time is cho for emptying and filling and cleaning the reactor.) The problems given alternates are equally straight forward. The only problem more strai forward than this one is CDP4-J_B.

P4-6. Real liquid phase reaction and data. Parts (a-d) are fairly straight forward provide reinforcement of principles for liquid phase reactions. Part (e open-ended and is similar to part (e) for **P4-4**. **P4-4** and **P4-5** could alternated from year to year.

P4-7. A gas phase reaction with a change in the total number of moles volumetric flow rate v. If either **P4-4** or **P4-5** is assigned at the same time this problem, I would suggest assigning only parts (a) and (b) and perh part (e). In part (e) they must solve for X and different temperatures to the optimum. *(Also see CDP4-F_A for a gas phase reaction with a change the total number of moles. Problem CDP4-F_A, which was often assig from the second edition, is straight forward and reinforces the principles and can be alternated form year to year with* ***P4-7*** *problem.)*

P4-8. This problem is somewhat open-ended and requires some creativit figure why the pressure conversion is GREATER than the predi conversion. Ask the students to do some brainstorming. Depending on time available, I would only assign part (a), especially if part (e) of P4-7 is assigned at the same time.

P4-9. Troubleshooting Problem. Students need to brainstorm ideas of what could be wrong with the reactor. Troubleshooting problems are being given to our students more and more as first or second assignments in industry. Perhaps point out Kepner-Tregoe Strategies (See Ch.5 *Strategies for Creative Problem Solving*, , Prentice Hall, 1995).

P4-10. Parts (a), (b), and (c) are straight forward to calculate PFR and CSTR volumes and a batch reaction time. Part (d) is similar to Part (e) of **P4-4** and **P4-5**. This problem could be alternated with **P4-4** and **P4-5** from year to year.

Problems **P4-11**, **P4-12**, **P4-13**, **P4-14**, and **P4-15**. These problems are great motivators for the students because they show the competency level to obtain they must rise to pass the professional engineers exam. A few years ago, and it still may be true. The California exam was one of the toughest, if not the toughest in the nation. There was no curve, you had to have 75% to pass. There were six problems (stoichiometry, fluids, thermo, heat transfer, reaction engineering, and plant design) and you were given 3 hours (1/2 hour per problem).

P4-16. This problem requires a bit of thinking and manipulation of equaitons.

P4-17. The student cannot use any of the equations presented in the text thus far and must use a model balance to derive a new equation relating conversion and distance. This problem also serves as a motivational problem because it shows how CRE principles are applied to the new field of ECOLOGICAL ENGINEERING. Parts of this problem are solved on the web module "Wetlands".

Problems P4-18, P4-19, P4-20, P4-21, P4-22, P4-23, and P4-24. are all problems involving pressure drop.

P4-18. Straight forward reinforcement of CRE principles. This problem is similar to **P4-22**.

P4-19. Trial and error solution using POLYMATH neither the specific reaction rate constant, k, or the pressure drop parameter, α, are given.

P4-20. Trial and error using POLYMATH. This problem is a much shorter version of the analysis required in P4-21.

P4-21. Parts (a) and (b) are straight forward, plug and chug calculations. Parts (c) through (g) requires some analysis. This problem can be quite long depending on how may parts are assigned.

P4-22. Fairly straight forward problem using POLYMATH. Alternate to **P4-20**.

P4-23. Tough problem. Need to solve for the conversion several times to plot conversion vs. particle diameter in order to find the optimum catalyst size.

P4-25. Reinforces that the algorithm can be applied to a reactor of a completely different slope, a spherical reactor. Fairly straight forward problem using POLYMATH.

P4-26. This straight forward problem is the recommended problem to assign to reinforce the principles of semibatch reactors.

P4-27. This problems is an alternative to P4-26. Also see CDP4-I$_B$ and CDP4-J$_B$.

P4-28. Tough problem involving CSTR with recycle.

P4-29. Apply the unsteady state mole balances to three CSTRs in series. Use POLYMATH to solve three coupled ODEs.

P4-30. Membrane reactor. There should be enough time for the students to carry out part (d) parameter variation and ask *"What if. . ."* questions.

P4-31. Membrane reactor problem that is an alternative to P4-30.

CDP4-A Good problem concerning batch reactions. solved on the web.

CDP4-B Alternative to problem P4-17.

CDP4-C Reversible batch reaction.

CDP4-D Alternative to CDP4-13.

CDP4-E California problem that takes 30 minutes to solve.

CDP4-F Very straight forward problem. Good to reinforce principles

CDP4-G Optimization problem - not too straight forward.

CDP4-H Very straight forward batch reactor.

CDP4-I Semibatch - alternative to P4-26.

CDP4-J Most straight forward problem in the chapter.

Problems CDP4-K through CDP4-M all involve recycle.

CDP4-N Radial flow reactor. New equations must be derived.

CDP4-O Bacteria growth in a batch reactor.

CDP4-P Fairly straight forward California registration problem where you must carry out a number of calculations involving conversion factors to calculate CSTR and PFR reactor volumes and a batch reaction time.

CDP4-Q I might assign this again if hell freezes over.

Summary

	Assigned	Alternates	Difficulty	Time	Solution Given
P4-1	O	8		--	No
● P4-2				30	Yes
P4-3	I		SF	20	Yes
P4-4	I	A,C,D,O*	SF	30	Yes
● P4-5		7(a,b),10(a,b),F,H,J	SF	60	Yes
● P4-6		7,10,16,	FSF	75	Yes
P4-7	A A	5,6,F,G,H,J	FSF	60	Yes
● P4-8		1		25	Yes
P4-9	O			25	Yes
P4-10	A A	5,6,7,F,G,H	FSF	60	Yes
P4-11	A A	12,13,14,15,E	FSF	40	Yes
● P4-12	A A	11,13,14,15,E	FSF	40	Yes
● P4-13	A A	11,12,14,15,E	FSF	40	Yes
P4-14	A A	11,12,13,15,E	FSF	40	Yes
P4-15	A A	11,12,13,14,E	FSF	40	Yes
P4-16	I	5,A,C,D		30	Yes
P4-17	O	B		35	Yes
● P4-18	A A	19,24	SF	45	Yes
P4-19	A A	18,24	SF	45	Yes
P4-20	A A	21,22,23		60	Yes
P4-21	A A	20,22,23		60	Yes
P4-22	A A	20,21,23	FSF	60	Yes
● P4-23	A A	20,21,22	FSF	75	Yes
P4-24	I			45	Yes
● P4-25				2	Yes
P4-26	A A	27,I,J,Q		60	Yes
P4-27	A A	26,I,J,Q		60	Yes
P4-28	S			50	Yes
P4-29	S			60	Yes
P4-30	A A	31		45	Yes
P4-31	A A	30		45	Yes
CDP4-A	A A	4,C,D	SF	45	Yes
CDP4-B		17	SF	45	Yes
CDP4-C	A A	A,D,O,4	SF	45	Yes
CDP4-D	A A	A,C,O,4	SF	45	Yes
CDP4-E	A A	11,12,13,14,15		40	Yes

●	CDP4-F	A	4,J	SF	60	Yes
	CDP4-G	AA	F,H,5,6,7,10,	SF	30	Yes
	CDP4-H				30	Yes
	CDP4-I	AA	26,27,Q		60	Yes
●	CDP4-J		26,27,Q		45	Yes
	CDP4-K		L,M		50	Yes
	CDP4-L		K,M		50	Yes
	CDP4-M		K,L		50	Yes
	CDP4-N				50	Yes
	CDP4-O	AA	A,C,4		50	Yes
	CDP4-P				60	Yes
	CDP4-Q		26,27,I,J		45	Yes

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 th problems, either the problem with a dot or any one of the alternates ar always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve th problem.

Difficulty

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

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

Table 4.1 Solution Manual

	CSTR	PFR	Membrane Reactor	PBR ΔP	Batch Reactor	Semibatch Reactor
Liquid Phase	5,6,8,28	5,6,17			3,6,7,10	26,27
Gas Phase	9,10	7,10		18,19,20, 21,22,23, 24		
Straight Forward	7(a),10(c), F,J	5(a,b), 10(b),18	30,31	18,20	4,5(b,c), 10(a),C,D, H	26,27
Fairly Straight Forward	3	11		20	10(e),A	
More Difficult	7(d),14,16, B,P	2(h),7(d), 13,15,19, P,N		23,24	3,5(e),6(e), 7(c,d),E,O	
Intermediate Calculations		12,13,14		19		
Parameter Variation	7(e),8(b), 29(e)	17(d)	2(f),30(e)	2		26(e)
Competing Effects	6(e),7(e)			23		
Open-ended	2(j,k),8,9, 17(f)		31(e)		6(e)	
Critical Thinking	4(f),5(f), 19(c)	4(f),5(f)		20(c)	26(f), 27(d)	

Chapter 4

P4-1 No solution will be given.

P4-2

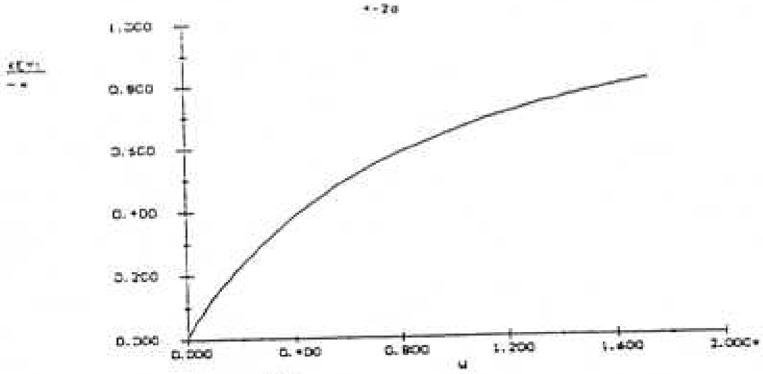
(a) Cooking food (effect of temperature), removing a stain with bleach (effect of bleach concentration), dissolution of sugar in coffee or tea.

(b) Accept catalyst:
  1) X is small and pressure drop is unaffected
  2) cost savings

Reject catalyst:
  1) Pressure drop now too high therefore lower conversion
  2) Catalyst not as active as it should be

(c) Bad idea for 100 tubes in series. Pressure drop will be too great because of greater mass flow rate through a single tube and because of the tube length.

(d) Using POLYMATH and the set of equations given in example 4-8, graph conversion as a function of catalyst weight:



$$\alpha = \frac{2\beta_0}{A_c\rho_c(1-\phi)P_o} \qquad (4\text{-}29)$$

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3}[small + 1.75G] \qquad (E4.\text{-}8.7)$$

$$\frac{\beta_0}{P_0} - \frac{1}{DP_0}$$

$$\frac{1}{\frac{1}{5} * \frac{5}{1}} = 1$$

Therefore, there is no effect. In future experiments, run it so that they do not increase and decrease at the same rate.

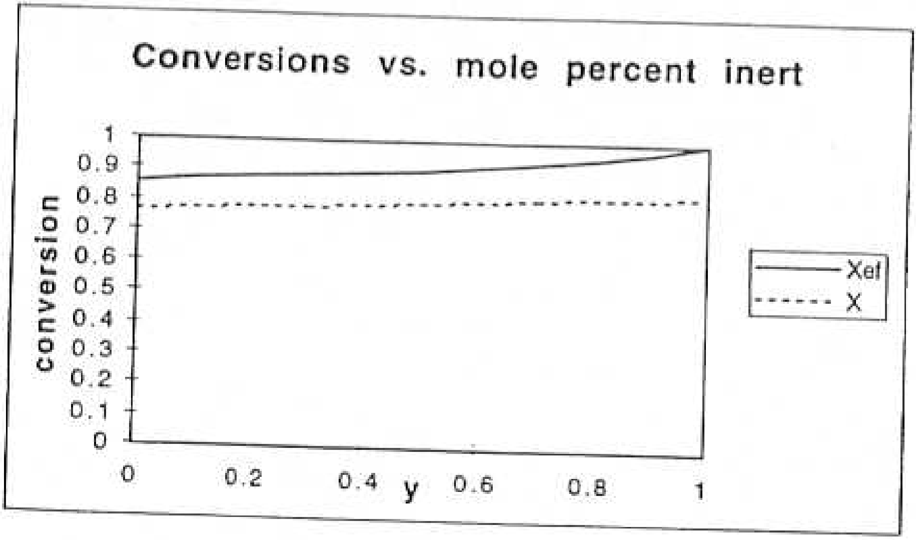
e) To determine the equilibrium conversion use the following equation

$$Xef = \sqrt{\frac{K_c * (1 - Xef) * (1 + \varepsilon X)}{4C_{A0}}}$$

have C_{A0} be a function of the mole fraction of inert and plug it into POLYMATH and change the inert value from 0 to .9 record the results. To determine final conversion use the POLYMATH program given in the example and make F_{A0} a function of the mole fraction of the inert and use the equation

$$X = \frac{F_{A0} - F_A}{F_{A0}}$$

to find the conversion. Record the results and graph the two conversions as a function of mole fraction:



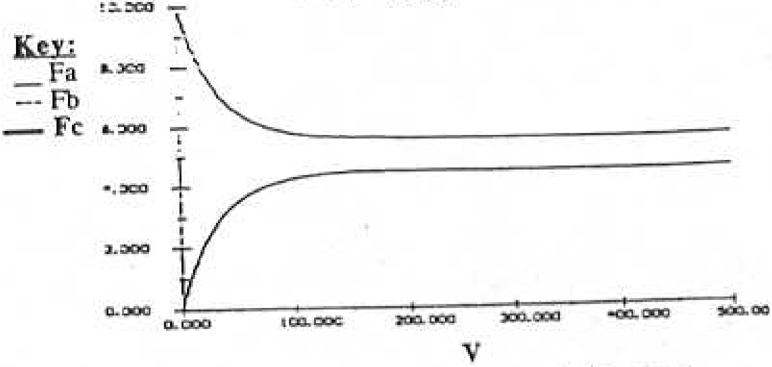
The advantages of the inert are obvious by the graph; as more inert is added the conversion increases. The disadvantage is that the more inert you add the less of A you will have and thus the less of B you will create.

(f) The following graphs show the flow rates of A,B, and C as a function of volume. Each graph represents a different k_c value.

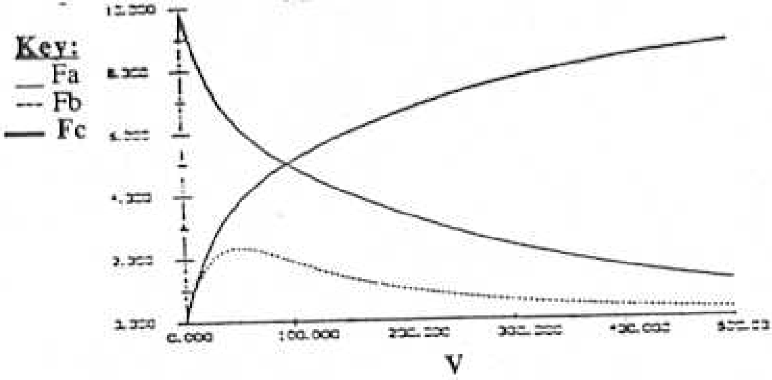
For k_c values not shown it should be noted that as k_c increases, the maximum value of F_B decreases, while the other flow rates are mostly unaffected.

4-2 cont'd

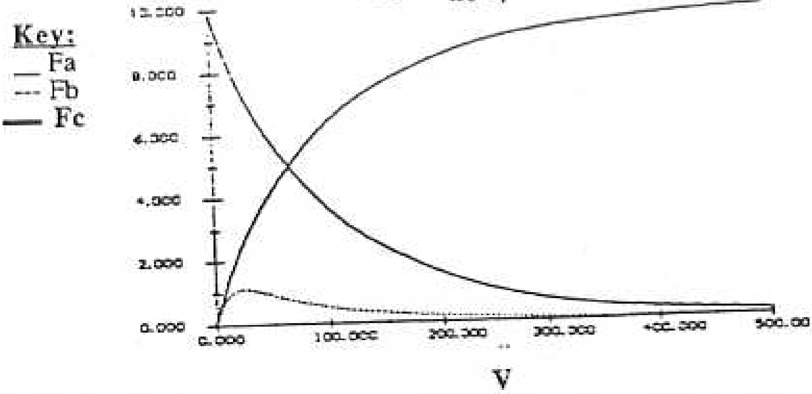
4-2f kc=0



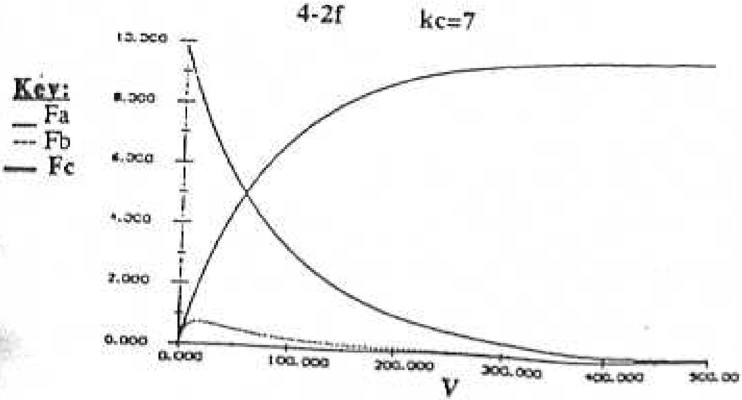
4-2f kc=1



4-2f kc=4

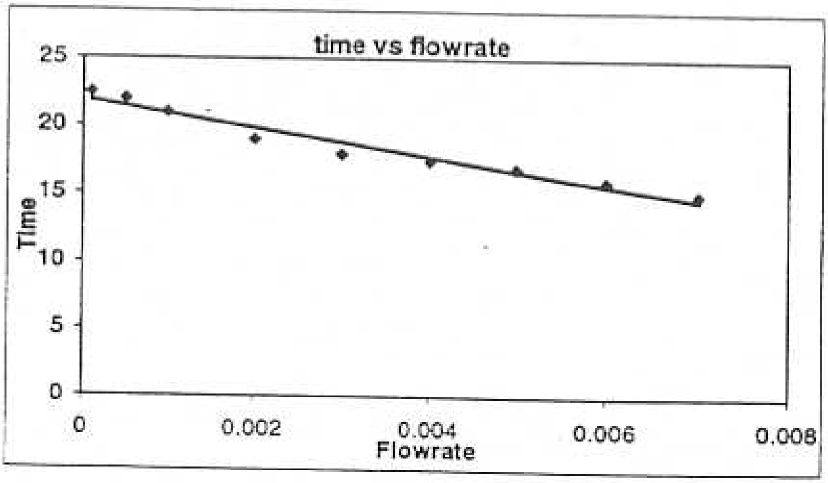


4-2 cont'd



By varying the parameters, k,k_c,K_c,F_{A0}, it can be determined that keeping the k to k_c ratio high would optimize the process getting the reaction done in less volume. K_c has little effect on the reaction as a whole. Keeping F_{A0} low also helps keep the volume down, but on the other hand it keeps it from having too much reacted. If the temperature were raised the volume needed would decrease.

g)



The maximum concentration of C and D in Example 4-22 is the derivative of C_A set to equal zero.

$$\frac{dC_C}{dt} = kC_AC_B - \frac{v_0 C_C}{V} = 0$$

$$\frac{dC_D}{dt} = kC_AC_B - \frac{v_0 C_D}{V} = 0$$

h) If one substitutes the numbers

$$\text{profit} = \left[.150\frac{\text{lb mol}}{\text{s}} * 44.04 * 3600 * 24 * 365 * .6\right] -$$
$$[0.04 * .425 * 30.06 * 3600 * 24 * 365]$$
$$-[0.043 * 0.0736 * 3600 * 24 * 365] - 8{,}000{,}000 = 92 million$$

$$[200{,}000{,}000 * 0.38] - ([0.04 * .425 * 30.06] - [0.043 * 0.0736]) * 3600 * 24 * 365 = 52 \text{ million}$$

they will not make as much money

It looks unfavorable. However, ethylene oxide is dangerous to transport and therefore, it will be made at the same location.

i)

$$\tau = \tau_0 + t \qquad \tau_0 = \frac{V_0}{v_0}$$

mole balance goes to :

$$C_{B0} - C_B(1 + k\tau_0) = \tau\frac{dC_B}{d\tau}$$

$$\frac{C_{B0}}{1 + \tau k} - C_B = \frac{\tau}{1 + k\tau_0}\frac{dC_B}{d\tau}$$

$$\frac{1 + k\tau_0}{\tau}d\tau = \frac{dC_B}{\frac{C_{B0}}{1 + \tau k} - C_B}$$

$$1 + k\tau_0 \ln\tau = \ln\frac{\frac{C_{B0}}{1 + k\tau_0}}{\frac{C_{B0}}{1 + k\tau_0} - C_B}$$

$$In\,\tau^{1+k\tau}\Big|_{\tau_0}^{\tau} = \ln\frac{\frac{C_{B0}}{1 + k\tau_0}}{\frac{C_{B0}}{1 + k\tau_0} - C_B}$$

$$\ln\left(\frac{\tau_0}{\tau}\right)^{(1+k\tau_0)} = \ln\frac{\frac{C_{B0}}{1 + k\tau_0}}{\frac{C_{B0}}{1 + k\tau_0} - C_B}$$

4-2 **cont'd**

$$\left(\frac{\tau_0}{\tau}\right)^{(1+k\tau_0)} = \frac{\dfrac{C_{B0}}{1+k\tau_0}}{\dfrac{C_{B0}}{1+k\tau_0} - C_B}$$

$$\left(\frac{\tau}{\tau_0}\right)^{-(1+k\tau_0)} = \frac{\dfrac{C_{B0}}{1+k\tau_0} - C_B}{\dfrac{C_{B0}}{1+k\tau_0}}$$

$$C_B = \frac{C_{B0}}{1+k\dfrac{V_0}{v_0}}\left[1-\left(\frac{V_0+v_0t}{V_0}\right)\right]$$

j) Immediately flush eyes or skin with lots of water for at least 15 minutes while removing contaminated clothing.

k) Ethylene oxide-Use safety goggles, use butyl rubber gloves, Keep from fire, prevent contact with air.

Bromine cyanide-use in closed system with a vent, use protective clothing and gloves, safety goggles, prevent contact with warm surfaces.

P4-3.

Location	Elevation	Pressure	Boiling Pt.	Time
	km	mm Hg	°C	min
Ann Arbor	0.21	739	99.2	15
Boulder	1.630	625	94.6	17
Cuzco	3.416	493	88.3	?

Assume reaction is zero order with respect to spaghetti conversion:

$$-r_A = k = Ae^{-E/RT} = -\frac{dC_A}{dt}$$

So

$$-C_A \Big|_{C_{Ao}}^{C_A} = (Ae^{-E/RT})t$$

For complete conversion (i.e.: well cooked) $C_A = 0$ at time t

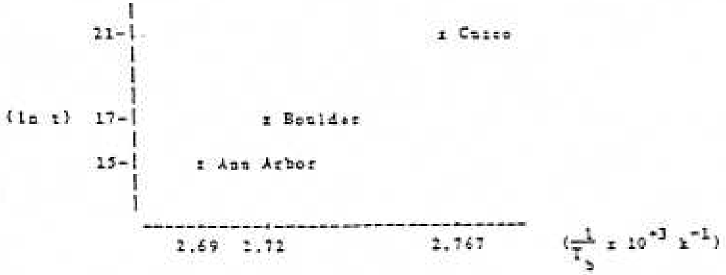
Therefore

$$C_{Ao} = Ae^{-E/RT}t$$

$$\frac{C_{Ao}}{A} = t\ e^{-E/RT}$$

$$\ln(C_{AO}/A) = \ln k = \ln t - \frac{E}{R}\frac{1}{T_b}$$

--> Can plot the natural log of the cooking time vs. $\frac{1}{T_b}$ and get a linear relationship. Extrapolation to T_b = 88.3°C = 361.45 K yields t = 21 minutes



P4-4. Assume constant volume batch reactor.

Mole balance:
$$C_{AO}\frac{dX}{dt} = -r_A$$

Rate law and stoichiometry:
$$-r_A = kC_A = kC_{AO}(1-X)$$

Specific reaction rate:
$$k(25°C) = .0022 \text{ weeks}^{-1}$$

Combine:

$$t = C_{AO}\int_0^X \frac{dX}{kC_{Ao}(1-X)} = \frac{-1}{k}\ln(1-X)$$

$$52.2 weeks = \frac{-1}{.0022 weeks^{-1}}\ln(1-X)$$

$$X = .108$$

$$C_A = C_{AO}(1\text{-}X)$$

Since, volume and molecular weight are constant the equation can be rewritten as

$$m_A = m_{AO}(1\text{-}X)$$

$$6500 \text{ IU} = m_{AO}\,(1\text{-}0.108)$$

$$m_{AO} = 7287 \text{ IU}$$

$$\%OU = \frac{C(t=0) - C(t=1yr)}{C(t=1yr)} X100 = 12.1\%$$

P4-4 (cont'd)

b) Serving size = 30 g. 10,000,000 lbs/year (4.58×10^9 g/year)of cereal made.

Number of servings per year = $(4.58 \times 10^9)/30 = 1.51 \times 10^8$

Each serving uses excess of 787 IU (1.02×10^{-6} lb) of nutrients.

Total excess per year = $(1.51 \times 10^8) * (1.02 \times 10^{-6}) = 154.11$ lb/year

Total overuse cost = \$5/lb * 154.11 lb/year = \$770.60/year

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.

d) $k(40°C) = 0.0048\ \text{weeks}^{-1}$ 6months = 26 weeks

$$t = C_{AO}\int_0^X \frac{dX}{kC_{Ao}(1-X)} = \frac{-1}{k}\ln(1-X)$$

$$26weeks = \frac{-1}{.0048weeks^{-1}}\ln(1-X)$$

$$X = 0.12$$

$$C_A = C_{AO}(1-X)$$

Since, volume and molecular weight are constant the equation can be rewritten as

$$m_A = m_{AO}(1-X)$$

$$6500\ \text{IU} = m_{AO}(1-0.108)$$

$$m_{AO} = 7367.12\ \text{IU}$$

$$\%OU = \frac{C(t=0) - C(t=1/2yr)}{C(t=1/2yr)} X100 = 13.34\%$$

P4-5. $A + B \Rightarrow C$

$C_{AO} = C_{BO} = 2\ \text{mol/dm}^3$ $k_1 = 0.07\ \text{dm}^3\text{/mol/min}$

$v_A = v_B = 5\ \text{dm}^3\text{/min}$ $E_A = 20{,}000\ \text{cal/mol}$

$T_1 = 300\text{K}$

Rate Law: $r_A=-kC_AC_B$ $C_A=C_{AO}(1-X)$ $C_j=F_{jo}/v_j$

a) <u>CSTR</u> $V=200\ \text{dm}^3$ $T=350\ \text{K}$

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

$$X = \frac{(200dm^3)(8.45\dfrac{dm^3}{mol*\min})(1\dfrac{mol}{dm^3})^2(1-X)^2}{10\dfrac{mol}{\min}}$$

From the quadratic equation: $X=0.925$

<u>PBR</u> $V=800\ \text{dm}^3$ $T=300\text{K}$

Design Equation:

$$F_{AO}\frac{dX}{dV} = -r_A$$

$$dX = \frac{(0.07\dfrac{dm^3}{mol*\min})(1\dfrac{mol}{dm^3})^2(1-X)^2}{10\dfrac{mol}{\min}}dV$$

$$\int_0^X \frac{dX}{(1-X)^2} = 0.007\int_0^{800} dV$$

$$X = 0.85$$

P4-5 (cont'd)

b) <u>Batch Reactor</u> V=200dm^3 N_{AO}=N_{BO}=200 moles X=0.90 Assume Isothermal

Design Equation:

$$t = N_{AO}\int_0^X \frac{dX}{-r_A V}$$

$$t = \frac{(200 moles)}{(8.45\frac{dm^3}{mol * \min})(1\frac{mol}{dm^3})^2(200dm^3)}\int_0^{.9}\frac{dX}{(1-X)^2}$$

$$t = 1.06 \min$$

c) T=273 K

Find the specific reaction rate at the new temperature of 273 K using the Arrhenius Equation.

$$k = 2.54 \times 10^{-3}$$

$$t = \frac{(200)(9)}{(2.54 \times 10^{-3})(200)} = 3543 \text{ min} = 2.5 \text{ days}$$

d) At higher temperatures the rate of the reaction may be extremely high. If the reaction is extremely exothermic, the temperature in the reactor may get too high making the process unsafe.

e) Assume for each batch it takes three hours to fill, empty, clean, and heat to the reaction temperature. The reaction takes one minute to complete, therefore we can carry out eight batches a day.

In one day, the reactor processes: (10 mol/min)(60 min/hr)(24 hr/day) = 1800 mol/batch

$$C_{Ao} = \frac{1 \text{ mol}}{\text{dm}^3} = \frac{N_{Ao}}{V} = \frac{1800 \text{ mol}}{V}$$

$$V = 1800 \text{ dm}^3$$

Use a 500 gallon reactor at a cost of $67,000. (1997 prices)

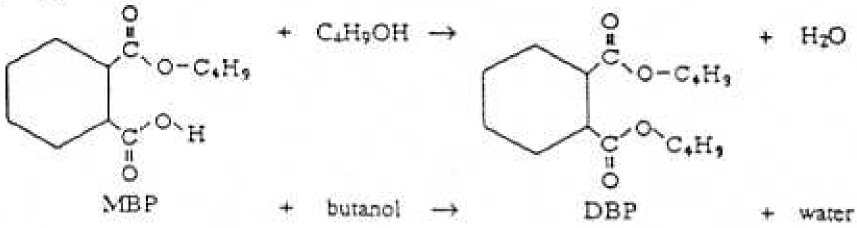
f) The points of the problem are:

(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 $F_{butanol} = 5\,F_{MBP,O}$

$-r_A = k\,C_A\,C_B$ elementary reaction

$-r_A = k\,(F_A/\upsilon)\,(F_A/\upsilon)$ for liquid systems

volumetric flow $\upsilon = \upsilon_O$

$$\boxed{-r_A = k\,C_{AO}^2\,(1-X)\,(5-X)}$$

$$V_{CSTR} = \frac{F_{A0}X}{-r_A} = \frac{F_C}{kC_{A0}^2(1-X)(5-X)}$$

$\dot{m}_c = 4 \times 10^6 \frac{lb}{yr}$, $F_C = 4 \times 10^6$ lb / yr , 30d / yr operation

$$F_C = 4 \times 10^6 \frac{lb}{yr} \times \frac{1\ yr}{30d}\ \frac{1\ d}{24\ hr} \times \frac{1\ lb\ mol}{278\ lb} = 20.0\ \frac{mol}{hr}$$

$$V_{CSTR} = 1000\ gal \times \frac{1\ ft^3}{7.48\ gal} = 133.7\ ft^3$$

$$133.7\ ft^3 = \frac{20\ lbmole/hr}{1.2\ \frac{ft^3}{lbmole \bullet hr}\left(\frac{0.2\ lbmole}{ft^3}\right)^2 (1-X)\,(5-X)}$$

$$X^2 - 6X + 1.89 = 0$$

$$X = 0.33$$

b) To increase conversion, X, use PFR, higher temperature, θ_B, or use a better catalyst.

P4-6 (cont'd)

(c)

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

RL $$-r_A = kC_AC_B$$

S $$C_A = C_{A0}(1-X)$$ $$C_B = C_{A0}(5-X)$$ $$F_{A0} = \frac{1\ \text{lbmol}}{\text{min}} = \frac{60\ \text{lbmol}}{\text{hr}}$$

C $$V = \frac{F_{A0}X}{kC_{A0}^2(1-X)(5-X)}$$

E $$V = \frac{(60\ \text{lbmol/h})(.85)}{\left(\frac{1.2\text{ft}^3}{\text{lbmol}\cdot\text{h}}\right)\left(\frac{0.2\text{lbmol}}{\text{ft}^3}\right)^2(1-.85)(5-.85)}$$

d) PFR Design Equation

$$\frac{dX}{dV} = \frac{-r_a}{F_{A0}}$$

$$\frac{dX}{dV} = \frac{kC_{A0}^2(1-X)(5-X)}{F_{A0}}$$

$$V = 535dm^3$$

e) Mw (DBP) = 278 lb/lbmol V=1000gal = 133.7 ft^3

therefore 14.4 X 10^3 lbmol of DBP need to be produced in 30 days

Mole balance: $$t = N_{A0}\int_0^X \frac{dX}{-r_AV}$$

$$t = \frac{1}{kC_{A0}}\frac{1}{(5-1)}\ln\left(\frac{5-X}{5(1-X)}\right)$$

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?

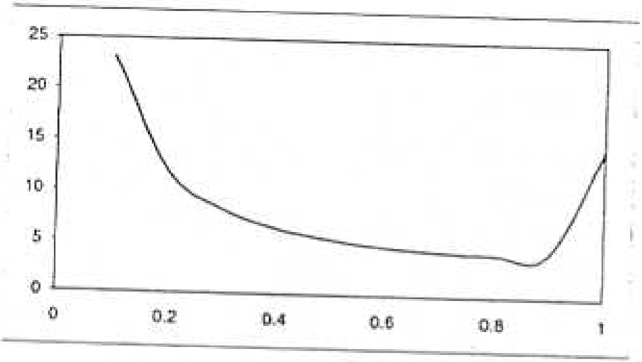
$$N_{A0} = 133.7\text{ ft}^3 * C_{A0} \qquad C_{A0} = 0.2lbmol/ft^3$$

$$\frac{\text{Product}}{reactor * day} = \frac{N_{A0}X * 24hr}{t_{batch}} = \frac{N_{A0}X24}{t_{rxn}+3} = \frac{N_{A0}X24}{\frac{1}{kC_{A0}}\ln\left(\frac{5-X}{5-5X}\right)+3} = f(X)$$

$$\frac{Moleproduct}{day} = \frac{4*10^6 lbs}{30days}\frac{lbmol}{278lb} = 480\frac{mol}{day}$$

$$n = \frac{480mol/day}{f(X)mol/day/reactor}$$

P4-6 (cont'd)



The minimum occurs at X = 0.82 and corresponds to 4.192 or 5 reactors

P4-7 (a)

$$A \rightarrow B + 2C$$

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

$$-r_A = kC_A$$

$$C_A = C_{A0}\frac{(1-X)}{(1+\varepsilon X)} \qquad \varepsilon = y_{A1}\delta = (1)(2+1-1) = 2$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{10}{(0.082)(400)} = 0.3\,\frac{\text{mol}}{\text{dm}^3}$$

$$V = \frac{F_{A0}X(1+\varepsilon X)}{C_{A0}k(1-X)}$$

$$k = 10^{-4}e^{\frac{85{,}000}{8.31}\left(\frac{1}{323}-\frac{1}{400}\right)} = 0.044$$

$$V = \frac{(2.5\,\text{mol/min})(0.9)(1+2(.9))}{(0.044\ \text{m}^{-1})(0.3\,\text{mol/dm}^3)(1-.9)} = 4772\ \text{dm}^3$$

(b)

$$V = F_{A0}\int_0^x \frac{dX}{-r_A} = \frac{F_{A0}}{kC_{A0}}\int_0^x \frac{(1+\varepsilon X)}{(1-X)}dX$$

$$= \frac{F_{A0}}{kC_{A0}}\left[(1+\varepsilon)\ln\frac{1}{1-X} - \varepsilon X\right]$$

$$= \left(\frac{(2.5\,\text{mol/min})}{(0.044\ \text{min}^{-1})(0.3\,\text{mol/dm}^3)}\right)\left((1+2)\ln\frac{1}{1-.9} - 1.8\right)$$

$$= (189.4\ \text{dm}^3)(5.11)$$

$$V = 967\ \text{dm}^3$$

P4-7 (cont'd)

(d) $A \Leftrightarrow B + 2C$

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: $C_A = \dfrac{C_{A0}(1-X)}{1+\varepsilon X}$, $C_B = \dfrac{C_{A0}X}{1+\varepsilon X}$, $C_C = \dfrac{2C_{A0}X}{1+\varepsilon X}$

$$K_C = \frac{C_B C_C^2}{C_A} = \left(\frac{C_{A0}X}{1+\varepsilon X}\right)\left(\frac{2C_{A0}X}{1+\varepsilon X}\right)^2\left(\frac{1+\varepsilon X}{C_{A0}(1-X)}\right) = \frac{4C_{A0}^2X^3}{(1+\varepsilon X)^2(1-X)}$$

$\varepsilon = 2$ and $C_{A0} = 0.3$

$X_{eq} = 0.52$

$X = (0.90)X_{eq} = 0.47$

CSTR

$$-r_A = \frac{kC_{A0}}{(1+\varepsilon X)}\left((1-X) - \frac{4C_{A0}^2X^3}{(1+\varepsilon X)^2K_C}\right)$$

$$V = \frac{F_{A0}X(1+\varepsilon X)}{kC_{A0}\left((1-X) - \dfrac{4C_{A0}^2X^3}{(1+\varepsilon X)^2K_C}\right)} = \frac{(2.5\text{ mol/min})(0.47)(1+2(0.47))}{(0.044\text{ min}^{-1})(0.3\text{ mol/dm}^3)\left((1-0.47) - \dfrac{4(0.3\text{ mol/dm}^3)^2(0.47)^3}{(1+2(0.47))^2 0.025}\right)}$$

$V = 1300\text{ dm}^3$

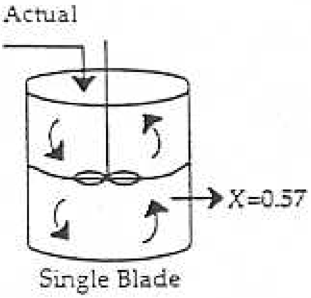
PFR

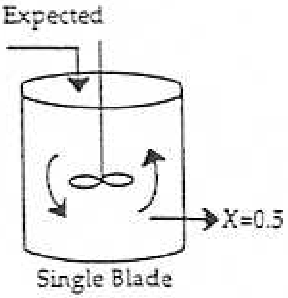
$F_{A0}\dfrac{dX}{dV} = -r_A$ or $\dfrac{dV}{dX} = \dfrac{F_{A0}}{-r_A}$

$$-r_A = \frac{kC_{A0}}{(1+\varepsilon X)}\left((1-X) - \frac{4C_{A0}^2X^3}{(1+\varepsilon X)^2K_C}\right)$$

Using these equations in the POLYMATH program below we get the volume to be 290 dm^3.

P4-8





P4-7 (cont'd)

c) $$t = C_{A0}\int_0^X \frac{dX}{-r_A} = \frac{1}{0.044\ \text{min}^{-1}}\int_0^X \frac{1+2X}{1-X}dX = 116\ \text{min}$$

It takes 116 min for the reaction to reach 90% conversion in the batch reactor. Assume that down time (table 4-1) is six hours (360 min.).

Therefore, total cycle time = 116min + 360min =476min

In one day there are 1440/476 = 3.03 ~ 3 runs

Therefore N_{A0} = 3600/3 = 1200 moles

Volume Calculations:

$$t = \frac{N_{A0}}{V}\int_0^X \frac{dX}{-r_A} =$$

$$116\ \text{min} = \frac{1200 mole}{V * 0.044\ \text{min}^{-1} * 3\dfrac{mole}{dm^3}}\int_0^X \frac{1+2X}{1-X}dX$$

$$V = 4000 dm^3$$

(d) A ⇔ 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 : $C_A = \dfrac{C_{A0}(1-X)}{1+\varepsilon X}$, $C_B = \dfrac{C_{A0}X}{1+\varepsilon X}$, $C_C = \dfrac{2C_{A0}X}{1+\varepsilon X}$

$$K_C = \frac{C_B C_C^2}{C_A} = \left(\frac{C_{A0}X}{1+\varepsilon X}\right)\left(\frac{2C_{A0}X}{1+\varepsilon X}\right)^2\left(\frac{1+\varepsilon X}{C_{A0}(1-X)}\right) = \frac{4C_{A0}^2X^3}{(1+\varepsilon X)^2(1-X)}$$

$\varepsilon = 2$ and $C_{A0} = 0.3$

$X_{eq} = 0.52$

$X = (0.90)X_{eq} = 0.47$

<u>CSTR</u>

$$-r_A = \frac{kC_{A0}}{(1+\varepsilon X)}\left((1-X) - \frac{4C_{A0}^2X^3}{(1+\varepsilon X)^2K_C}\right)$$

$$V = \frac{F_{A0}X(1+\varepsilon X)}{kC_{A0}\left((1-X) - \dfrac{4C_{A0}^2X^3}{(1+\varepsilon X)^2K_C}\right)} = \frac{(2.5\ \text{mol/min})(0.47)(1+2(0.47))}{(0.044\ \text{min}^{-1})(0.3\ \text{mol/dm}^3)\left((1-0.47) - \dfrac{4(0.3\ \text{mol/dm}^3)^2(0.47)^3}{(1+2(0.47))^2 0.025}\right)}$$

$V = 1300\ \text{dm}^3$

P4-8 (cont'd)

Predicted

$$V=\frac{F_{A0}X(1+\varepsilon X)}{C_{A0}^2k(1-X)^2}=a\frac{X}{(1-X)^2}$$

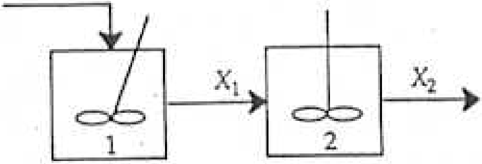
$$[a]=\frac{F_{A0}}{C_{A0}^2k}=\frac{\frac{\text{mol}}{\text{min}}}{\frac{\text{gal}}{\text{mol min}}\left(\frac{\text{mol}}{\text{gal}}\right)^2}$$

$$a=[\text{gal}]$$

$$1000\text{ gal}=a\frac{X}{(1-X)^2}=a\frac{.5}{.25}=2a$$

$$a=500\text{ gal}$$

Measured



$$V=a\frac{X}{(1-X)^2}\text{ For Reactor 1}$$

$$500\text{ gal}=\frac{500\text{ gal }X_1}{(1-X_1)^2}$$

$$1-2X_1+X_1^2=X$$

$$1-3X_1+X_1^2=0$$

$$X_1=\frac{3\sqrt{9-4}}{2}=.38$$

Reactor 2

$$500=\frac{500\,(X_2-.38)}{(1-X_2)^2}$$

$$1-2X_2+X_2^2=X_2-.38$$

$$X_2^2-3X+1.38=0$$

$$X_2=\frac{3\pm\sqrt{9-4(1.38)}}{2}=.57$$

P4-10

(a) Benzene is A

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

for equilibrium $-r_A = 0 \quad \therefore \quad C_A^2 - \frac{C_B C_C}{K_C} = 0$

$$C_A^2 = \frac{C_B C_C}{K_C}$$

$$C_A = C_{Ao}(1-X) \quad C_B = \frac{C_{Ao}X}{2} \quad C_c = \frac{C_{Ao}X}{2}$$

$$C_{Ao}^2(1-X_e)^2 = \frac{C_{Ao}^2 X_e^{\,2}}{4K_e}$$

$$4K_e(1-X_e)^2 = X_e^{\,2}$$

$$4K_e - 8K_eX_e + 4K_eX_e^{\,2} = X_e^{\,2}$$

$$0.2X^2 - 2.4X_e + 1.2 = 0$$

$$X_e = 0.52$$

(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 : $C_A = C_{Ao}(1-X) \quad C_B = \frac{C_{Ao}X}{2} \quad C_c = \frac{C_{Ao}X}{2}$

$$C_{Ao} = \frac{P}{RT} = \frac{5\ \text{atm}}{\left(0.73\frac{\text{ft}^3\cdot\text{atm}}{\text{lbmol}\cdot{}^\circ\text{R}}\right)(1859.67^\circ\text{R})} = 0.0037\frac{\text{lbmol}}{\text{ft}^3}$$

P4-10 (cont'd)

Combine:
$$V = \frac{F_{A0}}{kC_{A0}^2}\int_0^X \frac{dX}{\left[(1-X)^2 - \frac{X^2}{4K_c}\right]}$$

$$V = \frac{(10\,\text{lbmol/min})(1\,\text{min}/60\text{s})}{(1800\,\text{ft}^3/\text{lbmol}\cdot\text{s})(0.0037)^2}\int_0^X \frac{dX}{\left[(1-X)^2 - 0.833X^2\right]}$$

$$V = 6.76\,\text{ft}^3\int_0^X \frac{dX}{\left[1-2X+0.167X^2\right]}$$

$$V = 6.76\left(\frac{1}{(0.617)(11.45-0.523)}\ln\left[\frac{0.523}{11.45}\left(\frac{X-11.45}{X-0.523}\right)\right]\right)$$

$$V = 13.5\,\text{ft}^3$$

(c) CSTR

Design Equation: $V = \dfrac{F_{A0}X}{-r_A}$

Rate Law: $-r_A = k_A\left(C_A^2 - \dfrac{C_B C_C}{K_C}\right)$

Stoichiometry: $C_A = C_{A0}(1-X)$ $\quad C_B = \dfrac{C_{A0}X}{2}$ $\quad C_c = \dfrac{C_{A0}X}{2}$

Combine:
$$V = \frac{F_{A0}X}{k_A C_{A0}^2\left[(1-X)^2 - \left(\frac{X^2}{4K_c}\right)\right]}$$

$$V = \frac{(10)(0.51)(1/60)}{(1800)(0.0037)^2\left[(1-0.51)^2 - \left(\frac{0.51^2}{4(0.3)}\right)\right]} = 147.73\,\text{ft}^3$$

(d)

Amount processed in CSTR:

$(10\,\text{lbmol/min})(60\,\text{min/hr})(24\,\text{hr/day}) = 14{,}400\,\text{lbmol/day}$

P4-10 (cont'd)

Batch

$$t = C_{Ao}\int\frac{dX}{-r_A} = \frac{C_{Ao}}{kC_{Ao}^2}\int\frac{dX}{\left[(1-X)^2 - \frac{X^2}{4K_c}\right]}$$

$$t = \frac{1}{kC_{Ao}}\left(\frac{1}{(0.167)(11.45-0.523)}\ln\left[\frac{0.523}{11.45}\left(\frac{X-11.45}{X-0.523}\right)\right]\right)$$

$$t = 0.30\text{ s}$$

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.

$$\frac{14{,}400\text{ lbmol/day}}{6\text{ runs/day}} = 2400\text{ lbmol/run}$$

$$t = \frac{N_{Ao}}{V}\int\frac{dX}{-r_A} \qquad \therefore \qquad V = \frac{N_{Ao}}{t}\int\frac{dX}{-r_A}$$

$$V = \frac{N_{Ao}}{t}\frac{1}{kC_{Ao}^2}\left(\frac{1}{(0.167)(11.45-0.523)}\ln\left[\frac{0.523}{11.45}\left(\frac{X-11.45}{X-0.523}\right)\right]\right)$$

$$V = \frac{2400}{(4)(1800)(0.0037)^2}\left(\frac{1}{(0.167)(11.45-0.523)}\ln\left[\frac{0.523}{11.45}\left(\frac{X-11.45}{X-0.523}\right)\right]\right)$$

$$V = 48{,}690\text{ ft}^3$$

(e) $E = 30{,}202$ btu/lbmol

for $X = 0$, $-r_A = kC_{Ao}^2$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = \frac{k_{800}C_{Ao}^2}{k_{1400}C_{Ao}^2} = \frac{k_{800}}{k_{1400}} = \exp\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = \exp\frac{30{,}202\text{ btu/lbmol}}{1.987\text{ btu/lbmol}\cdot{}^\circ\text{R}}\left(\frac{1}{1259.67^\circ\text{R}}-\frac{1}{1859.67^\circ\text{R}}\right)$$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = 49$$

P4-11. Given: Gaseous reaction in a tubular reactor:

$A \longrightarrow B \qquad -r_A = k\,C_A,\ k = .0015\ \text{min}^{-1}$ at 80°F

$E = 25{,}000$ cal/gmole

$X = 0.90$

$M_B = 1000$ lb/hr

$(MW)_A = 58$ lb/lb-mole

$(MW)_B = 58$ lb/lb-mole

D_t = tube diameter = 1 inch (I.D.)

L = tube length = 10 feet

$P = 132$ psig = (132+14.7)psia=146.7 psia

$T = 260°F = 720°R$

n_t = number of tubes

$$F_B = \frac{1000\ \text{lb/hr}}{58\ \text{lb/lb-mole}} = \frac{17.2\text{lb-mole}}{\text{hr}}\ ;\ F_{AO} = \frac{F_B}{X} = (17.2\text{lbmole/hr})/0.9$$

$$= 19.1\ \text{lbmole/hr.}$$

For a plug flow reactor: $V = \dfrac{n_t P D_t^2 L}{4} = F_{AO}\displaystyle\int_0^{0.90} \frac{dX}{-r_A}$

$\delta = 1-1=0 \qquad y_A = 1.0 \qquad \varepsilon = y_A\delta = 0$

$\therefore\ -r_A = kC_{AO}(1-X\ ) \qquad C_{AO} = \dfrac{P_A}{RT} = \dfrac{P}{RT}$

$$\therefore\ V = F_{AO}\int_0^{0.90} \frac{dX}{-r_A} = F_{AO}\int_0^{0.90} \frac{dX}{kC_{AO}(1-X)} = \frac{F_{AO}}{kC_{AO}} \ln\frac{1}{1-.90} = \frac{F_{AO}RT}{k\,P} \ln 10$$

At $T_2 = 260°F = 720°R$, with $k_1 = .0015\ \text{min}^{-1}$ at $T_1 = 80°F = 540°R$,

$k_2 = k_1 \exp[\frac{E}{R}(\frac{1}{T_1} - \frac{1}{T_2})] =$

P4-11 (cont'd)

$$.0015\ \exp\left\{\frac{\dfrac{25{,}000\ \text{cal}}{\text{gmole}}}{\dfrac{1.99\text{BTU}}{\text{lbmole}°\text{R}}}\left(\frac{1}{540°\text{R}}-\frac{1}{720°\text{R}}\right)\cdot\frac{\dfrac{1.8\ \text{BTU}}{\text{lbmole}}}{\dfrac{\text{cal}}{\text{gmole}}}\right\}$$

$$k_2 = .0015\ \text{min}^{-1}\ \exp\left(\left[\frac{25{,}000}{1.99}\right]\left[\frac{180(1.8)}{(540)\ (720)}\right]\right) = .0015\ e^{10.487}\text{min}^{-1}$$

$$k_2 = (.0015)\ (3.52\text{x}10^4)\ \text{min}^{-1} = 52.8\ \text{min}^{-1}$$

$$\therefore\ V = \left(\frac{19.1\ \text{lbmole}}{\text{hr}}\right)\left(\frac{1\ \text{min}}{52.8}\right)\left(\frac{1\ \text{hr}}{60\ \text{min}}\right)\left[\frac{\dfrac{10.73\text{ft}^3}{\text{lbmole}°\text{R}}\text{psia x } 720°\text{R}}{146.7\ (\text{psi})}\right]\ln 10$$

$$= 0.73\ \text{ft}^3$$

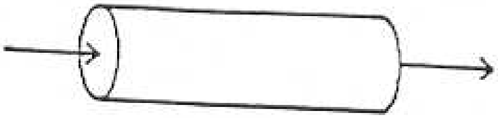
$$V = \frac{n_t\pi\ D_t^2 L}{4}\ ;\ \therefore\ n_t = \frac{4V}{\pi\ D_t^2 L} = \frac{(4)(0.73)\text{ft}^3}{3.14(1/12)^2\text{ft}^3(10)\text{ft}} = 13.4$$

$\therefore\ n_t = 14$ pipes

P4-12. Given: Tubular flow reactor:

$F_{AO} = F_{CO}$

$F_{BO} = 0$



Case 1:

Rearrange reaction: $A \rightarrow \frac{1}{2}B$ Then: $\delta = \frac{1}{2} - 1 = -1/2$

$$\Theta_B = 0\ ;\quad \Theta_C = 1\ ;\quad y_{AO} = \frac{F_{AO}}{F_{AO} + F_{BO} + F_{CO}} = \frac{1}{2}\ ;\ \varepsilon = y_{AO}\ \delta = -1/4$$

For a plug flow reactor:

$$V_{PF} = F_{AO}\int_o^X \frac{dX}{-r_A}\ ;\quad -r_A = k\ C_A^2 = \frac{k\ C_{AO}{}^2(1-X)^2}{(1+\varepsilon X)^2}$$

P4-12 (cont'd)

$$\therefore \frac{kC_{AO}^{2}V_{PF}}{F_{AO}} = \frac{k\,V_{PF}\,P^2}{4F_{AO}R^2T^2} \quad \text{and} \quad \frac{k\,C_{AO}'^{2}V_{PF}}{F_{AO}'} = \frac{2\,k\,V_{PF}\,P^2}{9\,F_{AO}R^2T^2}$$

$$\therefore \frac{k\,C_{AO}^{2'}\,V_{PF}}{F_{AO}'} = \frac{8}{9} \times \frac{k\,C_{AO}^{2}V_{PF}}{F_{AO}} = \frac{8}{9} = (2.90) = 2.58$$

$$\therefore 2.58 = \varepsilon'^{2}X' + 2\varepsilon'(1+\varepsilon')\ln[1-X'] + \underline{\underline{\frac{(\varepsilon'+1)^2X'}{(1-X')}}}$$ Must be

solved by trial and error. Dominating term is underlined. Rearranging the above equation

$$X' = \left(\frac{[2.58-\varepsilon'^{2}X' - 2\varepsilon'(1+\varepsilon')\ln[1-X']]}{(1+\varepsilon')^2 + [2.58 - \varepsilon'^{2}X' - 2\varepsilon'(1+\varepsilon')\ln(1-X')]}\right)$$

Solution (1) Assume a value of X'

(2) Calculate a new X' from L.H.S. of the above equation

(3) Compare or use new value of X' in L.H.S. of the equation and repeat steps (2) and (3).

$$X' = \frac{2.58 - 0.0278X' + 0.278\ln[1-X']}{3.27 - 0.0278X' + 0.278\ln[1-X']}$$

X' Assumed	X' Calculated	% Difference
0.700	0.763	9.0%
0.763	0.758	0.7%
0.758	0.758	----

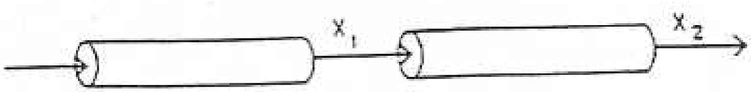
$\therefore X = 0.758$

P4-13. Given: The metal catalyzed isomerization, $A \rightleftarrows B$, liquid phase

$$-r_A = k_1\,[C_A - C_B/K_{eq}] \qquad \text{with } K_{eq} = 5.8$$

For a plug flow reactor with $y_A = 1.0$, $X_1 = 0.55$

Case I: P.F. reactor connected in series with that described above



Since $y_A = 1.0$, $\theta_B = 0$ For a liquid phase reaction, $C_A = C_{A0}(1-X)$,

$C_B = C_{A0}X$; $\quad -r_A = k\, C_{A0}\left[(1-X) - \frac{X}{K_{eq}}\right]$

For the first reactor,

$$V_1 = F_{A0}\int_0^{X_1} \frac{dX}{-r_A} = F_{A0}\int_0^{X_1} \frac{dX}{k\, C_{A0}[(1-X)-X/K_{eq}]} \quad \text{or}$$

$$\frac{kC_{A0}V_1}{F_{A0}} = \int_0^{X_1} \frac{dX}{1-(1+1/K_{eq})X]} = -\frac{1}{(1+1/K_{eq})}\ln\left[1-(1+\frac{1}{K_{eq}})X]\right|_0^{X_1}$$

$$\frac{kC_{A0}V_1}{F_{A0}} = -\frac{1}{(1+\frac{1}{K_{eq}})}\ln\left[1-(1+\frac{1}{K_{eq}})X_1\right] \qquad (a)$$

For the second reactor $\quad V_2 = F_{A0}\int_{X_1}^{X_2} \frac{dX}{-r_A}$ or upon rearrangement

$$\frac{k\,C_{A0}V_2}{F_{A0}} = \int_{X_1}^{X_2} \frac{dX}{[1-(1+\frac{1}{K_{eq}})X]} = -\frac{1}{(1+1/K_{eq})}\ln\left|\frac{1-(1+\frac{1}{K_{eq}})X_2}{1-(1+\frac{1}{K_{eq}})X_1}\right| \qquad (b)$$

but $\frac{k\,C_{A0}V_1}{F_{A0}} = \frac{k\,C_{A0}V_2}{F_{A0}}$, and thus, from Eqns. (a) and (b)

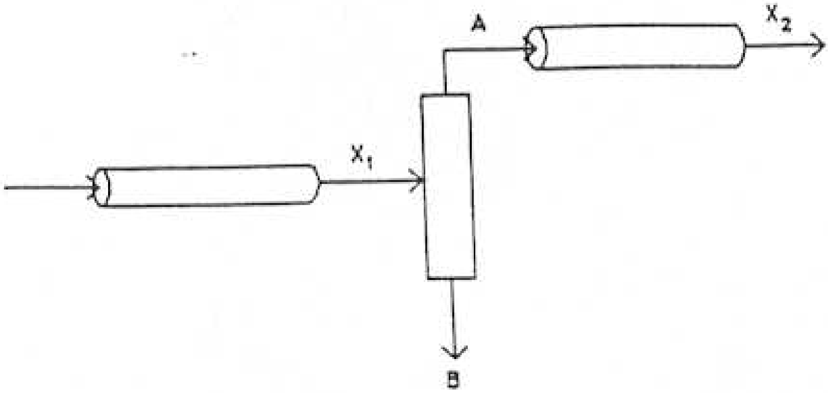
$$-\frac{1}{(1+1/K_{eq})}\ln\left[1-(1+\frac{1}{K_{eq}})X_1\right] = -\frac{1}{(1+1/K_{eq})}\ln\left[\frac{1-(1+\frac{1}{K_{eq}})X_2}{1-(1+\frac{1}{K_{eq}})X_1}\right]$$

or

$$1-(1+\frac{1}{K_{eq}})X_2 = \left[1-(1+\frac{1}{K_{eq}})X_1\right]^2$$

$$X_2 = \frac{1-\left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right]^2}{\left[1+\frac{1}{K_{eq}}\right]} = \frac{1-[1-(1.173)(.55)]^2}{1.173} = \frac{1-(.356)^2}{1.173} = .74 \text{ ans}$$

(b) Case II: Product from first reactor separated and pure A sent to second reactor:



Analysis for first reactor same as before

$$\therefore \quad \frac{kC_{AO}V_1}{F_{AO}} = \frac{-1}{(1+1/K_{eq})}\ln[1-(1+1/K_{eq})X_1]$$

By material balance on separator, $F_{AO,2} = F_{AO}(1-X_1)$

Since pure A enters second reactor $C_{AO,2} = C_{AO}$, $C_{BO} = 0$, $\theta_B = 0$

$\therefore \quad C_A = C_{AO}(1-X)$, $C_B = C_{AO}X$ for second reactor

$$V_2 = F_{AO,2}\int_0^{X_2}\frac{dX}{-r_A} = \frac{F_{AO}(1-X_1)}{k\,C_{AO}}\int_0^{X_2}\frac{dX}{[(1-X)-X/K_{eq}]}$$

$$\therefore \quad \frac{kC_{AO}V_2}{F_{AO}(1-X_1)} = -\frac{1}{(1+1/K_{eq})}\ln[1-(1+1/K_{eq})X_2]$$

But: $\frac{kC_{AO}V_2}{F_{AO}} = \frac{kC_{AO}V_1}{F_{AO}}$, or

P4-13 (cont'd)

$$-\frac{1}{(1+1/K_{eq})}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right] = -\frac{(1-X_1)}{(1+1/K_{eq})}\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)X_2\right]$$

$$1-\left(1+\frac{1}{K_{eq}}\right)X_2 = \left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right]^{\left(\frac{1}{1-X_1}\right)}$$

$$X_2 = \frac{1-\left[1-\left(1+\frac{1}{K_{eq}}\right)X_1\right]^{\frac{1}{1-X_1}}}{1+\frac{1}{K_{eq}}} = \frac{1-(.356)^{\frac{1}{.45}}}{1.174} = \frac{1-.102}{1.174} = 0.766$$

Overall conversion for this scheme:

$$\bar{X} = \frac{F_{AO}-F_{AO,2}\,(1-X_2)}{F_{AO}} = \frac{F_{AO}-F_{AO}(1-X_1)(1-X_2)}{F_{AO}} = 1-(1-X_1)(1-X_2)$$

$$= .89$$ ans.

P4-14. Given: Ortho to meta and para isomerization of xylene

$$M \xrightarrow{k_1} P$$

$$M \xrightarrow{k_2} O$$

$O \longrightarrow P$ (neglect.)

$\pi = 300$ psig
$T = 750°F$
$V = 1000\ ft^3$ cat.

Assume that reactions are irreversible first order

Then: $-r_M = k_1C_M + k_2C_M = kC_M;\ k = k_1 + k_2$

$\varepsilon = 0$

Check to see what type of reactor is being used

Case I:

$(v_o)_{Case\ I} = 2500$ gal/hr.; $X_{Case\ I} = .37$

Case II:

$(v_o)_{Case\ II} = 1667$ gal/hr.; $X_{Case II} = .50$

P4-14 (cont'd)

Assume plug flow reactor conditions: $F_{MO}dX = -r_M dV$ or

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

$$V = \int_0^X \frac{C_{AO}v_o\,dX}{-r_M} = v_o\int_0^X \frac{dX}{k(1-X)} = -\frac{v_o}{k}\ln[1-X]$$

C_{AO}, k and V should be the same for Case I and Case II.

$$\therefore (kV)_{\text{Case I}} = -(v_o)_{\text{Case I}}\ln[1-X_{\text{Case I}}] = -\frac{2500\text{gal}}{\text{hr}}\ln(1-.37)$$

$$= 1155 \text{ gal/hr.}$$

$$\therefore (kV)_{\text{Case II}} = -(v_o)_{\text{Case II}}\ln[1-X_{\text{Case II}}] = -\frac{1667\text{ gal}}{\text{hr}}\ln[1-.50]$$

$$= 1155 \text{ gal/hr.}$$

Reactor appears to be plug flow since $\left(\frac{kV}{C_{AO}}\right)_{\text{Case I}} = \left(\frac{kV}{C_{AO}}\right)_{\text{Case II}}$;

As a check, assume that the reactor behaves as a CSTR:

$$F_{MO}X = C_{MO}v_oX = (-r_M)V$$

$$\therefore V = \frac{C_{MO}X}{-r_M}v_o = \frac{v_oX}{k[1-X]} \text{ or } kV = \frac{v_oX}{1-X}$$

Again, (kV) should be the same for Case I and Case II:

$$(kV)_{\text{Case I}} = \frac{(v_o)_{\text{Case I}}X_{\text{Case I}}}{1-X_{\text{Case I}}} = \frac{(2500\text{ gal/hr})(.37)}{1-.37} = 1468 \text{ gal/hr.}$$

$$(kV)_{\text{Case II}} = \frac{(v_o)_{\text{Case II}}X_{\text{Case II}}}{1-X_{\text{Case II}}} = \frac{1667\text{ gal}}{\text{hr}} \times \frac{.50}{1-.50} = 1667 \text{ gal/hr.}$$

$(kV)_{\text{Case I}} \neq (kV)_{\text{Case II}}$ using the CSTR assumption, reactor can be modeled as a plug flow reactor:

P4-14 (cont'd)

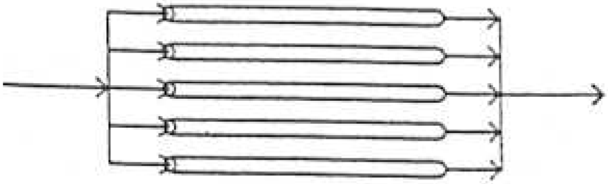
$$\therefore k = \frac{1155 \text{ gal/hr}}{1000 \text{ cu.ft}} = \frac{1.155 \text{ gal}}{\text{hr.ft}^3 \text{cat.}}$$

For the new plant, with v_o = 5500 gal/hr, X_F = .46, the required catalyst volume is:

$$V = \frac{-v_o}{k} \ln\,[1-X_F] = \frac{-5500 \text{ gal/hr}}{\frac{1.155 \text{ gal/hr}}{\text{ft}^3 \text{ cat}}} \ln\,[1-.46] = 2931 \text{ ft}^3 \text{ cat.}$$

This assumes that the same hydrodynamic conditions are present in the new reactor as in the old.

P4-15. Given A --> B in a tubular reactor



L_t = 40 ft = length of reactor tubes

D_t = .75 in = tube diameter

n_t = 50 = number of tubes

$$\therefore V = \frac{n_t \pi D_t^2}{4} L_t =$$

$$(50)(.785)\left[\frac{.75 \text{ in}}{12 \text{ in/ft}}\right]^2 [40 \text{ ft}] = 6.13 \text{ ft}^3$$

$$F_{AO} = \frac{m_a}{(M_w)_a} = \frac{500 \text{ lb/hr}}{\frac{73 \text{ lb}}{\text{lbmole}}} = 6.86 \text{ lbmole/hr}$$

$$\left[\frac{v_o}{(M_\omega)_a} = \frac{500 \text{ lb/hr}}{73 \frac{\text{lb}}{\text{lbmole}}}\right]$$

$$V = F_{AO} \int_0^X \frac{dX}{-r_A} \; ; \; -r_A = \frac{k\, C_{AO}[1-X]}{[1+\varepsilon X]} = k\, C_{AO}[1-X]$$

$$\therefore \; V = F_{AO} \int_0^X \frac{dX}{-r_A} = F_{AO} \int_0^X \frac{dX}{kC_{AO}(1-X)} = \frac{F_{AO}}{kC_{AO}} \ln \frac{1}{1-X}$$

P4-15 (cont'd)

With $C_{AO} = \frac{P}{RT} = \frac{y_{AO}P}{RT}$, $V = \frac{\dot{F}_{AO}RT}{k\ y_{AO}P} \ln \frac{1}{1-X}$ eqn. (a)

Assume Arrhenius equation applies to the rate constant

at $T_1 = 600°R$ $k_1 = .00152$; $k_1 = A\ e^{-E/RT_1}$

at $T_2 = 760°R$ $k_2 = .0740$; $k_2 = A\ e^{-E/RT_2}$

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

$$\therefore \frac{E}{R} = \left(\frac{T_1T_2}{T_1-T_2}\right) \ln \frac{k_2}{k_1} = \frac{(660)(760)°R^2}{100\ °R} \ln \frac{.0740}{.00152} = 19{,}500°R$$

$$A = k_1\ e^{+E/RT_1} \qquad \therefore\ k = k_1\ e^{-E/R\ (\frac{1}{T} - \frac{1}{T_1})}$$

From Eqn. a,

$$\frac{k}{T} = \frac{k_1\ e^{-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_1})}}{T} = \frac{F_{AO}R}{V\ y_{AO}P} \ln \frac{1}{1-X_{AF}} =$$

$$\text{or} \quad \frac{e^{-19{,}500\ [\frac{1}{T} - \frac{1}{660°R}]}}{T} = \frac{F_{AO}R}{k_1Vy_{AO}P} \ln \frac{1}{1-X_{AF}}$$

$$\frac{[\frac{6.86 \times \text{lbmole}}{\text{hr}}]\ [\frac{10.73\ \text{psia-ft}^3}{\text{lbmole}\ °R}] \ln 5}{[\frac{.00152}{\text{sec}} \times \frac{3600\ \text{sec}}{\text{hr}}][6.13\ \text{ft}^3][114.7\ \text{psia}]}$$

$$\frac{e^{-19{,}500\ [\frac{1}{T} - \frac{1}{660°R}]}}{T} = .0308°R^{-1}$$ Solving, $T = 738°R = 278°F$

P4-16. Plug flow reactor A --> B

X_{Ad} = design conversion = 0.632

X_{Af} = actual conversion = $0.927X_{Ad}$

= 0.586

$\theta_B=0$; $y_{AO}=1$; $\delta=1-1=0$; $\varepsilon=0$

$-r_A = k\ C_{AO}[1-X]$

P4-17 (cont'd)

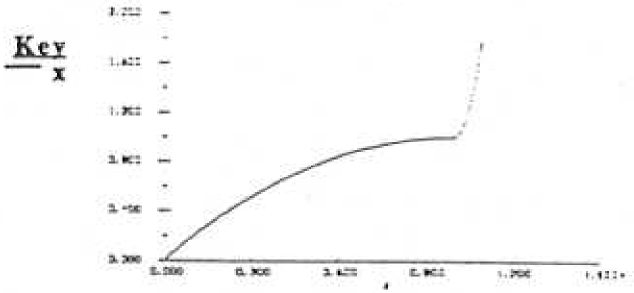
(2) Evaporation

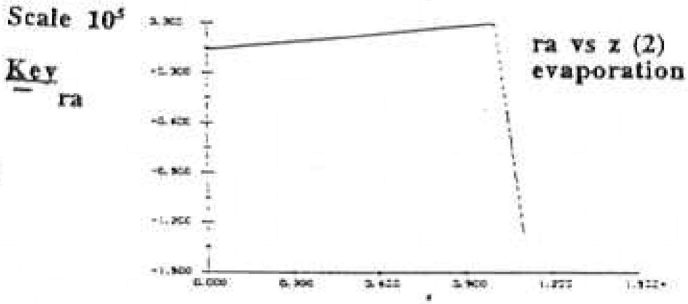
Equations:

```
d(X)/d(z)=-ra*w*d/fao
k=16e-5
w=100
d=0.25
cao=0.01
vo=2
Q=1.11e-3
rho=55.5
fao=cao*vo
fa=fao*(1-X)
v=vo-Q*w*z/rho
ca=fa/v
ra=-k*ca
```

$z_0 = 0, \quad z_f = 1100$

x vs z (2) evaporation





ra vs z (2) evaporation

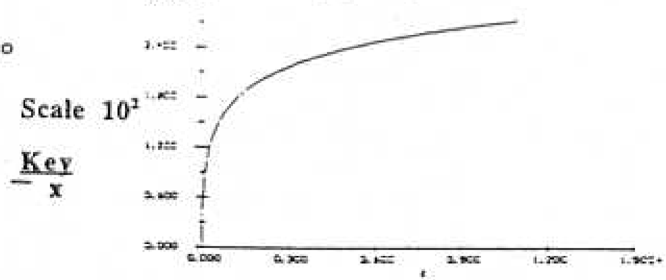
(3) Evaporation and condensation

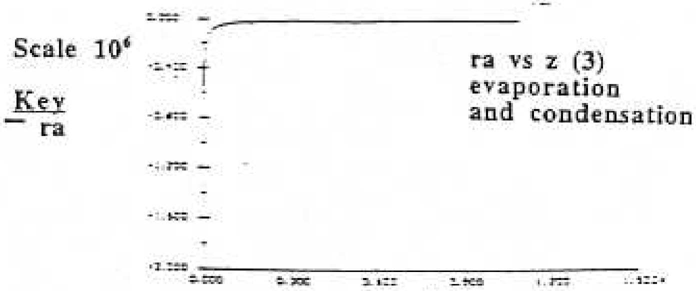
Equations:

```
d(X)/d(z)=-ra*w*d/fao
k=16e-5
w=100
d=0.25
cao=0.01
vo=2
Q=(1.11e-3)-0.5
rho=55.5
fao=cao*vo
fa=fao*(1-X)
v=vo-Q*w*z/rho
ca=fa/v
ra=-k*ca
```

$z_0 = 0, \quad z_f = 1100$

x vs z (3) evaporation and condensation





ra vs z (3) evaporation and condensation

d) Making the ratio Q/kC_{A0} a small positive number immediately puts the conversion close to 1. Conversly making that ratio any negative number makes the conversion go down very quickly.

e) No solution will be given.

P4-18.

a) Assume isothermal and $\varepsilon=0$

therefore, $P = P_0 (1 - \alpha W)^{.5}$ $1=10 (1-.01\ g^{-1}W)^{.5}$

$W = 99g.$

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

P4-19 (cont'd)

b) Since turbulent flow

$$\alpha_2 = \alpha_1 (G_2/G_1)^2 (D_{p1}/D_{p2})(A_{C1}/A_{C2})$$

$$= \alpha_1 (1/4)^2 (1/2) = \alpha_1 / 32$$

$$\alpha_2 = .938 / 32 = .029$$

$$a_2 = a_1 (F_{ao1}/F_{ao2}), \qquad C_{ao1} = C_a$$

$$a_2 = a_1 (1/(1/4)) = 4a_1 = 2.78$$

By using trial and error in POLYMATH we get <u>X=0.861</u>

<u>P4-20</u>

PBR

$$\frac{dX}{dW} = \frac{kC_A}{F_{A0}} = \frac{kC_{A0}}{F_{A0}} \frac{(1-X)}{(1+\varepsilon X)} y$$

$$\frac{dy}{dW} = \frac{-(1+\varepsilon X)\alpha}{2y}$$

$$a = \frac{kC_{A0}}{F_{A0}}$$

Trial and error by POLYMATH gets us the following:

Guess a, α, ε at X = 0.064 y = .123

a =.000101, α = .000948, ε =1

```
Equations:                                              Initial value
d(x)/d(w)=a*(1-x)/(1+eps*x)*y                           0
d(y)/d(w)=-(1+eps*x)*alp/(2*y)                          1
alp=.000948
a=.000101
eps=1
w0 = 0,    wf = 1000
```

P4-20 cont'd

a) 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:

$$W = \frac{X(1+\varepsilon X)}{a(1-X)}$$

$$X = 0.37$$

b)

$$\frac{dX}{dW} = \frac{a(1-X)}{1+\varepsilon X}y$$

$$\frac{dy}{dW} = \frac{-(1+\varepsilon X)\alpha}{2y}$$

We will make the approximation that ε*X will be neglected with respect to 1 and then use the above equations. k will increase as D_p will decrease as per Chapter 12 and that alpha increases as D_p decreases so that y decreases and there is a competition for the effect on $-r_A$. Alpha also decreases as G decreases therefore y increases and rate also increases therefore higher conversion.

c) No solution will be given.

P4-21.

a) $P/P_o = 1/20 = (1 - \alpha * 1000\ \text{kg})^{.5}$ $\alpha = 9.975 \times 10^{-4}\ \text{kg}^{-1}$

b) PBR

MB: $\frac{dX}{dW} = \frac{-r_A}{F_{AO}}$

Rate Law: $-r_A = k\, C_A$ $C_A = C_{AO}(1-X)$

Combine:

$$\int_0^{.141} \frac{dX}{1-X} = \left(\frac{kC_{AO}}{F_{AO}}\right)\int_0^{W} (1-W\alpha)^{.5}\, dW$$

$$.152 = \left(\frac{kC_{AO}}{F_{AO}}\right)\int_0^{1000} (1-8x10^{-4}W)^{.5}\, dW$$

$$\frac{kC_{AO}}{F_{AO}} = 2x10^{-4}$$

CSTR

MB: $W = \frac{F_{AO}X}{-r_A}$

Combine:

$$W = \frac{F_{AO}}{kC_{AO}}\frac{X}{(1-X)}$$

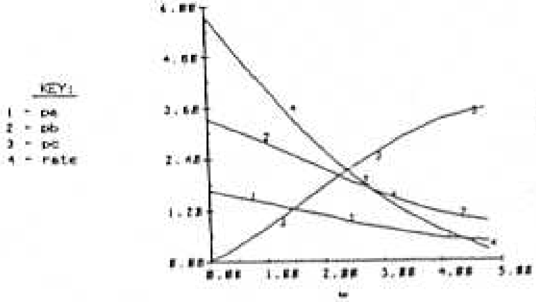
$$1000 = \frac{1}{2x10^{-4}}\frac{X}{(1-X)}$$

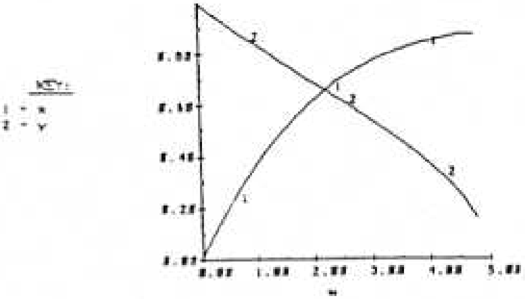
$$X = .18$$

c) α is inversely proportional to cross sectional area and therefore the pipe diameter so increasing the diameter will decrease α. Since this is limited by internal diffusion, the specific reaction rate is inversely proportional to the particle diameter. So to increase the conversion it is wise to increase the pipe diameter and decrease the particle size.

d) Increase is cross sectional area decreases α. Increase in particle diameter decreases α. α could stay constant if cross sectional area is increased and particle diameter

P4-22 (cont'd)





4-22 (c)

Case II $\alpha = 0.34$

$$C_A = C_{AO}\frac{(1-X)}{(1-.66X)}$$

$$C_B = 2C_{AO}\frac{(1-X)}{(1-.66X)}$$

$$C_C = \frac{C_{AO}X}{(1-.66X)}$$

$$\dot{m}_1 = \dot{m}_2$$

$$G_1\frac{\pi D_1^2}{4} = G_2\frac{\pi D_2^2}{4}$$

$$G_2 = G_1\left(\frac{D_1}{D_2}\right)^2$$

Now $D_2 = 2D_1$

$$G_2 = \frac{1}{4}G_1$$

Slow Flow

$$\alpha \sim G$$

$$\alpha_2 = \frac{1}{4}\alpha_1$$

Rapid Flow

$$\alpha \sim G^2$$

$$\alpha_2 = \frac{1}{16}\alpha_1$$

Either way its a good idea

P4-22 (cont'd)

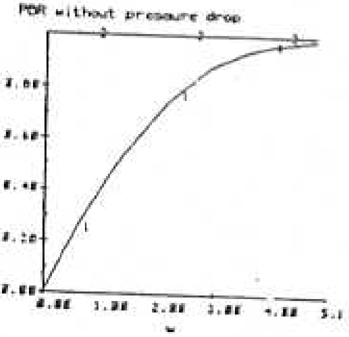
Case I $\alpha = 0$, $y = 1$

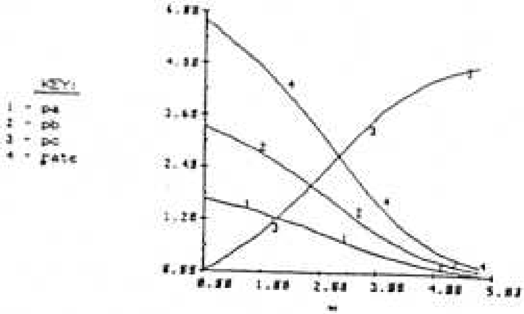
$$\frac{dX}{dW} = \frac{2\,k\,P_{AO}}{F_{AO}} \frac{(1-X)}{(1-.66X)}$$

$$W = \frac{2\,k\,P_{AO}}{F_{AO}} \left[(1+\varepsilon)\ln\frac{1}{1-X} - \varepsilon X\right]$$

4-22 (a)

```
                    PBR without pressure drop
The equations:
     d(x)/d(w)=-ra/fa0
     y=1
     k=1.74
     pa0=.333*5
     ra=-k*pa0^2*(1-x)*y/(1-.666*x)
     fa0=13.33
     rate=-ra
     pa=5*.333*(1-x)/(1-.666*x)
     pb=2*pa
     pc=.333*5*x/(1-.666*x)
Initial values: w0= 0.0, x0= 0.0
Final value:  wf= 4.0000
```





4-22 (b)

```
                    PBR with pressure drop
The equations:
     d(x)/d(w)=-ra/fa0
     d(y)/d(w)=-.34*(1-.666*x)/(2*y)
     k=1.74
     pa0=.333*5
     ra=-k*pa0^2*(1-x)*y/(1-.666*x)
     fa0=13.33
     rate=-ra
     pa=5*.333*(1-x)/(1-.666*x)
     pb=2*pa
     pc=.333*5*x/(1-.666*x)
Initial values: w0= 0.0, x0= 0.0, y0= 1.0000
Final value:  wf= 4.0000
```

P4-23. Solution:

Mole Balance

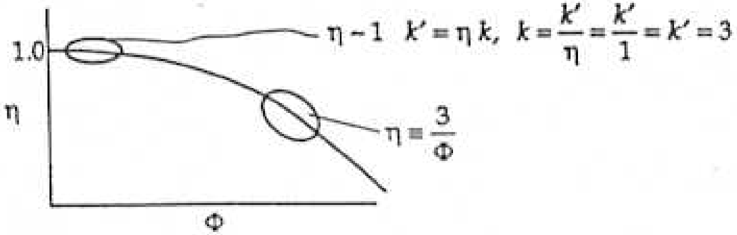
$$\frac{dX}{dW} = r_A'/F_{A0}$$

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 $\qquad$ $cD_p \longrightarrow$ Increasing Particle Size

Then

$$\eta = \frac{3}{\Phi} = \frac{3}{cD_P}$$

when $D_p = 2$ mm, $k' = 0.06$, $\eta = \frac{k'}{k} = \frac{.06}{3} = 0.02$

$$0.02 = \frac{3}{c(2)}$$

$$c = 75$$

$$\boxed{\Phi = 75\,D_P}$$

Stoichiometry

Gas, $\varepsilon = 0$, $C_A = C_{A0}(1-X)y$

$\frac{dy}{dW} = -\frac{\alpha}{2y}$, where $\alpha = \alpha_1\left(\frac{D_{P1}}{D_P}\right)$

$$\alpha_1 = \frac{2\beta_o}{P_o(1-\phi)\rho_C A_C} = \frac{2\left(10^{-3}\text{ atm}\cdot\text{dm}^{-1}\right)}{20\text{ atm}(1-0.35)\left(2.65\text{ kg/dm}^3\right)\left(0.82\text{ dm}^2\right)} = 7.08\times10^{-5}\text{ kg}^{-1}$$

P4-23 (cont'd)

Combine

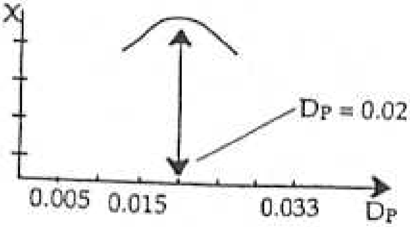
$$\frac{dX}{dW} = \left(\frac{k' C_A^2}{F_{A0}}\right)(1-X)^2 y^2 \quad \text{and} \quad \frac{dy}{dW} = -\frac{\alpha}{2y}$$

$$k' = k\overset{\eta}{\left[\frac{1}{\Phi^2}(\Phi\coth\Phi - 1)\right]} \quad \text{where } k = 3 \text{ and } \Phi = 75D_p$$

$$\alpha = 7.08 * 10^{-5}\, kg\left(\frac{D_{p1}}{D_p}\right)$$

$D_{p1} = 1$, $C_{A0} = 0.207$, $F_{A0} = 5$
$W = 0$ $X = 0$ $y = 1.0$
$W_f = 100$
See POLYMATH program Vary D_p

D_p	α	y	η	k	X
1.0	$7.08*10^{-5}$	0.996	.0039	0.12	0.092
0.1	0.0007	0.54	0.35	1.04	0.37
0.05	0.0014	0.93	0.59	1.76	.58
0.03	0.00236	0.87	0.77	2.3	0.64
0.025	.0028	0.85	0.82	2.5	0.64
0.015	.0035	0.73	0.92	2.8	0.65
0.01	.007	0.54	0.96	2.89	0.64
0.00725	.0098	0.15	0.98	2.4	0.56



```
4-23
Equations:                                                   Initial value
d(y)/d(w)=-alpha/2/y                                         1
d(x)/d(w)=-ra/fao                                            0
fao=5
cao=0.207
dp=.00725
k1=3
alp=0.0000708
dp1=1
ca=cao*(1-x)*y
phi=75*dp
eta=3/phi**2*(phi*((exp(phi)+exp(-phi))/(exp(phi)-exp(-ph
   i)))-1)
alpha=alp*dp1/dp
k=k1*eta
ra=-k*ca**2
w0 = 0,   wf = 100
```

$$\frac{d(y)}{d(w)}$$

Ca = Cao (1-x)*Y , phi = 75 * dp

$$eta = \left[\frac{3}{\Phi^2}\left(\Phi \operatorname{Coth}\phi - 1\right)\right]$$

P4-24

1. Mole Balance: $$\frac{dX}{dz} = \frac{-r_A A_C}{F_{A0}}$$

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: $$C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} y$$

$$\varepsilon = y_{A0}\delta = (1)\left(1+\tfrac{1}{2}-1\right) = \tfrac{1}{2}$$

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 $\varepsilon > 0$.)

P4-24 (cont'd)

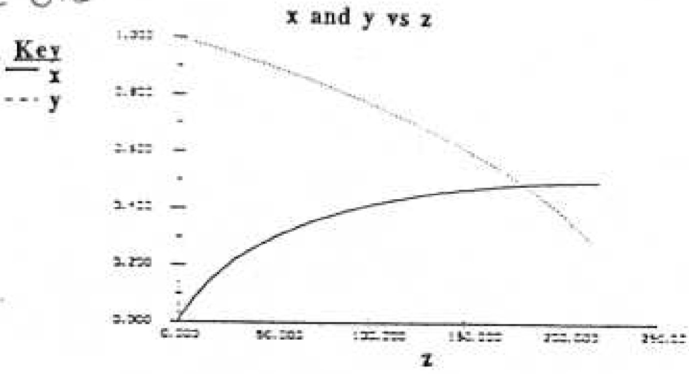
Case	POLYMATH y	POLYMATH X	Remedy	Effect on y	Effect on X
1	too HIGH	too HIGH	raise B	lowers y	lowers X
2	too HIGH	too LOW	raise k_o	lowers y	raises X
3	too LOW	too HIGH	lower k_o	raises y	lowers X
4	too LOW	too LOW	lower B	raises y	raises X

Once the correct values of B and k_o are found, one can proceed with the standard spherical algorithm.

a) From POLYMATH:
B=843
k=0.21
x=.67
$P=yP_0=.973*1500=1459.5$

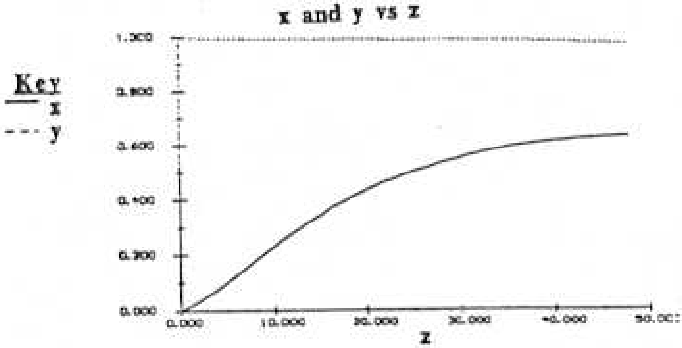
```
Equations:
d(y)/d(z)=-beta/(po*y)*(1+eps*x)
d(x)/d(z)=-ra*Ac/Fao
po=1500
eps=0.5
Fao=950
R=10
Cao=0.4
k=0.21
B=843
Ac=3.1416*(R**2)
Ca=Cao*y*(1-x)/(1+eps*x)
beta=B/Ac
ra=-k*Ca**2
z0 = 0,    zf = 220
```

eps= 0.5
Fao=950



P4-24 (cont'd)

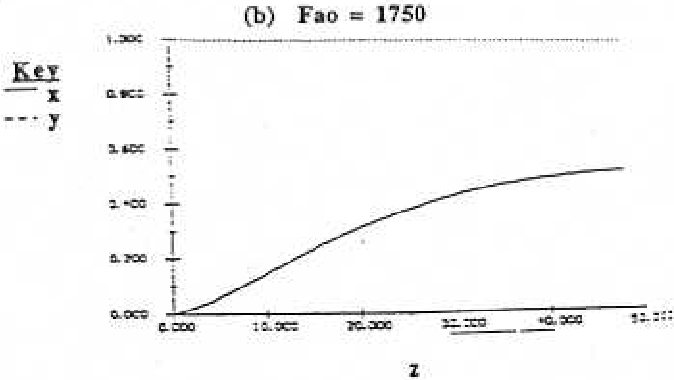
```
Equations:
d(y)/d(z)=-beta/(po*y)*(1+eps*x)
d(x)/d(z)=-ra*Ac/Fao
po=1500
eps=0.5
Fao=950
R=26
Cao=0.4
k=0.21
B=843
L=24
Ac=3.1416*(R**2-(z-L)**2)
Ca=Cao*y*(1-x)/(1+eps*x)
ra=-k*Ca**2
beta=B/Ac
z0 = 0,    zf = 48
```



b) From POLYMATH:

maximum flowrate=1750mol/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
z0 = 0,    zf = 48
```

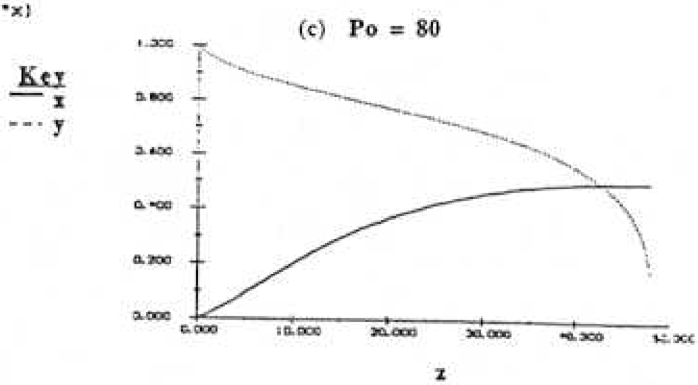


P4-24 (cont'd)

c) From POLYMATH

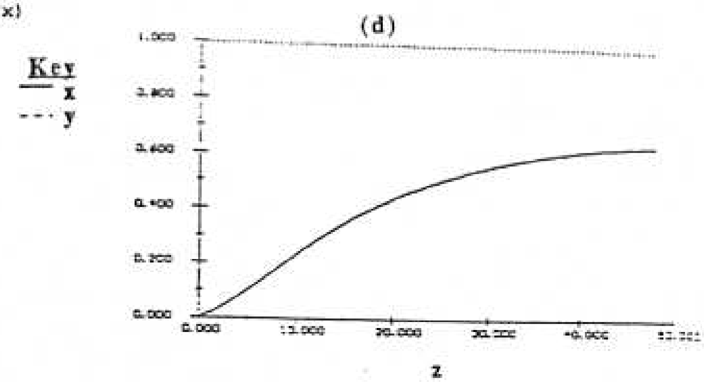
Minimum pressure=80 kPa

```
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
z0 = 0,    zf = 48
```



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
z0 = 0,    zf = 48
```



4-25 No solution will be given

P4-26 (cont'd)

$$X_{Aeq} = \frac{-b-\sqrt{b^2-4ac}}{2a}$$

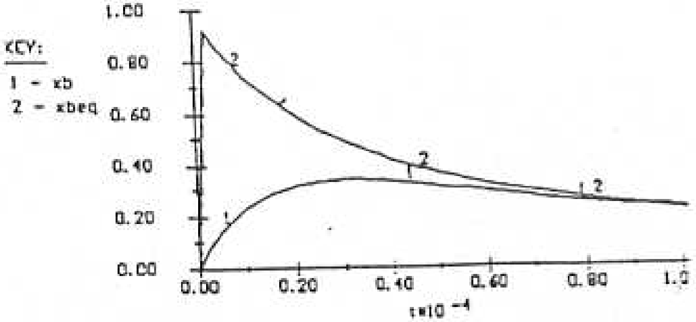
where

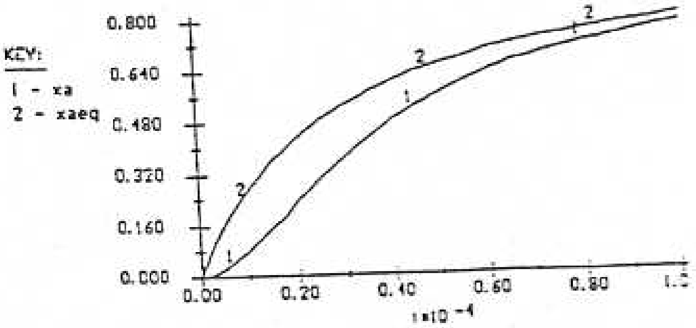
$$a = \left(1-\frac{1}{K_e}\right)$$

$$b = \left(\frac{v_0 C_{B0} t}{N_{A0}} + 1\right) \qquad c = \left(\frac{v_0 C_{B0} t}{N_{A0}}\right)$$

4-26 (a)

```
The equations:
    d(vol)/d(t)=.05
    d(na)/d(t)=-r*vol
    d(nb)/d(t)=.05*10.93-r*vol
    d(nc)/d(t)=r*vol
    d(nd)/d(t)=r*vol
    r=9*10**(-5)*((na/vol)*(nb/vol)-((nc/vol)*(nd/vol))/1.08)
    xa=(1544-na)/1544
    xb=(.05*10.93*t-nb)/(.05*10.93*(t+1.**(-10)))
    b=-(.05*10.93*t/1544+1)
    xaeq=(-b-(b*b-4*.0741*(-b-1))**.5)/(2*(1-1/1.08))
    xbeq=(1544/(.05*10.93*t+1.*10**(-3)))*xaeq
 Initial values: t0= 0.0, vol0= 200.00, na0= 1544.0, nb0= 0.0, nc0= 0.0
 nd0= 0.0
 Final value:  tf = 0.100*10^5
```

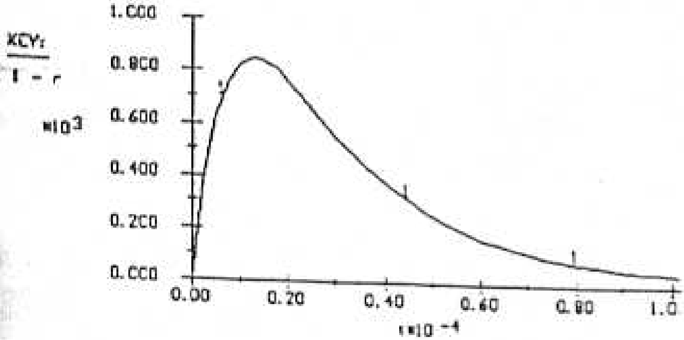


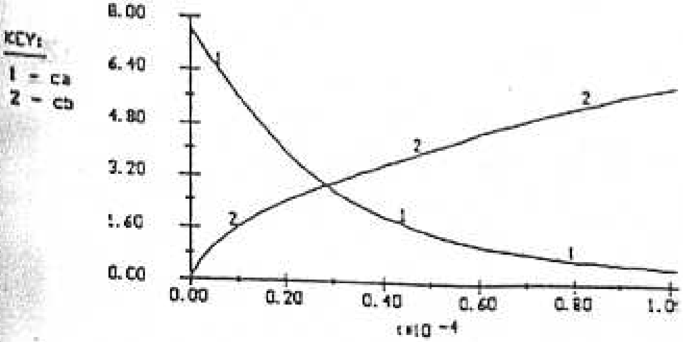


P4-26 (cont'd)

4-26 (b)

```
The equations:
    d(vol)/d(t)=.05
    d(na)/d(t)=-r*vol
    d(nb)/d(t)=.05*10.93-r*vol
    d(nc)/d(t)=r*vol
    d(nd)/d(t)=r*vol
    r=9*10**(-5)*((na/vol)*(nb/vol)-((nc/vol)*(nd/vol))/1.08)
    xa=(1544-na)/1544
    xb=(.05*10.93*t-nb)/(.05*10.93*(t+1.**(-10)))
    b=-(.05*10.93*t/1544+1)
    ca=na/vol
    cb=nb/vol
Initial values: t0= 0.0, vol0= 200.00, na0= 1544.0, nb0= 0.0, nc0= 0.0
nd0= 0.0
Final value:  tf = 0.100*10^5
```

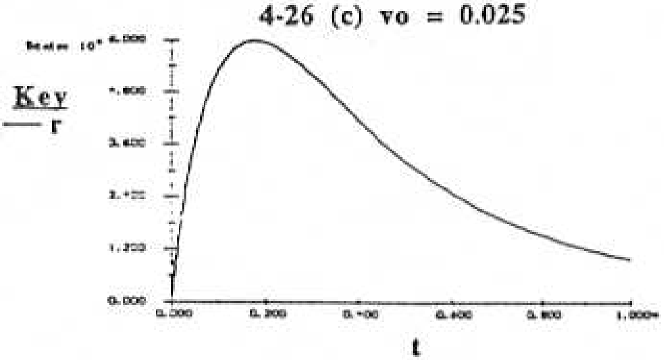


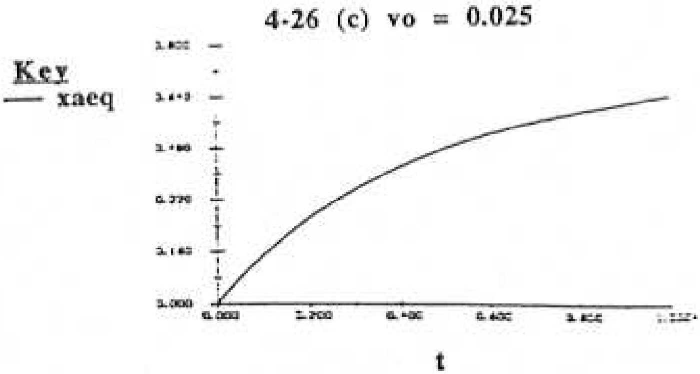


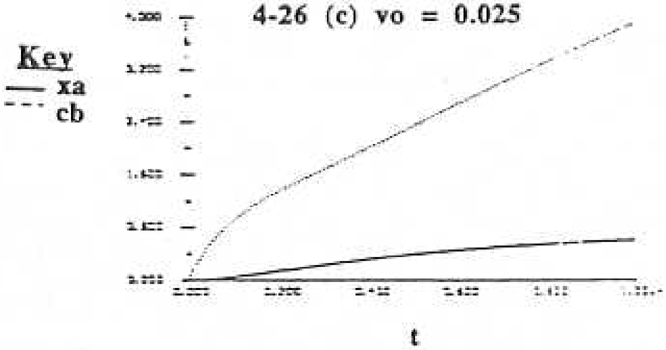
P4-26 (cont'd)

(c) Using the same POLYMATH equations, and changing values for V and v_o.

Change v_o from 0.050 dm^3/s from 0.025 dm^3/s:



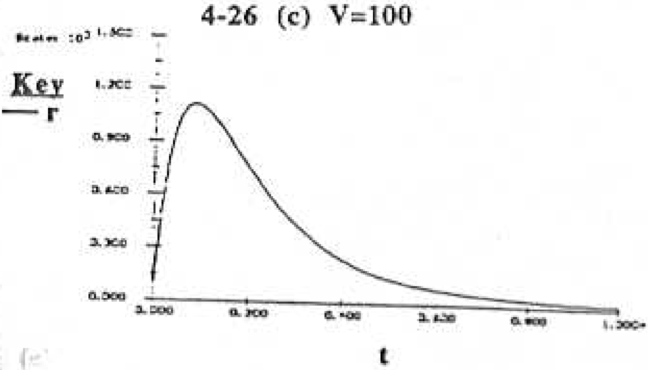


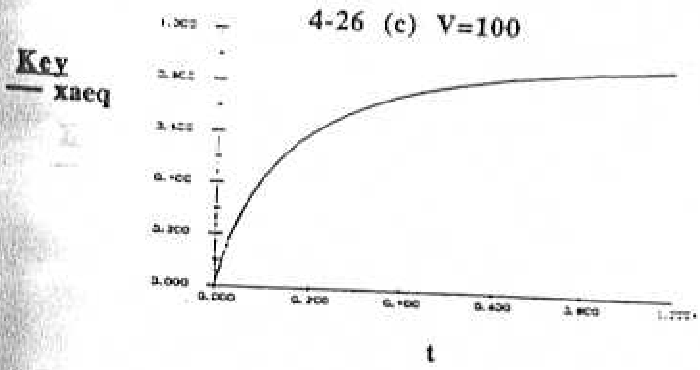


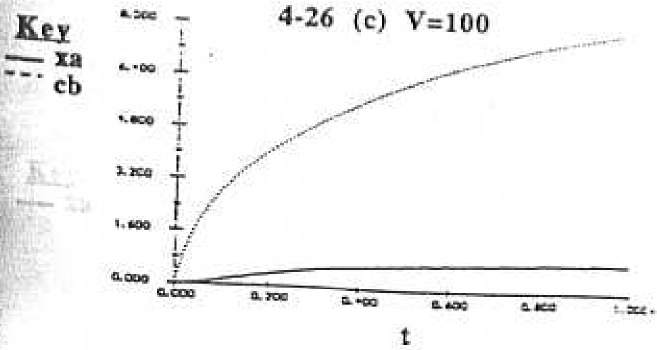
4-51

P4-26 (cont'd)

Change V from 200 dm^3 to 100 dm^3:







P4-26 (cont'd)

(d) Evaporation of D at a rate of 0.5 mol/s changes the mole balance for species D.

$$\frac{dN_D}{dt} = -0.5 + rV$$

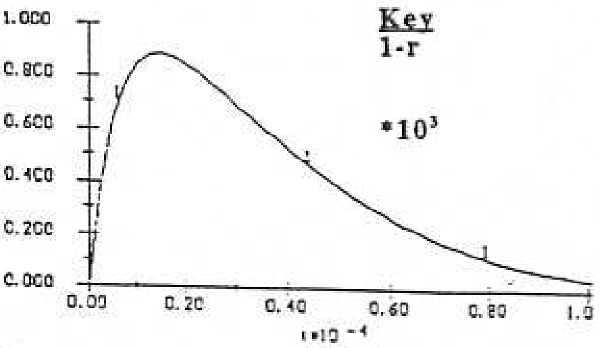
Simulations show that N_D is always negative. Therefore, set

$$\frac{dN_D}{dt} = 0, \quad \text{where } N_D = 0 \text{ at } t = 0$$

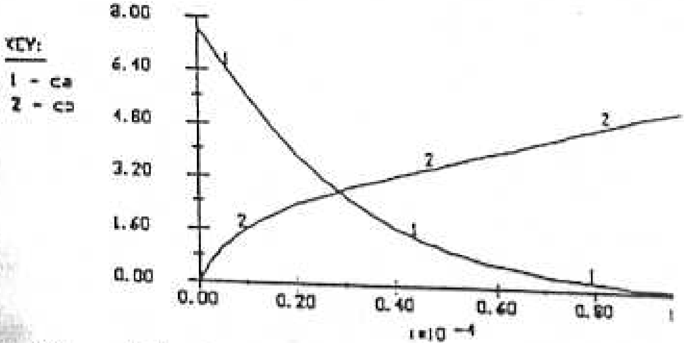
See POLYMATH solution below.

4-26 (d)

```
The equations:
     d(vol)/d(t)=.05
     d(na)/d(t)=-r*vol
     d(nb)/d(t)=.05*10.93-r*vol
     d(nc)/d(t)=r*vol
     d(nd)/d(t)=0.0
     r=9*10**(-5)*((na/vol)*(nb/vol)-((nc/vol)*(nd/vol))/1.08)
     xa=(1544-na)/1544
     xb=(.05*10.93*t-nb)/(.05*10.93*(t+1.**(-10)))
     ca=na/vol
     cb=nb/vol
Initial values:  t0= 0.0,  vol0= 200.00,  na0= 1544.0,  nb0= 0.0,  nc0= 0.0
nd0= 0.0
Final value:  tf = 0.100*10^5
```

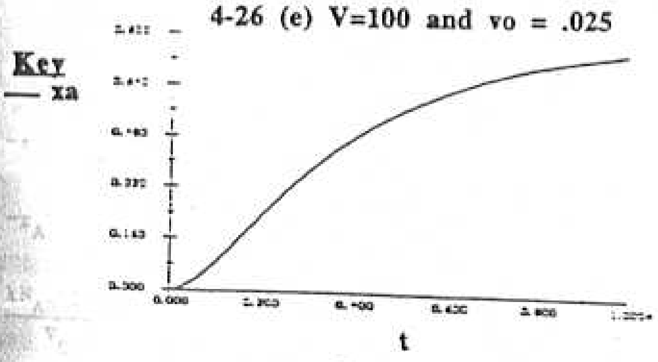


P4-26 (cont'd)

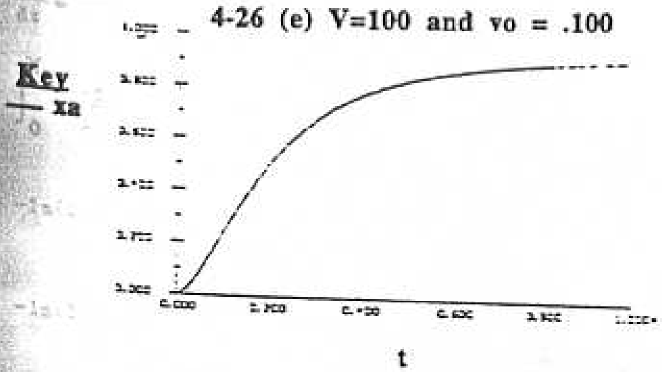


(e) Using the same equations in POLYMATH and varying vo and V.

$V = 100\ dm^3$ and $v_o = 0.025\ dm^3/s$

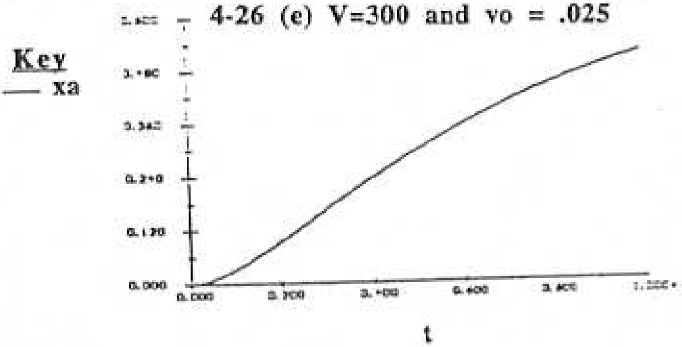

4-26 (e) V=100 and vo = .025

$V = 100\ dm^3$ and $v_o = 0.100\ dm^3/s$

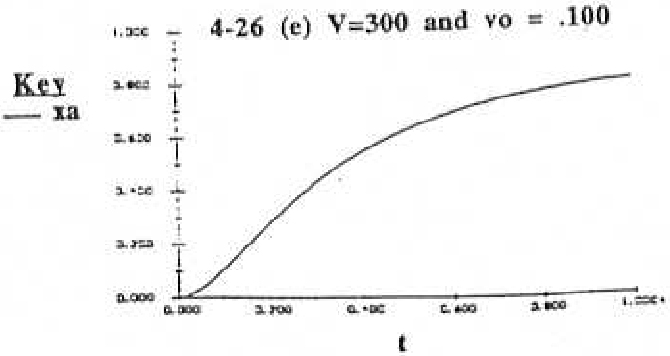

4-26 (e) V=100 and vo = .100

P4-26 (cont'd)

V = 300 dm^3 and v$_o$ = 0.025 dm^3/s



V = 300 dm^3 and v$_o$ = 0.100 dm^3/s



P4-27.

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

$$-r_A = kC_AC_B,\ k = 0.2\ ft^3/lbmol\ min$$

$$C_{AO} = 2\ lbmol/ft^3,\ C_{BO} = 0$$

$$V_0 = 100\ ft^3$$

$$v = 5\ ft^3/min,\ C'_{BO} = 0.5\ lbmol/ft^3$$

a) $N_{AO} = C_{AO}V_0 = 2(lbmol/ft^3)\ 100(ft^3) = 200\ lbmol$

$V = V_0 + vt$ $\qquad$ $N_c = N_{AO}X$

$$C_A = \frac{N_A}{V} = \frac{N_{AO}(1-X)}{V_0 + v\ t}$$

$$C_B = \frac{N_B}{V} = \frac{C'_{BO}vt}{V_0 + vt}$$ —Note that B is used at same rate as it is produced

$$-r_A = kC_AC_B = k\ \frac{N_{AO}\ (1-X)C'_{BO}\ vt}{(V_0 + v\ t)^2}$$

$$-r_AV = N_{AO}\frac{dX}{dt}$$

$$\frac{kN_{AO}(1-X)C'_{BO}vt}{V_0 + vt} = N_{AO}\frac{dX}{dt}$$

$$\frac{dX}{dt} = \frac{kC'_{BO}vt(1-X)}{V_0 + vt}$$

$$\int_0^X \frac{dX}{1-X} = \int_0^X \frac{kC_{BO}'\ v\ t}{V_0 + v\ t}\,dt$$

$$-\ln(1-X) = kC'_{BO}\ v\left[\frac{t}{v} - \frac{V_o}{v^2}\ln\ (V_o+vt)\right]_0^{30}$$

$$-\ln(1-X) = kC'_{BO}\ [30 - \frac{V_0}{v}(\ln(V_0 + 30v)-\ln(V_0))]$$

$$-\ln(1-X)=(0.2)\frac{ft^3}{lbmol\ min}(0.5)\frac{lbmol}{ft^3}[30_{min} - \frac{100\ ft^3}{5ft^3/min}(\ln(100+30(5))\ -\ln(100)]$$

$$-\ln(1-X) = 0.1[30-20(0.916)] = 1.167$$

$$X = 0.689$$

$$N_c = N_{A0}X = (200)\,\text{lbmol}\,(0.689) = 137.80\ \text{lbmol C}$$

b) $$-\ln(1-X) = kC_{B0}'\left[t - \frac{V_0}{v}\ln(V_0+vt)\right]\Big|_0^t$$

$$-\ln(1-X) = (0.2)(0.5)[t - \frac{100}{5}(\ln(100+5\ t) - \ln(100))]$$

$$\ln(1-X) = -\,0.1t + 2\ln(100+5t) - 2\ln(100)$$

$$1-X = e^{-0.1t}\,(100+5t)^2(100)^{-2}$$

$$X = 1 - \left(\frac{100+5t}{100}\right)^2 e^{-0.1t}$$

t(min)	X
0	0
5	0.052
10	0.172
15	0.317
20	0.459
25	0.584
30	0.689
35	0.772
40	0.835
45	0.883
50	0.917
55	0.943
60	0.960
10,000	1

c) $$C_A = \frac{N_A}{V} = \frac{C_{A0}'\,vt - N_{B0}\,X}{V_0 + vt}$$

$$C_B = \frac{N_B}{v} = \frac{N_{B0}}{V_0 + vt}$$ -Note that B is used up at the same rate as it is produced.

$$N_c = N_{B0}\,X$$

$$N_{B0} = C_{B0}\,V_0 = (0.5)\ \text{lbmol/ft}^3\ (100)\text{ft}^3 = 50\ \text{lbmol}$$

$$-r_A = kC_AC_B = \frac{k(C_{A0}'vt - N_{B0}X)N_{B0}}{(V_0 + vt)^2}$$

P4-27 (cont'd)

$$-r_A V = N_{BO}\frac{dX}{dt}$$

$$N_{BO}\frac{k(C'_{AO}\,vt - N_{BO}X)}{(V_O + vt)} = N_{BO}\frac{dX}{dt}$$

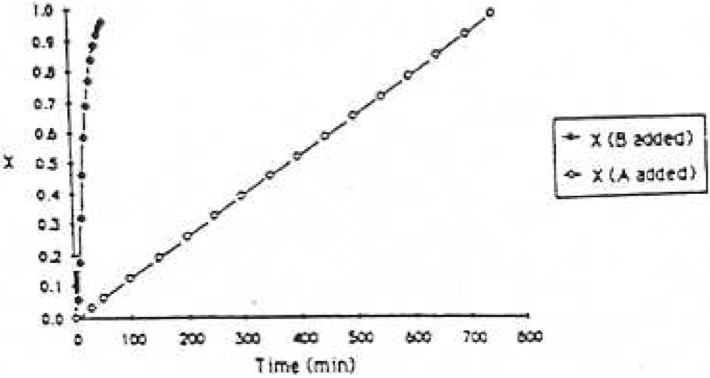
$$\frac{dX}{dt} = \frac{k\,(C'_{AO}vt - N_{BO}X)}{V_O + vt}$$

$$\frac{dX}{dt} = \frac{(0.2)((0.02)(5)\ t - 50X)}{100+5t}$$

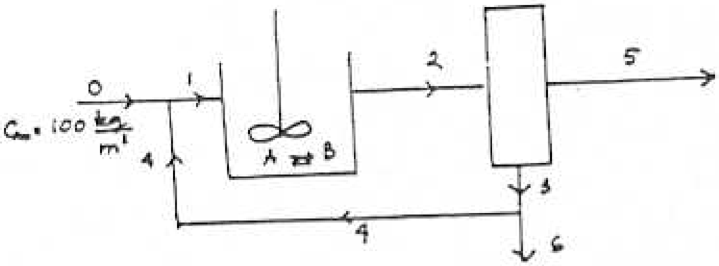
$$\frac{dX}{dt} = \frac{0.02t - 10X}{100+5t}$$

A modified version of the Runge-Kutta program yields

t(min)	X	t(min)	X
0	0	650	0.853
30	0.0301	700	0.920
50	0.0597	750	0.987
100	0.122		
150	0.188		
200	0.254		
250	0.320		
300	0.387		
350	0.454		
400	0.520		
450	0.587		
500	0.653		
550	0.720		
600	0.787		



P4-28.



Note - A and B have the same molecular weight

$F_{A2} = F_{A3}$

$F_{A4} = y\ F_{A3}$

$F_{A1} = F_{A0} + y\ F_{A3}$

$F_{A2} = F_{A1}\ (1-X)$ where X is conversion defined with respect to F_{A1}

$F_{A5} = F_{B2}$ (by problem specification)

$F_{B1} = 0$ (by problem specification)

$F_{A1} = F_{A0} + y\ F_{A1}\ (1-X)$ have $F_{A1} = \dfrac{F_{A0}}{1-y(1-X)}$ (1)

Stoichiometric table

Inlet	Outlet
F_{A1}	$F_{A1}(1-X)$
$F_{B1} = 0$	$F_{B1} + F_{A1}X = F_{A1}X$

Hence

$$F_{B2} = F_{A1}X = \frac{F_{A0}X}{1-y(1-X)}$$

Also

$v_1 = v_0 + v_4$

$v_2 = v_3 + v_5$

$v_1 = v_2$ (no volume change)

$$C_{A1} = \frac{F_{A1}}{v_1} = 100$$

$$v_1 = \frac{F_{A1}}{C_{A1}} = \frac{F_{A1}}{100}$$

P4-29.

This problem was solved using POLYMATH. The equations used for parts a, b, and c are given below.

```
d(ca1)/d(t)=(((voa/vo)*cao-ca1)/tau)-k*ca1**2
d(ca2)/d(t)=((ca1-ca2)/tau)-k*ca2**2
d(ca3)/d(t)=((ca2-ca3)/tau)-k*ca3**2
tau=10
k=0.025
cao=2
voa=10
vo=20
x=(voa*cao-vo*ca3)/(voa*cao)
```

$t_0 = 0$

$ca1_0 = 0$

$ca2_0 = 0$

$ca3_0 = 0$

$t_f = 70$

a) From POLYMATH, the steady state conversion of A is approximately 0.39.

b) 99% of the steady state concentration of A (the concentration of A leaving the 3rd reactor) is:

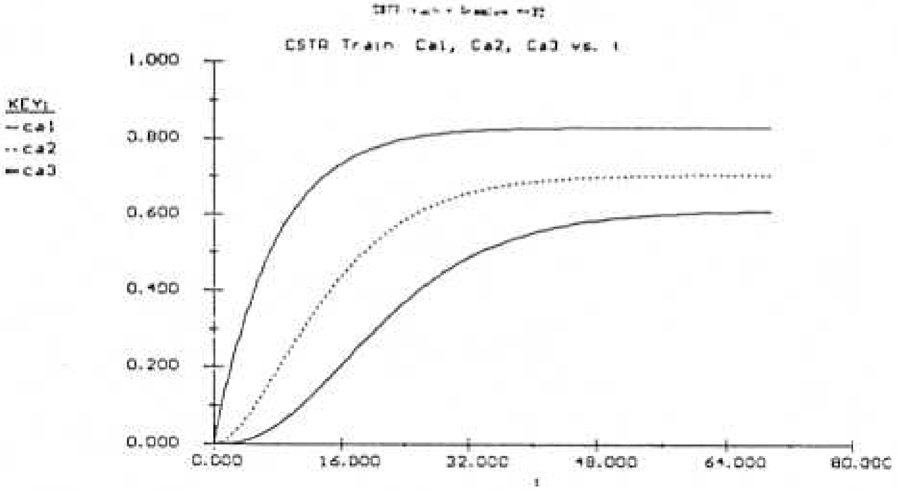
(0.99)(0.6110)=(0.605)

A concentration of 0.605 mol/dm^3 of A corresponds to a time of approximately 64.0 minutes.

c) Below is a plot of the concentration of A exiting each reactor as a function of time.

P4-29 (cont'd)

```
Variable      Initial value  Maximum value  Minimum value  Final value
t             0              70             0              70
ca1           0              0.828378       0              0.828378
ca2           0              0.703875       0              0.703875
ca3           0              0.608412       0              0.608412
voa           10             10             10             10
vo            20             20             20             20
cao           2              2              2              2
tau           10             10             10             10
k             0.025          0.025          0.025          0.025
x             1              1              0.391588       0.391588
```



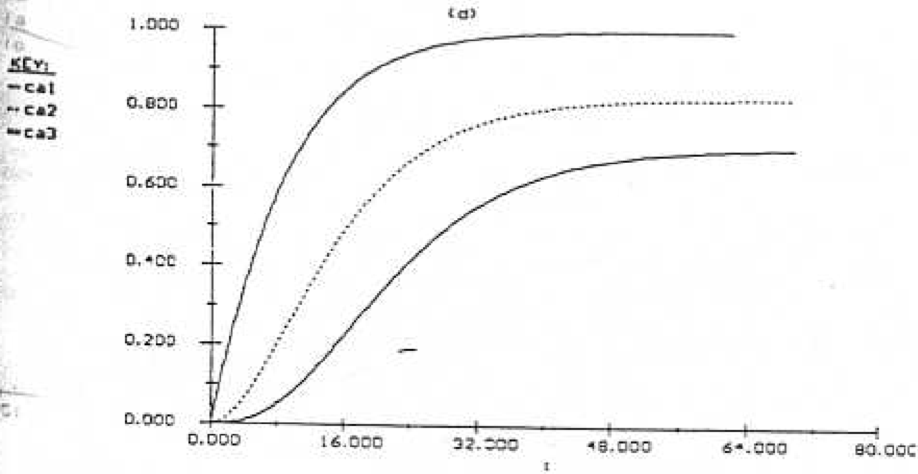
d) From POLYMATH, we found the conversion to be 0.30
99% of the steady state concentration of A is
(0.99)(0.70)=(.693)
That corresponds to 48 minutes
Below is a plot of concentration of A exiting the three CSTRs as a function of time.

e) Varying any of the parameters effects the results rather dramatically. Increasing v_0 to 50 caused the conversion to go to .69 and decreasing it to 11 decreased the conversion to .12. Increasing V to 1000 dm^3 increased the conversion to .87 while decreasing it to 20 dm^3 caused the conversion to decrease to 0.068. Increasing k to .1 caused the conversion to increase to 0.67 while decreasing k to 0.001 caused the conversion to decrease to .054. A person can see that k and V have the most significant effects on the conversion in this case.

P4-29 (cont'd)

```
Equations:                                                   Initial value
d(ca1)/d(t)=(((voa/vo)*cao-ca1)/tau1)-k*ca1**2               0
d(ca2)/d(t)=((ca1-ca2)/tau2)-k*ca2**2                        0
d(ca3)/d(t)=((ca2-ca3)/tau2)-k*ca3**2                        0
voa=10
vo=15
cao=2
k=0.025
tau1=13.3
tau2=10
x=(voa*cao-vo*ca3)/(voa*cao)
t_0 = 0,   t_f = 70
```

```
Variable    Initial value   Maximum value   Minimum value   Final value
t           0               70              0               70
ca1         0               1.00031         0               1.00031
ca2         0               0.82789         0               0.82789
ca3         0               0.701217        0               0.701217
voa         10              10              10              10
vo          15              15              15              15
cao         2               2               2               2
k           0.025           0.025           0.025           0.025
tau1        13.3            13.3            13.3            13.3
tau2        10              10              10              10
x           1               1               0.474088        0.474088
```



P4-30

(a)

$$K_C = \frac{C_B}{C_A}$$

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

$$K_C = \frac{C_{A0}X}{C_{A0}(1-X)} = \frac{X}{1-X}$$

$$X_{eq} = \frac{K_C}{1+K_C} = \frac{0.5}{1+0.5} = 0.33$$

(b) For a conventional PFR:

$$F_{A0}\frac{dX}{dV} = -r_A$$

$$-r_A = k\left(C_A - C_B/K_C\right) = kC_{A0}\left((1-X) - X/K_C\right)$$

For the IMRCF:

$$\frac{dF_A}{dt} = r_A v_o$$

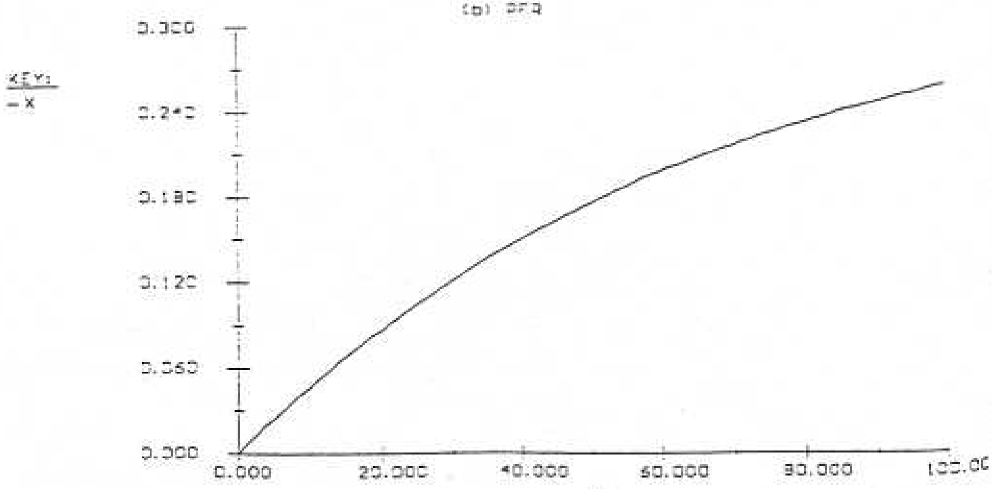
$$\frac{dF_B}{dt} = -r_A v_o - v_o k_C C_B$$

$$-r_A = k\left(C_A - C_B/K_C\right)$$

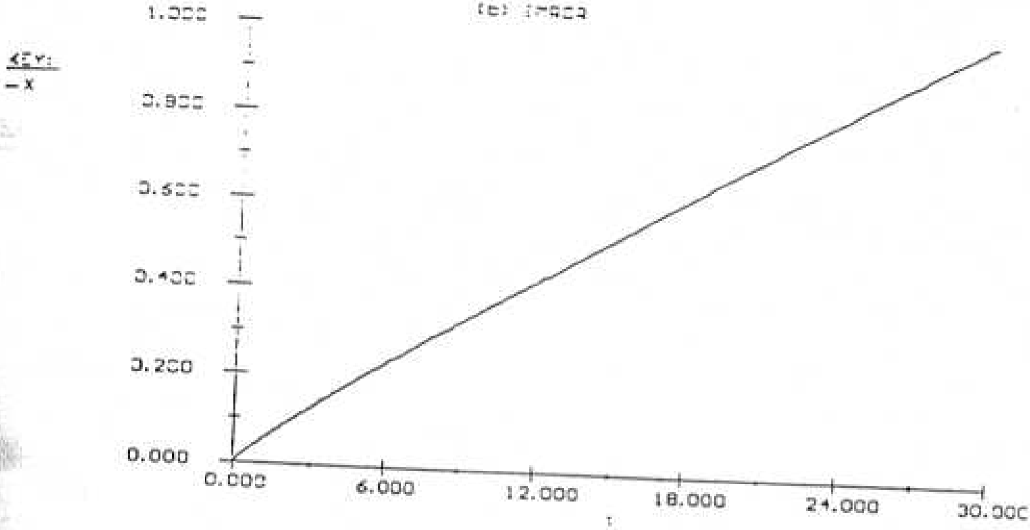
$$C_A = F_A/V\ ,\ C_B = F_B/V$$

$$V = v_o\frac{\left(F_A + F_B\right)}{F_{A0}}$$

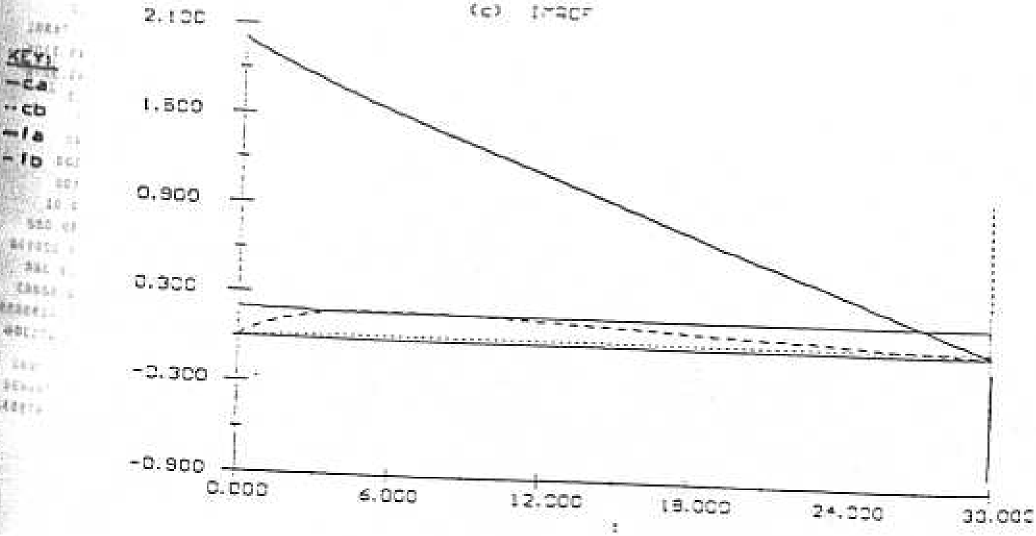
Use these equations in POLYMATH to generate plots of the conversion profile.



P4-30 (cont'd)



(c) Use the same equations for the IMRCF in POLYMATH to generate the desired plot.



P4-30 (cont'd)

(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_e), 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.

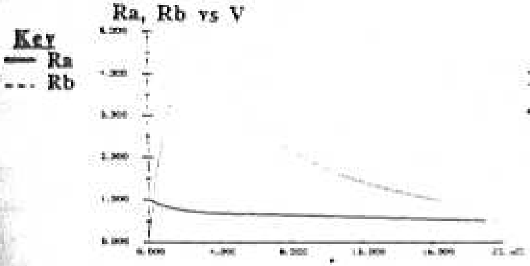
P4-31

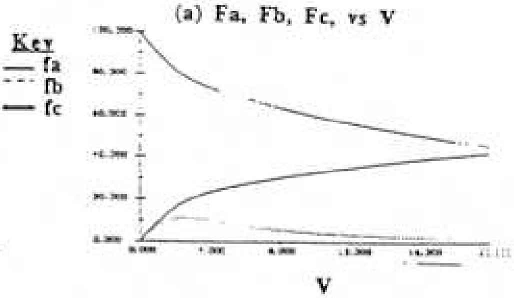
(a) Use the following POLYMATH program to generate the necessary graphs:

```
4-31 (a)
Equations:
d(fb)/d(v)=-ra-Rb
d(fa)/d(v)=ra-Ra
d(fc)/d(v)=-ra
k=10
kca=1
kcb=40
vo=100
fao=100
ke=.01
ft=fa+fb+fc
x=fc/(2*fao)
vf=vo*ft/fao
ca=fa/vf
cb=fb/vf
cc=fc/vf
Ra=kca*fa/vf
Rb=kcb*fb/vf
ra=-k*(ca-cb*cc^2/ke)
v0 = 0,    vf = 20
```

```
4-31 (a)
Variable   Initial value   Maximum value   Minimum value   Final value
v          0               20              0               20
fb         0               11.3351         0               1.74981
fa         100             100             45.3306         45.3306
fc         0               41.9875         0               41.9875
k          10              10              10              10
kca        1               1               1               1
kcb        40              40              40              40
vo         100             100             100             100
fao        100             100             100             100
ke         0.01            0.01            0.01            0.01
ft         100             109.126         89.088          89.088
x          0               0.209938        0               0.209938
vf         100             109.126         89.088          89.088
ca         1               1               0.50883         0.50883
cb         0               0.102822        0               0.0198659
cc         0               0.471304        0               0.471304
Ra         1               1               0.50883         0.50883
Rb         0               4.11288         0               0.794636
ra         -10             -0.675532       -10             -0.675532
```

P4-31 (cont'd)





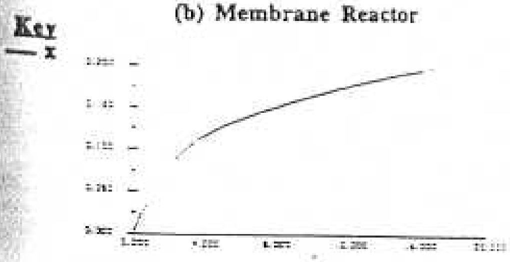
(b) Conventional PFR

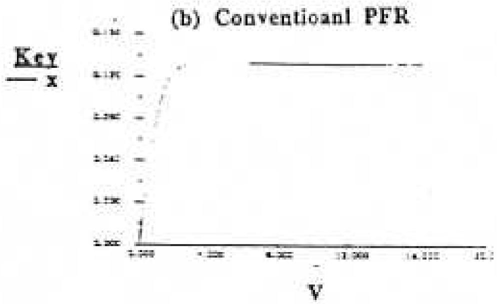
Mole Balance: $F_{A0}\frac{dX}{dV} = -r_A$

Rate Law: $-r_A = k\left(C_A - C_B C_C^2/K_C\right)$

Stoichiometry: $C_A = C_{A0}(1-X)$, $C_B = C_{A0}X$, $C_C = 2C_{A0}X$

Use these equations and the program above in POLYMATH to generate curves for X vs. V.





CDP4-A $CH_3I + AgClO_4 \longrightarrow CH_3ClO_4 + AgI$

0.7 mol/l $CH_3I = C_{BO}$

0.5 mol/l $AgClO_4 = C_{AO}$

$V_o = 30\ dm^3$

$r_{CH_3I} = -k\, C_{CH_3I}\, C_{AgClO_4}^{3/2}$

$k = 0.00042\ (dm^3/mol)^{3/2}(sec)^{-1}$ T=298 K

$X = 0.98$

Let $A = AgClO_4$, $B = CH_3I$

$$t = N_{AO}\int_0^X \frac{dX}{-r_A V}$$

$V = V_O$ (liquid phase)

$$t = \frac{C_{AO}V_O}{V_O}\int_0^X \frac{dX}{k\, C_B C_A^{3/2}}$$

$$t = \frac{C_{AO}}{k}\int_0^X \frac{dX}{C_{AO}(7/5 - X)\, C_{AO}^{3/2}(1 - X)^{3/2}}$$

$$t = \frac{1}{k\, C_{AO}^{3/2}}\int_0^X \frac{dX}{(7/5 - X)(1- X)^{3/2}}$$

Integration for X = 0.98, solved numerically

$$t = \frac{1}{0.00042\ (0.5)^{3/2}}\ (24.18)$$

$t = 1.628x10^5$ sec = 45.2 hr

CDP4-B

(a)

Mole Balance :

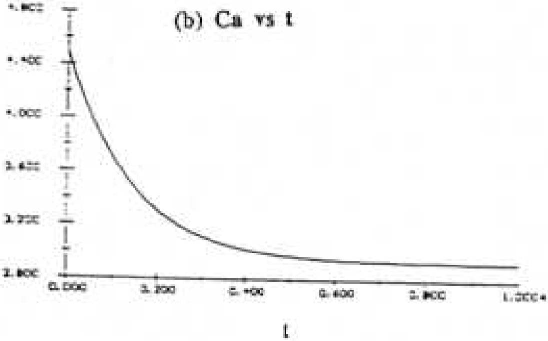
$$\frac{dN_A}{dt} = F_{A0} - F_A + r_A V$$

$$V\frac{dC_A}{dt} = C_{A0}v_0 - C_A v_0 - kC_A V$$

$$\frac{dC_A}{dt} = \frac{C_{A0}v_0}{V} - \frac{C_A(v_0 + V)}{V}$$

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
t0 = 0,    tf = 1000
```



For steady-state:

$$t = 4.6\frac{\tau}{1 + \tau k} = 641 \text{ hrs}$$

$$C_A = \frac{C_{A0}v_0}{kV + v_0} = 2.930 \text{ mg/dm}^3$$

99% of this is 2.946 mg/dm^3, which is below the standard of 3.0 mg/dm^3.

(b)

Mole Balance :

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

$$\frac{dN_A}{dt} = C_{A0}v_0 - C_A v_{out} - kC_A V$$

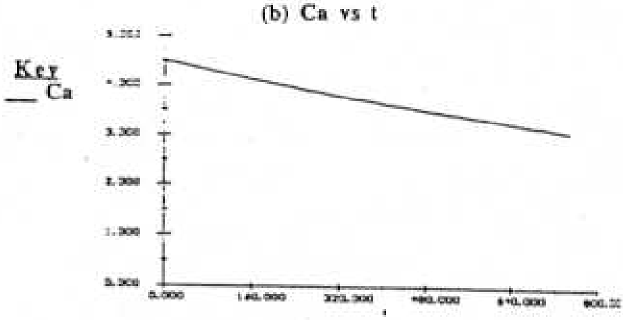
Use POLYMATH to generate plot of C_A and N_A vs. t.

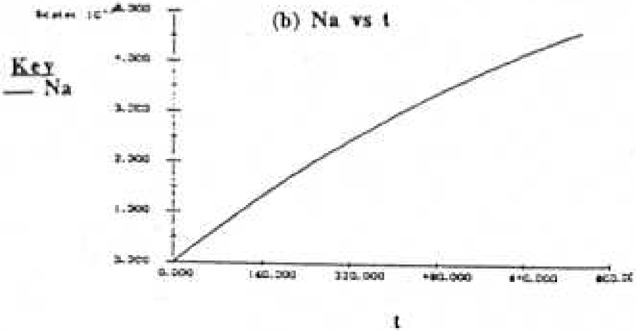
CDP4-B (cont'd)

Equations:

```
d(na)/d(t)=cao*vo-ca*vout-k*ca*v
cao=4.5
vo=70000
vout=50000
k=0.0025
v=20000*t
ca=na/v
```

$t_0 = 1, \quad t_f = 750$





(c)

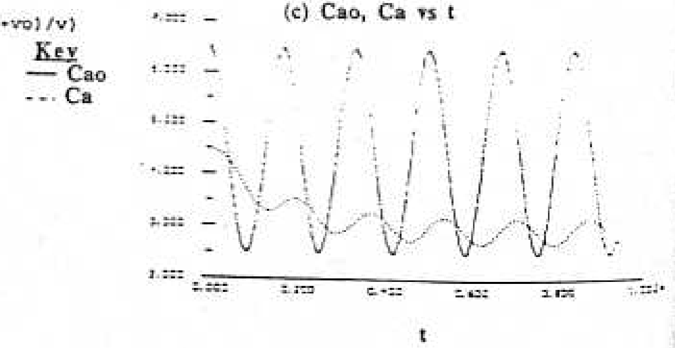
Use same equations as in part (a),

but change $C_{A0} = 4.5$ to $C_{A0} = 4.5 + 2.0\cos\left(\frac{\pi}{84}t\right)$

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
```

$t_0 = 0, \quad t_f = 1000$



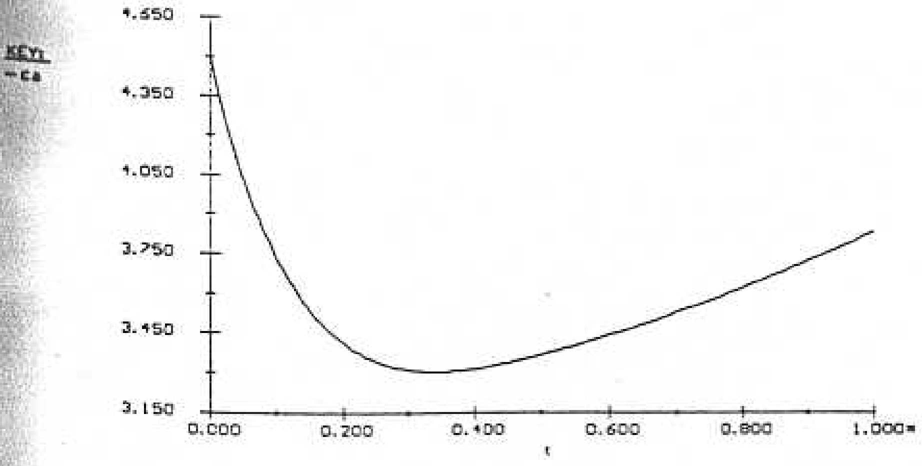
(d) Use the same equations in (a) except two values change:

$V = 15000000 - 10000t$
$v_0 = 80000$

The reason the graph looks so different from (a) is that pure water is evaporated, but water with atrazine is coming in.

```
4-b (a)
Equations:                                                         Initial value
d(ca)/d(t)=(cao*vo/v)-(ca*(k*v+vo)/v)                              4.5
cao=4.5
vo=80000
v=15000000-10000*t
k=0.0025
t0 = 0,    tf = 1000
```

```
4-b (d)
Variable     Initial value  Maximum value  Minimum value  Final value
t            0              1000           0              1000
ca           4.5            4.5            3.30411        3.8315
cao          4.5            4.5            4.5            4.5
vo           80000          80000          80000          80000
v            1.5e+07        1.5e+07        5e+06          5e+06
k            0.0025         0.0025         0.0025         0.0025
```



CDP4-C

a)Find the number of moles of receptors:

$$1\times10^{6}\ \frac{\text{cells}}{\text{mL}}*1\times10^{5}\ \frac{\text{receptors}}{\text{cell}}*\frac{1\ \text{mole receptors}}{6.022\times10^{23}\ \text{receptors}}*\frac{1000mL}{L}=1.66\times10^{-10}\ \text{M}$$

$$1.66\times10^{-10}\frac{mol}{L}*.01L=1.66\times10^{-12}\,moles$$

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:

$$\frac{dX}{(1-X)(\theta_B-X)}=\frac{kC_{A0}^2dt}{N_{A0}}$$

$$\frac{1}{\theta_B-1}\ln\frac{\theta_{B-X}}{\theta_B(1-X)}=\frac{kC_{A0}^2t}{N_{A0}}$$

$$t=0.071\,\text{min}$$

b) Assume $C_B=C_{B0}$

Design Equation:

$$N_{A0}\frac{dX}{dt}=-r_A$$

Rate Law:

$$-r_A=kC_AC_B$$

Stoichiometry:

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

$$C_B=C_{B0}$$

CDP4-C (cont'd)

Combine and solve:

$$\frac{dX}{1-X}=\frac{kC_{A0}C_{B0}dt}{N_{A0}}$$

$$\ln\frac{1}{1-X}=\frac{kC_{A0}C_{B0}t}{N_{A0}}$$

$$t=0.069\text{ min}$$

A very good approximation.

c) Design Equation:

$$N_{A0}\frac{dX}{dt}=-r_A$$

Rate Law:

$$-r_A=k_fC_AC_B-k_rC_C$$

Stoichiometry:

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

$$C_B=C_{B0}$$

$$C_C=C_{A0}X$$

Combine and solve:

$$N_{A0}\frac{dX}{dt}=k_fC_{A0}(1-X)C_{B0}-k_rC_{A0}X$$

$$\frac{dX}{k_fC_{A0}C_{B0}-k_fC_{A0}C_{B0}-k_rC_{A0}X}=\frac{dt}{N_{A0}}$$

$$\int_0^X\frac{dX}{k_fC_{B0}-X(k_fC_{B0}+k_r)}=\int_0^5\frac{C_{A0}dt}{X}$$

$$\frac{1}{k_fC_{B0}+k_r}\ln\frac{k_fC_{B0}}{k_fC_{B0}-X(k_fC_{B0}+k_r)}=\frac{5C_{A0}}{N_{A0}}$$

$$\frac{1}{.1+.1}\ln\frac{.1}{.1-X(.1+.1)}=500$$

$$X=0.5$$

CDP4-D Batch $2A+B \longrightarrow 2C$

$$-r_A = k_1 C_A C_B + k_2 C_A C_B^{\,2}$$

$$k_1 = 1.98 \text{ ft}^3/\text{lbmol}/\text{min}$$

$$k_2 = 9.2\text{x}10^3 \ (\text{ft}^3/\text{lbmol})^2/\text{min}$$

$$V = 5 \text{ gal} = 0.67 \text{ ft}^3$$

$$C_{A0} = \frac{0.002 \text{ lbmol}}{0.67 \text{ ft}^3} = 2.98\text{x}10^{-3} \text{ lbmol}/\text{ft}^3$$

$$C'_{A0} = \frac{0.34 \text{ lb}}{0.67 \text{ ft}^3} = 0.507 \text{ lb}/\text{ft}^3$$

$$C_{B0} = \frac{0.0018 \text{ lbmol}}{0.67 \text{ ft}^3} = 2.69\text{x}10^{-3} \text{ lbmol}/\text{ft}^3$$

$$C'_{B0} = \frac{0.288 \text{ lb}}{0.67 \text{ ft}^3} = 0.430 \text{ lbmol}/\text{ft}^3$$

X = 0.65 based on A

$$t = N_{A0}\int_0^X \frac{dX}{-r_A V}$$

$$V = V_0$$

(liquid phase)

$$t = \frac{C_{A0} V_0}{V_0}\int_0^X \frac{dX}{(1+\varepsilon X)[k_1 C_A C_B + k_2 C_A C_B^{\,2}]}$$

$$t = C_{A0}\int_0^X \frac{dX}{(1+\varepsilon X)\ [k_1 C_{A0}^2(1-X)(1-X/2) + k_2 C_{A0}^3(1-X)(1-X/2)^2]}$$

$$t = \frac{C_{A0}}{C_{A0}^2}\int_0^X \frac{dX}{(1+\varepsilon X)(1-X)(1-X/2)(k_1 + k_2 C_{A0}(1-X/2)}$$

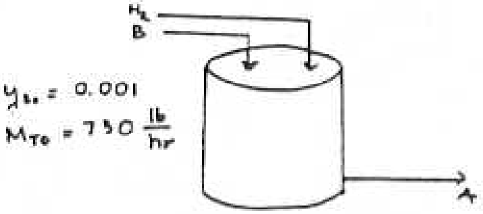
$$t = \frac{1}{2.98\text{x}10^{-3}}\,\frac{\text{lbmol}}{\text{ft}^3}\int_0^{0.65} \frac{dX}{(1-0.526X)(1-X)(1-X/2)[1.98 + (9.2\text{x}10^3)(2.98\text{x}10^{-3})(1-X/2)]\text{ft}^3/\text{lbmol}\cdot\text{min}}$$

$$t = \frac{1}{2.98\text{x}10^{-3}}\int_0^{0.65} \frac{dX}{(1-0.526X)(1-X)(1-X/2)(29.40-13.71X)}$$

Numerical integration yields

$$t = \frac{5.56\text{x}10^{-2}}{2.98\text{x}10^{-3}} \text{ min} = 18.7 \text{ min}$$

CDP4-E Given: CSTR with reaction: $B + H_2 \rightarrow A$



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. $\therefore y_{A0} = 1 - y_{B0} = .999$

Because of the low concentration of B in the feed, such properties as, SG, the specific gravity, MW, 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 500 psig,

$$C_{H_2,f} = \left[\frac{5.0g}{l}\right] \times \left[\frac{1gmole}{2g}\right] \times \left[\frac{1\ lbmole}{454\ gmoles}\right] \times \left[\frac{3.785l}{gal}\right] = \frac{.0208\ lbmole}{gal}$$

$$F_{A0} \simeq F_{Af} \text{ because } y_B \ll 1\ ,\ F_{Af} = \frac{M_T}{(M_{WA})} = \frac{730\ lb/hr}{\frac{196\ lb}{lbmole}} = 3.72\ lbmole/hr$$

Assume that there is no volume change accompanying absorption of H_2: Then

$$\therefore v_0 = \frac{M_T}{SG\ \rho_{H_2O}} = v = \text{constant, or}$$

$$v = \left[\frac{730\ lbA}{hr.}\right] \times \left[\frac{lb \times H_2O}{.980\ lbA}\right] \times \frac{1\ ft^3}{62.41\ lb} \times \left[\frac{7.48\ gal}{ft^3}\right] = 89.3\ gal/hr.$$

CDP4-E (cont'd) $\circledast \frac{X_{B0} F_{T0}}{V_0}$

$$C_{BO} = \frac{F_{BO}}{V_o} = \frac{x_{BO}F_{TO}}{v_o} = \frac{(10^{-3})(3.72)\,\text{lbmole/hr}}{(89.3)\,\text{gal/hr}} = 4.17 \times 10^{-5}\,\text{lbmole/gal}$$

Using equation for a CSTR

$$V = \frac{F_{BO}X}{-r_B}$$

$$k = \frac{F_{BO}X}{V\,C_{BO}(1-X)C_{H_{2,f}}} = \frac{v_o\,X}{V(1-X)C_{H_{2,f}}}$$

$$k = \frac{(89.3\ \text{gal/hr})(0.99)}{50\ \text{gal}\ \left(\frac{0.0208\ \text{lbmol}}{\text{gal}}\right)\ (0.01)}$$

$$k = 8.49 \times 10^3\ \text{gal/(lbmole - hr)}$$

With reactor at 300 psig, Henry's law is: $C_{H_2} \propto P$

$$\therefore\ C_{H_2}\ (300\ \text{psig}) = C_{H_2}\ (500\ \text{psig}) \times \left(\frac{300+14.7}{500+14.7}\right) = (.0208)\left[\frac{314.7}{514.7}\right]\frac{\text{lbmole}}{\text{gal}}$$

$$C_{H_2} = 0.0127\ \text{lbmole/gal}$$

Let conversion be X_2 when pressure = 300 psig

$$V = \frac{F_{BO}X_2}{k\,C_{BO}(1-X_2)C_{H_{2,300}}} = \frac{v_o\,X_2}{k(1-X_2)C_{H_{2,300}}}$$

$$\frac{X_2}{1-X_2} = \frac{(50\ \text{gal})(8.49\times10^3\ \text{gal/lbmol-hr})(0.0127\ \text{lbmol/gal})}{89.3\ \text{gal/hr}}$$

$$F_{H_{2,F}} = C_{H_{2,F}}\,v_o = \left(\frac{.0127\ \text{lbmole}}{\text{gal}}\right)\left(\frac{39.4\ \text{gal}}{\text{hr}}\right) = 1.134\ \text{lbmole/hr}$$

$$y_{BF} = \frac{F_{BO}\ (1-X_2)}{F_{H_{2,F}}+F_{TO}} = \frac{(3.72\times10^{-3})\ (1-0.984)}{1.134+3.72} = 1.23\times10^{-5}$$

CDP4-F $A + 2B \longrightarrow 2D$

a) Stoichiometric table - Basis: 1 mole of A fed

Species	In	Change	Out
A	1	$-X$	$1-X$
B	5/2	$-2X$	$5/2-2X$
D	0	$+2X$	$2X$
I	3/2	0	3/2
	5	$-X$	$5-X$

$$v = \frac{F_T}{F_{To}} v_o = \frac{F_{AO}(5-X)}{5 F_{AO}} = (1-0.2X)v_o$$

b) $$C_A = \frac{F_A}{v} = \frac{F_{AO}(1-X)}{v_o(1-0.2X)} = C_{AO}\frac{(1-X)}{(1-0.2X)}$$

$$C_B = \frac{F_B}{v} = \frac{F_{AO}(5/2-2X)}{v_o(1-0.2X)} = C_{AO}\frac{(5/2-2X)}{(1-0.2X)}$$

$$C_D = \frac{F_D}{v} = \frac{F_{AO}(2X)}{v_o(1-0.2X)} = C_{AO}\frac{(2X)}{(1-0.2X)}.$$

c) $$C_{AO} = \frac{F_{AO}}{v_o} = \frac{y_{AO}\,F_{T_o}}{v_o} = \frac{y_{AO}\,P_{T_o}}{RT_o} = \frac{(0.2)(5\ \text{atm})}{(.082)\text{dm}^3\text{atm/mol K}\ (55+273)\text{K}}$$

$$C_{AO} = 0.037\ \text{mol/dm}^3$$

d) $$-r_A = 2.5\ C_A^{1/2}\ C_B = 2.5\ C_{AO}^{3/2}\frac{(1-X)^{1/2}(5/2-2X)}{(1-0.2X)^{3/2}}$$

PFR

$$V = F_{AO}\int_o^X \frac{dX}{-r_A}$$

$$V = C_{AO}\ v_o \int_o^X \frac{dX\ (1-0.2X)^{3/2}}{2.5\ C_{AO}^{3/2}\ (1-X)^{1/2}(5/2-2X)}$$

$$V = \frac{C_{AO}v_o}{2.5C_{AO}^{3/2}}\int_o^X \frac{(1-0.2X)^{3/2}}{(1-X)^{1/2}\ (5/2-2X)}dX$$

CDP4-F (cont'd)

$$V = \frac{50\ \text{dm}^3/\text{min}}{(2.5)(0.037)^{1/2}\ (1/\text{min})} \int_0^{0.70} \frac{(1-0.2X)^{3/2}}{(1-X)^{1/2}\ (5/2-2X)}\, dX$$

$$V = 103.98 \int_0^{0.70} \frac{(1-0.2X)^{3/2}}{(1-X)^{1/2}\ (5/2-2X)} dX\ \text{dm}^3$$

Numerical integration yields

$V = 103.98\ (0.483)\ \text{dm}^3$

$V = 50.21\ \text{dm}^3$

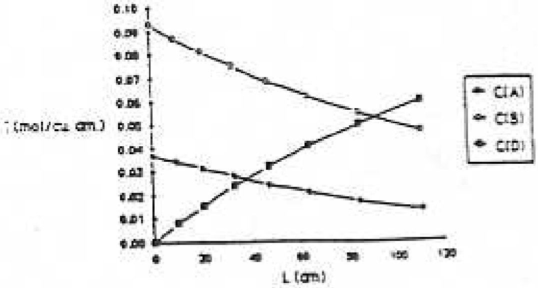
e) Have C_A, C_B, C_D and v as functions of X, so only need an equation for X as a function of reactor length.

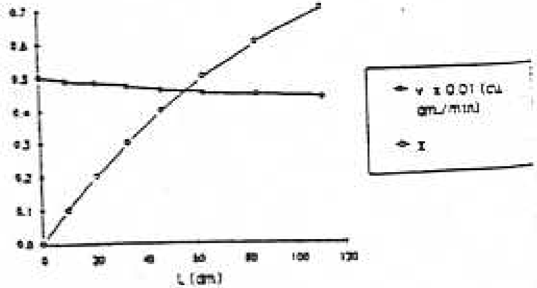
$V = \pi r^2 L = \pi(0.76/2)^2\ L = 0.454\ L$

$$\Rightarrow\ L = \frac{V}{0.454} = \frac{103.98}{0.454} \int_0^X \frac{(1-0.2X)^{3/2}}{(1-X)^{1/2}(5/2-2X)}$$

So if we take X from 0 to 0.70 in 0.10 intervals, we can get values of the other unknowns.

X	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
$C_A(\text{mol/dm}^3)$	0.037	0.034	0.031	0.028	0.024	0.021	0.017	0.013
$C_B(\text{mol/dm}^3)$	0.093	0.087	0.081	0.075	0.068	0.062	0.055	0.047
$C_D(\text{mol/dm}^3)$	0	0.008	0.015	0.024	0.032	0.041	0.050	0.060
$v(\text{dm}^3/\text{min})$	50	49	48	47	46	45	44	43
$V(\text{dm}^3)$	0	4.37	9.25	14.87	21.32	28.91	38.26	50.21
L(dm)	0	9.62	20.38	32.75	46.95	63.67	84.28	110.59





f) CSTR

$$V = \frac{F_{AO}(X-X_o)}{-r_A} \quad \text{from } X=0.70 \text{ to } 0.85$$

$$V = \frac{C_{AO}\ v_o\ (X-X_o)(1-0.2X)^{3/2}\ \text{mol/min}}{2.5\ C_{AO}^{3/2}(1-X)^{1/2}(5/2-2X)\ \text{mol/dm}^3\text{/min}}$$

$$V = \frac{(50)(0.85-0.70)(1-0.2(0.85))^{3/2}}{2.5\ (0.037)^{1/2}(1-0.85)^{1/2}(5/2-2(0.85))}$$

$$V = 38.06\ \text{dm}^3$$

g) $-r_A = F_{AO}\frac{dX}{dW} = 2.5\ C_A^{1/2}\ C_B$

$$C_A = C_{AO}\frac{(1-X)}{(1-0.2X)}\frac{P}{P_o}\ ;\ C_B = C_{AO}\frac{(2.5-2X)}{(1-0.2X)}\frac{P}{P_o} \quad \text{where } \frac{P}{P_o} = (1-\alpha W)^{1/2}$$

$$-r_A = 2.5\ C_{AO}^{3/2}\ \frac{(1-X)^{1/2}(2.5-2X)}{(1-0.2X)^{3/2}}\ (1-\alpha W)^{3/4} = F_{AO}\frac{dX}{dW}$$

$$\alpha = \frac{2\beta_o}{A_c(1-\phi)\rho_c P_o}\ ,\quad \beta_o = \frac{G(1-\phi)}{\rho_o g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right]$$

$$A_c = \frac{\pi}{4}d^2 = \frac{\pi}{4}\left(\frac{1}{12}\right)^2 \text{ft}^2 = 5.454\text{x}10^{-3}\ \text{ft}^2$$

$$\phi = 0.45$$

$$\rho_c = 2\ \text{g/cm}^3 = 124.74\ \frac{\text{lbm}}{\text{ft}^3}$$

$$P_o = 5\ \text{atm}$$

$$G = \frac{\dot{m}_T}{A_c} = \frac{\left[\left(0.037\ \frac{\text{mol A}}{\text{dm}^3}\right)\left(\frac{100\text{g A}}{\text{mol A}}\right) - \left(0.093\ \frac{\text{mol B}}{\text{dm}^3}\right)\left(\frac{50\text{g B}}{\text{mol B}}\right)\right]\left(50\frac{\text{dm}^3}{\text{min}}\right)}{5.454\ \text{x}\ 10^{-3}\ \text{ft}^2}$$

$$G = 7.655\text{x}10^4\ \frac{\text{g}}{\text{ft}^2\text{.min}} = 168.61\ \frac{\text{lbm}}{\text{ft}^2\text{.min}} = 10{,}117\ \frac{\text{lbm}}{\text{ft}^2\text{.hr}}$$

$$\rho_o = 0.4\ \frac{\text{lbm}}{\text{ft}^3}$$

CDP4-F (cont'd)

$$g_c = 4.17x10^8 \ \frac{lbm\ ft}{lb_f\ hr^2}$$

$$D_p = 0.5mm = 5x10^{-2}cm = 1.64x10^{-3}ft$$

$$\mu = 0.0673 \ \frac{lbm}{ft.hr}$$

$$\beta_o = \frac{(168.61\ \frac{lbm}{ft^2.min})(0.55)(60\frac{min}{hr})}{(0.4\frac{lbm}{ft^3})(4.17x10^8\frac{lbmft}{lbf\ hr^2})(1.64x10^{-3}ft)(0.45)^3}$$

$$\left[\frac{(150)(0.55)(0.0673)\frac{lbm}{ft.hr}}{1.64x10^{-3}ft} + (1.75)(10{,}117\frac{lbm}{ft^2hr}\right]$$

$$\beta_o = (4708\ \frac{lbf}{ft^3})(\frac{1ft^2}{144^{\cdot 2}_{m}})(\frac{1atm\ldots}{14.7lb_f\ 1in^2}) = 2.22\ \frac{atm}{ft}$$

$$\alpha = \frac{(2)(2.22\ atm/ft)}{(5.454x10^{-3}ft^2)(0.55)(124.74\ lbm/ft^3)(5atm)} = 2.37$$

$$-r_A = 2.5\ C_{AO}^{3/2}\ \frac{(1-X)^{1/2}(2.5-2X)(1-2.37X)^{3/4}}{(1-0.2X)^{3/2}}$$

$$V = F_{AO}\int_0^{0.95} \frac{dX}{-r_A} = \frac{C_{AO}\ v_o}{2.5\ C_{AO}^{3/2}}\int_0^{0.95} \frac{(1-0.2X)^{3/2}dX}{(1-X)^{1/2}(2.5-2X)(1-2.37X)^{3/4}}$$

$$V = (103.98)(0.55) = 57.2\ dm^3$$

Volume of each tube: $V_t = \frac{\pi D^2}{4}L = \frac{\pi}{4}(\frac{1}{12})^2(20) = 0.109\ ft^3$

$$n = \frac{V}{V_t} = (\frac{57.2\ dm^3}{0.109\ ft^3})(\frac{1ft}{0.254x12dm})^3 = 19$$

h) $-r_A = k_2\ (C_A^{1/2}\ C_B - \frac{C_D}{K_e})$; $C_{AO} = \frac{0.2(5)}{0.082(373)} = 0.033\ \frac{mol}{l}$

$k = Ae^{-E/RT}$ ==> $k_2 = k_1\ e^{-E/R(1/T_2\ -\ 1/T_1)}$

CDP4-F (cont'd)

$$k_2 = 2.5\ e^{-30x10^3 J/mol/8.31J/mol/K(1/373-1/328)}\ \bullet K^{-1}$$

$$k_2 = 9.43$$

$$-r_A = 9.43\ (C_{AO}^{3/2}\ \frac{(1-X)^{1/2}(5/2-2X)}{(1-0.2X)^{3/2}} - 0.1\ C_{AO}\ \frac{2X}{(1-0.2X)})$$

$$-r_A = \frac{9.43\ C_{AO}}{(1-0.2X)^{3/2}}\ (C_{AO}^{1/2}\ (1-X)^{1/2}(5/2-2X)\ -0.2X(1-0.2X)^{1/2})$$

At equilibrium $-r_A = 0$

$$(0.033)^{1/2}(1-X_e)^{1/2}(5/2-2X_e)-0.2X_e(1-0.2X_e)^{1/2} = 0$$

$$X_e = 0.664$$

PFR $X = 0.70\ (0.664) = 0.465$

$$V = F_{AO}\int_o^X \frac{dX}{-r_A}$$

$$V = C_{AO}\ v_o\int_o^X \frac{(1-0.2X)^{3/2}\ dX}{9.43C_{AO}\ (C_{AO}^{1/2}(1-X)^{1/2}(5/2-2X)-0.2X(1-0.2X)^{1/2})}$$

$$V = \frac{50dm^3/min}{9.43(1/min)}\int_o^{0.465} \frac{(1-0.2X)^{3/2}\ dX}{(0.037)^{1/2}(1-X)^{1/2}(5/2-2X)-0.2X(1-0.2X)^{1/2}}$$

Numerical integration yields

$V = 5.302\ (1.614)$

$V = 8.559\ dm^3$

CSTR $X = 0.85(0.664) = 0.564$

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

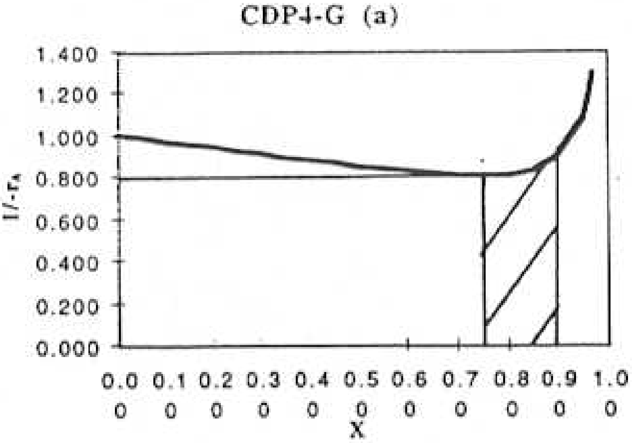
$$V = \frac{C_{AO}\ v_o\ (X-X_o)(1-0.2X)^{3/2}}{9.43\ C_{AO}\ (C_{AO}^{1/2}(1-X)^{1/2}(5/2-2X)-0.2X(1-0.2X)^{1/2})}$$

$$V = \frac{50\ dm^3/min\ (0.564-0.465)(1-0.2(0.564))^{3/2}}{9.43(0.037^{1/2}(1-0.564)^{1/2}(5/2-2(0.564)-0.2(0.564)(1-0.2(0.564))^{1/2})}$$

$V = 6.45\ dm^3$

CDP4-G

(a) Plot 1/-rA vs. X to find the optimal system:



From the chart it is apparent that to minimize volume the best system would be a CSTR followed by a PFR.

(b) To find the volume of the CSTR, calculate the area of the rectangle drawn in the chart and multiply it times the initial flow rate of A:

$$V = (\text{area of rectangle})(F_{Ao}) = (0.80)(0.75)(100) = 60\ \text{ft}^3$$

To find the volume of the PFR, calculate the area under the curve between X=0.75 and 0.90, and multiply times the initial flow rate of A:

$$\text{Using the trapezoidal rule:} \qquad A = \frac{0.90 - 0.75}{2}(0.885 + 0.800) = 0.126$$

$$V = (\text{area under the curve})(F_{Ao}) = (0.126)(100) = 12.6\ \text{ft}^3$$

(c)

$$\text{Design Equation:} \qquad \frac{dX}{dV} = \frac{-r_A}{F_{Ao}} \quad \text{or} \quad \frac{dV}{dX} = \frac{F_{Ao}}{-r_A}$$

$$\text{Rate Law:} \qquad -r_A = \frac{k_1 C_A^{1/2}}{1 + k_2 C_A}$$

$$\text{Stoichiometry:} \qquad C_A = C_{Ao}(1 - X)$$

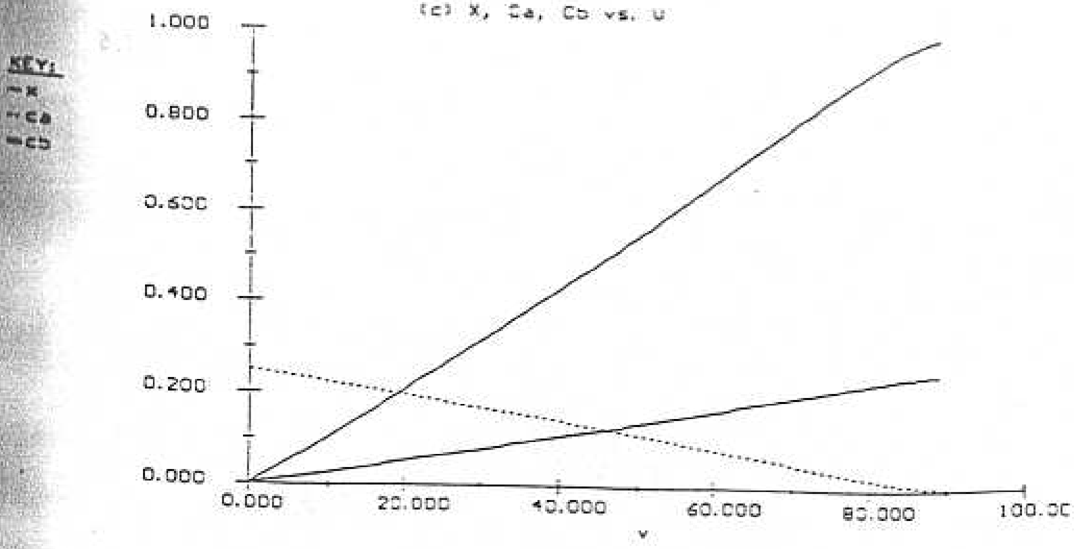
$$C_B = C_{Ao}X$$

Use these equations in POLYMATH to generate the plot of X, C_A, and C_B vs. V.

CDP4-G (cont'd)

```
Equations:                                          Initial value
d(v)/d(x)=fao/ra                                    0
k1=10
fao=100
k2=16
cao=0.25
ca=cao*(1-x)
cb=cao*x
ra=k1*ca**.5/(1+k2*ca)
x0 = 0,    xf = 0.99
```

```
Variable      Initial value   Maximum value   Minimum value   Final value
x             0               0.99            0               0.99
v             0               89.28           0               89.28
k1            10              10              10              10
fao           100             100             100             100
k2            16              16              16              16
cao           0.25            0.25            0.25            0.25
ca            0.25            0.25            0.0025          0.0025
cb            0               0.2475          0               0.2475
ra            1               1.24994         0.480769        0.480769
```



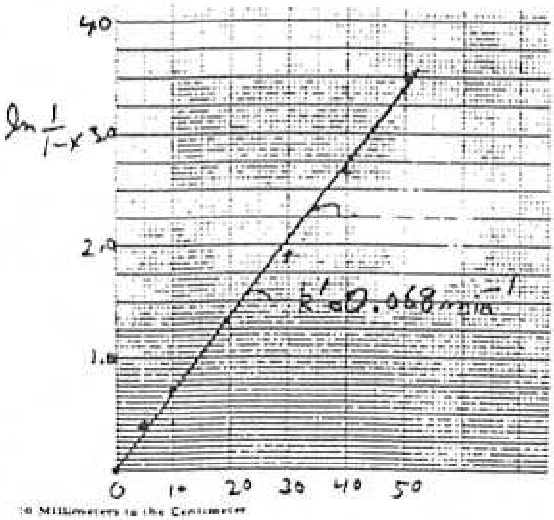
CDP4-H $N_{A0}\frac{dX}{dt} = V\rho_C\left(-r_A'\right) = V\rho_C\, kC_A$

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

$$\frac{dX}{dt} = \rho_C\, k\,(1-X)$$

$$\ln\frac{1}{1-X} = \frac{k'}{k\rho_c}\, t$$

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 $k'=0.068\ \text{min}^{-1}$

$$\ln\left[\frac{-r_A(T_2)}{r_A(T_1)}\right] = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln 4 = \frac{E}{R}\left[\frac{1}{353} - \frac{1}{383}\right]$$

$$\frac{E}{R} = \frac{\ln 4}{\frac{30}{(353(383))}} = 6248\ ^\circ K$$

$$E = 12{,}414\ \frac{cal}{mol}$$

at 90°C = 363K

$$k\,(363) = \left[e^{6248\left(\frac{1}{373} - \frac{1}{363}\right)}\right] k\,(373)$$

$$k\,(363) = 0.63\ k\,(373)$$

CDP4-H (cont'd)

$$k_2' = \frac{k_2}{k_1}\,\frac{\rho_{C2}\,k_1'}{\rho_{C1}} = (.63)\,(2)\,k_1' = 1.26\,k_1'$$

$$k_1' = 0.0857$$

$$\ln\frac{1}{1-X} = k't$$

$$X = 1 - e^{-k't}$$

t	0	10	20	30	40	50
X	0	0.57	0.82	0.42	0.97	0.99

CDP4-I

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

$N_{B0} = 0.005$ kmol, $C_{B0} = 0.015$ kmol/m^3 $V_o = 0.33$ m^3
$C_{A0F} = 0.03$ kmol/m^3 $v = 4\times10^{-3}$ m^3/min.

Feed stopped when $V = 0.53$ m^3

$$0.33 + 4x10^{-3}t = 0.52$$

$$t = 50\,\text{min}$$

a) $-r_B = -\dfrac{r_A}{2} = \dfrac{k}{2}C_A C_B$

From t = 0 to t = 50 min.

$$V = V_0 + vt$$

$$C_B = \frac{N_{B0}(1-X_B)}{V_0 + vt} = \frac{0.005(1-X_B)}{0.33 + 4x10^{-3}t}$$

$$C_A = \frac{C_{A0F}vt - 2N_{B0}X_B}{V_0 + vt} = \frac{1.2x10^{-4}t - 0.01X_B}{0.33 + 4x10^{-3}t}$$

$$C_C = C_D = \frac{N_{B0}X_B}{V_0 + vt} = \frac{0.005X_B}{0.33 + 4x10^{-3}t}$$

$$-r_B V = N_{B0}\frac{dX_A}{dt}$$

$$\frac{k}{2}\frac{\left(C_{A0F}vt - 2N_{B0}X_B\right)\left(N_{B0}(1-X_B)\right)^{0.5}}{\left(V_0 + vt\right)^{0.5}} = N_{B0}\frac{dX_B}{dt}$$

$$\frac{dX_B}{dt} = 6000\frac{\left(1.2x10^{-4}t - 0.01X_B\right)\left(0.005(1-X_B)\right)^{0.5}}{\left(0.33 + 4x10^{-3}t\right)^{0.5}}$$

CDP4-I (cont'd)

Plugging that into POLYMATH we get the following table:

```
Equations:                                                          Initial value
d(xb)/d(t)=6000*(1.2e-4*t-.01*xb)*(.005*(1-xb))^.5/(.33+4           0
   e-3*t)^.5
Vo=.33
vo=4e-3
Cb=0.005*(1-xb)/(.33+4e-3*t)
ca=(1.2e-4*t-.01*xb)/(.33+4e-3*t)
cc=.005*xb/(.33+4e-3*t)
V=Vo+vo*t
t0 = 0,    tf = 50
t              xb             ca              Cb              cc
0              0              0               0.015151515     0
10             0.11817128     4.9424906e-05   0.011916604     0.0015969092
20             0.23792992     5.0489792e-05   0.0092935376    0.0029015844
30             0.35763903     5.246591e-05    0.0071373441    0.003973767
40             0.47727115     5.5690825e-05   0.0053339679    0.0048701138
50             0.59677332     6.0880811e-05   0.0038040253    0.005629937
```

after t = 50 min, treat as a batch reactor with a volume of 0.53 m^3 and starting conditions:

$$N'_{A0} = C'_{A0}\,V = (5.7\times10^{-4})\ \text{kmol/m}^3\ (0.53)\text{m}^3 = 3.02\times10^{-4}\ \text{kmol}$$
$$N'_{B0} = C'_{B0}\,V = (40.6\times10^{-4})\ \text{kmol/m}^3\ (0.53)\text{m}^3 = 2.15\times10^{-4}\ \text{kmol}$$
$$N'_{C0} = N'_{D0} = (53.8\times10^{-4})\ \text{kmol/m}^3\ \ (0.53)\text{m}^3 = 2.85\times10^{-4}\ \text{kmol}$$

Now A is the limiting reactant

$$C_A = \frac{N'_{A0}(1-X_A)}{V_F} = C'_{A0}(1-X_A)$$

$$C_B = \frac{N'_{A0}\left(\theta_B - \frac{X_A}{2}\right)}{V_F} = C'_{A0}\left(\theta_B - \frac{X_A}{2}\right)$$

$$C_C = C_D = \frac{N'_{D0} + N'_{A0}\frac{X_A}{2}}{V_F} = C'_{D0} + C'_{A0}\frac{X_A}{2}$$

$$-r_A = kC_{A0}^{1.5}(1-X_A)\left(\theta_B - \frac{X_A}{2}\right)^{0.5}$$

$$\theta_B = \frac{40.6}{5.7} = 7.12$$

$$C_{A0}\frac{dX}{dt} = -r_A$$

$$\frac{dX_A}{dt} = 0.143(1-X_A)\left(7.12 - \frac{X_A}{2}\right)^{0.5}$$

Plugging into POLYMATH get the following table.

```
4-I
Equations:                                                    Initial value
d(xa)/d(t)=.143*(1-xa)*(7.12-xa/2)^.5                         0
cao=6.09e-5
cco=.0056
ca=cao*(1-xa)
cb=cao*(62.48-xa/2)
cc=cco+cao*xa/2
t0 = 50,    tf = 68.6
4-I
t        xa            ca              cb              cc
50       0             6.09e-05        0.003805032     0.0056
53.1     0.68819307    1.8989042e-05   0.0037840765    0.0056209555
56.2     0.90114376    6.0203448e-06   0.0037775922    0.0056274398
59.3     0.96848514    1.9192549e-06   0.0037755416    0.0056294904
62.4     0.98992685    6.1345493e-07   0.0037748887    0.0056301433
65.5     0.99678108    1.9603251e-07   0.00377468      0.005630352
68.6     0.99897206    6.2601823e-08   0.0037746133    0.0056304187
```

Now we need to combine the two conversion equations to obtain one equation for the conversion of A, A'_A and another for the conversion of B, X'_B.

During the semibatch operation, $X'_B = X_B$. During the batch stage.

$$X'_B = \frac{N_{B0} - N_B}{N_{B0}} = \frac{N_{B0} - C_B V}{N_{B0}}$$

During the semibatch stage.

$$X_A' = \frac{N_{At} - N_A}{N_{At}}$$

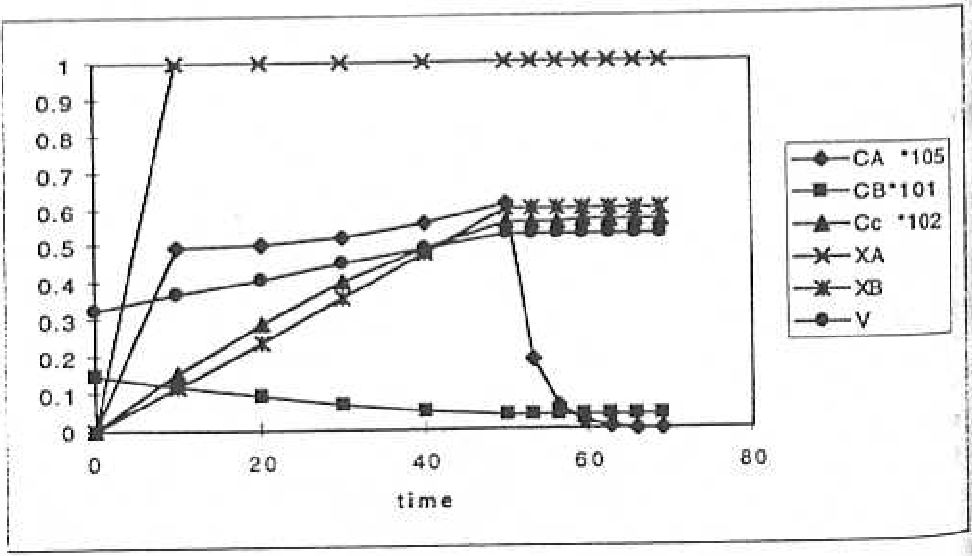
where N_{At} is the total amount of A introduced in the reactor by the time t, and N_A is the amount of A left in the reactor at that time, so

$$X_A' = \frac{C_{A0F} vt - C_A(V_0 + vt)}{C_{A0F} vt}$$

During the batch stage.

$$X_A' = \frac{C_{A0F} vt_0 - C_A V}{C_{A0F} vt_0}$$

where t_0 is the time at which the flow of feed was stopped. (i.e. 50 minutes)



CDP4-I (cont'd)

t	X_A	X_B
0	0	0
10	0.99847683	0.118
20	0.999139	0.238
30	0.999345	0.358
40	0.9994314	0.477
50	0.99946293	0.597
53.1	0.99983827	0.59932
56.2	0.99995048	0.599532
59.3	0.9999847	0.599744
62.4	0.99999526	0.5998606
65.5	0.99999852	0.5998818
68.6	0.99999954	0.5998924

b) From the table $X_A = 0.97$ at t = 9.71 min

c) From the table $X_B = 0.59$ at t = 49.42

d) New reaction rate

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

$$k = 6\exp\left[-\frac{35}{8.3\times10^{-3}}\left(\frac{1}{343}-\frac{1}{298}\right)\right]$$

$$= 38.3$$

$$-r_A = k\left(C_A C_B^{0.5} - \frac{C_C^{0.5}C_D^{0.5}}{K}\right), K = 10$$

Semibatch reactor

the concentration equations are the same as before, so, with

$$-r_B = \frac{-r_A}{2}$$

and

$$-r_B V = N_{B0}\frac{dX_B}{dt}$$

$$\frac{k}{2}\left(\frac{(C_{A0F}vt - 2N_{B0}X_B)(N_{B0}(1-X_B))^{0.5}}{(V_0+vt)^{1.5}} - \frac{N_{B0}X_B}{K(V_0+vt)}(V_0+vt)\right) = N_{B0}\frac{dX_B}{dt}$$

CDP4-I (cont'd)

$$\frac{dX_B}{dt}=\frac{k}{2}\left[\frac{\left(C_{A0F}vt-2N_{B0}X_B\right)\left(N_{B0}(1-X_B)\right)^{0.5}}{N_{B0}\left(V_0+vt\right)}-\frac{X_B}{K}\right]$$

$$\frac{dX_B}{dt}=3830\left(\frac{\left(1.2*10^{-4}t-0.01X_B\right)\left(0.005(1-X_B)\right)^{0.5}}{.033+4*10^{-3}t}\right)-1.915*X_B$$

Recall that in the semibatch reactor stage $X'_B = X_B$

The equation for the conversion of A remains the same as in part a,

$$X'_A=\frac{1.2*10^{-4}t-C_A\left(.033+4*10^{-3}t\right)}{1.2*10^{-4}t}$$

at equilibrium, $-r_B = 0$

$$C_A C_B^{0.5}=\frac{C_C}{K}$$

$$K\frac{\left(C_{A0F}vt-2N_{B0}X_{BE}\right)\left(N_{B0}(1-X_B)\right)^{0.5}}{\left(V_0+vt\right)^{1.5}}=\frac{N_{B0}X_{BE}}{V_0+vt}$$

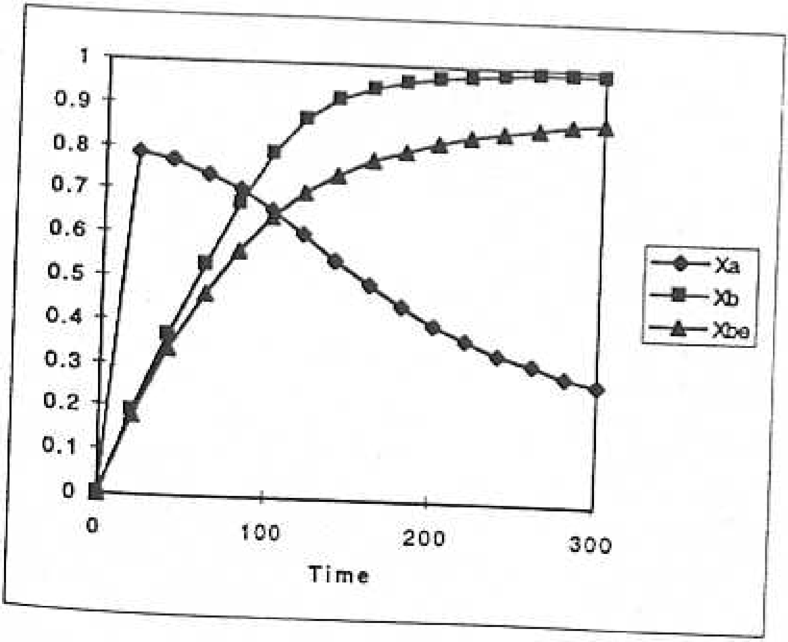
$$\frac{\left(C_{A0F}vt-2N_{B0}X_{BE}\right)}{\left(V_0+vt\right)^{0.5}}-\frac{N_{B0}^{0.5}X_{BE}}{K\left(1-X_{BE}\right)^{0.5}}=0$$

$$\frac{\left(1.2*10^{-4}t-0.01X_{BE}\right)}{.033+4*10^{-3}t}-\left(\frac{0.005}{1-X_{BE}}\right)^{0.5}\frac{X_{BE}}{10}=0$$

Solving for X_B, X_A and X_{BE} we obtain

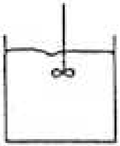
CDP4-I (cont'd)

t	Xa	Xb	Xbe
0	0	0	0
20	0.788	0.189	0.182
40	0.769	0.369	0.337
60	0.741	0.534	0.464
80	0.705	0.677	0.566
100	0.659	0.791	0.644
120	0.604	0.87	0.702
140	0.547	0.919	0.747
160	0.493	0.947	0.78
180	0.446	0.964	0.805
200	0.406	0.974	0.825
220	0.371	0.981	0.84
240	0.342	0.985	0.853
260	0.317	0.988	0.863
280	0.295	0.99	0.871
300	0.276	0.992	0.878



CDP4-J Liquid phase reaction

$$A + B \rightarrow C$$



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, p. 725.

a)

$$t = \frac{1}{(0.01\ \text{dm}^3/\text{mol min})\ (2\ \text{mol/dm}^3)}\left[\frac{0.9}{1-0.9}\right]\ ,\ t = 450\ \text{min}$$

1. Mole balance on CSTR

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

CDP4-J(cont'd)

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

$$V = \frac{10\text{ mol/min }(0.9)}{(0.01\text{ dm}^3\text{/mol min})(2\text{ mol/dm}^3)^2(1-0.9)^2}$$

b) $V = 22500\text{ dm}^3$

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, $-r_A = 0$

$$K_C = \frac{C_{Ce}}{C_{Ae} C_{Be}} = \frac{C_{A0} X}{C_{A0}^2 (1-X)^2} = \frac{X}{C_{A0}(1-X)^2}$$

$$K\, C_{A0} = \frac{2\text{dm}^3}{\text{mol}} \times \frac{2\text{mol}}{\text{dm}^3} = 4$$

$$1 - 2X + X^2 = \frac{X}{K\, C_{A0}} = \frac{X}{4}$$

$$X^2 - 2.25\, X + 1 = 0$$

$$X_e = 0.61$$

CSTR

$$V = \frac{F_{A0}X}{-r_A} = \frac{F_{A0}X}{k\, C_{A0}\left[C_{A0}(1-X)^2 - \frac{X}{K_C}\right]}$$

$$X = (.98)\, X_e = .60$$

$$V = \frac{(10)\,(.6)}{(.01)\,(2)\left[(2)\left((1-.6)^2 - \frac{.6}{2}\right)\right]} = 15{,}000 \text{ dm}^3$$

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-K

$$V = F_{A1}\int_0^{X_1}\frac{dX}{-r_A}$$

$$-r_A = kC_A$$

$$F_A = F_{A1}(1-X) = F_{A0}\left[1+R(1-X_o)\right](1-X)$$

$$v = v_{01}(1+\varepsilon_s X) = v_0\left[1+R(1+\varepsilon_0 X_0)\right](1+\varepsilon_S X)$$

$$\varepsilon_S = y_{A0}\delta\left(\frac{1+R(1-X_0)}{1+R(1+\varepsilon_0 X_0)}\right)$$

$$\varepsilon_0 = y_{A0}\delta = 1$$

$$R = 5$$

$$C_A = \frac{F_A}{v} = C_{A0}\left(\frac{\left[1+R(1-X_0)\right](1-X)}{\left[1+R(1+X_0)\right](1+\varepsilon_S X)}\right)$$

$$F_{A1} = F_{A0} + F_{AR} = F_{A0} + RF_{A0}(1-X_0)$$

Combining:

$$V = \frac{\left(F_{A0}+F_{A0}R(1-X_0)\right)\left(1+R(1+X_0)\right)}{1+R(1+X_0)}\int_0^{X_1}\frac{(1-\varepsilon_S X)}{1-X}$$

We also know that $X_S = \dfrac{X_0}{1+R(1-X_0)}$.

$F_{A0} = 1$ so R = 5. $\varepsilon_S = y_{A0}\delta\left(\dfrac{1+R(1-X_0)}{1+R(1-\varepsilon_0 X_0)}\right)$, $\varepsilon_0 = y_{A0}\delta = 1$

Two equations with two unknowns is solvable and the answer is $X_0 = .495$.

CDP4-L

$$\frac{dP}{dL} = -0.0025$$

$$\frac{dx}{dL} = \frac{-r_A * A}{F_{A0}}$$

$$-r_A = kC_A$$

$$C_A = \frac{F_A}{v_0}\frac{P}{P_0} = \frac{F_{A0}P\left[1+R*(1-x_0)\right](1-x)}{10P_0}$$

$$x_0 = \frac{x+Rx}{Rx+1}$$

Plugging into POLYMATH gets the following:

CDP4-L cont'd

```
Equations:                                              Initial value
d(p)/d(l)=-.0025                                        2
d(x)/d(l)=-ra*A/fao                                     0
A=.02
fao=.1
k=.25
cao=.01
po=2
R=5
xo=(x+R*x)/(R*x+1)
epss=(1+R*(1-xo))/(1+R*(1+xo))
ca=fao*p/po*(1+R*(1-xo))*(1-x)/10
ra=-k*ca
l0 = 0,   lf = 10
```

```
4-1
Variable   Initial value   Maximum value   Minimum value   Final value
l          0               10              0               10
p          2               2               1.975           1.975
x          0               0.0275011       0               0.0275011
A          0.02            0.02            0.02            0.02
fao        0.1             0.1             0.1             0.1
k          0.25            0.25            0.25            0.25
cao        0.01            0.01            0.01            0.01
po         2               2               2               2
R          5               5               5               5
xo         0               0.14506         0               0.14506
epss       1               1               0.784307        0.784307
ca         0.04            0.04            0.0506552       0.0506552
ra         -0.015          -0.0126638      -0.015          -0.0126638
```

$X_0 = .15$

CDP4-M

$$\frac{dV}{dX_0} = \frac{F_{A0}}{-r_A}$$

$$-r_A = kC_AC_B$$

$$C_A = \frac{F_A}{v} \qquad C_B = \frac{F_B}{v}$$

$$v = v_0\left[1 + R(1+\varepsilon_0 X_0)\right](1+\varepsilon_S X_S)$$

$$F_A = F_{A0}\left[1 + R(1-X_0)\right](1-X_S)$$

$$F_B = F_{A0}\left[1 + R(1-X_0)\right] - F_{A0}\left[1 + R(1-X_0)\right]X_S$$

$$\varepsilon_S = \varepsilon_0\left[\frac{1+R(1-X_0)}{1+R(1+\varepsilon_0 X_0)}\right]$$

$$\varepsilon_0 = y_{A0}\delta = .5 * -1 = -.5$$

$$R = 4$$

$$X_S = \frac{X_0}{1+R(1-X_0)}$$

Plugging into POLYMATH:

CDP4-M cont'd

```
4-m
Equations:                                                  Initial value
d(V)/d(xo)=fao/-ra                                          0
k=100
fao=1
vo=138.3
R=4
epso=-.5
xs=xo/(1+R*(1-xo))
epss=epso*(1+R*(1-xo))/(1+R*(1+epso*xo))
fa=fao*(1+R*(1-xo))*(1-xs)
fb=fao*(1+R*(1-xo))-fao*(1+R*(1-xo))*xs
v=vo*(1+R*(1+epso*xo))*(1+epss*xs)
ca=fa/v
cb=fb/v
ra=-k*ca*cb
xo0 = 0,   xof = 0.5
```

```
4-m
Variable     Initial value   Maximum value   Minimum value   Final value
xo           0               0.5             0               0.5
V            0               138.015         0               138.015
k            100             100             100             100
fao          1               1               1               1
vo           138.3           138.3           138.3           138.3
R            4               4               4               4
epso         -0.5            -0.5            -0.5            -0.5
xs           0               0.166667        0               0.166667
epss         -0.5            -0.375          -0.5            -0.375
fa           5               5               2.5             2.5
fb           5               5               2.5             2.5
v            691.5           691.5           518.625         518.625
ca           0.00723066      0.00723066      0.00482044      0.00482044
cb           0.00723066      0.00723066      0.00482044      0.00482044
ra           -0.00522824     -0.00232366     -0.00522824     -0.00232366
```

$V=138\ m^3$

CDP4-N

a) Develop new design equation:

$$F_A|_r - F_A|_{r+\Delta r} + h r_A \pi r \Delta r$$

$$-\frac{F_A|_{r+\Delta r} - F_A|_r}{\Delta r} + h r_A \pi r$$

$$\frac{dF_A}{dr} = h r_A \pi r$$

$$F_A = F_{A0}(1-X)$$

$$F_{A0}\frac{dX}{dr} = -r_A \pi h r$$

Then make r_A a function of X and solve.

$$-r_A = k_1 C_A C_B$$

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} y$$

$$C_B = \frac{C_{A0}(\theta_B - X)}{(1+\varepsilon X)} y$$

$$\theta_B = 1$$

$$\varepsilon = 0$$

$$\frac{dX}{dr} = \frac{k C_{A0}^2 (1-X)^2 \pi h r}{F_{A0}}$$

$$\frac{dx}{(1-X)^2} = \frac{k C_{A0}^2 \pi h r d(r)}{F_{A0}}$$

$$\frac{X}{1-X} = \frac{k C_{A0}^2 \pi h r^2}{2F_{A0}}$$

$$X = \frac{k C_{A0}^2 \pi h r^2}{2F_{A0}} - \frac{k C_{A0}^2 \pi h r^2 X}{2F_{A0}}$$

$$X\left(1 - \frac{k C_{A0}^2 \pi h r^2}{2F_{A0}}\right) = \frac{k C_{A0}^2 \pi h r^2}{2F_{A0}}$$

$$X = \frac{\dfrac{k C_{A0}^2 \pi h r^2}{2F_{A0}}}{1 - \dfrac{k C_{A0}^2 \pi h r^2}{2F_{A0}}}$$

b) Now with pressure drop

$$\frac{dX}{dr} = \frac{-r_A \pi h r}{F_{A0}}$$

$$r_A = -kC_A C_B$$

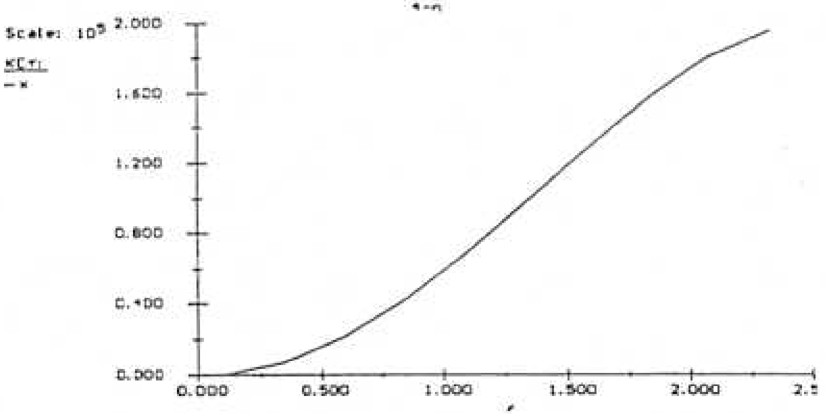
$$C_A = C_B = C_{A0}(1-X)y$$

$$y = (1-\alpha W)^{0.5}$$

$$W = \rho_b \pi (r - r_0)^2 h$$

Plugging this into POLYMATH, the following graph is made:

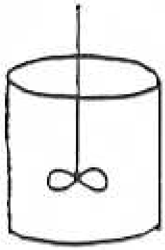
```
4-n
Equations:                                   Initial value
d(x)/d(r)=-ra*3.1416*r*h/fao                 0
k=.01
h=.4
fao=10
cao=.1
alp=.07
rho=2
ro=.1
W=rho*3.1416*(r-ro)^2*h
w=W
y=(1-alp*w)^.5
ca=cao*(1-x)*y
cb=ca
ra=-k*ca*cb
r0 = 0.1,   rf = 10
```



c) Increasing the value for k increases the 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 a decrease in height causes only a small decrease in conversion. Increasing R_o decreases the volume of the reactor, therefore decreasing conversion. Increasing R_i will increase the conversion as volume increases.

CDP4-O

a)



$X_0 = .1 \text{ g/dm}^3$

$S_0 = 50 \text{ g/dm}^3$

$V = 5 \text{ dm}^3$

$Y = .5$ g cell formed/g substrate consumed

Cell balance,

$$\text{Accumulation} = \underbrace{\text{In} - \text{Out}}_{\substack{\text{No flow}\\ \text{terms}}} + \text{generation}$$

$$\frac{d(VX)}{dt} = \mu VX$$

Constant volume,

$$\frac{dX}{dt} = \mu X \qquad (1)$$

$$\frac{dX}{dt} = \frac{\mu_{max} S}{K_s + S} X \qquad (2)$$

Substrate balance,

$$\frac{d(VS)}{dt} = \underbrace{-\frac{\mu VX}{Y}}_{\text{growth}} \underbrace{- mVX}_{\text{maintenance}}$$

Constant volume,

$$\frac{dS}{dt} \quad \frac{\mu X}{Y} - mX \qquad (3)$$

$$\frac{dS}{dt} = \frac{-\mu_{max} S X}{(K_S + S) Y} - m X \qquad (4)$$

growth rate (μ)
(μ)
growth rate
(μ)

b) In order to do this exactly, one would have to solve equations (3) and (4) simultaneously. This could be done numerically. However, the growth rate is essentially constant except when the substrate concentration becomes very small:

μ	S
$.8298\,hr^{-1}$	50 g/1
.8292	10
.8283	5
.8218	1
.692	.05

As a first approximation, set $\mu = \mu_{max} = .83\ hr^{-1}$ and solve equation (1). It can then be determined from Eq. (5) whether the substrate concentration is indeed still high enough to justify the approximation that $\mu = \mu_{max}$.

From (1),

$$\int_{X_0}^{X} \frac{dX}{X} = \mu_{max} \int_0^t dt$$

$$\ln \frac{X}{X_0} = \mu_{max} t \qquad \text{or} \qquad X = X_0\, e^{\mu_{max} t}$$

$$t = \frac{\ln (20/.1)}{.83}$$

$$t = 6.38\ hr$$

From (3),

$$\frac{dS}{dt} = -\left(\frac{\mu_{max}}{Y} + m\right) X$$

$$\int_{S_0}^{S} dS = -\left(\frac{\mu_{max}}{Y} + m\right) X_0 \int_0^t e^{\mu_{max} t}\, dt$$

$$S - S_0 = -\left(\frac{\mu_{max}}{Y} + m\right) X_0 \left.\frac{e^{\mu_{max} t}}{\mu_{max}}\right|_0^t$$

$$S = S_0 - \left(\frac{\mu_{max}}{Y} + m\right) \frac{X_0}{\mu_{max}} \left(e^{\mu_{max} t} - 1\right) \qquad (5)$$

At $t = 6.38\ hr$

$$S = 50 - \left(\frac{.83}{.5} + .1\right)\left(\frac{.1}{.83}\right)\left(e^{(.83)(6.38)} - 1\right)$$

$$= 7.93\ g/1$$

From Eq. (4) part d),

$$X = \frac{(F/V)(S_0-S)}{(\mu_{max}S/(K_S+S)Y) + m}$$

Substitute the relation for S into the above equation. After some algebra,

$$X = \frac{YS_0\mu_{max}\tau-Y(S_0+K_S)\tau^2}{\mu_{max}mY-(\mu_{max}-mY)\tau-\tau^2}$$

where

$$\tau = \frac{F}{V}$$

To find the maximum cell concentration, differentiate and set equal to zero:

$$\frac{dX}{d\tau} = \frac{[\mu_{max}mY+(\mu_{max}-mY)\tau-\tau^2][YS_0\mu_{max}-2Y(S_0+K_S)\tau]-[YS_0\mu_{max}\tau-Y(S_0+K_S)\tau^2][\mu_{max}-mY-2}{[\mu_{max}mY+(\mu_{max}-mY)\tau-\tau^2]^2}$$

Set equal to zero. The only unknown is τ. After some algebra,

$$0 = \frac{.496\ \tau^2 - .8304\ \tau + .34445}{(.0415 + .78\tau - \tau^2)^2}$$

$$0 = .496\ \tau^2 - .8304\ \tau + .34445$$

Solving with the quadratic equation:

$$\tau = .9163,\ .7579$$

These corresponding flow rates are 91.63 l/hr, 75.79 l/hr. The 91.63 l/hr flow rate is a meaningless solution because this is greater than the maximum allowable flow rate (part e).

$\therefore$ At F = 75.79 l/hr, the cell concentration is maximum.

The maximum cell concentration can be calculated using $\tau = .7579$.

$$X = \frac{YS_0\mu_{max}\ \tau - Y(S_0 + K_S)\ \tau^2}{\mu_{max}\ mY + (\mu_{max} - mY)\ \tau - \tau^2}$$

$$X_{max} = 9.324\ g/l$$

$$F = 75.79\ l/hr$$

At this substrate concentration, the actual growth rate is:

$$\mu = \frac{.83(7.93)}{.01 + 7.93}$$

$$= .8290 \text{ hr}^{-1}$$

The approximation that $\mu = \mu_{max} = .83 \text{ hr}^{-1}$ at all times is indeed valid.

c) Divide Equations (2) and (4) from part (b).

$$\frac{dS}{dX} = \frac{(-\mu_{max}SX/(K_S+S)Y) - m X}{(\mu_{max}SX/K_S + S) X}$$

After some algebraic manipulation,

$$\frac{dS}{dX} = \frac{-mK_SY - (\mu_{max} + mY) S}{\mu_{max} YS}$$

$$\int_{S_0}^{S} \frac{S}{m K_SY + (\mu_{max} + mY)S} dS = \frac{-1}{\mu_{max}Y} \int_{X_0}^{X} dX$$

From table of integrals,

$$\int \frac{XdX}{a + bX} = \frac{X}{b} - \frac{a}{b^2} \ln (a + bX)$$

Integrating,

$$\frac{S-S_0}{\mu_{max} + mY} - \frac{mK_SY}{(\mu_{max} + mY)^2} \ln \frac{[mK_SY + (\mu_{max} + mY)S]}{[mK_SY + (\mu_{max} + mY)S_0]} = \frac{X_0-X}{\mu_{max}Y}$$

The max. cell concentration will occur when all the substrate is consumed (i.e. S=0).

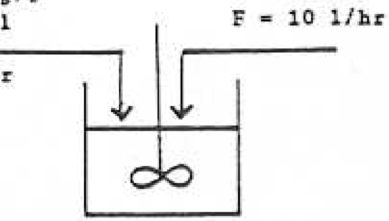
$$\frac{-50}{.83 + (.1)(.5)} - \frac{(.1)(.01)(.5)}{[.83 + (.1)(.5)]^2} \ln \frac{(.1)(.01)(.5)}{(.1)(.01)(.5) + (.88)(50)} = \frac{.1 - X}{(.83)(.5)}$$

Solving for X,

X = 23.69 g/l

d) S_0 = 20 g/l

F = 10 l/hr



V = 100 l

CDP4-O (cont'd)

From Eq. (4) part d),

$$X = \frac{(F/V)(S_0-S)}{(\mu_{max}S/(K_S+S)Y) + m}$$

Substitute the relation for S into the above equation. After some algebra,

$$X = \frac{YS_0\mu_{max}\tau-Y(S_0+K_S)\tau^2}{\mu_{max}mY-(\mu_{max}-mY)\tau-\tau^2}$$

where

$$\tau = \frac{F}{V}$$

To find the maximum cell concentration, differentiate and set equal to zero:

$$\frac{dX}{d\tau} = \frac{[\mu_{max}mY+(\mu_{max}-mY)\tau-\tau^2][YS_0\mu_{max}-2Y(S_0+K_S)\tau]-[YS_0\mu_{max}\tau-Y(S_0+K_S)\tau^2][\mu_{max}-mY-2}{[\mu_{max}mY+(\mu_{max}-mY)\tau-\tau^2]^2}$$

Set equal to zero. The only unknown is τ. After some algebra,

$$0 = \frac{.496\,\tau^2 - .8304\,\tau + .34445}{(.0415 + .78\tau - \tau^2)^2}$$

$$0 = .496\,\tau^2 - .8304\,\tau + .34445$$

Solving with the quadratic equation:

$$\tau = .9163,\ .7579$$

These corresponding flow rates are 91.63 l/hr, 75.79 l/hr. The 91.63 l/hr flow rate is a meaningless solution because this is greater than the maximum allowable flow rate (part e).

∴ At F = 75.79 l/hr, the cell concentration is maximum.

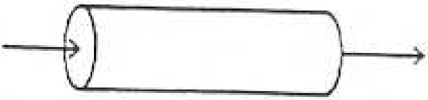
The maximum cell concentration can be calculated using $\tau = .7579$,

$$X = \frac{YS_0\mu_{max}\,\tau - Y(S_0 + K_S)\,\tau^2}{\mu_{max}\,mY + (\mu_{max} - mY)\,\tau - \tau^2}$$

$$X_{max} = 9.324 \text{ g/l}$$

$$F = 75.79 \text{ l/hr}$$

CDP4-P Given: $A + B \longrightarrow C + D$ in a tubular reactor:



M_A = 210 lb/hr $\qquad\qquad X = 0.50$

M_B = 260 lb/hr

$$F_{AC} = \frac{M_A}{(M_W)_A} = \frac{210\text{lb/hr}}{\frac{139\ \text{lb}}{\text{lbmole}}} = 1.51\ \text{lbmole/hr}$$

$$F_{BO} = \frac{M_B}{(M_W)_B} = \frac{260\ \text{lb/hr}}{\frac{172\ \text{lb}}{\text{lbmole}}} = 1.51\ \text{lb/lbmole/hr}$$

$$\Theta_B = \frac{F_{BO}}{F_{AO}} = 1$$

For a tubular reactor:

$$V = F_{AO}\int_0^X \frac{dX}{-r_A} \qquad\qquad -r_A = k\,C_A C_B$$

No volume changes on mixing: $\varepsilon = 0$; $C_{AO} = C_{BO}$:

$$\therefore\ -r_A = k\,C_{AO}^{\ 2}\,[1-X]^2\ ; \quad V = F_{AO}\int_0^X \frac{dX}{k\,C_{AO}^2[1-X]^2} = \frac{F_{AO}X}{kC_{AO}^{\ 2}(1-X)}$$

or, solving for k, $k = \dfrac{XF_{AO}}{C_{CA}^2\ V(1-X)} = \dfrac{v_oX}{C_{AO}V[1-X]}$

$$v_o = \frac{M_A}{\rho_A} + \frac{M_B}{\rho_B} = \frac{210\ \text{lb/hr}}{47.8\ \text{lb/ft}^3} + \frac{260\ \text{lb/hr}}{54.0\ \text{lb/ft}^3}$$

$$v_o = 4.39\ \text{ft}^3/\text{hr} + 4.82\ \text{ft}^3/\text{hr} = 9.21\ \text{ft}^3/\text{hr}$$

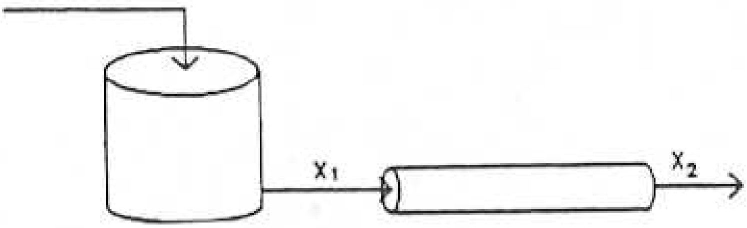
$$\therefore\ C_{AO} = F_{AO}/v_o = \frac{1.51\ \text{lbmole/hr}}{9.21.\text{ft}^3/\text{hr}} = 0.164\ \text{lbmole/ft}^3$$

$$\therefore\ k = \frac{9.21\ \text{ft}^3/\text{hr}\ \ (0.5)}{\frac{0.164\text{lbmole}}{\text{ft}^3}\text{x}5.33/\text{ft}^3(1-0.5)} = \frac{10.55\text{ft}^3}{\text{lbmole-hr.}}$$

CDP4-P (cont'd)

<u>Alternative scheme</u> - same feed as before

$F_{AO} = F_{BO} = 1.51$ lbmole/hr



$$V = V_{CSTR} = \frac{100 \text{ gal} \times 1 \text{ ft}^3}{7.48 \text{ gal}} = 13.37 \text{ ft}^3 = \frac{F_{AO}X_1}{-r_A} = \frac{F_{AO}X_1}{kC_{AO}{}^2[1-X_1]^2}$$

$$V = \frac{v_o X_1}{kC_{AO}[1-X_1]^2}$$

$$\text{or:} \quad X_1{}^2 - [2 + \frac{v_o}{kC_{AO}V}] X_1 + 1 = 0$$

$$X_1 = \frac{[2 + \frac{v_o}{kC_{AO}V}] \pm [(2 + \frac{v_o}{kC_{AO}V})^2 - 4]^{1/2}}{2} = \frac{1.075}{2} = 0.538$$

$$V_{PF} = F_{AO}\int_{X_1}^{X_2} \frac{dX}{kC_{AO}{}^2(1-X)^2} = \frac{v_o}{kC_{AO}}\int_{X_1}^{X_2} \frac{dX}{(1-X)^2} = \frac{v_o}{kC_{AO}}[\frac{1}{1-X_2} - \frac{1}{1-X_1}]$$

$$\frac{1}{1-X_2} = \frac{1}{1-X_1} + \frac{kC_{AO}V_{PF}}{v_o} = \frac{1}{1-.538} + \frac{(10.55)(.164)(5.33)}{(9.21)}$$

$$\frac{1}{1-X_2} = 2.16 + 1; \qquad X_2 = 1 - \frac{1}{3.16} = .684$$

CDP4-Q

a) From the mole balance for H_2SO_4:

$$F_B - 0 + 0 = \frac{dN_B}{dt}$$

$$N_B = 10t$$

Concentration:

$$\frac{F_B}{V} = \frac{dC_B}{dt}$$

$$V = V_0 + v_0 t$$

$$\frac{F_B dt}{V_0 + v_0 t} = dC_B$$

Integrating:

$$C_B = \frac{F_B}{y_0} \ln\left(\frac{V_0 + v_0 t}{V_0}\right)$$

For species A mole balance:

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

$$-r_A = kC_A C_B$$

$$C_A = \frac{N_A}{V}$$

$$C_B = \frac{F_B}{v_0} \ln\left(\frac{V_0 + v_0 t}{V_0}\right)$$

$$-kN_A \frac{F_B}{v_0} \ln\left(\frac{V_0 + v_0 t}{V_0}\right) = \frac{dN_A}{dt}$$

For Concentration:

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

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

$$-r_A = kC_A C_B$$

$$C_B = \frac{F_B}{v_0} \ln\left(\frac{V_0 + v_0 t}{V_0}\right)$$

$$-kCA \frac{F_B}{v_0} \ln\left(\frac{V_0 + v_0 t}{V_0}\right) = \frac{dC_A}{dt}$$

CDP4-Q (cont'd)

b) From POLYMATH, the answer comes out this way

```
Equations:                     Variable   Initial value  Maximum value  Minimum value  Final value
d(ca)/d(t)=ra                  t          0              30             0              30
k=0.05                         ca         10             10             2.05676        2.05676
fb=10                          k          0.05           0.05           0.05           0.05
vo=5                           fb         10             10             10             10
Vo=100                         vo         5              5              5              5
V=Vo+vo*t                      Vo         100            100            100            100
cb=fb/vo*ln((Vo+vo*t)/Vo       V          100            250            100            250
ra=-k*ca*cb                    cb         0              1.83258        0              1.83258
t0 = 0,   tf = 30              ra         -0             -0             -0.354348      -0.183459
```

c) Species A:

$$0-0+r_AV=\frac{dN_A}{dt}$$

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

$$-r_A=kC_AC_B-\frac{C_C}{K_C}$$

$$C_B=\frac{F_B}{v_0}\ln\left(1+\frac{v_0t}{V_0}\right)$$

Species C:

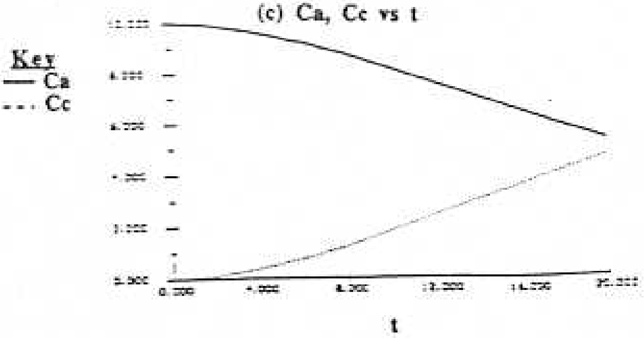
$$0-0+r_C=\frac{dC_C}{dt}$$

$$r_C=kC_AC_B-\frac{C_C}{K_C}$$

$$C_B=\frac{F_B}{v_0}\ln\left(1+\frac{v_0t}{V_0}\right)$$

Plugging into POLYMATH gives the following graph:

```
Equations:
d(ca)/d(t)=ra
d(cc)/d(t)=rc
k=0.05
ke=2
fb=10
vo=5
Vo=100
cb=fb/vo*ln(1+vo*t/Vo)
ra=-k*(ca*cb-cc/ke)
rc=-ra
t0 = 0,   tf = 20
```



CDP4-Q (cont'd)

d) The concentration of A will never get very high for the irreversible part because as soon as it enters the reactor it reacts. For the irreversible part it will increase and the concentration of C will also increase.

e) Species B(H_2SO_4):

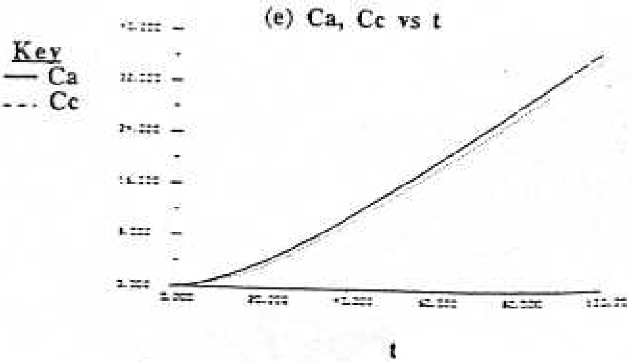
$$0-0-0=\frac{dN_B}{dt}$$
$$N_B=N_{B0}$$
$$C_B=\frac{N_{B0}}{V_0+v_0t}$$

Species A:

$$10-0+r_AV=\frac{dN_A}{dt}$$
$$-r_A=kC_A$$
$$C_A=\frac{N_A}{V}$$
$$10-kN_A=\frac{dN_A}{dt}$$
$$\frac{dN_A}{10-kN_A}=t$$
$$-\frac{1}{k}\left[\ln(10-kN_A)-\ln(10-kN_{A0})\right]=t$$
$$\ln\left(\frac{10-kN_A}{10-kN_{A0}}\right)=-kt$$
$$\frac{10-kN_A}{10-kN_{A0}}=e^{-kt}$$
$$N_A=\frac{10-e^{-kt}(10-kN_{A0})}{k}$$
$$C_A=\frac{N_A}{V_0+v_0t}$$

After 30 min the concentration is 0.44 mol/dm^3

```
Equations:
d(na)/d(t)=10-ra*V
d(nc)/d(t)=rc*V
k=0.5
Kc=2
Vo=200
vo=5
V=Vo+vo*t
ca=na/V
cc=nc/V
ra=-k*ca-cc/Kc
rc=k*ca-cc/Kc
t0 = 0,   tf = 100
```



Chapter 5

General: In Chapters 3 and 4, the students were given the rate law. The problems in this chapter reinforce how to obtain the rate law from experimental data.

P5-1. An open-ended problem that requires students to create and original problem and solution.

P5-2. "What if. . ." problem.

Problems **P5-3**, **P5-5**, **P5-7**, and **P5-18** all involve batch reactor experiments to find the reactor order and specific reaction rate. The students can use different techniques to differential the data or can use regression. These problems can be alternated from year to year.

P5-4. This problem usually trips up some students because many go blindly ahead and differentiate the data (dC_A/dt) not realizing the data were taken in a CSTR at steady state.

P5-6. Differentiate the data down a PFR to find the rate law parameters. Note the reaction is reversible. Quite tricky and time consuming.

P5-8. California Exam Problem where one first needs to determine in the rate law parameters from a batch experiment. Part **(a)** is quite straight forward but part **(b)** usually trips the students. Good problem. Requires thinking and not just choosing a formula.

P5-9. Straight forward problem involving the method of half lives.

P5-10. Good problem involving regression AND thinking. May be time consuming if the students don't get the hint and see it is the sum of two rate laws, zero and first order.

P5-11. Very short problem once the students realize the % decomposition is the same for different entering concentrations. No calculation is necessary to determine the reaction order.

P5-12. Fairly straight forward problem to determine the reaction order and speci reaction rate. Shows the application of CRE principles to the electroni industry.

Problems **P5-13**, **P5-14**, **P5-15**, **P5-19**, **P5-20**, and **P5-21** are straight forward problems using nonlinear regression. They can be alternated from year to year.

P5-16. Shows an important concept where lumping of reactants is used to mod first and second order reactions.

P5-17.	A problem on designing experiments.
P5-18.	Can be used alternatively with P5-3, P5-5, and P5-8.
CDP5-A	Alternative to problems P5-3, P5-5, and P5-7. Read data.
CDP5-B	Alternative to P5-6, but simpler.
CDP5-C	Fairly difficult problem. Usually assigned at the graduate level.
CDP5-D	Alternative to P5-9.
CDP5-E	More difficult to alternative P5-7.

Summary

	Assigned	Alternates	Difficulty	Time	Solution Given
P5-1				60	No
P5-2				15	No
P5-3	AA	5,7,8,18,A,B,C,E	SF	30	Yes
● P5-4			SF	20	Yes
● P5-5	AA	3,7,8,18,A,B,C	SF	20	No
P5-6	G		SF	60	Yes
P5-7	AA	3,5,8,18,A,B,C,E		40	Yes
● P5-8		3,5,7,18,A,B,C,E		40	Yes
P5-9	I	D		25	Yes
P5-10	AA	13,14,15,19,20,21		60	Yes
P5-11	O			15	Yes
P5-12	I			60	Yes
P5-13	AA	10,14,18,19,20,21		30	Yes
P5-14	AA	10,13,18,19,20,21		45	Yes
P5-15	G			40	Yes
P5-16	G			60	Yes
P5-17	G			(a) 40	Yes
P5-18	AA	3,5,7,8,A,B,C,E		60	Yes
● P5-19	AA	10,13,14,15,20,21		45	Yes
P5-20	AA	10,13,14,15,19,21		45	Yes
P5-21	AA	10,13,14,15,19,20		30	Yes
CDP5-A		5,7,8,18,B,C,E		30	Yes
CDP5-B		5,7,8,18,A,C,E		45	Yes
CDP5-C		5,7,8,18,A,B,E		60	Yes
CDP5-D		5-9		20	Yes
CDP5-E		5,7,8,18,A,B,C		60	Yes

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.

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

Summary Table Ch-5

	Reasoning	Graphical, Numerical Polynomial Analysis	Method of Half Lines	Regressi
Straight Forward	4,11	3,5,6,7,8,12,18	9	5
Fairly Straight Forward		A	D	13,19,20,
More Difficult	16	C,E		10,14,
Critical Thinking	17	3(b,c),4(c),5(b), 7(c,d),8(c)		14(b),16 18(d)

Chapter 5

P5-1 No solution will be given.

P5-2 No solution will be given.

P5-3

$$-r_A = kC_A^{\alpha} = -\frac{dC_A}{dt}$$

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 $\alpha = 0.5$

$$k_A = \frac{-\frac{dC_A}{dt}}{C_A^{0.5}} = \frac{.15}{0.65^{0.5}} - 0.19\frac{mol^{0.5}}{dm^{1.5}\ \text{min}}$$

P5-4

a)

$$\frac{C_{A0} - C_A}{\tau} = kC_A^{\alpha}$$

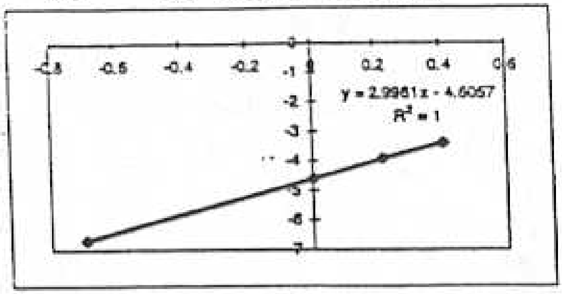
$$\ln\left(\frac{C_{A0} - C_A}{\tau}\right) = \ln k + \ln C_A$$

Plotting $\ln\left(\frac{C_{A0} - C_A}{\tau}\right)$ vs. $\ln C_A$

P5-4 cont'd

Problem 5-4

space time	Ca	ln(Ca)	ln((Cao-Ca)/t)
15	1.5	0.405465	-3.40119738
38	1.25	0.223144	-3.92526823
100	1	0	-4.60517019
1200	0.5	-0.69315	-6.68461173



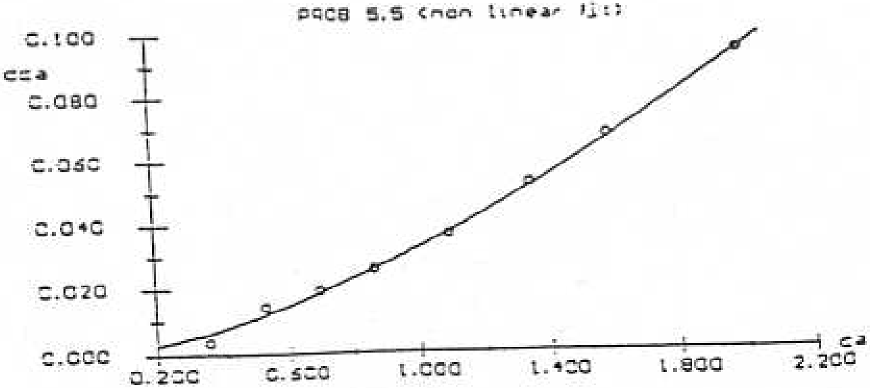
α = slope ≅ 3
ln k = intercept = -4.6
k = 0.01

P5-5

$$\frac{dC_A}{dt} = kC_A^n$$

From a non - linear fit, we get

k = 0.033
n = 1.54



```
model: dca = k*(ca^n)
k = 0.0326929
n = 1.53995
4 positive residuals, 4 negative residuals.  Sum of squares = 1.49367e-0
```

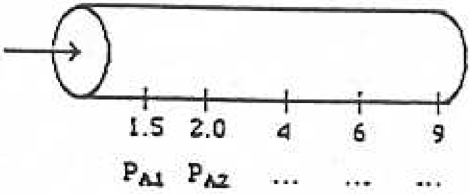
$AsH_3 = 1.5$	Z	P	$-\frac{dP}{dZ}$
	0	129	45.3
	1.5	70	28.63
	2.5	50	19.4
	4.0	30	9.5
	6.5	18	1.3
	9.0	16	(1.7)

$AsH_3 = 3.0$	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
	2.5	85	13.3
	4.0	80	10.8
	6.5	42	6.2
	9.0	40	1.3

PFR

$$A + B \rightleftarrows C$$



Task 1. Rewrite the design equation (i.e., mole balance) in terms of the measurement variables. Recall $V = A_C Z$, then

$$\frac{dX}{dZ} = \frac{-r_A A_c}{F_{A0}}$$

5-6

5-6 cont'd

For isothermal operation and no pressure drop.

$$C_A = C_{AO}\frac{(1-X)}{(1+\varepsilon X)},\quad C_A = P_A/RT$$

$$P_A = P_{AO}\frac{(1-X)}{(1+\varepsilon X)}$$

$$(1+\varepsilon X)\,P_A = P_{AO}\,(1-X)$$

$$\boxed{X = \frac{1-P_A/P_{AO}}{1+\varepsilon X\, P_A/P_{AO}}}$$

$$\boxed{\frac{d\left[\dfrac{1-P_A/P_{AO}}{\left(1+\varepsilon\dfrac{P_A}{P_{AO}}\right)}\right]}{dZ} = \frac{-r_A A_C}{F_{A0}}}$$

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.

$$\varepsilon = y_{AS}\,\delta = \frac{0.129}{152}(-1) = \left(8\times10^{-4}\right) - 0$$

$\varepsilon \equiv 0$ therefore neglect volume change.

$$\text{Then:}\quad -\frac{dP_A}{dZ} = \overbrace{\frac{P_{A0}\,k\,A_C}{F_{A0}}}^{k'}\left[P_A^{\alpha}P_B^{\beta} - \frac{P_C^{\gamma}}{K_P}\right]$$

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

$$-r_A = k'\,P_{B0}^{\beta}P_A^{\alpha} = k'\,P_A^{\alpha}$$

$$-\frac{dP_A}{dZ} = k''\,P_A^{\alpha}\qquad \text{Algorithm}$$

P5-6 cont'd

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

$$\frac{\left(\frac{-dP_A}{dZ}\right)_{03}}{\left(\frac{-dP_A}{dZ}\right)_{01}} = \frac{k\, P_{A03}\, P_{B03}^{\beta}}{k\, P_{A01}\, P_{B01}^{\beta}} = \left(\frac{P_{B03}}{P_{B01}}\right)^{\beta}$$

$$\frac{90}{46} = \left(\frac{3}{1.5}\right)^{\beta}$$. 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

$$-\frac{dP_A}{dZ} = 90 \times 10^{-3}\,\frac{\text{torr}}{\text{cm}} = k'\,(.129 \text{ torr})\,(3.0 \text{ torr})$$

$$k' = 0.23\ (\text{torr cm})^{-1}$$

P5-7 Given: Data for the decomposition of dimethylether in a gas phase, constant volume reactor at T = 504°C = 777°K

Time	0	390	777	1195	3155	∞
P	312	408	488	562	799	931

$(CH_3)_2O \rightarrow CH_4 + H_2 + CO$ or $A \rightarrow M + H + C$

cont'd

$_{A0} = 1,\ \delta = 3-1 = 2\ \therefore \varepsilon = 2$ $\quad V = V_0\left(\frac{P_0}{P}\right)(1-\varepsilon X) = V_0$ const. vol.

arranging

$P = P_0(1+\varepsilon X)$, at $t = \infty, X = X_{AF}$

$= \frac{\ - P_o}{\varepsilon P_o} = \frac{931-312}{2(312)} = \frac{619}{624} = 1.0$ ∴ Assume reaction is irreversible.

$- \frac{N_{AO}}{V_o}\frac{dX}{dT} = r_A$; Assume: $-r_A = k\ C_A$ (i.e. 1st order)

) $[1-X]$ (V = const.) Then: $C_{AO}\frac{dX}{dt} = k\ C_{AO}\ [1-X]$

$\frac{P_o}{o} \Longrightarrow \frac{dX}{dt} = \frac{1}{\varepsilon P_o}\frac{dP}{dt}$

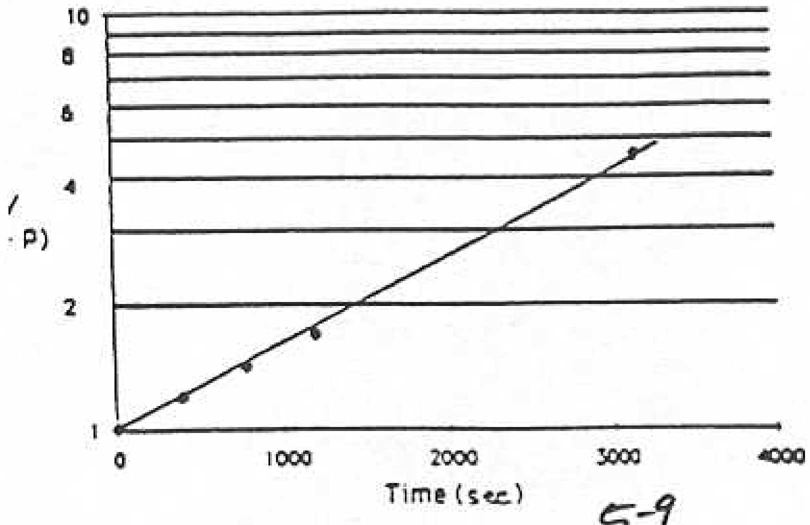
$\frac{dP}{dt} = k\ [1 - \frac{P - P_o}{\varepsilon P_o}] = \frac{k}{\varepsilon P_o}([1+\varepsilon]\ P_o - P)$

$\frac{dt}{[1-\varepsilon]P_o-P} = \int_0^t k\,dt$, or $\ln\frac{\varepsilon P_o}{[1+\varepsilon]P_o-P} = \ln\frac{2P_o}{3P_o-P} = kt$

.log plot of $\frac{2P_o}{3P_o-P} = \frac{624}{936-P}$

is linear, reaction is 1st order; it is evident from the plot that

$c = 0.00048$ $\qquad$ ∴ $-r_A = 4.8 \times 10^{-4}\ \text{sec}^{-1}\ C_A$



5-9

P5-8

t(min)	10	20	30	40	50	60
C_A(ppm)	2.45	1.74	1.23	0.88	0.62	0.44

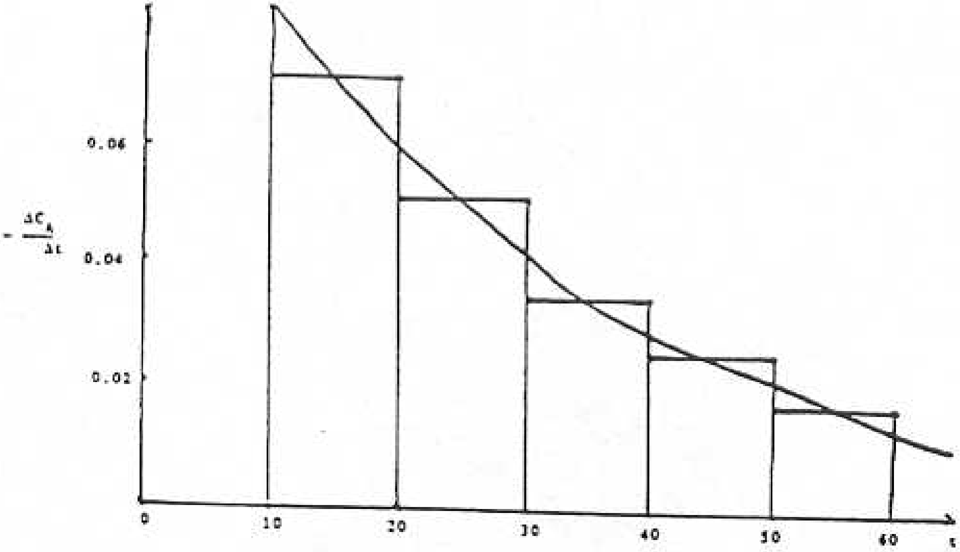
(a) Mole Balance: constant V

$$\frac{dC_A}{dt} = r_A = -k\, C_A^{\alpha}$$

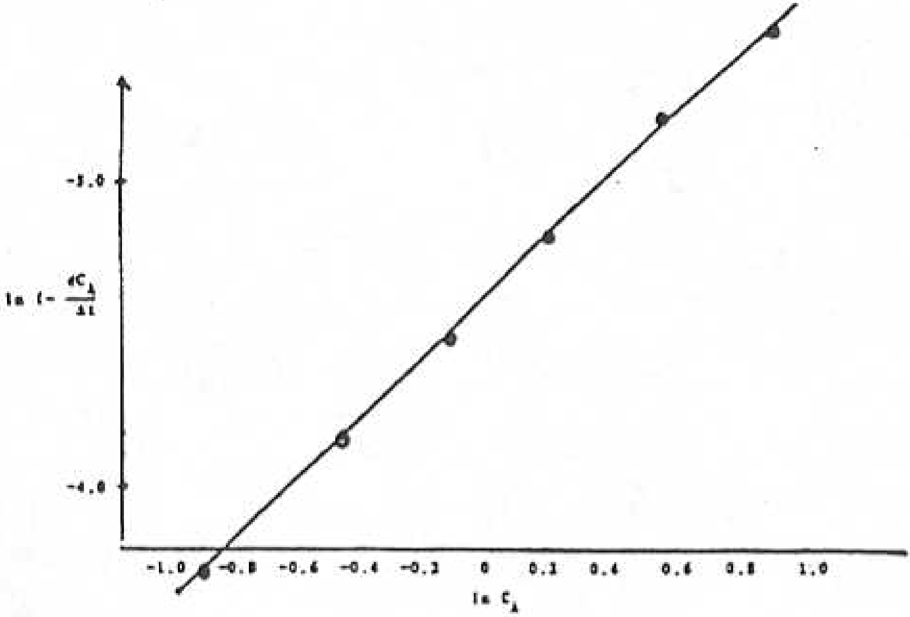
$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

Differentiation

t(min)	10		20		30		40		50		60
Δt(min)		10		10		10		10		10	
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	
$\frac{\Delta C_A}{\Delta t}$ $\left(\frac{ppm}{min}\right)$		-0.071		-0.051		-0.035		-0.026		-0.018	



P5-8 cont'd



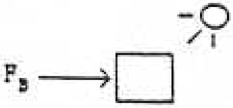
After plotting and differentiating by equal area

$-dC_A/dt$	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: $\alpha = 1.0$

$\ln k = -3.3864 \rightarrow k = 0.0344\ \text{min}^{-1}$

(b)



$$\frac{dN_A}{dt} = Vr_A = F_B$$

$$r_A = -0.0344\ \frac{\text{ppm}}{\text{min}} \doteq -0.0344\ \frac{\text{mg}}{1\ \text{min}}\ \text{at}\ C_A = 1\ \text{ppm}$$

$$F_B = (25000\ \text{gal})\left(0.0344\ \frac{\text{mg}}{1\ \text{min}}\right)\frac{60\ \text{min}}{\text{hr}}\ \frac{1\ \text{g}}{1000\ \text{mg}}\left(\frac{3.7851}{453.6}\right)\frac{1}{\text{gal}} = 0.429\ \frac{\text{lbm}}{\text{hr}}$$

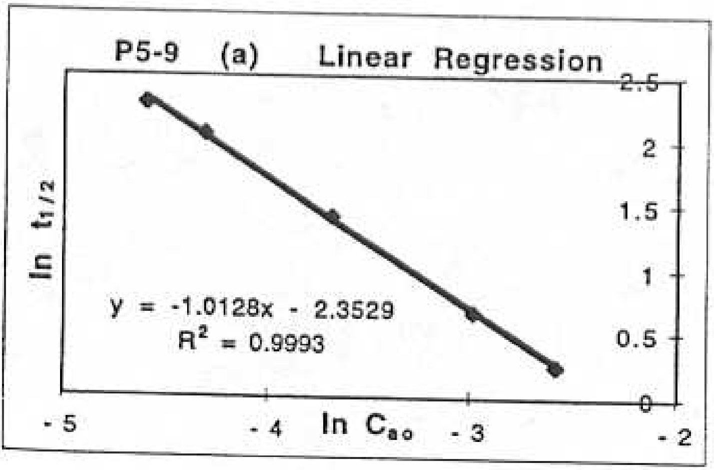
P5-9

(a) Method of Half Lives

Linear Regression:

Run	C_{Ao}	$t_{1/2}$	ln C_{Ao}	ln $t_{1/2}$
1	0.025	4.1	-3.689	1.411
2	0.0133	7.7	-4.320	2.041
3	0.01	9.8	-4.605	2.282
4	0.05	1.96	-2.996	0.673
5	0.075	1.3	-2.590	0.262
6	0.025	2		

Plot ln Cao vs. ln t1/2



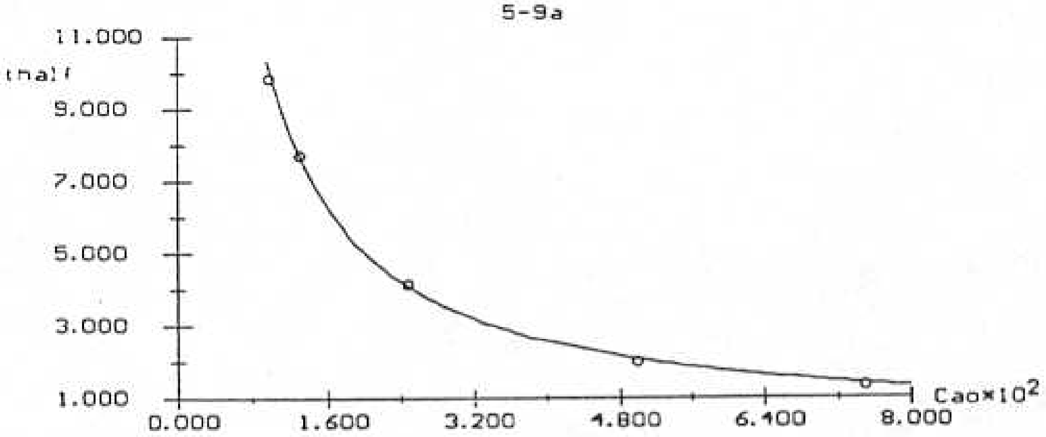
From Linearization:

$$\alpha = 1 - \text{slope} = 2.1029 \cong 2$$

$$k = \frac{\left(2^{(\alpha-1)} - 1\right)e^{-\text{intercept}}}{\alpha - 1} = 10.52$$

P5-9 cont'd

Using POLYMATH we can come up with the following



```
Model: thalf=(2^(alp-1)-1)/(k*(alp-1))*(1/Cao^(alp-1))
alp = 1.97725
k = 8.99184
2 positive residuals, 3 negative residuals.  Sum of squares = 0.070594
```

(b)

Using the equation : $$k = \frac{\left(2^{(\alpha-1)}-1\right)}{t_{1/2}(\alpha-1)}\left(\frac{1}{C_{Ao}^{\alpha-1}}\right)$$

Solve for k at 110°C.

k @ 110°C is 20

k @ 100°C is 10.52

From these values of k we can calculate the activation energy (E).

$$E = \frac{-\ln\frac{k_2}{k_1}R}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} = -5876 \text{ J/mol}$$

P5-10

O_3 + wall → loss of O_3 $\quad k_1$

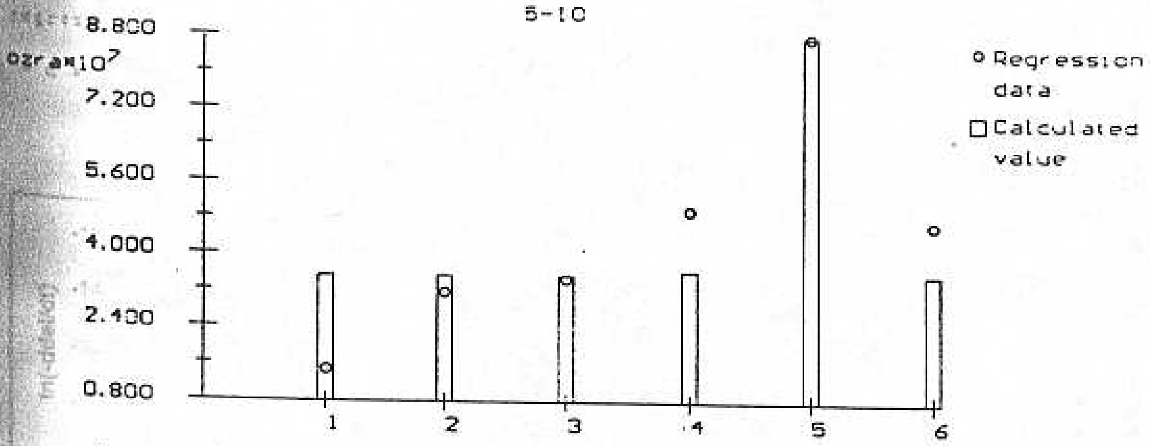
O_3 + alkene → products $\quad k_2$

$$-r_{O_3} = \frac{dC_{O_3}}{dt} = k_1 + k_2 \frac{C_B}{C_{O_3}}$$

Using POLYMATH's non-linear regression we can find the values for k_1 and k_2.

```
5-10
ozra
Coz
Cbu
```

0	ozra	Coz	Cbu
1	1.5e-07	0.01	1e-12
2	3.2e-07	0.02	1e-11
3	3.5e-07	0.015	1e-10
4	5e-07	0.005	1e-09
5	8.8e-07	0.001	1e-08
6	4.7e-07	0.018	1e-09



```
Model: ozra=k1+k2*Cbu/Coz
k1 = 3.54558e-07
k2 = 0.0528758
2 positive residuals, 4 negative residuals.  Sum of squares = 7.39236e-14
```

P5-11 Given: Plot of percent Decomposition of NO_2 vs. V/F_{AO}

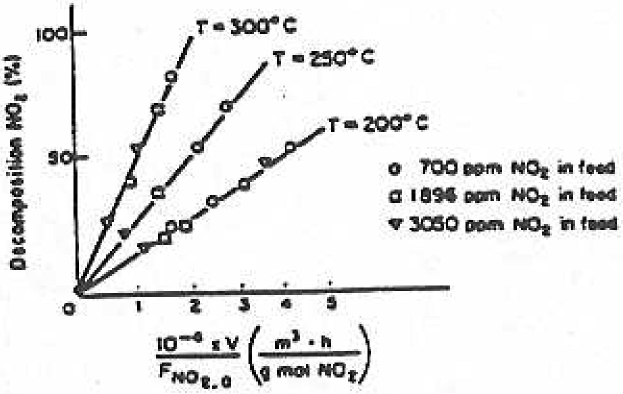
$$X = \frac{\%\text{ Decomposition of } NO_2}{100}$$

Assume that $-r_A = k\,C_A^n$

For a CSTR $V = \dfrac{F_{AO}\,X}{-r_A}$

or $\dfrac{V}{F_{AO}} = \dfrac{X}{-r_A} = \dfrac{X}{k\,C_A^n}$

with $n = 0$ $X = k\,(\dfrac{V}{F_{AO}})$



X is linear with V/F_{AO}, as figure to the right shows

∴ reaction is <u>zero order</u>. <u>ans</u>.

P5-12 $SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$

N_S = moles of $SiO_2 = \dfrac{A_c \rho_s \delta}{MW_s}$

A_c = cross sectional area

ρ_s = silicon dioxide density

MW_s = molecular weight of SiO2 = 60.0

δ = depth of Si

N_F = moles of HF = $\dfrac{w\rho V}{100\ MW_F}$

w = weight percentage HF in solution

ρ = density of solution

V = volume of solution

MW_F = molecular weight of HF 20.0

Assume the rate law is $-r_s = kC_F^a$

ont'd

ole balance $\frac{dN_S}{dt} = r_s V$

$$-\frac{A_c \rho_s}{MW_s}\frac{d\delta}{dt} = k\left(\frac{w\rho V}{100V\ MW_F}\right)^\alpha V$$

$$-\frac{d\delta}{dt} = \frac{k\ MW_S}{(100)^\alpha A_c \rho_s}\left(\frac{\rho}{MW_F}\right)^\alpha V_w{}^\alpha$$

$$-\frac{d\delta}{dt} = \beta w^\alpha \text{ where } \beta = \frac{kMW_S}{(100)^\alpha A_c \rho_S}\left(\frac{\rho}{MW_F}\right)^\alpha V$$

$$\ln\left(-\frac{d\delta}{dt}\right) = \ln\beta + \alpha\ln w$$

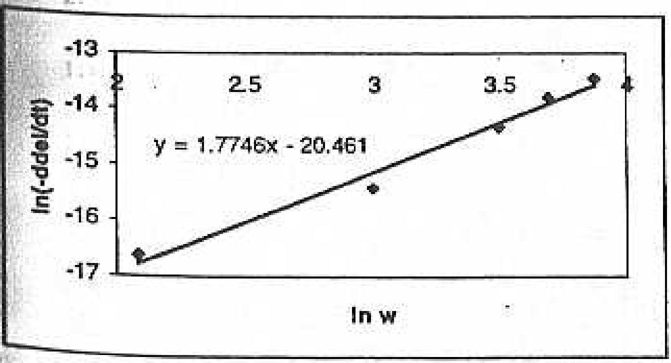
$\ln\left(-\frac{d\delta}{dt}\right)$	-16.629	-15.425	-14.326	-13.816	-13.479
ln w	2.079	2.996	3.497	3.689	3.871

here $\left(-\frac{d\delta}{dt}\right)$ in $\left(\frac{m}{min}\right)$

Linear regression between $\ln\left(-\frac{d\delta}{dt}\right)$ vs. lnw, we have:

Slope = α = 1.775 ; intercept = $\ln\beta$ = -20.462

or $\beta = 1.2986\text{x}10^{-9}$



P5-12 cont'd

$$\beta = \frac{kMW_s}{A_c\rho_s}\left(\frac{\rho}{MW_F}\right)^{1.775} V$$

$$A_c = (10\times10^{-6}\,m)(10\,m)(2\text{ sides})(1000\text{ wafers}) = 0.2\ m^2$$

$$MW_s = 60\ g/gmol$$

$$\rho_s = 2.32\ \frac{g}{ml} = 2.32\times10^{+6}\ \frac{g}{m^3}$$

(Handbook of Chemistry and Physics, 57th ed., p. B-155)

$$\rho = 1\ \frac{g}{ml} = 1\times10^{6}\ \frac{g}{m^3}$$

$$MW_F = 20\ g/gmol$$

$$V = 0.5\ dm^3 = 0.5\times10^{-3}\ m^3$$

$$\beta = 1.2986\times10^{-9}$$

$$1.2986\times10^{-9} = \frac{k\left(60\ \frac{g}{gmol}\right)\left(\frac{1\times10^{6}\,g/m^3}{20\ g/gmol}\right)^{1.775}}{(0.2\ m^2)\left(2.3\times10^{6}\ \frac{g}{m^3}\right)(100)^{1.775}}\times 0.5\times10^{-3}\ m^3$$

$$k = 3.224\times10^{-7}\left(\frac{m^3}{gmol}\right)^{0.775} min^{-1}$$

Volume of SiO_2 removed = 2(50*10^{-6})(10*10^{-6})(10)(1000) = 1*$10^{-5}$$m^3$

Moles of SiO_2 removed = 1*10^{-5}(2.32*10^{6})/60 = 0.386 mol

Moles of HF used = 6(0.386) = 2.316 moles

Moles of HF available = 0.5*10^{-3}/5*1*10^{6}/20=5 moles

$$\text{Final }[HF] = \frac{5-2.316}{5}(0.2) = 0.107\text{ weight fraction} = 10.7\%$$

$$\text{Initial }[HF] = 0.2\text{ (given)} = 20\%$$

$$\text{Mole balance for HF: }\frac{dN_F}{dt} = 6\,\frac{dN_S}{dt}$$

$$-\frac{\rho V}{MW_F}\frac{dw}{dt} = 6\,k\left(\frac{w\rho}{100MW_F}\right)^{\alpha} V \qquad \text{where } \alpha=1.775$$

P5-12 cont'd

$$-\int_{20}^{10.7} \frac{dw}{w^{1.775}} = 6\ k\left(\frac{\rho}{100HW_F}\right)^{0.775}\int_0^t dt$$

$$\frac{1}{(0.775)}\left(\frac{1}{w^{0.775}}\right)\Bigg|_{20}^{10.7} = (6)(3.224x10^{-7})\left(\frac{1x10^6}{20x100}\right)^{0.775} t$$

$$\frac{1}{(0.775)}\left[\frac{1}{(10.7)^{0.775}} - \frac{1}{(20)^{0.775}}\right] = 2.389x10^{-4}\ t$$

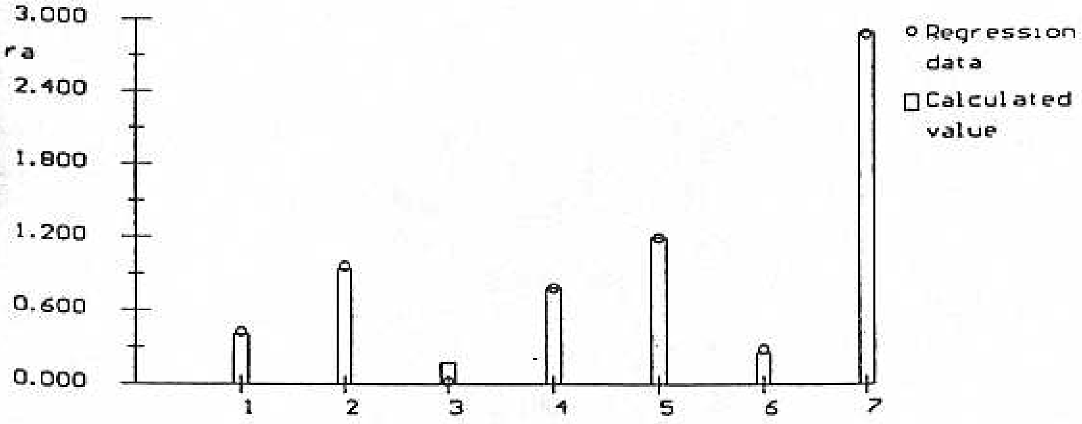
$$t = 330 \text{ min}$$

P5-13

First,

$$r_A = \frac{F_A}{\Delta W}$$
$$\Delta W = 0.5$$

Using POLYMATH's non-linear regression, the following results were found:
k = 6.8 α = 1 β = .2



```
Model: ra=k*Pp^alp*Po2^bet
k = 6.80214                          bet = 0.201097
alp = 1.03491
5 positive residuals, 2 negative residuals.  Sum of squares = 0.024629
```

P5-14

	F_{To} gmole/hr	P_{AO} atm	P_{BO} atm	θ_B	y_p	X	P_A atm	P_B atm	$-r'_A$ gmole/hr-kg
1	1.7	0.5	0.5	1	0.05	0.05	0.475	0.475	1.0625
2	1.2	0.5	0.5	1	0.07	0.07	0.465	0.465	1.0500
3	0.6	0.5	0.5	1	0.16	0.16	0.420	0.420	1.200
4	0.3	0.4	0.6	1.5	0.16	0.2	0.320	0.520	0.600
5	0.75	0.6	0.6	1	0.10	0.10	0.540	0.540	0.9375
6	2.75	0.6	0.4	0.67	0.06	0.05	0.570	0.370	2.0625

$$F_T = F_{T0}$$

$$P_A = C_A RT = C_{A0}RT(1-X) = P_{A0}(1-X)$$

$$P_B = C_B RT = C_{A0}RT(\theta_B - X) = P_{A0}(\theta_B - X)$$

$$X = \frac{y_P F_{T0}}{2F_{A0}} = \frac{y_P}{2y_{A0}} = \frac{y_P(1-\theta_B)}{2}$$

$$-r'_A = \frac{1}{2}r'_B = \frac{F_{A0}X}{W} = \frac{F_P}{2W} = \frac{y_P F_{T0}}{2W}$$

$$-r'_A = kP_A^{\alpha}P_B^{\beta}$$

$$\ln(-r'_A) = \ln k - \alpha \ln P_A - \beta \ln P_B$$

$$y = A_0 - A_1X_1 - A_2X_2$$

P5-14 cont'd

Summing over 'n' data points

$$\sum_{i=1}^{n} y_i = nA_o + A_1 \sum_{i=1}^{n} X_{1i} + A_2 \sum_{i=1}^{n} X_{2i}$$

$$\sum_{i=1}^{n} X_{1i}\, y_i = A_o \sum_{i=1}^{n} X_{1i} + A_1 \sum_{i=1}^{n} X^2_{ii} + A_2 \sum_{i=1}^{n} X_{1i}\, X_{2i}$$

$$\sum_{i=1}^{n} X_{2i}\, y_i = A_o \sum_{i=1}^{n} X_{2i} + A_1 \sum_{i=1}^{n} X_{1i}\, X_{2i} + A_2 \sum_{i=1}^{n} X_{2i}{}^2$$

Using the data from the following page

$$6\, A_o - 4.695\, A_1 - 4.642\, A_2 = 0.4403$$

$$-4.695\, A_o + 3.8837\, A_1 + 3.5733\, A_2 = -0.026$$

$$-4.695\, A_o + 3.5733\, A_1 + 3.6858\, A_2 = -0.5866$$

$\Delta = 0.097$

$\Delta_1 = -0.072$

$\Delta_2 = 0.0935$

$\Delta_3 = -0.1974$

$A_o = -0.7423 = \ln k$ ans || $k = 0.476^{\text{atm}}$ gmole/hr-kg

$A_1 = 0.9639 = \alpha \_ 1.0$ || ans

$A_2 = -2.035 = \beta \_ -2.0$

$-r_A'$ gmole/hr-kg	P_A atm	P_B atm	y_i $\ln(-r_A')$	X_{1i} $\ln P_A$	$X_{1i}{}^2$ $(\ln P_A)^2$	X_{2i} $\ln P_B$	$X_{2i}{}^2$ $(\ln P_D)^2$	$X_{1i}\, X_{2i}$ $\ln P_A$ ln
1.0625	0.475	0.475	0.0606	-0.7444	0.5542	-0.7444	0.5542	0.5542
1.0500	0.465	0.465	0.0488	-0.7657	0.5863	-0.7657	0.5863	0.5863
1.200	0.420	0.420	0.1823	-0.8675	0.7525	-0.8675	0.7525	0.7525
0.600	0.320	0.520	-0.5108	-1.139	1.298	-0.6539	0.4276	0.7448
0.9375	0.540	0.540	-0.0645	-0.6162	0.3767	-0.6162	0.3767	0.3767
2.0625	0.570	0.370	0.7239	-0.5621	0.3160	-0.9942	0.9885	0.5588
		$\sum_{i=1}^{n}$	0.4403	-4.695	3.8837	-4.642	3.6858	3.5733

P5-15

$$-r_A = k_o\, e^{(-E/RT)}\, C_A^{\alpha}$$

so $$\frac{-r_{Ai}}{-r_{A3}} = [\exp\{(-E/R)(1/T_i - 1/T_3)\}]\,(C_{Ai}/C_{A3})^{\alpha}$$

$$\ln(-r_{Ai}/-r_{A3}) = -E/R\,(1/T_i - 1/T_3) + \alpha \ln(C_{Ai}/C_{A3})$$

$$\frac{\ln(-r_{Ai}/-r_{A3})}{(1/RT_i - 1/RT_3} = -E + \alpha\,\frac{\ln(C_{Ai}/C_{A3})}{(1/RT_i - 1/RT_3)}$$

Run number	1	2	4	5
$\frac{\ln(-r_{Ai}/-r_{A3})}{(1/RT_i - 1/RT_3}$	-2792.94	-3035.27	-2472.3	-2301.14
$\frac{\ln(-C_{Ai}/-C_{A3})}{(1/RT_i - 1/RT_3}$	-739.50	-902.18	-524.47	-409.48

Linear regression yields

$E = 1690$ atm l/mol

$\alpha = 1.49$

Using any data point, we obtain

$k_o = 3.16 \times 10^{10}\ (\text{mol/l})^{-0.49}/\text{s}$

P5-16

I)

$$A \xrightarrow{k_A} \text{prod} \qquad -r_A = k_A C_A$$

$$B \xrightarrow{k_B} \text{prod} \qquad -r_B = k_B C_B$$

$$-r_I = k_A C_A + k_B C_B$$

$$-\frac{dC_I}{dt} = k_A C_{Ao}(1 - X_A) + k_B C_{Bo}(1 - X_B)$$

$$C_I(t) = C_A(t) + C_B(t) = C_{Ao}(1 - X_A) + C_{Bo}(1 - X_B)$$

$$C_I(t) = C_{Ao}(1 - X_A + \Theta_B - X_B) = C_{Ao}(1.75 - X_A - X_B)$$

$$-\frac{dC_I}{dt} = C_{Ao}(k_A - k_A X_A + k_B \Theta_B - k_B X_B)$$

$$-\frac{dC_I}{dt} = C_{Ao}(k_A - k_A X_A + 0.75 k_B \Theta_B - k_B X_B)$$

P5-16 cont'd

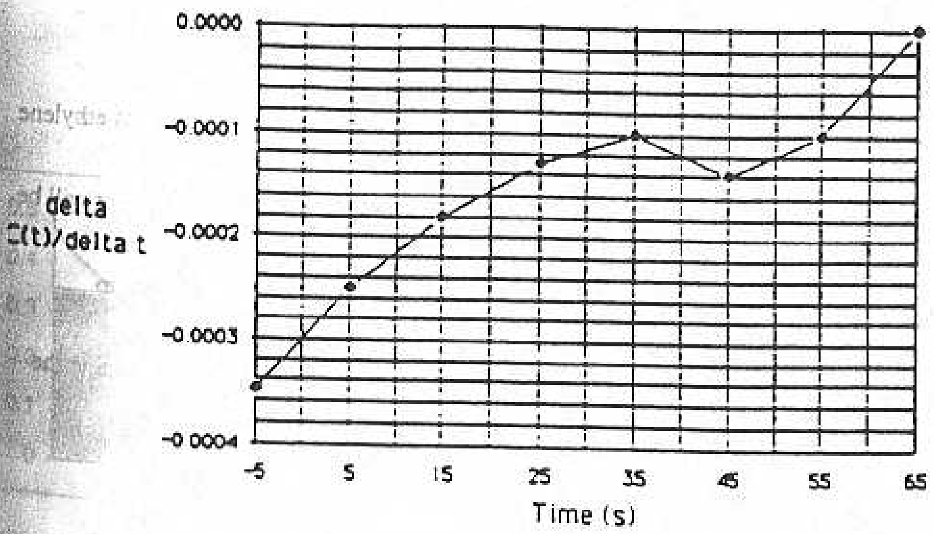
II) $D \xrightarrow{k_D} \text{prod} \qquad -\frac{dC_{II}}{dt} = -r_{II} = k_D C_D^2 = k_D\ C_{DO}^2\ (1-X_D)^2$

$C_{II}(t) = C_D(t) = C_{DO}\ (1-X_{D_O})$

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. $w = X_A + X_B$	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}	
$-\frac{dC(t)}{dt}$	$+2.7\times10^{-4}$	-2.2×10^{-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



P5-17

(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.

(c) Experimental Plan to find the rate law for the acid-catalyzed production of ethylene glycol form an aqueous solution of ethylene oxide:

1. Since this is an aqueous solution with a soluble catalyst, a batch reactor will be used.

2. Several different runs will be done with different acid concentrations to determine the effect of catalyst concentration on the rate of reaction.

3. For each run record C_A at equal time intervals. Use this data to determine the effect of C_A on the rate law.

P5-18

a) **Numerical Method**

Initial Point :
$$\left(\frac{dC_A}{dt}\right)_{t_0} = \frac{-3*2.00+4*1.31-0.95}{2*2} = -0.43$$

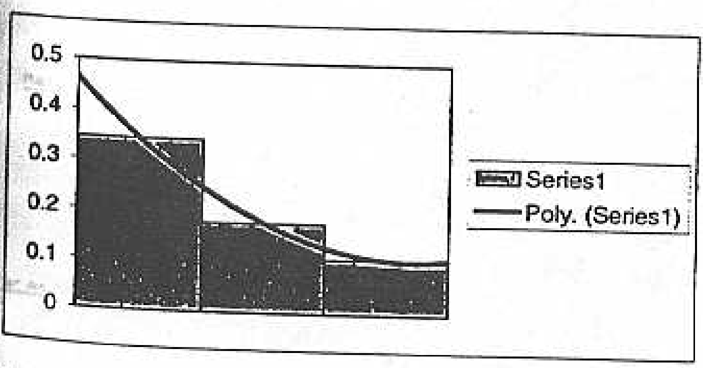
Interior Points :
$$\left(\frac{dC_A}{dt}\right)_{t_1} = \frac{0.95-2.00}{2*2} = -0.26$$

$$\left(\frac{dC_A}{dt}\right)_{t_2} = \frac{0.73-1.31}{4} = -0.15$$

Final Point :
$$\left(\frac{dC_A}{dt}\right)_{t_3} = \frac{1.31-4*0.95+3*0.73}{4} = -0.075$$

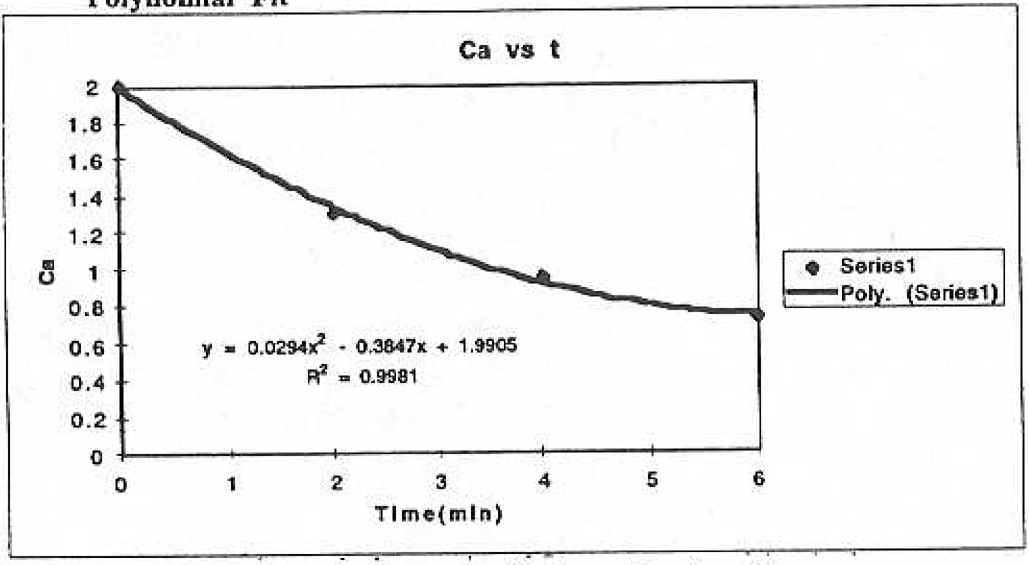
Graphical Method

t	Ca	Δt	Δca	Δca Δt	dCa/dt
0	2				0.46
		2	-0.69	-0.345	
2	1.31				0.251
		2	-0.36	-0.18	
4	0.95				0.144
		2	-0.22	-0.11	
6	0.73				0.111



Noticing where the trendline crosses the edges of the bars we will get our values for -dCa/dt.

5-18 cont'd
Polynomial Fit

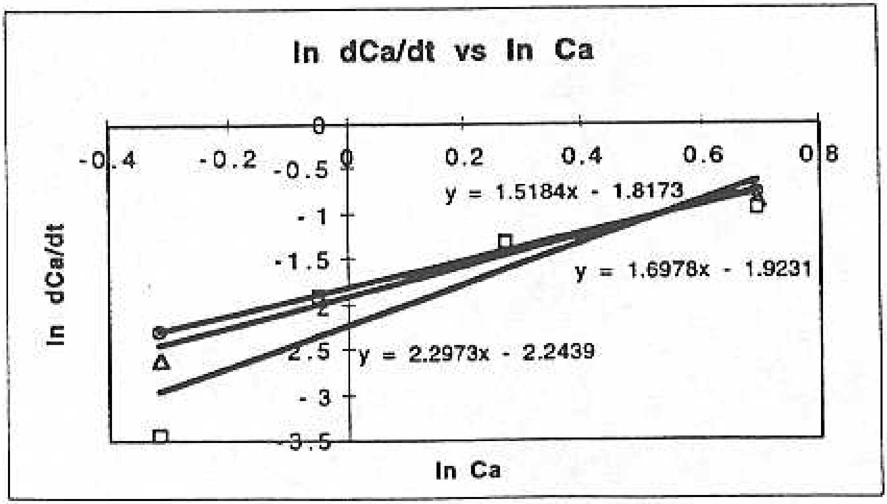


From the graph, we determine the equation for C_A as a function of time:

$$\frac{dC_A}{dt} = 0.0588t - 0.3847$$

Using that we can find and graph the derivative of C_A at any time.
Graphs of the natural log plot of the derivative are given below.

Triangles represent the plot made by the Numerical Technique; circles represent the Graphical Technique; and squares represent polynomial fitting



P5-18 cont'd

b) Reaction order approximations:
Numerical Technique - 1.5
Graphical Technique - 1.5
Polynomial Technique - 2

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

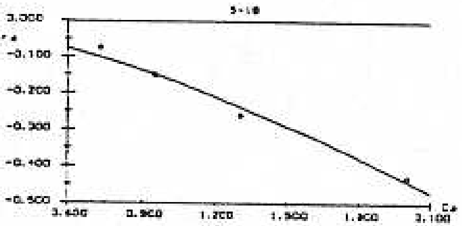
$$-r_A = kC_A^{\alpha}$$

Combine and then integrate from (0,C_{A0}) to (t, C_A) to get

$$C_A = \left[C_{A0}^{1-\alpha} - (1-\alpha)kt\right]^{1/1-\alpha}$$

Plug that into POLYMATH's non-linear regression and find that $\alpha = 1.5$ and k = .16

ra	Ca
-0.43	2
-0.26	1.31
-0.15	0.95
-0.075	0.73



```
Model: ra=-k*Ca^alp
k = 0.159354
alp = 1.4575
2 positive residuals, 2 negative residuals.  Sum of squares = 0.00129113
```

Matrix of correlation coefficients for the nonlinear correlation equation

	k	alp
k	1	-0.871145
alp	-0.871145	1

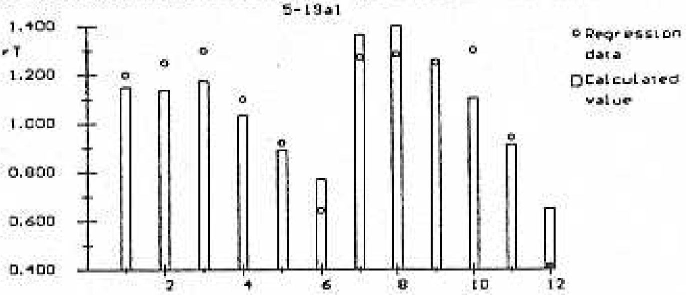
```
Param.    Converged     0.95 conf.     lower        upper
          Value         interval       limit        limit
k         0.159354      0.0671333      0.0922212    0.226488
alp         1.4575      0.714352       0.743149     2.17185
```

```
Model: ra=-k*Ca^alp
k = 0.159354
alp = 1.4575
2 positive residuals, 2 negative residuals.  Sum of squares = 0.00129113
```

d) No answer will be given.

P5-19

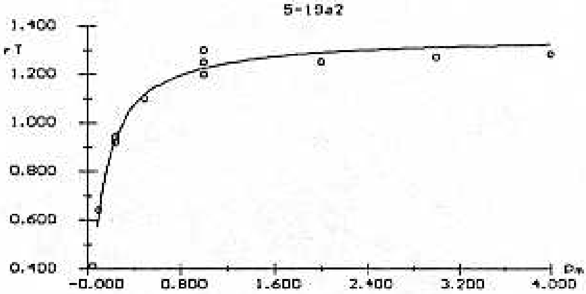
a) 1) From POLYMATH' s non-linear regression the following was obtained



```
Model: rT=k*Pm^alp*Ph2^bet
k = 1.14815                    bet = -0.0300691
alp = 0.184305
7 positive residuals, 5 negative residuals.  Sum of squares = 0.200197
```

k=1.15 $\alpha = .18$ $\beta = -.031$

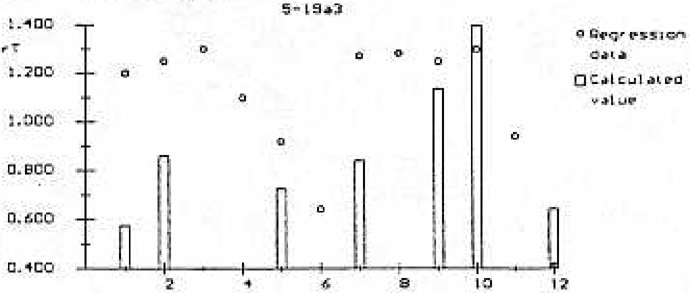
2) Again POLYMATH is used



```
Model: rT=k*Pm/(1+Km*Pm)
k = 12.2562
Km = 9.02516
3 positive residuals, 9 negative residuals.  Sum of squares = 0.0186383
```

k = 12.3 $K_M = 9.0$

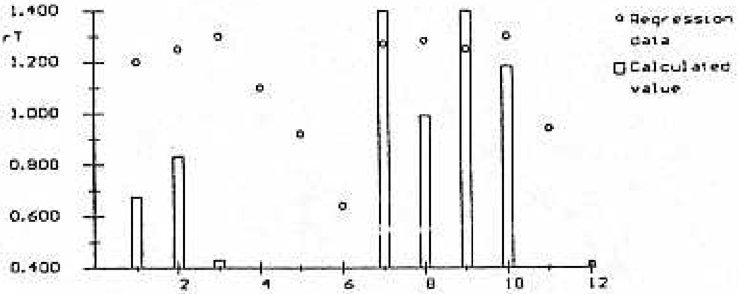
3) POLYMATH



```
Model: rT=k*Pm*Ph2/(1+Km*Pm)^2
k = 0.40943
Km = 2.8307
10 positive residuals, 2 negative residuals.  Sum of squares = 5.00106
```

$k = 8.4$ $K_M = 2.8$

4) POLYMATH



```
Model: rT=k*Pm*Ph2/(1+Km*Pm-Kh2*Ph2)
k = 3.25685e+18                    Kh2 = -2.06168e+18
Km = 2.77855e+18
10 positive residuals, 2 negative residuals.  Sum of squares = 3.89059
```

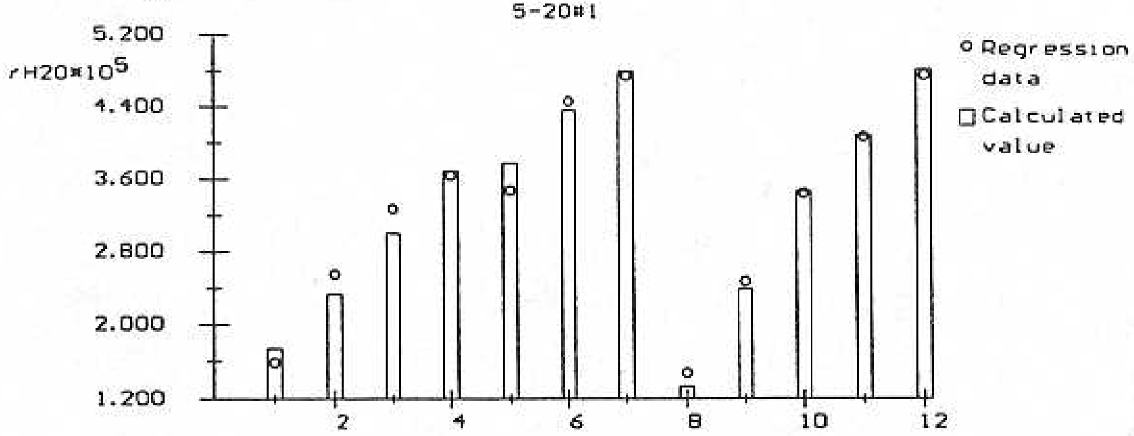
$k = 3.26*10^{18}$ $K_{H2} = 2.06*10^{18}$ $K_M = 2.78*10^{18}$

b) From the above POLYMATH regressions we can see that the best rate law is number two. This is evident because it has the lowest sum of squares.

c) No answer will be given.

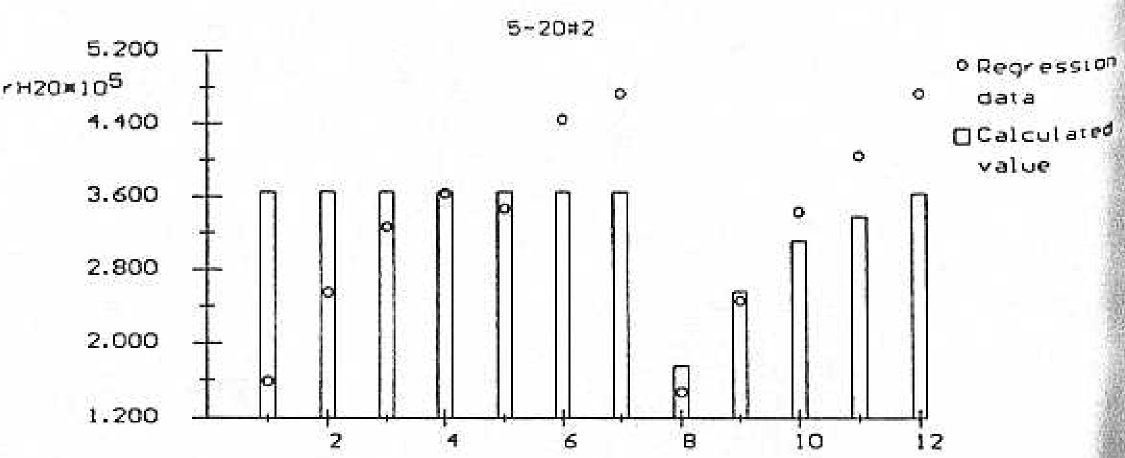
P5-20

Using POLYMATH's non-linear regression, the data was fit to the following parameters. For the first equation: $k = 0.0024$ $K_{NO} = 8.31*10^{15}$ $K_{H2} = 1.24*10^{16}$



```
Model:  rH20=k*KNO*PNO*PH2/(1+KNO*PNO+KH2*PH2)
k  =  0.0024218                       KH2  =  1.24056e+16
KNO  =  8.31397e+15
5 positive residuals, 7 negative residuals.   Sum of squares = 2.71177e-11
```

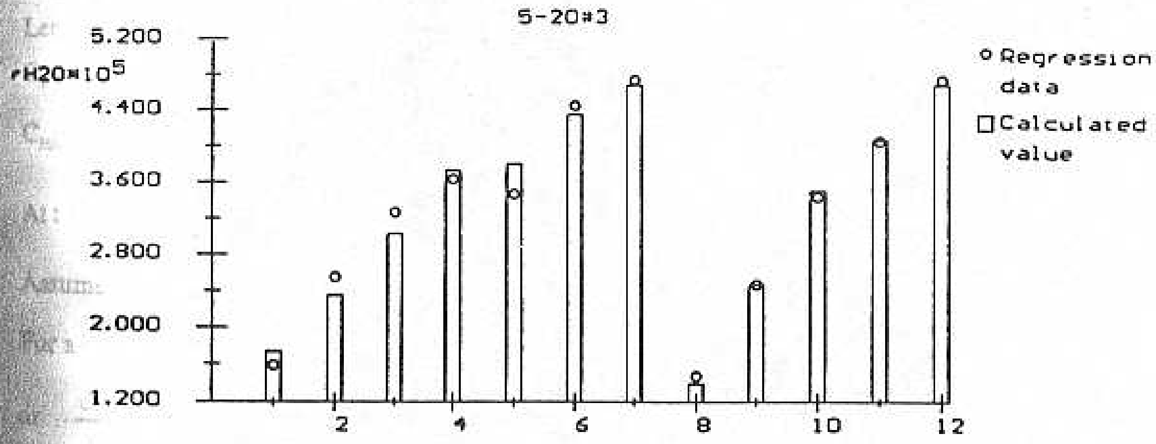
For the second equation: $k = 0.32$ $K_{NO} = 61.8$ $K_{H2} = 0.00015$



```
Model:  rH20=k*KH2*KNO*PNO/(1+KNO*PNO+KH2*PH2)
k  =  0.320466                        KNO  =  61.846
KH2  =  0.00015082
5 positive residuals, 7 negative residuals.   Sum of squares = 9.32207e-10
```

P5-20 cont'd

For the third equation: k = 0.00052 K_{NO} = 13.2 K_{H2} = 18.5



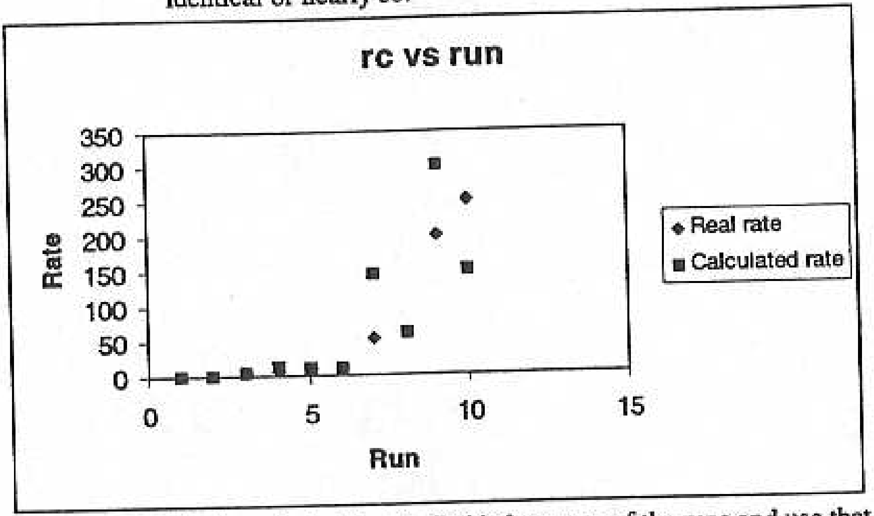
```
Model: rH20=k*KH2*KNO*PNO*PH2/(1+KNO*PNO+KH2*PH2)^2
k = 0.000518948                    KNO  =  13.1994
KH2 = 18.5102
6 positive residuals, 6 negative residuals.  Sum of squares = 2.60646e-11
```

$$r_{H_2O} = \frac{kK_{H_2}K_{NO}P_{NO}P_{H_2}}{\left(1+K_{NO}P_{NO}+K_{H_2}P_{H_2}\right)^2}$$

This is the best equation. In the second equation, the calculated value does not change with a change in Hydrogen pressure so it is not a reliable source. The first equation is somewhat reliable, but the values for the Ks are very high and do not make a good answer.

P5-21

a) This reaction is not elementary, if it were these two graphs would be identical or nearly so:



To obtain the calculated rate, find k from one of the runs and use that one throughout. The graph is similar in the smaller pressures, but as the pressure of A increases the rates differ greatly.

b) The sequence is specified this way so that r_c is always increasing.

c) No solution will be given.

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.)

$C_{HA} = C_{Po}X = KA \quad \therefore \quad X = \dfrac{KA}{C_{Po}}$ when $X = 1$ and $A = A_\infty$

At $t = \infty$, $A_\infty = \dfrac{C_{Po}}{K} \quad \therefore \quad X = \dfrac{A}{A_\infty}$

Assume reaction is irreversible: $-r_P = kC_P^n = kC_{Po}^n(1-X)^n$

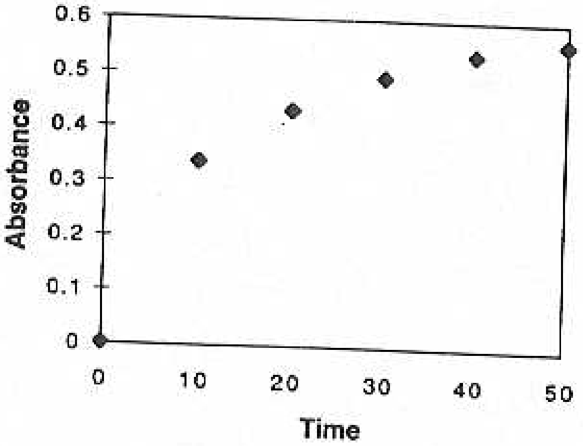
For a batch, constant volume reactor: $\dfrac{1}{V}\dfrac{dN_P}{dt} = \dfrac{dC_P}{dt} = r_P$

or $\dfrac{dC_P}{dt} = C_{Po}\dfrac{dX}{dt} = -\dfrac{C_{Po}}{A_\infty}\dfrac{dA}{dt} = -kC_{Po}^n(1-X)^n = -kC_{Po}^n(1-A/A_\infty)^n$

or $\dfrac{dA}{dt} = k\left(\dfrac{C_{Po}}{A_\infty}\right)^{n-1}(A_\infty - A)^n = K(A_\infty - A)^n$, where $K = k\left(\dfrac{C_{Po}}{A_\infty}\right)^{n-1}$

Try integral analysis first. Assume that reaction is zero order:

Then $\dfrac{dA}{dt} = K$ 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:



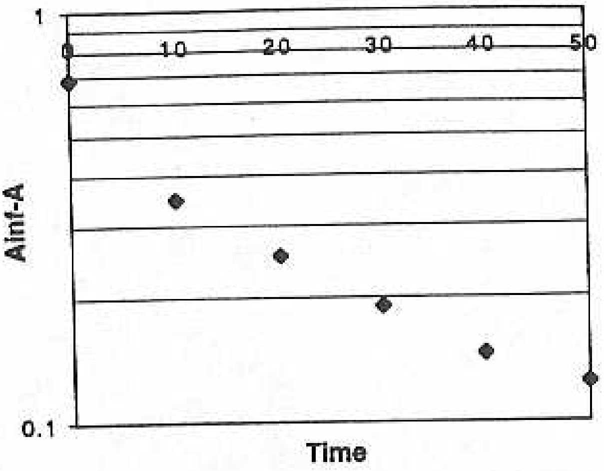
Next, assume that the reaction is first order:

$\dfrac{dA}{dt} = K(A_\infty - A)$ or $\int_0^A \dfrac{dA}{(A_\infty - A)} = \int_0^t Kdt = \ln\dfrac{(A_\infty - A)}{A_\infty} = -Kt$

$\therefore$ A plot of $(A_\infty - A)$ vs. t on semi-log paper should be linear.

CDP5-A (cont'd)

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

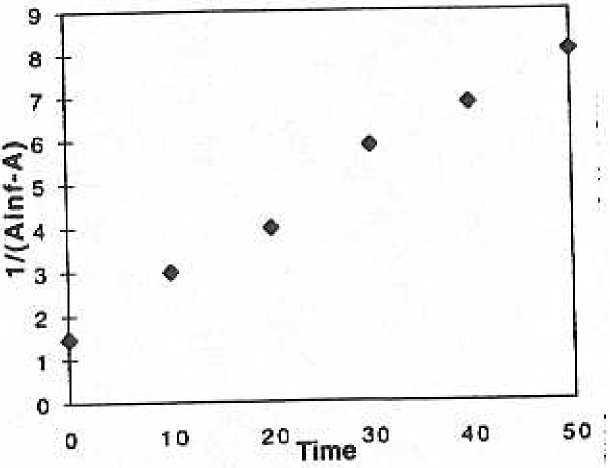


It is evident from the plot that the reaction is not first order. Try second order:

$$\frac{dA}{dt} = K(A_\infty - A)^2 \quad \therefore \quad \int_0^A \frac{dA}{(A_\infty - A)^2} = \frac{1}{(A_\infty - A)} - \frac{1}{A_\infty} = Kt$$

$$\text{or} \quad \frac{1}{(A_\infty - A)} = \frac{1}{A_\infty} + Kt \quad \therefore \quad \text{A plot of } \frac{1}{(A_\infty - A)} \text{ vs. t should be linear}$$

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 evident that a linear ralationship exists between (1/A_-A) and time; therefore the reaction is second order.

CDP5-B

The rate law for this reaction will be of the form:

$$-r_A = kC_A^n$$

Where n = the order of the reaction and k = the specific reaction rate constant. These are the two parameters we need to find using the data given.

First, we need to plot ln($-dC_A/dt$) vs. ln (C_A). To do this, we need to know how fast the solution is traveling and at what time the solution reaches an electrode position.

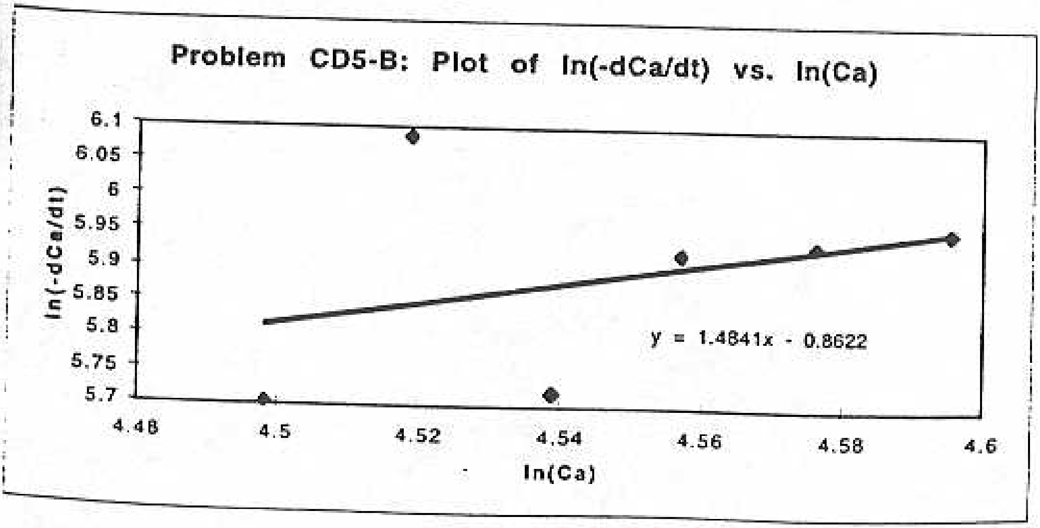
Since the tube diameter is 0.158 cm, the tube cross-sectional area is 0.0196 cm^2. This allows us to divide the solution volumetric flow rate by the cross sectional area and attain the velocity at which the solution is traveling:

Solution velocity = (19.6 cm^3/s)/(0.0196 cm^2) = 1000 cm/s

Now, if we consider the percent decomposition of HbO$_2$ as the conversion of the reaction, the percent of HbO$_2$ still remaining can be our C_A, since we do not know the initial concentration or molar flow rate of HbO$_2$ in solution.

Electrode Position	1	2	3	4	5	6	7
Time (s)	0	.005	.010	.015	.020	.025	.030
dt (s)	.005	.005	.005	.005	.005	.005	.005
% Decomposition HbO$_2$	0	1.93	3.82	5.68	7.2	9.4	10.9
% HbO$_2$ left (C_A)	100	98.07	96.18	94.32	92.8	90.6	89.1
dC_A	-	-1.93	-1.89	-1.86	-1.52	-2.2	-1.5
$-dC_A/dt$	-	386	378	372	304	440	300
Average C_A	-	99.035	97.125	95.25	93.56	91.7	89.85

A plot of ln($-dC_A/dt$) vs. ln(C_A) is then produced:



CDP5-B **cont'd**

As can be seen from this plot, the data points are not exactly linear. However, to use the method of differential analysis of rate data, we must find a best-fit line for the data. That best-fit ine is drawn in the plot, and the slope is 1.4841. This slope corresponds to the order of the rate law (n). Therefore, the rate law is now:

$$-r_A = kC_A^{1.5}$$

To calculate k, the specific reaction rate constant, we must evaluate the following equation, using the data gathered between electrode points 1 and 2:

$$k = \frac{-\left.\frac{dC_A}{dt}\right|_P}{\left.C_A^{n}\right|_P} = \frac{386 \quad \%/s}{99.035^{1.5} \ \%^{1.5}} 0.39166 s^{-1}\%^{-0.5}$$

Therefore, the specific reaction rate is 0.39166 $s^{-1}\%^{-0.5}$, and the final reaction rate law is:

$$-r_A = 0.39166 C_A^{1.5} \%/s$$

CDP5-C

Given: moles of ammonia formed at specific time
Find dC/dt also known as the rate of formation of ammonia
Use the graphical method and the following table is a summary of the results
First use a temperature of 351K

CDP5-C@351K

t	Cn	Δt	ΔCn	ΔCn/Δt	dCn/dt
0	0				0.033
		5	0.15	0.03	
5	0.15				0.027
		5	0.125	0.025	
10	0.275				0.023
		10	0.21	0.021	
20	0.485				0.019
		10	0.165	0.0165	
30	0.65				0.015
		10	0.12	0.012	
40	0.77				0.013
		10	0.1	0.01	
50	0.87				0.01
		10	0.08	0.008	
60	0.95				0.009
		20	0.13	0.0065	
80	1.08				0.008
		20	0.09	0.0045	
100	1.17				0.0074
		50	0.145	0.0029	
150	1.315				0.007

Ne:

: following way

Next, find the concentrations of GN and N_2H_4. Do this the following way

$$C_{NH_3} = \frac{N_{NH_3}}{V}$$

CDP5-C **cont'd**

$$X = \frac{C_{NH_3}}{3 * C_{GN0}}$$

$$C_{GN} = C_{GN0} * (1 - X)$$

$$C_{N_2H_4} = C_{GN0} * (\theta_B - 3 * X)$$

$$.5M + 2.575M = 3.075M$$

$$y_{GN} = \frac{.5}{3.075} = .16$$

$$y_{N_2H_4} = \frac{2.575}{3.075} = .84$$

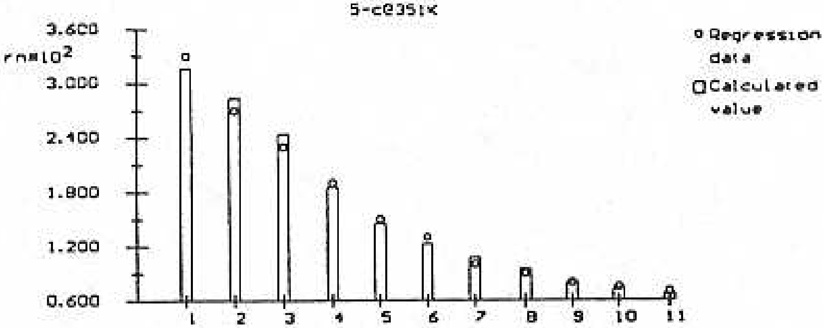
$$\theta_B = \frac{.84}{.16} = 5.23$$

Once that is done plug into POLYMATH's non-linear regression program with the following table.

```
5-30351
rn
X
Cgn
Ch
```

#	rn	X	Cgn	Ch
1	0.033	0	0.5	2.575
2	0.027	0.1	0.45	2.47
3	0.023	0.18	0.41	2.35
4	0.019	0.32	0.34	2.14
5	0.015	0.43	0.285	1.97
6	0.013	0.51	0.245	1.85
7	0.01	0.58	0.21	1.75
8	0.009	0.63	0.185	1.67
9	0.008	0.72	0.14	1.54
10	0.0074	0.78	0.11	1.45
11	0.007	0.88	0.06	1.3

CDP5-C **cont'd**



```
Model: rn=k*Cgn^alp*Ch^bet
k = 0.00035948                    bet = 4.25705
alp = -0.644973
6 positive residuals, 5 negative residuals.  Sum of squares = 7.38112e-06
```

5-c@351K

Matrix of correlation coefficients for the nonlinear correlation equation

	k	alp	bet
k	1	0.993351	-0.99832
alp	0.993351	1	-0.986061
bet	-0.99832	-0.986061	1

```
          Converged      0.95 conf.       lower           upper
Param.      Value         interval         limit           limit
 k        0.00035948    0.000628826  -0.000269345    0.000988306
 alp       -0.644973      0.574513       -1.21949     -0.0704596
 bet         4.25705       1.44931        2.80774        5.70636
```

```
Model: rn=k*Cgn^alp*Ch^bet
k = 0.00035948                    bet = 4.25705
alp = -0.644973
6 positive residuals, 5 negative residuals.  Sum of squares = 7.38112e-06
```

The answer we get is that $k = 0.00036$

$\alpha = -2/3$

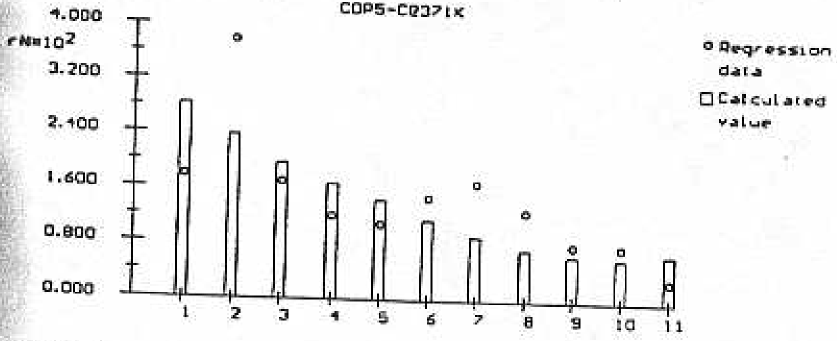
$\beta = 4.25$

For the higher temperature, we know alpha and beta so we will just solve for k. Create this chart to find dC/dt.

PS-C cont'd

CDPS-C @ 371

t	Cn	Δt	ΔCn	ΔCn/Δt	dCn/dt
0	0				0.017581
		5	0.19	0.038	
5	0.19				0.038167
		5	0.155	0.031	
10	0.345				0.01674
		10	0.13	0.013	
20	0.475				0.012
		10	0.105	0.0105	
30	0.58				0.011
		10	0.175	0.0175	
40	0.755				0.015
		10	0.13	0.013	
50	0.885				0.017
		10	0.18	0.018	
60	1.065				0.013
		20	0.12	0.006	
80	1.185				0.008
		20	0.135	0.006/5	
100	1.32				0.0079
		50	0.075	0.0015	
150	1.395				0



Model: rN=k*Cgn^(-.66)*CH^(4.25)
k = 0.000323653
6 positive residuals, 5 negative residuals. Sum of squares = 0.00046934

CDPS-C@371K

Matrix of correlation coefficients for the nonlinear correlation equation

	k
k	1

Param.	Converged Value	0.95 conf. interval	lower limit	upper limit
k	0.000323653	9.55865e-05	0.000228067	0.00041924

Model: rN=k*Cgn^(-.66)*CH^(4.25)
k = 0.000323653
6 positive residuals, 5 negative residuals. Sum of squares = 0.00046934

CDP5-C **cont'd**

So k = .00032

$$\log\left(\frac{0.00036}{0.00032}\right)=\frac{-E}{2.3*8.314}\left(\frac{1}{371}-\frac{1}{351}\right)$$
$$E=6368\text{ J}$$

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.

$$t_{1/2}=\frac{2^{\alpha-1}-1}{k(\alpha-1)}\left(\frac{1}{C_{NO_0}^{\alpha-1}}\right)=\frac{2^{3-1}-1}{k(3-1)}\left(\frac{1}{C_{NO_0}^{3-1}}\right)=\frac{2^{2}-1}{2k}\left(\frac{1}{C_{NO_0}^{2}}\right)$$

(a) For $C_{NO_0} = 3000\text{ppm}$:

$$t_{1/2}=\frac{3}{2\left(1.4\times10^{-9}\text{ ppm}^{-2}/\text{min}\right)}\left(\frac{1}{(3000\text{ ppm})^{2}}\right)=119.05\text{ min}$$

(b) For $C_{NO_0} = 1$ 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.

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

CDP5-E **cont'd**

Plug that into the design equation:

$$-\frac{dC_A}{dt} = kC_A^{\alpha}$$

$$-\frac{d\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)}{dt} = k'\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)^{\alpha}$$

$$k' = k\left(N_{A0}^{\alpha-1}\right)$$

$$\ln -\frac{d\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)}{dt} = \alpha \ln\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right) + \ln k'$$

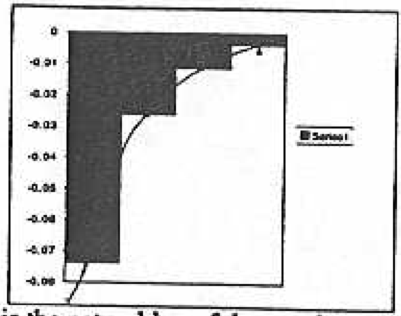
$$k' = \frac{-\dfrac{d\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)}{dt}}{\left(\dfrac{1-\dfrac{V-V_0}{V_0\varepsilon}}{V}\right)}$$

Now find the derivitive. To do that use the graphical method.

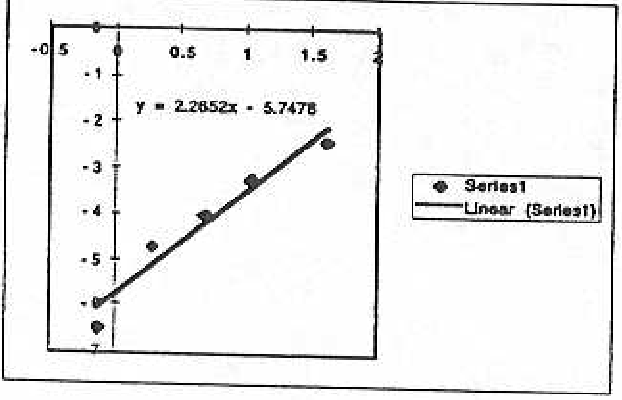
t	$(1-(V-V_0)/V_0\varepsilon)/V$	Δt	$\Delta 1-(V-V_0)/V_0\varepsilon)/V$	$\Delta 1-(V-V_0)/V_0\varepsilon)/V$ /Δt	$d1-(V-V_0)/V_0\varepsilon)/V$ /dt
0	5				-0.09
		30	-2.211	-0.0737	
30	2.789				-0.04
		30	-0.785	-0.0262	
60	2.003				-0.018
		60	-0.679	-0.011	
120	1.32				-0.009
		120	-0.448	-0.004	
240	0.88				-0.0015

CDP5-E **cont'd**

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.

$$V = \frac{F_{A0}X}{.9 * \left(\frac{P_{A0}}{RT}(1-X)\right)^2} = \frac{16.67 * .8}{.9 * \left[\frac{607.95}{8.314 * 313}(1-.8)\right]^2} = 6787 dm^3$$

Chapter 6

P6-1. An open-ended problem that requires students to create and original problem and solution.

P6-2. "What if. . ." problem. Parts (c), (d) and (e) can be used in conjunction with **Living Example Problems** E6-6 and E6-8.

P6-3. This problem concerns thermodynamic equilibrium and multiple reactions. It is usually assigned at the graduate level. The heat of isomerization must be calculated at temperature below 100°C where no other reactions are dominate alternate to **P6-5**.

P6-4. Straight forward problem to reinforce principles of how to choose reactor schemes to maximize the instantaneous selectivity S_{DU} for parallel reactions.

P6-5. Thermodynamics and multiple reactions. Alternative to **P6-3**.

P6-6. Maximize S_{DU} for parallel reactions. Parts (c) and (d) allow the student to explore the problem by varying the temperature and pressure.

P6-7. This problem concerning drinking and driving has always been a favorite with the students. It is quite straight forward.

P6-8. This problem is a new problem on drug medication which has been assigned for the past two years, is similar to P6-7. But it is a little more open-ended than P6-7 in that the student must decide on the amount (one dose or two) of drugs and the times to administer them.

P6-9. Maximizing S_{DU} and $ for series reaction. Parts (a), (b), and (c) are straight forward, and could be one problem by themselves. Parts (c) through (f) allow the student to explore the problem and learn the trends as each reaction is allowed to be reversible. Part (g) involves a packed bed reactor with pressure drop. If all parts are assigned, it would be a fairly long assignment. Good though!!!!! (Moose dung pie joke).

P6-10. Straight forward problem that is fairly short. Points out that the CSTR temperature can be adjusted to maximize overall selectivity.

P6-11. This problem is a medium-length (Ca.40 minutes) straight forward problem it reinforces relating relative rates of reaction. It is most always assigned as an "in class" problem.

P6-12. Fairly straight forward problem using POLYMATH. Allows for temperature variation to find optimum operating conditions.

P6-13.	This problem is usually assigned as it is straight forward and encompasses all the facets of liquid phase reactor design for multiple reactions.
P6-14.	This problem is a more complicated, alternative to **P6-12**. Parts (a) through (d) are reasonably straight forward.
P6-15.	Extends the **Living Example Problem** E6-6, to include a 3rd reaction. Allows for parameter variation, and because E6-6 can be loaded directly on to ones computer, it is a relatively short problem.
P6-16.	Fairly straight forward solution with POLYMATH or MatLab. This problem is a simpler version of P6-18. Allows for a small degree of open-endedness in part (c).
P6-17.	This problem is unique in that is one of the few problems with gas phase multiple reactions in which there is a change in the total number of moles. **CDP6-H, CDP6-I,** and **CDP6-J** extend this problem.
P6-18.	More complicated version of **P6-14**, however it is quite straight forward when using POLYMATH.
P6-19.	California Registration Exam Problem.
P6-20.	Short problem using living example problem E6-8.
P6-21.	Many reactions are shown. The point is to find which ones are dominate at what temperatures. Usually assigned at graduate level in conjunction with PSSH in Chapter 7.
P6-22.	Requires the student to go outside the text to develop an original problem.
P6-23.	New problem with **recent** (1996) real data for a gas phase reaction with a change in the total number of moles. It is open-ended in that it asks the student to select the best feed conditions.
P6-24.	Member Problem Hall of Fame. This problem is designed to help enhance the students critical thinking and creative thinking skills by varying the feed temperature and concentrations to maximize methanol production. Should count for more than one assignment.
P6-25.	This current (1996) problem is quite open-ended and probably be assigned only at the senior or gradate level. Real reactions and real numbers.
P6-26.	This problem is more straight forward than **P6-24** and **P6-25** and can rapidly be solved with POLYMATH.

P6-27. This problem requires the use of Attainable Region Analysis (ARA) to solve it and in fact is solved on the web.

CDP6-A Maximize S for parallel reactions. Alternative to problems **P6-4, CDP6-B.**

CDP6-B Rework of **P6-14** for different reaction order. Alternative to problems **P6-4, CDP6-A.**

CDP6-C Straight forward. Alternative to **P6-14.**

CDP6-D Straight forward.

CDP6-E Simpler alternative to **P6-9.**

CDP6-F Very straight forward problem to reinforce the principles.

CDP6-G Requires additional reading.

CDP6-H Good problem involving gas phase reactions with a change in the number of moles. Straight forward.

Problems CDP6-I and CDP6-J are extensions of Problem CDP6-H.

CDP6-K Have not assigned this graduate level problem.

CDP6-L Have not assigned this graduate level problem.

CDP6-M Straight forward. Alternative to F.

CDP6-N Graduate level problem has yet to be assigned.

CDP6-O Straight forward.

CDP6-P Graduate level problem yet to be assigned.

Summary

	Assigned	Alternates	Difficulty	Time	Solution Given
P6-1				20	No
P6-2				70	No
P6-3	G		SF	50	Yes
P6-4	AA	6,A,C,D		60	Yes
P6-5	G	3		60	Yes
P6-6	AA	4,10,12,C		45	Yes
P6-7		7	SF	50	Yes
P6-8		8	SF	75	Yes
P6-9	G	E		120	Yes

	P6-10	I	4,6	35	Yes
●	P6-11			40	Yes
	P6-12	I	6,10,15,23	30	Yes
●	P6-13		17	75	Yes
	P6-14	AA	16,B,C	75	Yes
	P6-15	AA	6,10,12,M	60	Yes
	P6-16	AA	14,18	45	Yes
●	P6-17	AA	13,H,I,J	25	Yes
	P6-18	AA	14,C,N	35	Yes
	P6-19	I		40	Yes
	P6-20	O		30	Yes
	P6-21	G		90	No
	P6-22	S			No
●	P6-23	AA	12,23,24,25,25,K,L	40	Yes
	P6-24	AA	23,25,26,K,L	60	Yes
	P6-25	AA	23,24,26,K,L	90	No
	P6-26	AA	23,24,25,K,L	75	Yes
	P6-27	G		45	No
	CDP6-A	AA	4,C,D	30	Yes
	CDP6-B	AA	16	45	Yes
	CDP6-C	AA	6,12,14,18,A,D	55	Yes
	CDP6-D	O	C	45	Yes
	CDP6-E	O	9	30	Yes
	CDP6-F	O	12	45	Yes
	CDP6-G	G	–	70	Yes
	CDP6-H	AA	13,17	30	Yes
	CDP6-I	AA	13,17	30	Yes
	CDP6-J	AA	13,17	30	Yes
	CDP6-K	G	23,24,25,26	60	Yes
	CDP6-M	O		45	Yes
	CDP6-N	G		90	Yes
	CDP6-Q			60	Yes

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-6

	Equilibrium	Maximize	Batch Reactor	PFR	PBR	CSTR	Semibatch Reactor	Othe
Series Reactions	3,5	9(b,c)	9,7,8,E			9		9
Parallel Reactions		6(d),A		13	12	6,12,13, A	13	6
Complex Reaction		M	P,C,25	15,16,17, B,H,I,J, 24	N	11,10,20, 19,18,H, ,?,P,23		
Straight Forward Reinforcement of Principles		6a	8(a), 9(a,c)	15(a),G, M	12(a),14(d)	11, 14(b,c), F,M		
Fairly Straight Forward		6(b)		13(a,b), 16(a), 18(a)	14(f)		13(c), 18(b)	
Parameter Variation		4(c),5(c), 6(c,d), 10(b),25	9(c,f)	14(a), 15(b,c,d), 16(a,b)	12(b),13(d),15(b), 16(a)	4(c), 14(a)		
Open-ended		8(b,d),25, N		16(b)	9(g),17(d)	4(e),6(d)	4(c)	
Critical Thinking		8(c)		16(c), N(e)		N(e)		N(
More Difficult		9(b),N	9(b)	10(a), 16(b)	N	10(a)	N	P

Chapter 6

P6-1 No solution will be given.

P6-2 No solution will be given.

P6-3

The equilibrium constant for the reaction

tr-OL $\rightleftarrows$ 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

$$\frac{-1.39-(-1.11)}{3.09-2.68} \times 1000 = -683 = \frac{\Delta H_R}{R}$$

$$\Delta H = -1.357 \ \frac{\text{cal}}{\text{mol}}$$

P6-4

a)

$$A + C \rightarrow D \qquad r_D = 800 e^{-2000/T} C_A^{0.5} C_C$$

$$A + C \rightarrow U_1 \qquad r_u = 10 e^{-300/T} C_A C_C$$

$$S_{DU1} = \frac{r_D}{r_{U1}} = 80 C_A^{-0.5} e^{-1700/T}$$

To maximize S_{DU1},

- Operate at high temperatures
- C_A should be kept low
- Tubular reactor with side streams of A
- Semi-batch reactor with A fed slowly into a solution of C

b)

$$D + C \rightarrow U_2 \qquad r_{U2} = 1000e^{-8000/T} C_C C_D$$

$$S_{DU2} = 0.8\frac{C_A^{0.5}}{C_D} e^{6000/T}$$

T (K)	$S_{DU1}\ C_A^{0.5}$	$S_{DU2}\ C_D/C_A^{0.5}$
273	0.158	$2.805*10^9$
473	2.198	$2.583*10^9$
873	11.412	$7.725*10^2$
1000	14.614	322.74
1250	20.532	97.208
1500	25.756	43.678
1750	30.283	24.616
2000	34.193	16.068

Hence to minimize selectivity we can use two reactors

1st CSTR: 2000K
2nd CSTR: 1250 K

c)

$$V = \frac{F_{D0} - F_D}{-r_D}; F_D = r_D V$$

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

$$Y_D = \frac{F_D}{F_{A0} - F_A} = \frac{r_D V}{-r_a V} = \frac{r_D}{-r_A}$$

$$r_A = -800e^{-2000/T} C_A^{0.5} C_C - 10e^{-300/T} C_A C_C$$

$$r_D = 800e^{-2000/T} C_A^{0.5} C_C - 1000e^{-8000/T} C_D C_C$$

$$C_A v_0 = F_A; v_0 = 1\frac{dm^3}{\text{min}}, C_A = F_A$$

$$C_A = C_{A0} + 2r_A$$

$$C_D = 2r_D$$

$$C_C = C_{C0} + 2r_C$$

$$r_C = r_A - 1000e^{-8000/T} C_D C_C$$

Using these equations in POLYMATH for different inlet concentrations, yield is maximized at different temperatures e.g.

T	C_{C0} (mol/dm^3)	Yield
850	1	0.977
500	0.5	0.987
1300	2	0.96

```
6-4 (c)
Equations:                                                    Initial value
f(ca)=ca-cao-2*ra                                             1
f(cd)=cd-2*rd                                                 0
f(cc)=cc-cco-2*rc                                             0.5
cao=1
cco=0.5
T=1300
ra=-800*exp(-2000/T)*ca^0.5*cc-10*exp(-300/T)*ca*cc
rd=800*exp(-2000/T)*ca^0.5*cc-1000*exp(-8000/T)*cd*cc
rc=ra-1000*exp(-8000/T)*cc*cd
Y=rd/-ra
```

All maximum yields greater than 0.95.

Lower concentration → higher temperatures to get right yield. See POLYMATH solution below.

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

```
6-4 (d)
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=10
rc=-k2
x=(fao-fa)/fao
avo=fto/cto
ca=cto*(fa/ft)
ra=-k1*ca
```

```
6-4 (d)
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
```

P6-5

a) Using the equation for the equilibrium constants:

$$K_{e1} = \frac{C_C C_D}{C_A C_B} \qquad \mathrm{K}_{e2} = \frac{C_X C_Y}{C_C C_B}$$

We can come up with the equations for C_A, C_D, and C_X.

$$C_A = \frac{C_C C_D}{K_{e1} C_B}$$

$$C_D = \frac{K_{e1} C_A C_B}{C_C}$$

$$C_X = \frac{K_{e2} C_C C_B}{C_Y}$$

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                 0.979598
cb                0.675961
```

$C_A = 0.0306$ $\quad C_B = 0.68$ $\quad C_C = 0.75$ $\quad C_D = 0.11$

$C_X = 0.71$ $\quad C_Y = 0.71$

We also find that X = 0.98

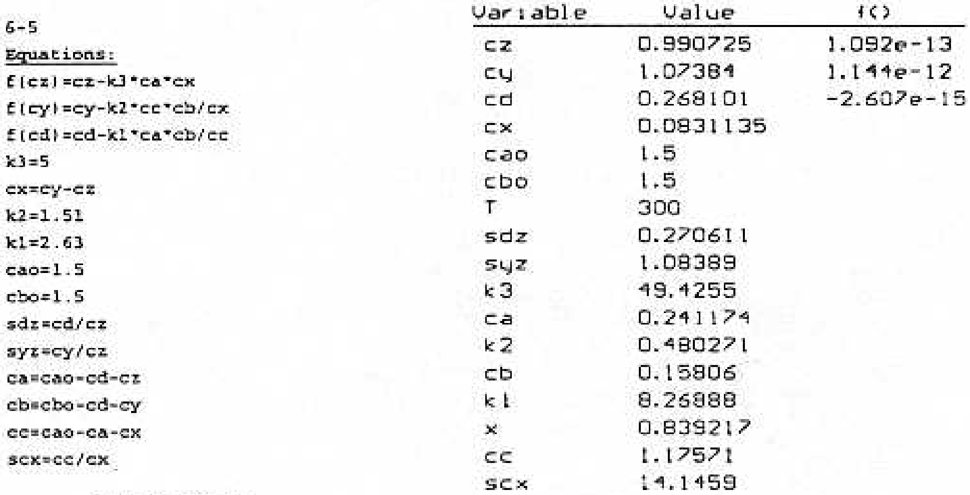
P6-5 cont'd

b) With the new equation we must find the new equilibrium equations.

$$C_Z = K_{e3} C_A C_X$$
$$C_Y = \frac{K_{e2} C_C C_B}{C_X}$$
$$C_D = \frac{K_{e1} C_A C_B}{C_C}$$

The rest are the same except for:

$$C_X = C_Y - C_Z$$
$$C_A = C_{A0} - C_D - C_Z$$



```
6-5
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            14.1459
```

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	312.5336841	Ca	0.016513937
k1	0.003919233	Cx	0.039192325
k2	0.230891512	Cb	0.038129279
k3	2.260443602	Cy	0.006164458

P6-7 US legal limit: 1 g/l

Sweden legal limit: 0.5 g/l

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$\frac{dC_A}{dt} = -k_1 C_A$; $k_1 = 10\ hr^{-1}$; A - Alcohol in gastrointestinal tract

$\frac{dC_B}{dt} = -k_2 + k_1 C_A$; $k_2 = 0.192 \frac{g}{l\text{-}hr}$; B - Alcohol in blood

$$C_A = C_{A0} e^{-k_1 t}$$

$$\frac{dC_B}{dt} = k_1 C_{A0} e^{-k_1 t} - k_2$$

$$C_B = -C_{A0} e^{-k_1 t} - k_2 t + C$$

If at $t = 0$; $C_B = 0 \Rightarrow C = C_{A0}$

$$C_B = C_{A0}(1 - e^{-k_1 t}) - k_2 t$$

or if at $t = 0$; $C_B = C_{B0} \Rightarrow C = C_{A0} + C_{B0}$

$$C_B = C_{A0}(1 - e^{-k_1 t}) + C_{B0} - k_2 t$$

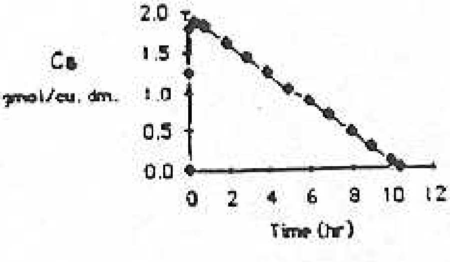
(a) Two tall martinis = 80 g ETOH

Body fluid = 40 l

$$C_{A0} = \frac{80\ g}{40\ l} = 2\ g/l$$

At $t = 0$; $C_B = 0$: $C_B = C_{A0}(1 - e^{-k_1 t}) - k_2 t$

$$C_B = 2\frac{g}{l}\left(1 - e^{-10t}\right) - 0.192t \quad \text{where } t \text{ in hours}$$



In U.S. for $C_B = 1\frac{g}{l}$, $t = 5.2$ hrs

P6-7 (cont'd)

(f) 60 g immediately ⇒ $C_{A0} = 1.5\ \frac{g}{l}$

$$C_B = C_{A0}\left(1 - e^{-k_1 t}\right) - 0.192t$$

$$C_B = 1.5\left(1 - e^{-10t}\right) - 0.192t$$

$C_B = 1\ \frac{g}{l}$ at $t = 0.115$ hr at $t = 2.6$ hr

(23g) A heavy person would be less affected by the alcohol than a thin one. That is, the reaction rate constant would be lower for a heavy person.

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:

$$-r_A = k_1C_A + k_2C_A$$

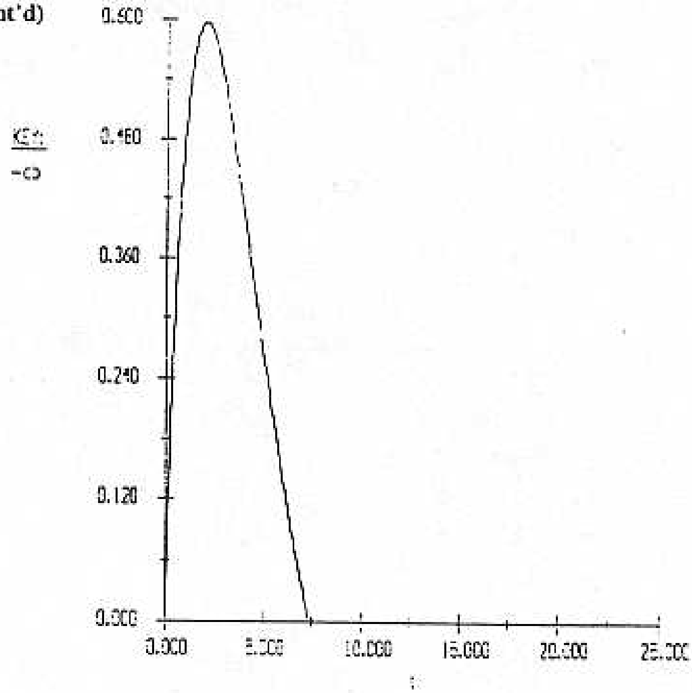
$$r_B = k_1C_A - k_3 - k_4C_B$$

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:

```
Equations:                                        Initial value
d(ca)/d(t)=-k1*ca-k2*ca                           6.25
d(cb)/d(t)=k1*ca-k3-k4*cb                         0
k1=0.15
k2=0.6
k4=0.2
k3=if(cb<0)then(k1*ca-k4*cb)else(0.1)
t0 = 0,    tf = 24
```

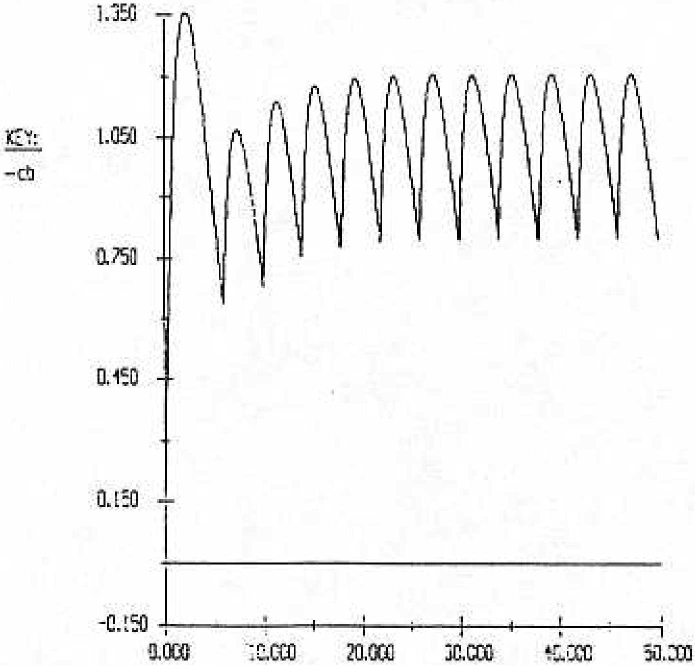
P6-8 (cont'd)



(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.



P6-9

a) Species A:

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

$$-r_A = k_1 C_A$$

Species B:

$$\frac{dC_B}{dt} = r_B$$

$$r_B = k_1 C_A - k_2 C_B$$

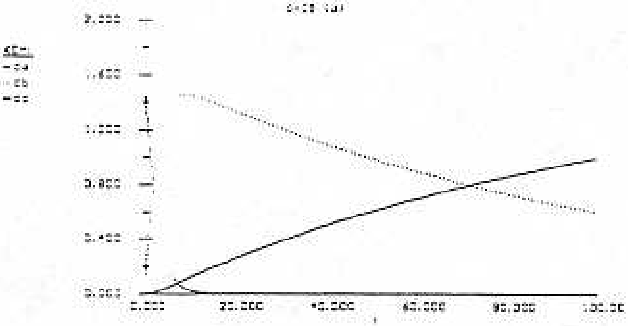
Species C:

$$\frac{dC_C}{dt} = r_C$$

$$r_C = k_2 C_B$$

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
t0 = 0,   tf = 100       rb         0.64            0.64             -0.0132417      -0.006037
```



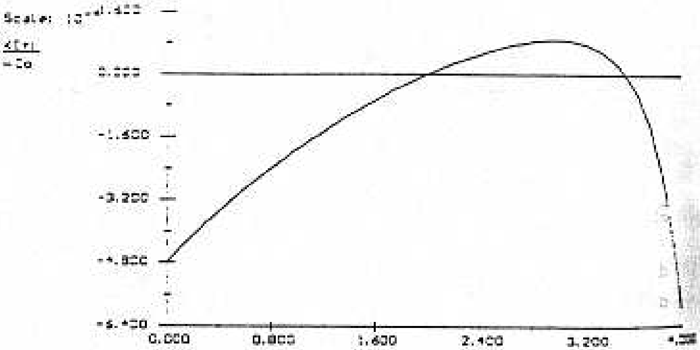
b)To find the maximum profit, take the above equations and add this one:

$$Cost = 50 * C_B * 500 - 10 * C_A * 500 - 50 * C_A * 500 - 30 * \left(e^{(3*C_C)} - 1\right)$$

Plugging into POLYMATH: gets the following.

P6-9 cont'd

```
Equations:                                                   Initial val
d(ca)/d(t)=ra                                                1.6
d(cb)/d(t)=rb                                                0
d(cc)/d(t)=rc                                                0
k1=.4
k2=.01
Co=50*cb*500-10*ca*500-50*ca*500-30*(exp(.5*cc*500)-1)
ra=-k1*ca
rc=k2*cb
rb=k1*ca-k2*cb
t0 = 0,    tf = 4
```



```
Variable      Initial value   Maximum value   Minimum value   Final value
t             0               4               0               4
ca            1.6             1.6             0.323034        0.323034
cb            0               1.24536         0               1.24536
cc            0               0.0316028       0               0.0316028
k1            0.4             0.4             0.4             0.4
k2            0.01            0.01            0.01            0.01
Co            -48000          8784.85         -59502.7        -59502.7
ra            -0.64           -0.129214       -0.64           -0.129214
rc            0               0.0124536       0               0.0124536
rb            0.64            0.64            0.11676         0.11676
```

Find the maximum profit occurs at t=3.2 h

c) First, find the values for the proportionality constant from the Arhennius equation.

$$0.4\text{h}^{-1} = 0.0001\text{s}^{-1}$$

$$0.01\text{h}^{-1} = 2.78\times10^{-6}\text{s}^{-1}$$

$$0.0001 = A_1e^{-(10000/(1.987*373))}$$

$$A_1 = 72$$

$$2.78\times10^{-6} = A_2e^{-(20000/(1.987*373))}$$

P6-9 cont'd

Using the CSTR design equation with respect to space-time, come up with equations for C_A and C_B.

$$t = \frac{C_{A0} - C_A}{k_1 C_A}$$

$$C_A = \frac{C_{A0}}{1 + tk_1}$$

$$t = \frac{-C_B}{-k_1 C_A + kC_B}$$

$$C_B = \frac{k_1 t C_A}{tk_2 + 1}$$

Using EXCEL's solver, come up with the temperature that maximizes B. The concentration and temperature are shown below.

T
437.941035

k1
0.0007354

k2
0.00015231

Ca
0.68854972

Cb
0.7153319

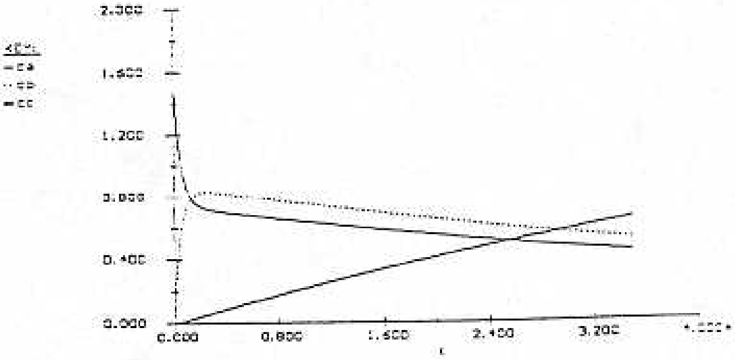
d)Part d is similar to part b except for two rate laws:

$$r_A = k_{-1}r * C_B - k_1 * C_A$$

$$r_B = k_1 * C_A - k_{-1} * C_B - k_2 * C_B$$

Using those rate laws inPOLYMATH produce the following:

```
Equations:                         Initial value
d(ca)/d(t)=ra                      1.6
d(cb)/d(t)=rb                      0
d(cc)/d(t)=rc                      0
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
t0 = 0,    tf = 350000
```



P6-9 cont'd

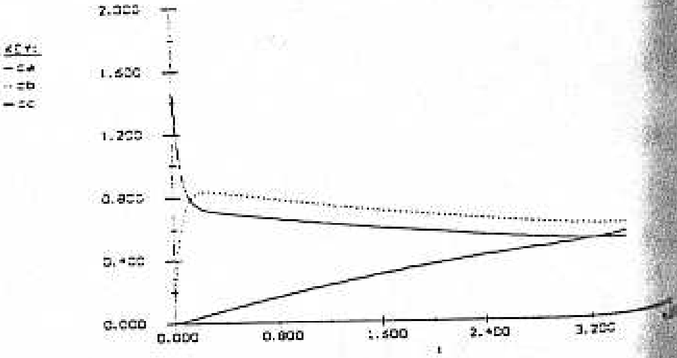
```
Variable          Initial value  Maximum value  Minimum value  Final value
t                 0              350000         0              350000
ca                1.6            1.6            0.436316       0.436316
cb                0              0.833237       0              0.5159
cc                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
```

e)Part e 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
t0 = 0,    tf = 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
```

P6-9 **cont'd**

f) 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.

g)

$$\frac{dF_A}{dW} = r_A'$$

$$r_A' = -k_1 C_A$$

$$C_A = \frac{N_A}{v}$$

$$v = v_0\left(\frac{P_0}{P}\right)$$

$$\left(\frac{P_0}{P}\right) = (1-\alpha W)^{1/2}$$

Combining:

$$\frac{dF_A}{dW} = \frac{-k_1 F_A (1-\alpha W)^{1/2}}{v_0}$$

Similarly:

$$\frac{dF_B}{dW} = r_B$$

$$r_B = k_1 C_A - k_2 C_B$$

$$C_A = \frac{F_A}{v} \qquad\qquad C_A = \frac{F_A}{v}$$

$$\frac{dF_B}{dW} = \frac{k_1 F_A (1-\alpha W)^{1/2} - k_2 F_B (1-\alpha W)^{1/2}}{v_0}$$

and:

$$\frac{dF_C}{dW} = \frac{k_2 F_C (1-\alpha W)^{1/2}}{v_0}$$

Once those are done we have to come up with a way to change α with the change in diameter of the particle. We know that

$$\alpha = J\beta_0 \qquad\qquad J = \frac{2}{A_C \rho_c (1-\phi) P_0}$$

$$\beta_0 = \frac{L}{D_p}\left[\frac{M}{D_p} + N\right]$$

Where J, L, M, and N are constants that won't change for this problem.

Starting at the given α and the following chart was made.

P6-9 cont'd

```
Equations:                                                    Initial value
d(fc)/d(w)=k2*fb*(1-alp*w)^.5/vo                              1e-06
d(fb)/d(w)=(k1*fa*(1-alp*w)^.5-k2*fb*(1-alp*w)^.5)/vo         0
d(fa)/d(w)=-k1*fa*(1-alp*w)^.5/vo                             10
k1=.25
k2=.15
alp=.00098
vo=10
fa0=10.0000001
Sbc=fb/fc
Yb=fb/(fa0-fa)
```

```
6-09g  dp=1
Variable     Initial value   Maximum value   Minimum value   Final
w            0               100             0               100
fc           1e-06           5.51973         1e-06           5.5197
fb           0               4.64738         0               3.606
fa           10              10              0.873606        0.873
k1           0.25            0.25            0.25            0.25
k2           0.15            0.15            0.15            0.15
alp          0.00098         0.00098         0.00098         0.000
vo           10              10              10              10
fa0          10              10              10              10
Sbc          0               177.571         0               0.653
Yb           0               0.994405        0               0.395
```

When D_p increases to 2 cm, according to the above equations, β_0 decreases by 3/4 and α also decreases by 3/4. The following chart was made and the selectivity has gone down.

```
6-09g  dp=2
Variable     Initial value   Maximum value   Minimum value   Final value
w            0               100             0               100
fc           1e-06           5.55377         1e-06           5.55377
fb           0               4.64749         0               3.5863
fa           10              10              0.859935        0.859935
k1           0.25            0.25            0.25            0.25
k2           0.15            0.15            0.15            0.15
alp          0.000735        0.000735        0.000735        0.000735
vo           10              10              10              10
fa0          10              10              10              10
Sbc          0               177.527         0               0.645741
Yb           0               0.994403        0               0.392371
```

P6-9 cont'd

When D_p decreases to 0.5, according to the above equations, β_0 increases by 6 and α also increases by 6. The following chart was made and the selectivity goes up.

```
Variable     Initial value   Maximum value   Minimum value   Final value
w            0               100             0               100
fc           1e-06           4.70888         1e-06           4.70888
fb           0               4.64701         0               4.04792
fa           10              10              1.24321         1.24321
k1           0.25            0.25            0.25            0.25
k2           0.15            0.15            0.15            0.15
alp          0.00588         0.00588         0.00588         0.00588
vo           10              10              10              10
fa0          10              10              10              10
Sbc          0               52.6414         0               0.859635
Yb           0               0.981359        0               0.46226
```

Therefore choose the smallest particle and the selectivity will be high.

P6-10

(a)

Mole Balances: $\frac{dF_A}{dV} = -r_B - r_C \qquad \frac{dF_B}{dV} = r_B \qquad \frac{dF_C}{dV} = r_C$

Rate Laws: $r_B = k_1 C_A^2 \qquad k_1 = 15$

$r_C = k_2 C_A \qquad k_2 = 0.015$

Stoichiometry: $C_A = C_{T0}\left(\frac{F_A}{F_T}\right) \qquad F_T = F_A + F_B + F_C$

$\$ = 60F_B - 15F_C - 10F_{A0}$

Use these equations in POLYMATH to find the necessary volume to maximize \$.
V = 1425 ft^3.

P6-10 (cont'd)

```
Equations:
d(fb)/d(V)=rb
d(fa)/d(V)=-rc-rb
d(fc)/d(V)=rc
cao=0.00447
k1=15
k2=0.015
ft=fa+fb+fc
fao=0.06705
cost=60*fb-15*fc-10*fao
ca=cao*(fa/ft)
rc=k2*ca
rb=k1*ca**2
```

$V_0 = 0, \quad V_f = 3000$

V	cost
1012.5	1.4570562
1050	1.4592956
1087.5	1.4611432
1125	1.4626513
1162.5	1.4638652
1200	1.4648239
1237.5	1.4655614
1275	1.4661071
1312.5	1.4664866
1350	1.4667222
1387.5	1.4668335
1425	1.4668376
1462.5	1.4667493
1500	1.4665818
1537.5	1.4663465
1575	1.4660535

(b)

Mole Balances: $F_A = F_{Ao} + r_A V \qquad F_B = r_B V \qquad F_C = r_C V$

Rate Laws: $r_A = -r_B - r_C \qquad r_B = k_1 C_A^2 \qquad r_C = k_2 C_A$

$$k_i = k_{io}\exp\left(\frac{E_i}{R}\right)\left(\frac{1}{T} - \frac{1}{919.67}\right) \qquad F_i = v_o C_i$$

$$\$ = v_o\left(60C_B - 15C_C - 10C_{Ao}\right)$$

Use these equations in POLYMATH and vary T from 860°R to 1160°R and find maximum value for \$.

\$ steadily rises with temperature and reaches a maximum at 970°R (510.33°F).

P6-10 (cont'd)

```
Equations:
f(ca)=ca-cao-ra*tau                                     0.00447
f(cb)=cb-rb*tau                                         0
f(cc)=cc-rc*tau                                         0
cao=0.00447
E1=10000
R=1.987
T=970
k2o=0.015
E2=20000
k1o=15
vo=15
V=400
tau=V/vo
cost=vo*(60*cb-15*cc-10*cao)
k1=k1o*exp(E1/R*(1/T-1/919.67))
k2=k2o*exp(E2/R*(1/T-1/919.67))
rb=k1*ca**2
rc=k2*ca
ra=-k1*ca**2-k2*ca
```

```
Variable      Value          f()
ca            0.00232126     1.257e-13
cb            0.00162253    -1.257e-13
cc            0.000526208    9.897e-18
cao           0.00447
E1            10000
R             1.987
T             970
k2o           0.015
E2            20000
k1o           15
vo            15
V             400
tau           26.6667
cost          0.671384
k1            11.2922
k2            0.0085009
rb            6.0845e-05
rc            1.97328e-05
ra           -8.05778e-05
```

P6-11

a)

$$r_{1A} = -k_{1A}C_A = -(.07)(.1) = -0.07\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{2A} = -\frac{r_{2D}}{3} = -\frac{(.3)(.51)^2(.1)}{3} = -0.0026\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{3A} = 0 * r_{3E} = 0\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

b)

$$r_{1B} = \frac{-r_{1A}}{3} = \frac{(.7)(.1)}{3} = 0.023\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{2B} = 0 * r_{2D} = 0\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{3B} = 0 * r_{3E} = 0\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

c)

$$r_{1C} = \frac{-r_{1A}}{3} = \frac{(.7)(.1)}{3} = 0.023\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{2C} = \frac{-2 * r_{2D}}{3} = \frac{-2(.3)(.51)^2(.1)}{3} = -0.0052\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{3C} = -r_{3E} = -(.2)(.049)(.51) = -0.005\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

P6-11 cont'd

d)

$$r_{1D} = 0 * r_{1A} = 0 \frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{2D} = (.3)(.51)^2(.1) = 0.0078 \frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_{3D} = \frac{-4r_{3E}}{3} = \frac{-4(.2)(.049)(.51)}{3} = -0.0067 \frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

e)

$$r_{1E} = 0 * r_{1A} = 0 \frac{mol}{dm^3 \bullet s}$$

$$r_{2E} = 0 * r_{2D} = 0 \frac{mol}{dm^3 \bullet s}$$

$$r_{3E} = (.2)(.049)(.51) = 0.005 \frac{mol}{dm^3 \bullet s}$$

f)

$$r_A = -0.07 - 0.0026 = -0.0726 \frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_B = 0.023 \frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_C = 0.023 - 0.0052 - 0.005 = 0.0128 \frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_D = 0.0078 - 0.033 = 0.0011 \frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

$$r_E = 0.005 \frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}$$

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 (cont'd)

(b)

CSTR

Mole Balances: $F_A = F_{Ao} + r_A V \qquad F_B = r_B V \qquad F_M = r_M V \qquad F_P = r_P V$

Rate Laws: $r_A = -C_A(k_1 + k_2) \qquad r_B = r_M = k_1 C_A \qquad r_P = k_2 C_A$

$$k_1 = k_{1o} \exp \frac{E_1}{R}\left(\frac{1}{T} - \frac{1}{946}\right) \qquad k_1 = k_{1o} \exp \frac{E_1}{R}\left(\frac{1}{T} - \frac{1}{946}\right)$$

Stoichiometry: $F_A = v_o C_A \qquad F_B = v_o C_B \qquad F_M = v_o C_M \qquad F_P = v_o C_P$

Use these equations in POLYMATH and vary T to maximize the yield of *p*-xylene.

The optimal temperature would be about 1455 K (1182°C).

```
Equations:                                              Initial value
f(ca)=ca-cao-ra*tau                                     0.0375
f(cb)=cb-rb*tau                                         0
f(cm)=cm-rm*tau                                         0
f(cp)=cp-rp*tau                                         0
cao=0.0375
tau=0.5
k1o=0.22
E1=20000
R=1.987
T=1455
k2o=0.71
E2=10000
Yp=cp/(0.0376-ca)
k1=k1o*exp(E1/R*(1/T-1/946))
k2=k2o*exp(E2/R*(1/T-1/946))
rb=k1*ca
rm=k1*ca
rp=k2*ca
ra=-ca*(k1+k2)
```

```
Variable        Value           f()
 ca             0.0354488       -9.558e-13
 cb             9.42926e-05     8.451e-15
 cm             9.42926e-05     8.451e-15
 cp             0.00195691      -8.008e-13
 cao            0.0375
 tau            0.5
 k1o            0.22
 E1             20000
 R              1.987
 T              1455
 k2o            0.71
 E2             10000
 Yp             0.909682
 k1             0.00531994
 k2             0.110408
 rb             0.000188585
 rm             0.000188585
 rp             0.00391383
 ra             -0.00410241
```

P6-13

a) Mole balance:

$$\frac{dC_A}{dV} = \frac{r_A}{v_0} \qquad \frac{dC_D}{dV} = \frac{r_D}{v_0}$$

$$\frac{dC_B}{dV} = \frac{r_B}{v_0} \qquad \frac{dC_E}{dV} = \frac{r_E}{v_0}$$

$$\frac{dC_C}{dV} = \frac{r_C}{v_0} \qquad \frac{dC_F}{dV} = \frac{r_F}{v_0}$$

Rate laws:

$$r_A = -r_{D1} - 3 * r_{E2} \qquad r_F = r_{F3}$$

$$r_B = -2 * r_{D1} - r_{F3} \qquad r_{D1} = k_{D1} C_A C_B^2$$

$$r_C = r_{D1} + r_{E2} - r_{F3} \qquad r_{E2} = k_{E2} C_A C_D$$

$$r_D = r_{D1} - 2 * r_{E2} + r_{F3} \qquad r_{F3} = k_{F3} C_B C_C^2$$

$$r_E = r_{E2}$$

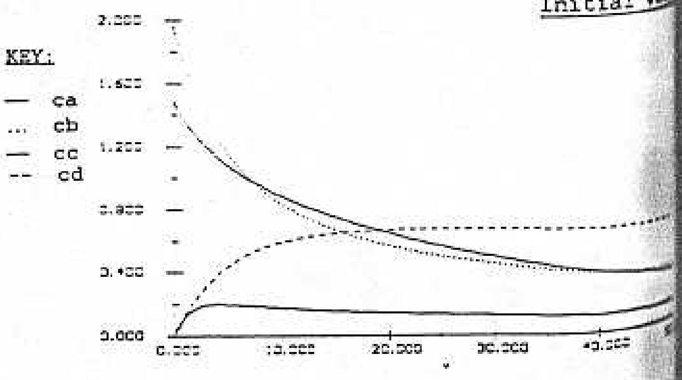
The equation for the conversion of A is this:

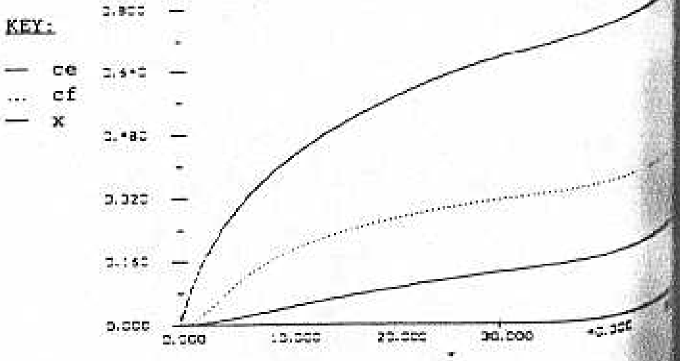
$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

The following is the POLYMATH program to give the graphs

Initial v

```
Equations:
d(cb)/d(v)=rb/vo
d(ca)/d(v)=ra/vo
d(cc)/d(v)=rc/vo
d(cd)/d(v)=rd/vo
d(ce)/d(v)=re/vo
d(cf)/d(v)=rf/vo
vo=10
kd1=.25
ke2=.1
kf3=5
cao=1.5
x=(cao-ca)/cao
rd1=kd1*ca*cb^2
re2=ke2*ca*cd
rf3=kf3*cb*cc^2
re=re2
rf=rf3
ra=-rd1-3*re2
rb=-2*rd1-rf3
rc=rd1+re2-2*rf3
rd=rd1-2*re2+rf3
v0 = 0,    vf = 50
```





P6-13 cont'd

b) With a CSTR, start with the mole balance:

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

$$F_{B0} - F_B = -r_B V$$

$$F_C = r_C V$$

$$F_D = r_D V$$

$$F_E = r_E V$$

$$F_F = r_F V$$

Next is the relative rate laws and the overall rate laws:

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1} = \frac{r_{1D}}{1} = k_{D1} C_A C_B^2$$

$$\frac{r_{2D}}{-2} = \frac{r_{2A}}{-3} = \frac{r_{2C}}{1} = \frac{r_{2E}}{1} = k_{E2} C_A C_D$$

$$\frac{r_{3B}}{-1} = \frac{r_{3C}}{-2} = \frac{r_{3D}}{1} = \frac{r_{3F}}{1} = k_{F3} C_B C_C^2$$

$$r_A = r_{1A} + r_{2A} = -k_{D1} C_A C_B^2 - 3k_{E2} C_A C_D$$

$$r_B = r_{1B} + r_{3B} = -2k_{D1} C_A C_B^2 - k_{F3} C_B C_C^2$$

$$r_C = r_{1C} + r_{2C} + r_{3C} = k_{D1} C_A C_B^2 + k_{E2} C_A C_D - 2k_{F3} C_B C_C^2$$

$$r_D = r_{1D} + r_{2D} + r_{3D} = k_{D1} C_A C_B^2 - 2k_{E2} C_A C_D + k_{F3} C_B C_C^2$$

$$r_E = r_{2E} = k_{E2} C_A C_D$$

$$r_F = r_{3F} = k_{F3} C_B C_C^2$$

Using stoichiometry, we can then combine it all in terms of conversion and rearrange to be plugged into POLYMATH.

$$F_i = \frac{C_i}{v_0}$$

$$\tau = \frac{V}{v_0}$$

$$f(C_A) = C_A - C_{A0} + (k_{D1} C_A C_B^2 + 3k_{E2} C_A C_D)\tau$$

$$f(C_B) = C_B - C_{B0} + \left(2k_{D1} C_A C_B^2 + k_{F3} C_B C_C^2\right)\tau$$

$$f(C_C) = \left(k_{D1} C_A C_B^2 + k_{E2} C_A C_D - 2k_{F3} C_B C_C^2\right)\tau - C_C$$

$$f(C_D) = \left(k_{D1} C_A C_B^2 - 2k_{E2} C_A C_D + k_{F3} C_B C_C^2\right)\tau - C_D$$

$$f(C_E) = \tau k_{E2} C_A C_D - C_E$$

$$f(C_F) = \tau k_{F3} C_B C_C^2 - C_F$$

That being done we can plug these into POLYMATH and get that $C_A = .61$, $C_B = .79$, $C_C = .11$, $C_D = .45$, $C_E = .45$, $C_E = .14$, $C_F = .25$

P6-13 cont'd

```
6-13 (b)
Equations:
f(ca)=ca-cao-ra*tau
f(cb)=cb-cbo-rb*tau
f(cc)=rc*tau-cc
f(cd)=rd*tau-cd
f(ce)=re*tau-ce
f(cf)=rf*tau-cf
cao=1.5
tau=50/10
cbo=2
kd1=.25
ke2=.1
kf3=5
re=ke2*ca*cd
rf=kf3*cb*cc^2
x=(cao-ca)/cao
ra=-kd1*ca*cb^2-3*ke2*ca*cd
rb=-2*kd1*ca*cb^2-kf3*cb*cc^2
rc=kd1*ca*cb^2+ke2*ca*cd-2*kf3*cb*cc^2
rd=kd1*ca*cb^2-2*ke2*ca*cd+kf3*cb*cc^2
```

```
Variable      Value          f()
--------------------------------------
ca            0.608316       3.608e-16
cb            0.792733       4.563e-14
cc            0.112666      -8.861e-14
cd            0.453528       4.481e-14
ce            0.137944       1.735e-17
cf            0.251565       4.454e-14
cao           1.5
tau           5
cbo           2
kd1           0.25
ke2           0.1
kf3           5
re            0.0275888
rf            0.050313
x             0.594456
ra           -0.178337
rb           -0.241453
rc            0.0225331
rd            0.0907056
```

c) For the first case where Ais fed into a vat of B. The following equations are the mole balances:

$$\frac{dC_A}{dt} = r_A + v_0 \frac{C_{A0} - C_A}{V}$$

$$\frac{dC_B}{dt} = r_B - v_0 \frac{C_B}{V}$$

$$\frac{dC_C}{dt} = r_C - v_0 \frac{C_C}{V}$$

$$\frac{dC_D}{dt} = r_D - v_0 \frac{C_D}{V}$$

$$\frac{dC_E}{dt} = r_E - v_0 \frac{C_E}{V}$$

$$\frac{dC_F}{dt} = r_F - v_0 \frac{C_F}{V}$$

The rate laws are the same as in part (a) so the only other equation needed is:

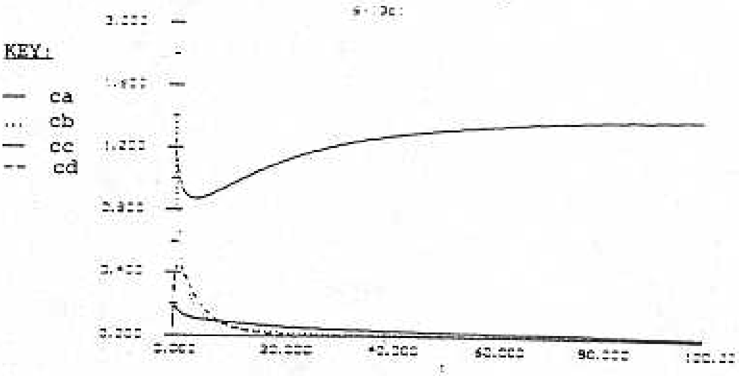
$$V = V_0 + v_0 t$$

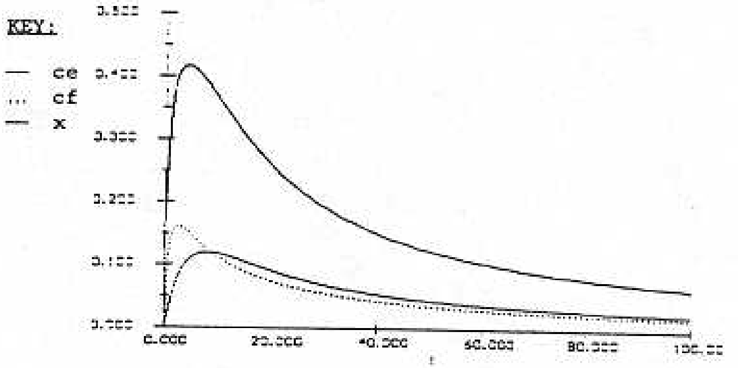
This gets plugged into POLYMATH:

P6-13 cont'd

```
Equations:
d(ca)/d(t)=ra+vo*(cao-ca)/V
d(cb)/d(t)=rb-vo*cb/V
d(cc)/d(t)=rc-vo*cc/V
d(cd)/d(t)=rd-vo*cd/V
d(ce)/d(t)=re-vo*ce/V
d(cf)/d(t)=rf-vo*cf/V
vo=10
cao=1.5
Vo=40
kd1=.25
ke2=.1
kf3=5
rd1=kd1*ca*cb^2
re2=ke2*ca*cd
rf3=kf3*cb*cc^2
x=(cao-ca)/cao
V=Vo+vo*t
re=re2
rf=rf3
ra=-rd1-3*re2
rb=-2*rd1-rf3
rc=rd1+re2-2*rf3
rd=rd1-2*re2+rf3
```

$t_0 = 0, \quad t_f = 100$





Variable	Initial value	Maximum value	Minimum value	Final value
t	0	100	0	100
ca	1.5	1.5	0.874392	1.40262
cb	2	2	0.00271086	0.00271086
cc	0	0.184965	0	0.0138917
cd	0	0.449824	0	1.99367e-05
ce	0	0.119804	0	0.0231828
cf	0	0.161163	0	0.0185589
vo	10	10	10	10
cao	1.5	1.5	1.5	1.5
Vo	40	40	40	40
kd1	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
kf3	5	5	5	5
rd1	1.5	1.5	2.57689e-06	2.57689e-06
re2	0	0.0456977	0	2.79638e-06
rf3	0	0.215642	0	2.61569e-06
x	0	0.417072	0	0.0649167
V	40	1040	40	1040
re	0	0.0456977	0	2.79638e-06
rf	0	0.215642	0	2.61569e-06
ra	-1.5	-1.0966e-05	-1.5	-1.0966e-05
rb	-3	-7.76946e-06	-3	-7.76946e-06
rc	1.5	1.5	-0.0128971	1.41886e-07
rd	1.5	1.5	-0.0256529	-4.0018e-07

P6-13 cont'd

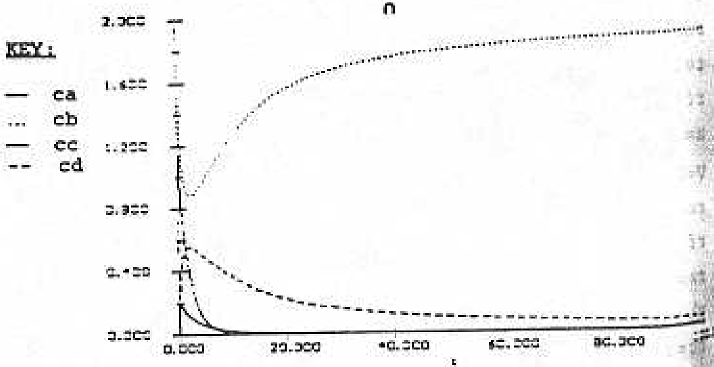
For the second case, B is fed into a vat of A. So the following changes to the above design equations are made:

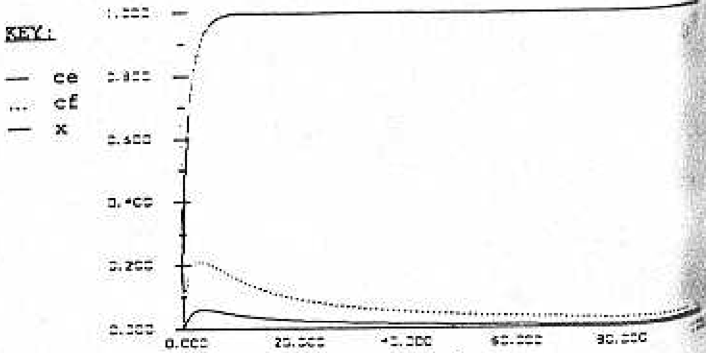
$$\frac{dC_A}{dt} = r_A - v_0\frac{C_A}{V}$$

$$\frac{dC_B}{dt} = r_B + v_0\frac{C_{B0} - C_B}{V}$$

All other equations are the same. Again plug into POLYMATH:

```
6-13c2
Equations:                                        Initial value
d(ca)/d(t)=ra-vo*ca/V                             1.5
d(cb)/d(t)=rb+vo*(cbo-cb)/V                       2
d(cc)/d(t)=rc-vo*cc/V                             0
d(cd)/d(t)=rd-vo*cd/V                             0
d(ce)/d(t)=re-vo*ce/V                             0
d(cf)/d(t)=rf-vo*cf/V
vo=10
cbo=2
cao=1.5
Vo=40
kd1=.25
ke2=.1
kf3=5
rd1=kd1*ca*cb^2
re2=ke2*ca*cd
rf3=kf3*cb*cc^2
x=(cao-ca)/cao
V=Vo-vo*t
re=re2
rf=rf3
ra=-rd1-3*re2
rb=-2*rd1-rf3
rc=rd1+re2-2*rf3
rd=rd1-2*re2+rf3
t0 = 0,    tf = 100
```





P6-13 cont'd

```
Variable         Initial value  Maximum value   Minimum value   Final value
t                0              100             0               100
ca               1.5            1.5             7.61455e-36     7.61455e-36
cb               2              2               0.885955        1.89683
cc               0              0.185797        0               0.000270977
cd               0              0.553101        0               0.0513271
ce               0              0.0603835       0               0.00584598
cf               0              0.210084        0               0.0228647
vo               10             10              10              10
cbo              2              2               2               2
cao              1.5            1.5             1.5             1.5
Vo               40             40              40              40
kd1              0.25           0.25            0.25            0.25
ke2              0.1            0.1             0.1             0.1
kf3              5              5               5               5
rd1              1.5            1.5             6.84919e-36     6.84919e-36
re2              0              0.038839        0               3.90832e-38
rf3              0              0.239239        0               6.96408e-07
x                0              1               0               1
V                40             1040            40              1040
re               0              0.038839        0               3.90832e-38
rf               0              0.239239        0               6.96408e-07
ra               -1.5           -6.96644e-36    -1.5            -6.96644e-36
rb               -3             -6.96408e-07    -3              -6.96408e-07
rc               1.5            1.5             -0.0276699      -1.39282e-06
rd               1.5            1.5             6.96408e-07     6.96408e-07
```

In case 1, A is the main species in the reactor after a good amount of time. In case 2, B is the main species after a time. The conversion of A is much greater in case 2 than in case 1. In case 1, however, E and F are formed more early on.

d) When $\theta_B = 1$, the reaction does not form as much of any of the products. When $\theta_B = 10$, the conversion goes to 1 and a lot of F, but very little E are formed.

P6-14

$$\upsilon_0 C_{A0} - \upsilon_0 C_A + r_A W = 0 \qquad r_A = -k_1 C_A - k_3 C_A$$

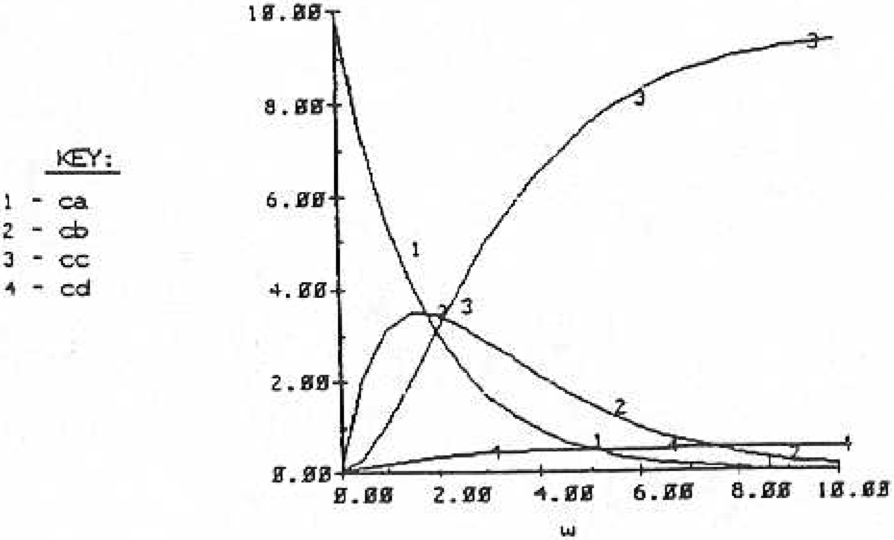
$$-\upsilon_0 C_B + r_B W = 0 \qquad r_B = k_1 C_A - k_2 C_B$$

$$r_C = k_2 C_B$$

$$-\upsilon_0 C_C + r_C W = 0 \qquad r_D = k_3 C_A$$

$$-\upsilon_0 C_D + r_D W = 0$$

P6-14 (cont'd)



P6-15

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:

P6-15 cont'd

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:

$$F_H = v_0 C_H$$

$$F_M = v_0 C_M$$

$$F_X = v_0 C_X$$

$$F_T = v_0 C_T$$

$$F_{Me} = v_0 C_{Me} = v_0 (C_{H0} - C_H)$$

$$F_B = v_0 C_B = v_0 [(C_{M0} - C_M) - C_X - C_T]$$

Combining all of these:

$$C_{H0} - C_H = (k_1 C_H^{0.5} C_M + k_2 C_H^{0.5} C_X + k_3 C_H^{0.5} C_T)\tau$$

$$C_{M0} - C_M = k_1 C_H^{0.5} C_M \tau$$

$$C_X = (k_1 C_H^{0.5} C_M - k_2 C_H^{0.5} C_X)\tau$$

$$C_T = (k_2 C_X C_H^{0.5} - k_3 C_H^{0.5} C_X)\tau$$

$$C_{Me} = C_{H0} - C_H$$

$$C_B = (C_{M0} - C_M) - C_X - C_T$$

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
```

P6-15 cont'd

The conversion of Hydrogen and Mesitylene are then:

$$X_H = \frac{C_{H0} - C_H}{C_{H0}} = \frac{0.021 - 0.0078}{0.021} = 0.63$$

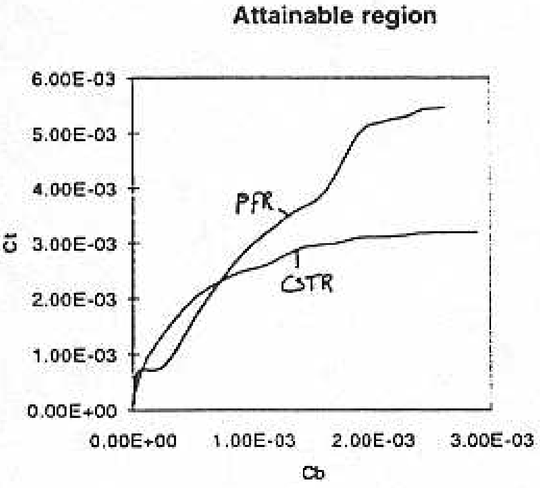
$$X_M = \frac{C_{M0} - C_M}{C_{M0}} = \frac{0.0105 - 0.0030}{0.0105} = .71$$

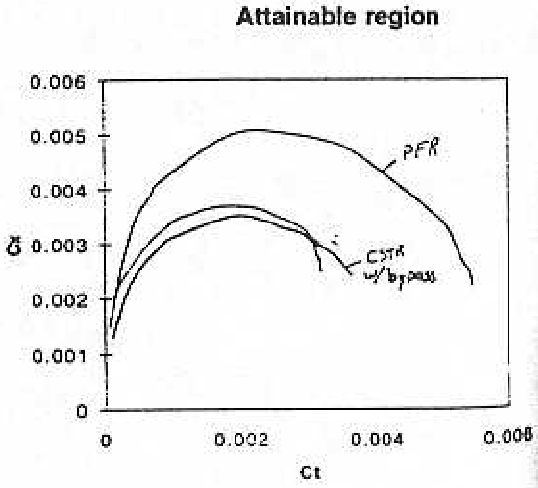
$C_H = 0.0078$ lb mol/ft^3 $C_M = 0.0030$ lb mol/ft^3 $C_X = 0.0032$ lb mol/ft^3

$C_T = 0.0029$ lb mol/ft^3 $C_{me} = 0.013$ lb mol/ft^3 $C_B = 0.0014$ lb mol/ft^3

b) When θ_M is reduced to 1.5, it now takes a τ of 0.24 h to achieve a maximum of xylene. Increasing θ_M to 10 now requires a τ of only 0.08 h.

c) To find out the reactor schemes needed, use the attainable region theory 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.

d) First find the proportionality constants of the rate constants using the Arrhenius equation.

$$k = Ae^{-(E/RT)}$$

$$55.2 = A_1 e^{-(20000/(1.987*833.3))}$$

$$A_1 = 9.72 \times 10^8$$

$$30.2 = A_2 e^{-(10000/(1.987*833.3))}$$

$$A_2 = 12674$$

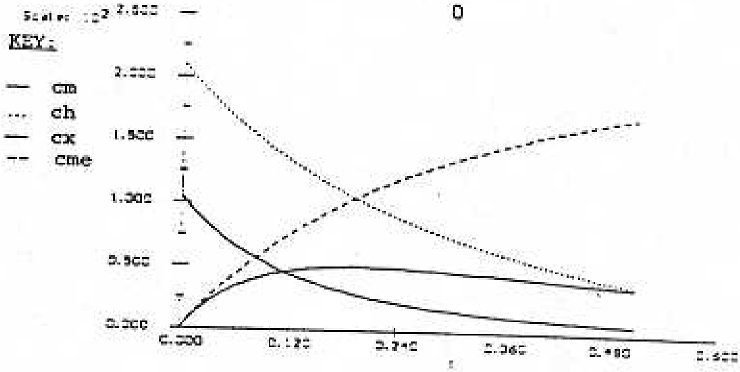
$$11.2 = A_3 e^{-(30000/(1.987*833.3))}$$

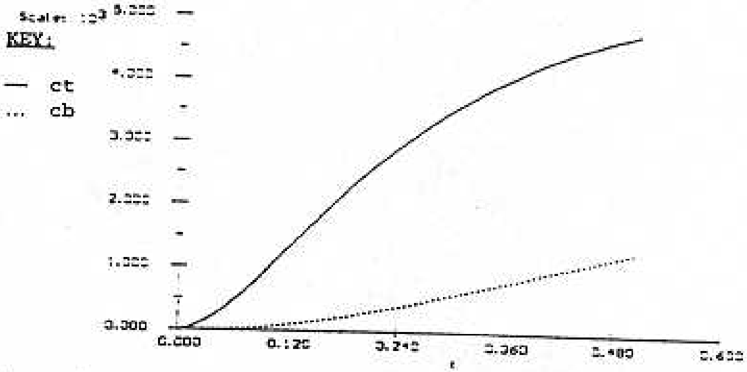
$$A_3 = 8.28 \times 10^8$$

Once that is done, by trial and error come up with the temperature where $\bar{S}_{XT} = \bar{S}_{TB}$ and the answer is then 862K or 1551.6°R.

P6-15 cont'd

```
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
t0 = 0,    tf = 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 τ = 0.19 h.

P6-16

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:

$$F = C \cdot v_o$$

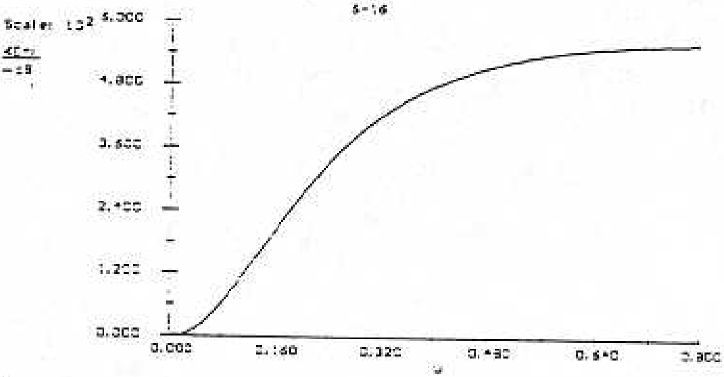
Putting all of those together and put it into POLYMATH and get the following program and answers.

```
P6-16 Hydodealkyation Reactions
 Equations:                                                   Initial value
 d(c11)/d(V)=r1/vo                                            0.137
 d(c9)/d(V)=(-r2+r3)/vo                                       0
 d(c10)/d(V)=(-r1+r2)/vo                                      0
 d(c8)/d(V)=(-r3+r4)/vo                                       0
 d(c7)/d(V)=(-r4+r5)/vo                                       0
 d(c6)/d(V)=-r5/vo                                            0
 d(ch)/d(V)=(r1+r2+r3+r4+r5)/vo                               0.389
 vo=1
 k5=2.1
 S87=c8/(c7+.0000001)
 s89=c8/(c9+.00001)
 c11o=.1
 s910=c9/(c10+.00001)
 s9o=c9/(c10+c8+c7+c6+.00000001)
 r5=-k5*ch^.5*c7
 k1=k5*17.6
```

P6-16 cont'd

```
k2=k5*10
k3=k5*4.4
k4=k5*2.7
x=1-c11/c11o
r2=-k2*ch^.5*c10
r3=-k3*ch^.5*c9
r1=-k1*ch^.5*c11
r4=-k4*ch^.5*c8
```

$v_0 = 0, \quad v_f = 10$



```
6-16
Variable    Initial value  Maximum value  Minimum value  Final value
v           0              0.800063       0              0.800063
c9          0              0.0661357      0              0.0452049
c11         0.137          0.137          0.000109711    0.000109711
c10         0              0.0651101      0              0.00526749
c8          0              0.0560404      0              0.0560404
c7          0              0.0270125      0              0.0270125
c6          0              0.00336495     0              0.00336495
ch          0.389          0.389          0.000326609    0.000326609
vo          1              1              1              1
k5          2.1            2.1            2.1            2.1
S87         0              84.4133        0              2.0746
s89         0              1.23942        0              1.23942
c11o        0.1            0.1            0.1            0.1
s910        0              8.56561        0              8.56561
s9o         0              0.978962       0              0.493044
r5          -0             -0             -0.00709141    -0.00102518
```

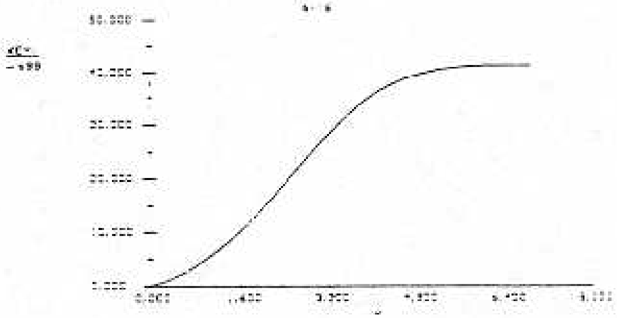
P6-16 cont'd

```
k1                36.96          36.96           36.96           36.96
k2                21             21              21              21
k3                9.24           9.24            9.24            9.24
k4                5.67           5.67            5.67            5.67
x                 -0.37          0.998903        -0.37           0.998903
r1                -3.15811       -7.32818e-05    -3.15811        -7.32818e-05
r2                -0             -0              -0.697704       -0.00199911
r3                -0             -0              -0.220371       -0.00754869
r4                -0             -0              -0.0623892      -0.00574247
```

The ratio of hydrogen to pentamethylbenzene is 2.83 and the volume is 0.8 m^3.

b) Shown in this POLYMATH program, which is the same as the first, we see that the ratio now becomes 4.8 to 1 and the volume increases to 6.8 m^3 to maximize S_{89}. To maximize S_{87} it follows that the volume would be smaller because the earlier the reaction is ended the less C7 that is formed.

```
6-16
Variable          Initial value  Maximum value   Minimum value   Final value
V                 0              6.88499         0               6.88499
c9                0              0.0444059       0               1.59259e-05
c11               0.092          0.092           2.56915e-18     2.56915e-18
c10               0              0.0437213       0               8.37446e-11
c8                0              0.0387026       0               0.00107129
c7                0              0.0464547       0               0.0238096
c6                0              0.0671031       0               0.0671031
ch                0.434          0.434           3.29003e-11     3.29003e-11
vo                1              1               1               1
k5                2.1            2.1             2.1             2.1
S87               0              75.7226         0               0.0449937
s89               0              41.3212         0               41.3212
c11o              0.1            0.1             0.1             0.1
s910              0              136.668         0               1.59258
s9o               0              0.978912        0               0.000173138
r5                -0             -0              -0.0272308      -2.86795e-07
k1                36.96          36.96           36.96           36.96
k2                21             21              21              21
k3                9.24           9.24            9.24            9.24
k4                5.67           5.67            5.67            5.67
x                 0.08           1               0.08            1
r1                -2.24009       -5.44655e-22    -2.24009        -5.44655e-22
r2                -0             -0              -0.538785       -1.00873e-14
r3                -0             -0              -0.204868       -8.44065e-10
r4                -0             -0              -0.0887499      -3.48409e-08
```



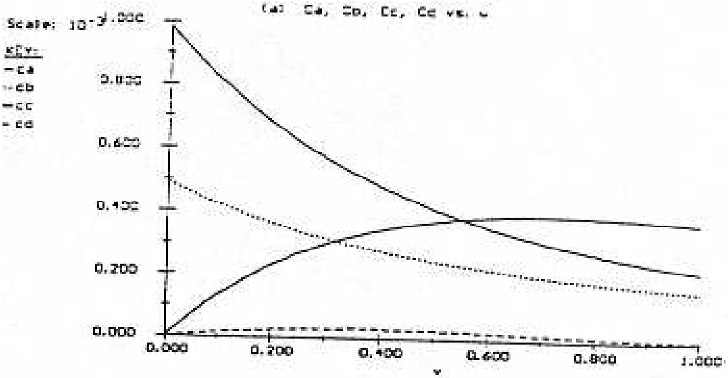
P6-17

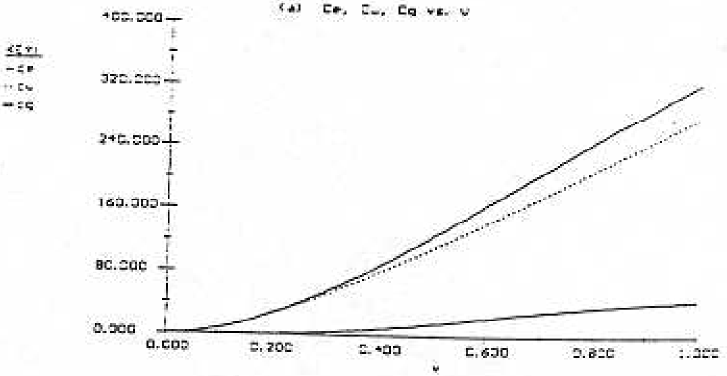
(a) Enter the given program into POLYMATH. Equations for the concentrations must be added.

The following maximums can be seen in the graph given. (More exact values can be found in the corresponding table in POLYMATH.)

$C_{C\max} = 0.0434$ and $C_{D\max} = 0.0033$

```
Equations:                                                        Initial value
d(fc)/d(v)=k1*(fa/ft)*(fb/ft)**(1/2)-k3*(fc/ft)+k4*(fw/ft        0
   )*(fd/ft)
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)
v0 = 0,    vf = 1000
```





P6-17 (cont'd)

(b)

Overall yield of HCOOH: $\tilde{Y}_C = \dfrac{F_C}{F_{Ao} - F_A}$

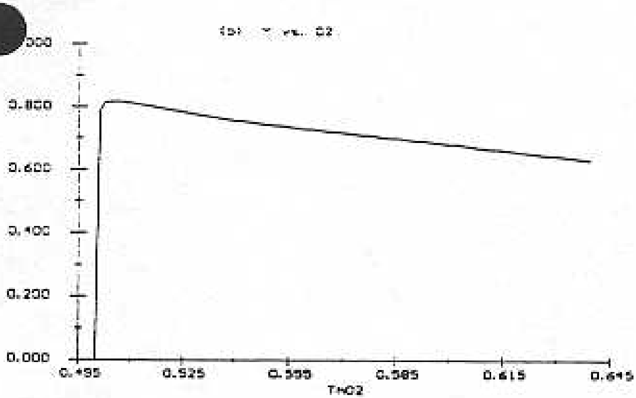
Selectivity of HCHO to CO: $\tilde{S}_{AE} = \dfrac{F_A}{F_E}$

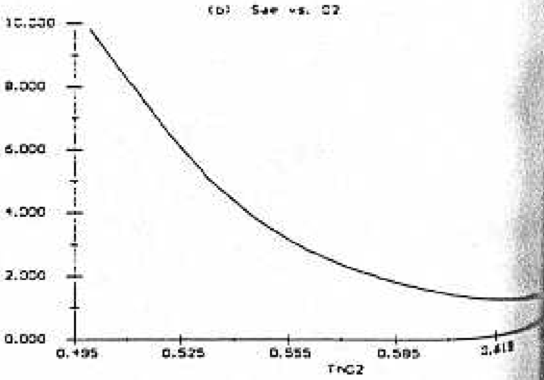
Selectivity of $HCOOCH_3$ to CH_3OH: $\tilde{S}_{DG} = \dfrac{F_D}{F_G}$

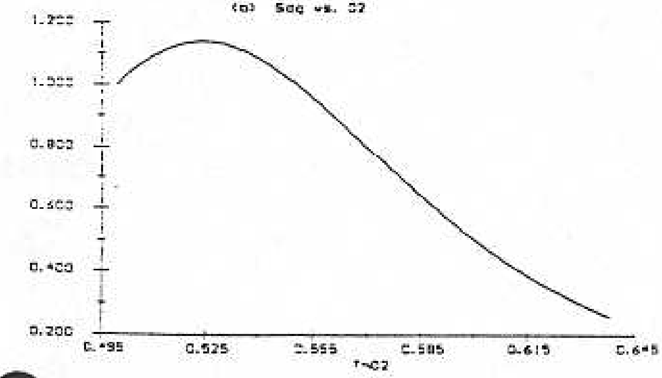
Selectivity of HCOOH to $HCOOCH_3$: $\tilde{S}_{CD} = \dfrac{F_C}{F_D}$

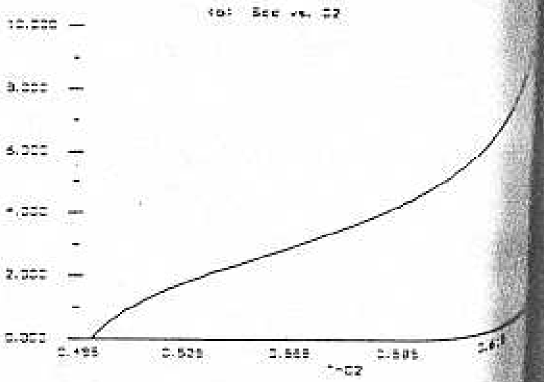
$$\Theta_{O_2} = \frac{C_B}{C_A}$$

Add these equations to the previous program and use it to generate the desired plots.









(c) Modify the original POLYMATH program by adding y to each of the concentration terms. Also add the following equation:

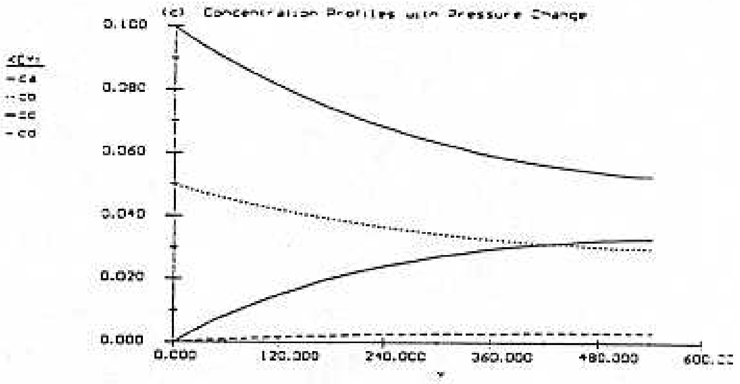
$$\frac{dy}{dV} = \frac{-\alpha}{2y}\left(\frac{F_T}{F_{To}}\right)$$

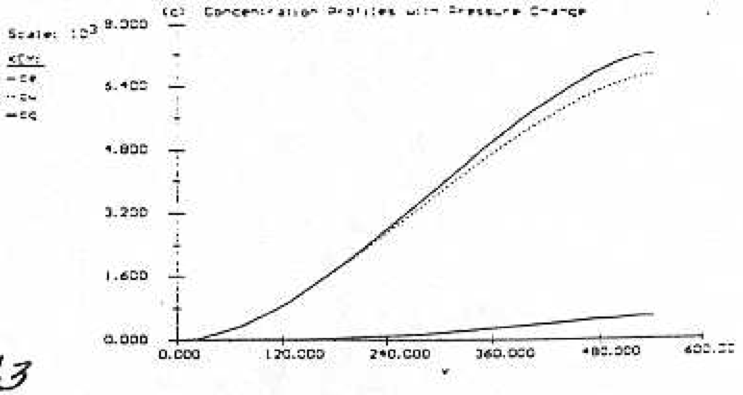
$\alpha = 0.002 \qquad F_{To} = 15$

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*(f             0
   w/ft)*(fd/ft)*y
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
```

$v_0 = 0, \quad v_f = 1000$





P6-17 (cont'd)

(d)

$$k_{i1} = k_{io}\exp\left(\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right)$$

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.

P6-18

(a)

Mole Balances: $\frac{dF_C}{dV} = r_C \quad \frac{dF_P}{dV} = r_P \quad \frac{dF_A}{dV} = r_A \quad \frac{dF_O}{dV} = r_O$

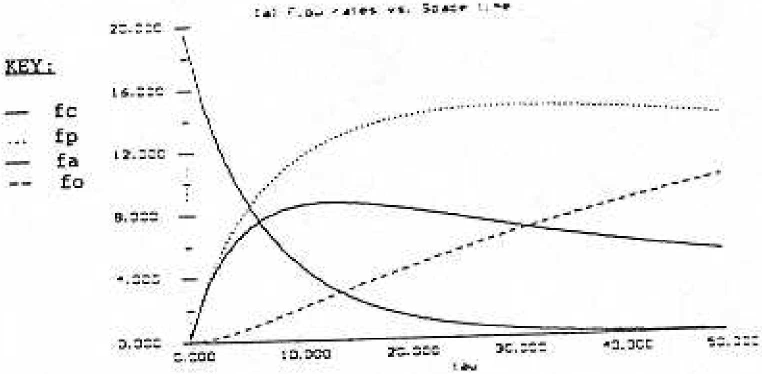
Rate Laws: $r_C = -k_1C_C - k_2C_C \qquad r_P = k_1C_C - k_3C_P + k_4C_A$

$r_A = k_1C_C + k_3C_P - k_4C_A - k_5C_A \qquad r_O = k_5C_A$

Stoichiometry: $C_C = C_{To}\left(\frac{F_C}{F_T}\right) \quad C_P = C_{To}\left(\frac{F_P}{F_T}\right) \quad C_A = C_{To}\left(\frac{F_A}{F_T}\right) \quad C_O = C_{To}\left(\frac{F_O}{F_T}\right)$

$F_T = F_C + F_P + F_A + F_O$

Use these equations in POLYMATH to generate a plot of the flow rates vs. τ.



(b) For a CSTR

Mole Balances: $F_C = F_{Co} + r_CV \qquad F_P = r_PV \qquad F_A = r_AV \qquad F_O = r_OV$

Rate Laws: $r_C = -k_1C_C - k_2C_C \qquad r_P = k_1C_C - k_3C_P + k_4C_A$

$r_A = k_1C_C + k_3C_P - k_4C_A - k_5C_A \qquad r_O = k_5C_A$

Stoichiometry: $F_C = v_o C_C \qquad F_P = v_o C_P \qquad F_A = v_o C_A \qquad F_O = v_o C_O$

Combine:

$$f(C_C) = 0 = C_C - C_{Co} + (k_1 + k_2) C_C \tau$$

$$f(C_P) = 0 = C_P - (k_1 C_C - k_3 C_P + k_4 C_A)\tau$$

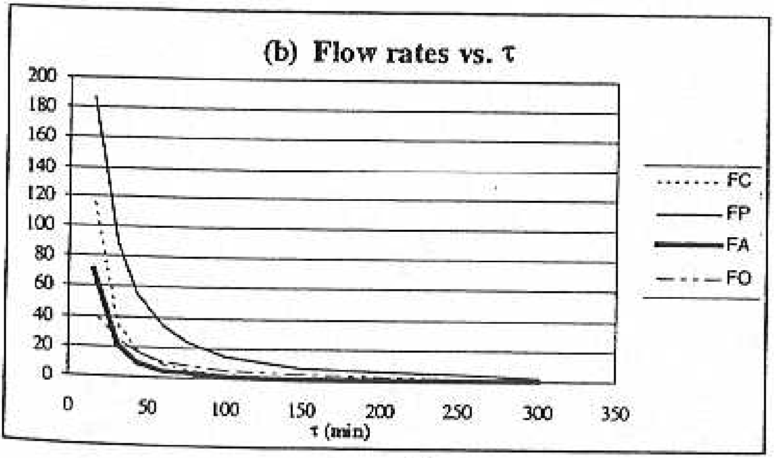
$$f(C_A) = 0 = C_A - (k_1 C_C - k_3 C_P - k_4 C_A - k_5 C_A)\tau$$

$$f(C_O) = 0 = C_O - k_5 C_A \tau$$

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.

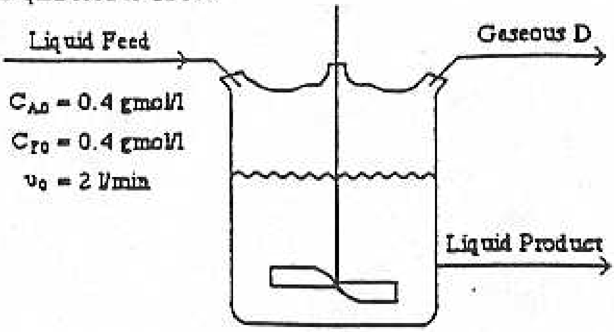
```
Equations:                                                   Initial value
f(cc)=cc-cco+(k1+k2)*cc*tau                                  2
f(cp)=cp-(k1*cc-k3*cp+k4*ca)*tau                             0
f(ca)=ca-(k1*cc-k3*cp-k4*ca-k5*ca)*tau                       0
f(co)=co-k5*ca*tau                                           0
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
```

```
                  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
```



P6-19

Given: Liquid feed to CSTR



$V = 120$ l

$\varepsilon = 0$

With the following reaction sequence

$A \xrightarrow{k_1} C \qquad -r_1 = k_1 C_A \qquad k_1 = 0.01 \text{ min}^{-1}$

$A \xrightarrow{k_2} B \qquad -r_2 = k_2 C_A \qquad k_2 = 0.02 \text{ min}^{-1}$

$B \xrightarrow{k_3} C \qquad -r_3 = k_3 C_B \qquad k_3 = 0.07 \text{ min}^{-1}$

$F \xrightarrow{k_4} B + D\uparrow \qquad -r_4 = k_4 C_F^2 \qquad k_4 = 0.50 \text{ l/gmol - min}$

(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: $\upsilon_0 C_{A0} - \upsilon_0 C_A = (-r_A) V = (-r_1 - r_2) V = (k_1 + k_2) C_A V$ (a)

$$\frac{C_{A0} - C_A}{C_A} = (k_1 + k_2)\frac{V}{\upsilon_0} = (k_1 + k_2)\tau$$

$$\text{or } C_A = \frac{C_{A0}}{1 + (k_1 + k_2)\tau} = \frac{0.4 \text{ gmol / l}}{1 + (0.01 + 0.02) \text{ min}^{-1}\left(\frac{120 \text{ l}}{2 \text{ l/min}}\right)} = \frac{0.4 \text{ gmol / l}}{1 + (0.03)(60)}$$

$C_A = 0.143$ gmol / l

Balance on F: $\upsilon_0 C_{F0} - \upsilon_0 C_F = (-r_F) V = k_4 C_F^2 V$ (b)

$$k_4 \tau C_F^2 + C_F - C_{F0} = 0 \quad \text{where } \tau = \frac{V}{\upsilon_0} = 60 \text{ min}$$

P6-20 (cont'd)

Rate Laws :

$-r_A = r_{1A} + r_{2A} + 2/3 r_{4C}$ $\quad$ $-r_B = 1.25 r_{1A} + 0.75 r_{2A} + r_{3B}$

$-r_C = -r_{1A} + 2r_{3B} + r_{4C}$ $\quad$ $-r_D = -1.5 r_{1A} - 1.5 r_{2A} - r_{4C}$

$-r_E = -0.5 r_{2A} - 5/6 r_{4C}$ $\quad$ $-r_F = -2 r_{3B}$

Use these equations in POLYMATH to find the exiting molar flow rates.

```
Equations:                                        Initial value
f(ca)=vo*ca-fao-ra*W                              1
f(cb)=vo*cb-fbo-rb*W                              1
f(cc)=vo*cc-rc*W                                  0
f(cd)=vo*cd-rd*W                                  0
f(ce)=vo*ce-re*W                                  0
f(cf)=vo*cf-rf*W                                  0
vo=10
fao=10
W=3
fbo=10
rho=0.0012
k1=5
k2=2
k3=10
k4=5
fa=vo*ca
fb=vo*cb
fc=vo*cc
fd=vo*cd
fe=vo*ce
ff=vo*cf
r1=rho*k1*ca*cb**2
r2=rho*k2*ca*cb
r4=rho*k4*cc*ca**(2/3)
r3=rho*k3*cc**2*cb
rf=2*r3
re=0.5*r2+(5/6)*r4
ra=-r1-r2-(2/3)*r4
rb=-1.25*r1-0.75*r2-r3
rc=r1-2*r3-r4
rd=1.5*r1+1.5*r2+r4
```

V₀

fao

W

fbo

rho

K1

K2

K3

K4

fa = V₀*Ca

fb = V₀*Cb

fc = V₀*Cc

fd = V₀*Cd

fe = V₀*Cf

ff

```
                                      Solution
Variable      Value          f()            Variable      Value          f()
ca            0.998927       -3.912e-16     fe            0.00361292
cb            0.997227       6.28e-16       ff            2.28744e-07
cc            0.00178488     -1.574e-16     r1            0.00596037
cd            0.00376122     -7.373e-17     r2            0.00239078
ce            0.000361292    6.614e-19      r4            1.07016e-05
cf            2.28744e-08    -9.264e-19     r3            3.81234e-08
vo            10                            rf            7.62468e-08
fao           10                            re            0.00120431
w             3                             ra            -0.00357672
fbo           10                            rb            -0.00924358
rho           0.0012                        rc            0.00594959
k1            5                             rd            0.0125374
k2            2
k3            10
k4            5
fa            9.98927
fb            9.97227
fc            0.0178488
fd            0.0376122
```

$\longrightarrow$

r₁ = rho * K1 * Ca * Cb ^ 2

r₂ = rho * K2 * Ca * Cb

r₄ = rho * K4 * Cc * Ca ^ (2/3)

r₃ = rho * K3 * Cc ^ 2 * Cb

r_f = 2 * r₃

(b)

$$\tilde{Y}_{AE} = \frac{F_E}{F_{Ao} - F_A} = \frac{3.6\times10^{-3}}{10-9.989} = 0.336$$

$$\tilde{Y}_{BF} = \frac{F_F}{F_{Bo} - F_B} = \frac{2.29\times10^{-7}}{10-9.973} = 8.25\times10^{-6}$$

$$\tilde{Y}_{AC} = \frac{F_C}{F_{Ao} - F_A} = \frac{0.0178}{10-9.989} = 1.663$$

r_e = 0.5*r₂+(5/6)r₄

r_a = −r₁ + r₂ − (2/3) r₄

r_b = −1.25r₁ − 0.75r₂ − r₃

r_c = r₁ − 2r₃ − r₄

r_d = 1.5r₁ + 1.5r₂ − r₄

P6-23 cont'd

```
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)
```

```
                                  Solution
Variable      Value         f()            Variable      Value          f()
 fh           63.5619       5.826e-13       Pho          1945.2
 fc           8232.08       1.847e-12       rb           -9.08426
 fca          852.181       2.842e-14       rca          0.852181
 V            1000                          rh           -9.93644
 fho          10000                         rc           8.23208
 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
```

The highest yield occurs at pressures: P_{BO} = 1400 kPa
P_{HO} = 1945.2 kPa

P6-24

(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:

$$C_i = C_{T0}\left(\frac{F_i}{F_T}\right)\left(\frac{T_0}{T}\right)$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_G$$

$$C_{T0} = \frac{P_0}{RT_0}$$

Use these equations in POLYMATH. Vary P_0 and T_0 to find the optimal conditions. We determine these to be:

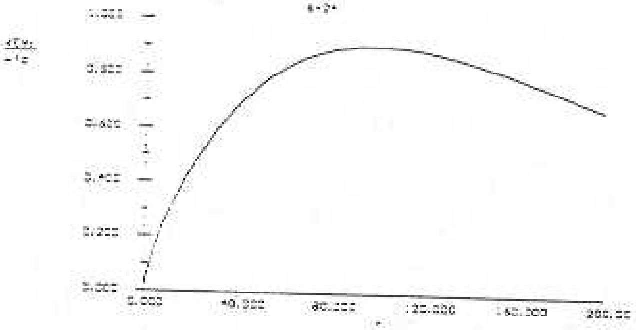
$$T_0 = 315.8 \text{ K} \qquad P_0 = 160 \text{ atm} \qquad V = 100 \text{ dm}^3$$

```
6-24
Equations:                        Initial value
d(fe)/d(v)=-r2a                   6
d(fb)/d(v)=2*r1a-r2a-r3c          14
d(fa)/d(v)=r1a+r2a                6
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=131667*(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)
v0 = 0,   vf = 200
```

P6-24 (cont'd)

```
6-24
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        2.24393
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
```

P6-24 (cont'd)

(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

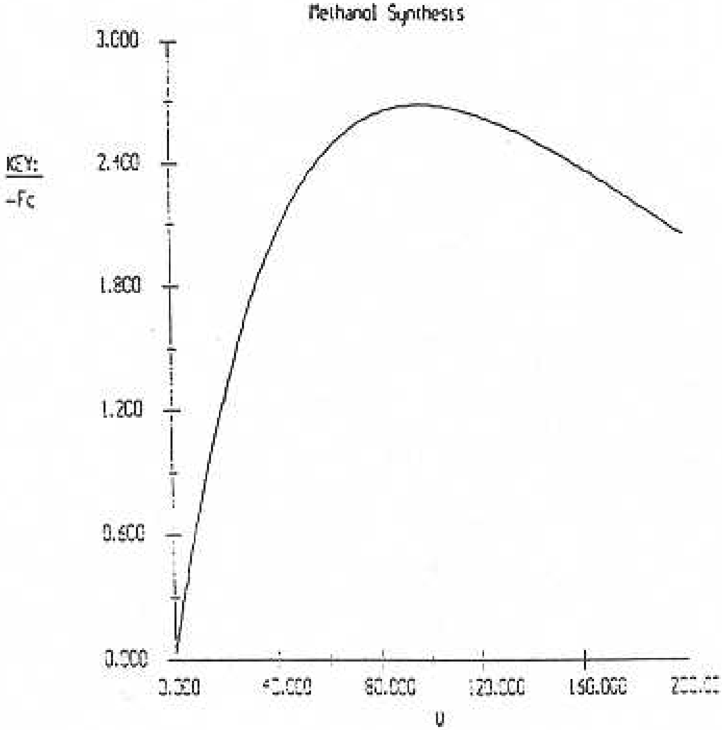
These results are similar to those in part (a) in that the optimal volume is still 100 dm^3, and the concentration profile is very similar in shape. The primary difference is that the F_C values are more than doubled.

```
        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)
V0 = 0.    Vf = 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              7.88788         7.88788
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         6.17865
Ca           1.64764         1.64764         0.547917        0.547917
Cb           3.29528         3.29528         2.22658         2.22658
Cc           0               0.724399        0               0.579233
Cd           0               0.000156781     0               0.000156781
Ce           1.23373         1.69351         1.23571         1.69351
r3c          -0              -0              -0.024912       -0.0199193
r1a          -0.076678       -0.0116408      -0.076678       -0.0116408
r2a          0.000287834     0.000287834     1.12794e-07     3.24112e-06
```

```
      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
```

P6-24 (cont'd)


Methanol Synthesis
KEY:
-Fc
3.000
2.400
1.800
1.200
0.600
0.000
0.000
40.000
80.000
120.000
160.000
200.00
V

P6-26

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 :

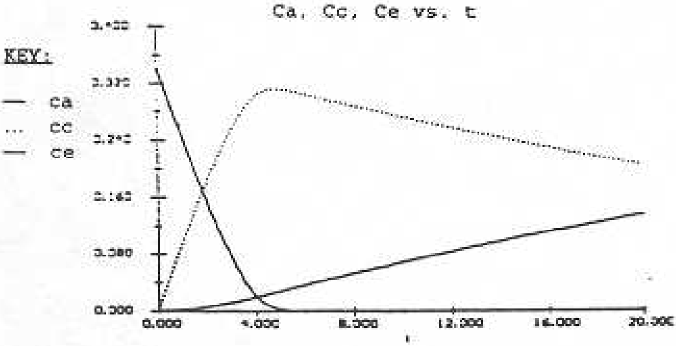
$$C_{Ao} = 5.9\ \text{MPa}\left(0.058\ \text{kmol/m}^3 \cdot \text{MPa}\right) = 0.3422\ \text{mol/dm}^3$$

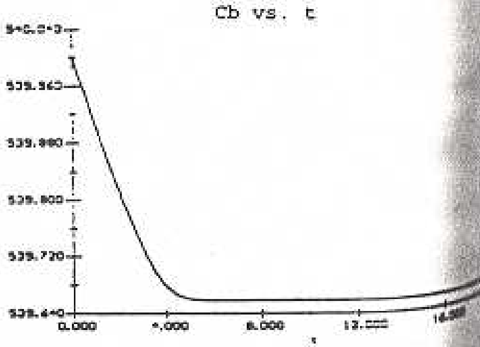
Use these equations in the following POLYMATH program to generate graphs of C_A, C_B, C_C, C_E, and C_F as a function of time.

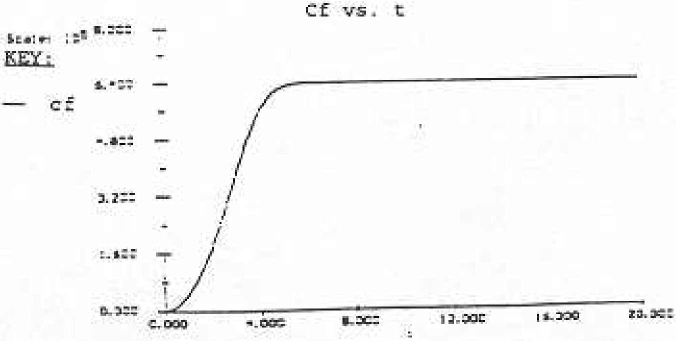
```
Equations:                                   Initial value
d(ca)/d(t)=ra                                0.3422
d(cb)/d(t)=rb                                540
d(cc)/d(t)=rc                                0
d(ce)/d(t)=re                                0
d(cf)/d(t)=rf                                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
t0 = 0,   tf = 20
```

P6-26 cont'd

```
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-A

Given: The following system of gas phase reactions:

$$A \rightarrow B \qquad -r_{A1} = 2\ \text{mol/dm}^3 \cdot \text{min}$$

$$A \rightarrow C \qquad -r_{A2} = 6\text{min}^{-1} C_A$$

$$A \rightarrow D \qquad -r_{A3} = 18 \frac{\text{dm}^3}{\text{mol} \cdot \text{min}} C_A^2$$

Finding selectivity:

$$S_{CB} = \frac{6 * C_A}{2} \qquad S_{CD} = \frac{6}{18 * C_A}$$

To minimize B, make C_A as high as possible. Therefore use a plug flow reactor. To minimize D, make C_A as low as possible. Therefore use a CSTR. The above two statements contradict each other. Therefore look at the numerical values.

$$C_{A0} = \frac{P_0}{RT} = \frac{405.3\text{kPa}}{\frac{8.314}{\text{mol} \cdot \text{K}} * 500\text{K}} = .097 \frac{dm^3}{mol}$$

and since $\delta = \delta_B + \delta_C + \delta_D = 0$,

$$C_{AF} = C_{A0}(1 - X_F) = 0.1 C_{A0}$$

Examining the ratios at final and initial conditions:

$$S_{CB0} = \frac{6 * .097}{2} = 0.291$$

$$S_{CBF} = \frac{6 * .1 * .097}{2} = .0291$$

$$S_{CD0} = \frac{6}{18 * .097} = 3.4$$

$$S_{CDF} = \frac{6}{18 * .097 * 0.1} = 34.4$$

r_B seems to be the undesirable dominant reaction the whole time so keeping C_A low will maximize C the best so use a CSTR. If we tried to change reactors, we would want $S_{CB} = S_{cd}$, but the only time that happens is when C_A equals 1/3 and it never can.

$$V = \frac{F_{A0} X}{-r_A} = \frac{1 * .9}{2 + 6 * .097 * .1 + 18 * (.097)^2 * .1^2} = .35 dm^3$$

CDP6-B

a)

$$\upsilon_0 C_{A0} - \upsilon_0 C_A + r_A W = 0$$

$$-\upsilon_0 C_B + r_B W = 0$$

$$-\upsilon_0 C_C + r_C W = 0$$

$$-\upsilon_0 C_D + r_D W = 0$$

$$r_A = -k_1 C_A^2 - k_3 C_A$$

$$r_B = k_1 C_A - k_2 C_B \qquad r_D = k_3 C_A$$

$$r_C = k_2 C_B$$

CDP6-B (cont'd)

```
The equations:
     f(cb)=-cb+(k1*ca*ca-k2*cb)*w/v0
     f(cc)=-cc+k2*cb*w/v0
     f(cd)=-cd+k3*ca*w/v0
     f(ca)=ca0-ca-(k1*ca*ca+k3*ca)*w/v0
     k1=.2
     k2=.0004
     k3=.0006
     ca0=.01
     v0=2.5
     w=5000
 Initial values: cb0= 0.100*10^-2, cc0= 0.100*10^-2
  cd0= 0.200*10^-3, ca0= 0.100*10^-2
```

```
               Solution
 Variable                  Value
   cb                 0.194*10^-2
   cc                 0.155*10^-2
   cd                 0.355*10^-2
   ca                 0.296*10^-2
   k1                 0.2000
   k2                 0.400*10^-3
   k3                 0.600*10^-3
   ca0                0.0100
   v0                 2.5000
   w                  5000.0
```

c)

$$\frac{dC_A}{dW} = \left(r'_{A1} + r'_{A3}\right) / \upsilon_0$$

$$\frac{dC_B}{dW} = \left(-r'_{A1} + r'_{B2}\right) / \upsilon_0$$

$$\frac{dC_C}{dW} = -r'_{B2} / \upsilon_0$$

$$\frac{dC_D}{dW} = r'_{A3} / \upsilon_0$$

$$r_{A1} = -k_1 C_A$$

$$r_{B2} = -k_2 C_B$$

$$r_{A3} = -k_3 C_A$$

```
The equations:
     d(ca)/d(w)=(ra1+ra3)/v0
     d(cb)/d(w)=(-ra1+rb2)/v0
     d(cc)/d(w)=-rb2/v0
     d(cd)/d(w)=-ra3/v0
     k1=.2
     ra1=-k1*ca*ca
     k2=.0004
     rb2=-k2*cb
     k3=.0006
     ra3=-k3*ca
     v0=2.5
Initial values: w0= 0.0, ca0= 0.0100, cb0= 0.0, cc0= 0.0
 cd0= 0.0
Final value:  wf= 10000
```

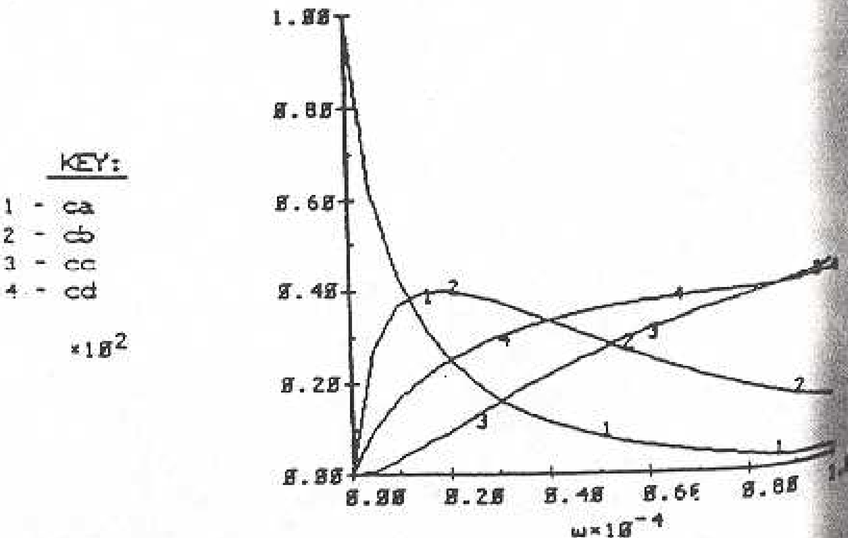
$k_1 = 0.0014$ m³/kg cat • s

$k_2 = 0.00146$

$k_3 = 0.0000765$

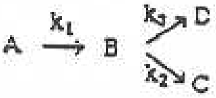
$\upsilon_0 = 2.5$

$C_{A0} = 0.01$



6-56

CDP6-C



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 min = 120 s, C_B = 0.136 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 min = 60 sec.

$$C_C = 0.003\left(\frac{15}{3}\right)[0 + 4(0.0449) + 2(0.0782) + 4(0.102) + 0.1183]$$

$$C_C = 0.0129 \text{ gmol/dm}^3$$

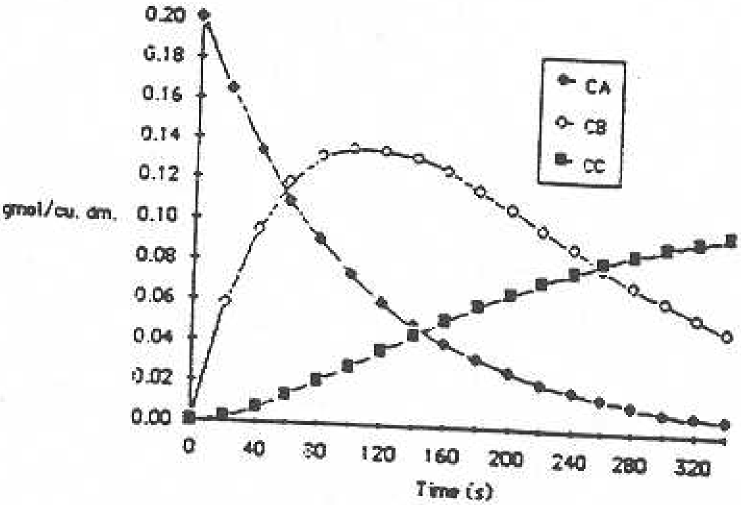
t = 2 min = 120 sec

$$C_C = 0.003\left(\frac{30}{3}\right)[0 + 4(0.0782) + 2(0.1183) + 4(0.134) + 0.1355]$$

$$C_C = 0.0366 \text{ gmol/dm}^3$$

(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 = 110 sec, where its value is 0.1363 gmol/dm³.

(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-D

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:

$$-r_{1I} = -r_{1O} = r_{1M} = k_1C_IC_{O0}$$

$$-r_{2I} = \frac{-4r_{2O}}{25} = \frac{1}{4}r_{2D} = k_2C_IC_{O0}$$

$$-r_{3I} = \frac{4r_{3O}}{-17} = \frac{1}{4}r_{3C} = k_3C_IC_{O0}$$

Combine all of these and come up with the following:

$$C_{I0} - C_I = (k_1C_IC_{O0} + k_2C_IC_{O0} + k_3C_IC_{O0})\tau$$

$$C_{O0} - C_O = (k_1C_IC_{O0} + \frac{25}{4}k_2C_IC_{O0} + \frac{17}{4}k_3C_IC_{O0})\tau$$

$$C_M = k_1C_IC_{O0}\tau$$

$$C_D = 4 * k_2C_IC_{O0}\tau$$

$$C_C = 4 * k_3C_IC_{O0}\tau$$

Before plugging into POLYMATH, evaluate the parameters and derive equations for conversion.

$$C_T = \frac{P}{RT} = \frac{2}{.082 * 700} = 0.034$$

$$C_{I0} = y_{A0}C_T = .1 * .034 = 0.0034$$

$$C_{O0} = 0.031$$

$$X_I = \frac{C_{I0} - C_I}{C_{I0}}$$

$$X_{1I} = \frac{C_M}{C_{I0}}$$

$$X_{2I} = \frac{C_D}{4C_{I0}}$$

$$X_{3I} = X_I - X_{1I} - X_{2I}$$

CDP6-D cont'd

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
```

$X_I = 0.496$ $X_{1I} = 0.25$ $X_{2I} = 0.037$ $X_{3I} = 0.21$

CDP6-E

$$\frac{dC_A}{dt} = r_A \qquad \frac{dC_B}{dt} = r_B \qquad C_C = KC_B$$

$$r_A = k_2C_B - k_1C_A \qquad r_B = k_1C_A - k_2C_B$$

Once that is done, then it gets plugged into POLYMATH and the composition can be found.

After 6.5 h, the answer is found to be:
$y_A = .44$
$y_B = .37$
$y_C = .19$

```
Equations:                                                Initial valu
d(ca)/d(t)=ra                                             1
d(cb)/d(t)=rb                                             0
cc=.5*cb
k2=.001
k1=.002
ra=k2*cb-k1*ca
rb=k1*ca-k2*cb
t0 = 0,   tf = 390
```

```
Variable      Initial value   Maximum value   Minimum value   Final value
t             0               390             0               390
ca            1               1               0.540245        0.540245
cb            0               0.459755        0               0.459755
cc            0               0.229878        0               0.229878
k2            0.001           0.001           0.001           0.001
k1            0.002           0.002           0.002           0.002
ra            -0.002          -0.000620734    -0.002          -0.000620734
rb            0.002           0.002           0.000620734     0.000620734
```

CDP6-F

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:

$$-r_A = k_1C_{A0}(1-X)$$

Combining all these and solving for τ when $X = .3$, $C_{A0} = .1$ and $k_1 = .412$

$$\tau = \frac{C_{A0}X}{k_1C_{A0}(1-X)} = \frac{.1*.3}{.412*.1*.7} = 1.04h$$

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:

$$-r_A = k_1C_A$$

$$-r_B = k_1C_A + k_2C_C$$

$$r_C = k_1C_A - k_2C_C$$

$$r_D = k_1C_A + k_2C_C$$

$$r_E = k_2C_C$$

Combining and rearranging into a function:

$$f(C_A) = 0 = C_A - C_{A0} + k_1C_A\tau$$

$$f(C_B) = 0 = C_B - C_{B0} + (k_1C_A + k_2C_C)\tau$$

$$f(C_C) = 0 = (k_1C_A - k_2C_C)\tau - C_C$$

$$f(C_D) = 0 = (k_1C_A + k_2C_C)\tau - C_D$$

$$f(C_E) = 0 = k_2C_C\tau - C_E$$

CDP6-F cont'd

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 $F_{co} = 10$

$$v_0 = \frac{F_C}{C_C} = \frac{10}{.028} = 357\,gal/h$$

$$V = \tau v_0 = 1.04 * 357 = 371.3\,gal$$

b)No solution will be given.

CDP6-G

First, write all of the equations in terms of symbols:

(1) $4A + 5B \Leftrightarrow 4C + 6D$

(2) $4A + 3B \Leftrightarrow 2E + 6D$

(3) $4C + B \Leftrightarrow 2F$

(4) $4A + 6C \Leftrightarrow 5E + 6D$

(5) $2C \Leftrightarrow E + B$

(6) $E + 2B \Leftrightarrow 2F$

Set up a coefficient matrix:

	Species					
	A	B	C	D	E	F
(1)	-4	-5	4	6	0	0
(2)	-4	-3	0	6	2	0
(3)	0	-1	-4	0	0	2
(4)	-4	0	-6	6	5	0
(5)	0	1	-2	0	1	0
(6)	0	-2	0	0	-1	2

CDP6-G (cont'd)

Now, reduce the numbers in column 1 and rows 2,3,4,5, and 6 to 0 by adding and subtracting with row 1:

$$\begin{array}{c} (1)\\ (2)\\ (3)\\ (4)\\ (5)\\ (6) \end{array} \begin{pmatrix} -4 & -5 & 4 & 6 & 0 & 0\\ 0 & 2 & -4 & 0 & 2 & 0\\ 0 & -1 & -4 & 0 & 0 & 2\\ 0 & 5 & -10 & 0 & 5 & 0\\ 0 & 1 & -2 & 0 & 1 & 0\\ 0 & -2 & 0 & 0 & -1 & 2 \end{pmatrix}$$

Next, repeat this for column 2, rows 3, 4, 5, and 6:

$$\begin{array}{c} (1)\\ (2)\\ (3)\\ (4)\\ (5)\\ (6) \end{array} \begin{pmatrix} -4 & -5 & 4 & 6 & 0 & 0\\ 0 & 2 & -4 & 0 & 2 & 0\\ 0 & 0 & -12 & 0 & 2 & 4\\ 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & -4 & 0 & 1 & 2 \end{pmatrix}$$

Finally, repeat for column 3, rows 4,5, and 6:

$$\begin{array}{c} (1)\\ (2)\\ (3)\\ (4)\\ (5)\\ (6) \end{array} \begin{pmatrix} -4 & -5 & 4 & 6 & 0 & 0\\ 0 & 2 & -4 & 0 & 2 & 0\\ 0 & 0 & -12 & 0 & 2 & 2\\ 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 1 & 2 \end{pmatrix}$$

From this final matrix it is apparent that there are four independent reactions.

We then use reactions 1, 2, 3, and 6 to define our X values:

$$X_1 = \frac{\Delta F_{A1}}{-F_{Ao}} = \frac{\Delta F_{B1}}{-1.25F_{Ao}} = \frac{\Delta F_{C1}}{F_{Ao}} = \frac{\Delta F_{D1}}{1.5F_{Ao}}$$

$$X_2 = \frac{\Delta F_{A2}}{-F_{Ao}} = \frac{\Delta F_{B2}}{-0.75F_{Ao}} = \frac{\Delta F_{E2}}{0.5F_{Ao}} = \frac{\Delta F_{D2}}{1.5F_{Ao}}$$

$$X_3 = \frac{\Delta F_{C3}}{-\Theta_B F_{Ao}} = \frac{\Delta F_{B3}}{-\Theta_B F_{Ao}} = \frac{\Delta F_{F3}}{2\Theta_B F_{Ao}}$$

$$X_6 = \frac{\Delta F_{E6}}{-0.5\Theta_B F_{Ao}} = \frac{\Delta F_{B6}}{-\Theta_B F_{Ao}} = \frac{\Delta F_{F6}}{\Theta_B F_{Ao}}$$

CDP6-G (cont'd)

From here we generate a Stoichiometric Table:

Species	Initial	Change	Final
A	F_{Ao}	$-F_{Ao}(1-X_1+X_2)$	$F_{Ao}(1-X_1+X_2)$
B	$\Theta_B F_{Ao}$	$-F_{Ao}(1.25X_1+0.75X_2+\Theta_B X_3+\Theta_B X_6)$	$F_{Ao}(\Theta_B-1.25X_1+0.75X_2+\Theta_B X_3+\Theta_B X_6)$
C	0	$F_{Ao}(X_1-4\Theta_B X_3)$	$F_{Ao}(X_1-4\Theta_B X_3)$
D	0	$F_{Ao}(1.5X_1+1.5X_2)$	$F_{Ao}(1.5X_1+1.5X_2)$
E	0	$F_{Ao}(0.5X_2-0.5X_6)$	$F_{Ao}(0.5X_2-0.5X_6)$
F	0	$F_{Ao}(2\Theta_B X_3+\Theta_B X_6)$	$F_{Ao}(2\Theta_B X_3+\Theta_B X_6)$

Balance on A:

$$\frac{dF_A}{dV} = r_A = -(-r_1 - r_2 - r_4)$$

$$F_A = F_{Ao}(1 - X_1 - X_2) \quad \Rightarrow \quad F_{Ao}\frac{dX_1}{dV} + F_{Ao}\frac{dX_2}{dV} = -r_1 - r_2 - r_4$$

Balance on B:

$$-F_{Ao}\left(1.25\frac{dX_1}{dV} + 0.75\frac{dX_2}{dV} + \Theta_B\frac{dX_3}{dV} + \Theta_B\frac{dX_6}{dV}\right) = -\tfrac{5}{4}r_1 - \tfrac{3}{4}r_2 - r_3 + \tfrac{1}{2}r_5 - r_6$$

Balance on C:

$$F_{Ao}\left(\frac{dX_1}{dV} - 4\Theta_B\frac{dX_3}{dV}\right) = -\left(r_1 - 4r_3 - \tfrac{3}{2}r_4 - r_5\right)$$

Balance on F:

$$F_{Ao}\Theta_B\left(2\frac{dX_3}{dV} + \frac{dX_6}{dV}\right) = -(2r_3 + r_6)$$

Combine and simplify to get:

$$F_{Ao}\frac{dX_1}{dV} = \tfrac{3}{2}r_4 + r_5 - \tfrac{8}{5}r_6$$

$$F_{Ao}\frac{dX_2}{dV} = -r_1 - r_2 - \tfrac{5}{2}r_4 - r_5 - \tfrac{8}{5}r_6$$

$$F_{Ao}\frac{dX_3}{dV} = \frac{\tfrac{1}{4}r_1 - r_3 - \tfrac{2}{5}r_6}{\Theta_B}$$

$$F_{Ao}\frac{dX_6}{dV} = \frac{-\tfrac{1}{2}r_1 + \tfrac{1}{5}r_6}{\Theta_B}$$

CDP6-H

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

$$2A \rightarrow D$$

$$A \rightarrow D/2$$

$C_{T0} = 0.15$ mol/dm^3

$k_1 C_{T0}^{3/2} = (0.7)(.15)^{3/2} = 0.04$

$k_2 C_{T0}^{2} = (0.6)(.15)^{2} = 0.0135$

$F_{A0} = 10$ mol/min

$F_{B0} = 5$ mol/min

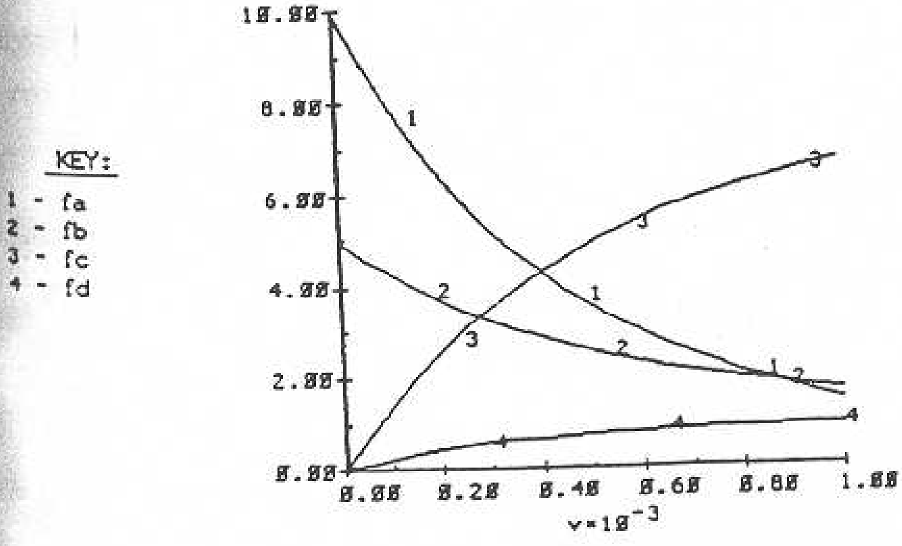
$$\frac{dF_A}{dV} = -.04\,\frac{F_A}{F_T}\left(\frac{F_B}{F_T}\right)^{1/2} - .0135\left(\frac{F_A}{F_T}\right)^2$$

$$\frac{dF_B}{dV} = -.02\left(\frac{F_A}{F_T}\right)\left(\frac{F_B}{F_T}\right)^{1/2}$$

$$\frac{dF_C}{dV} = .04\left(\frac{F_A}{F_T}\right)\left(\frac{F_B}{F_T}\right)^{1/2}$$

$$\frac{dF_D}{dV} = 0.00675\left(\frac{F_A}{F_T}\right)^2$$

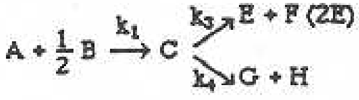
$$F_T = F_A + F_B + F_C + F_D + F_E$$



CDP6-H (cont'd)

```
The equations:
    d(fa)/d(v)=-.04*fa*(fb/ft)**.5/ft-.0135*(fa/ft)**2
    d(fb)/d(v)=-.02*fa*(fb/ft)**.5/ft
    d(fc)/d(v)=.04*fa*(fb/ft)**.5/ft
    d(fd)/d(v)=.00675*(fa/ft)**2
    ft=fa+fb+fc+fd
Initial values: v0= 0.0, fa0= 10.000, fb0= 5.0000, fc0= 0.0
 fd0= 0.0
Final value:  vf= 1000.0
```

CDP6-I



$$A \xrightarrow{k_1} \frac{D}{2}$$

$$k_3 C_{T0} = 1.05 \times 10^{-2}$$

$$k_4 C_{T0} = 1.35 \times 10^{-2}$$

$$k_3 C_{T0} + k_4 C_{T0} = 2.4 \times 10^{-2}$$

$$\frac{dF_E}{dV} = 2.1 \times 10^{-2}\left(\frac{F_C}{F_T}\right)$$

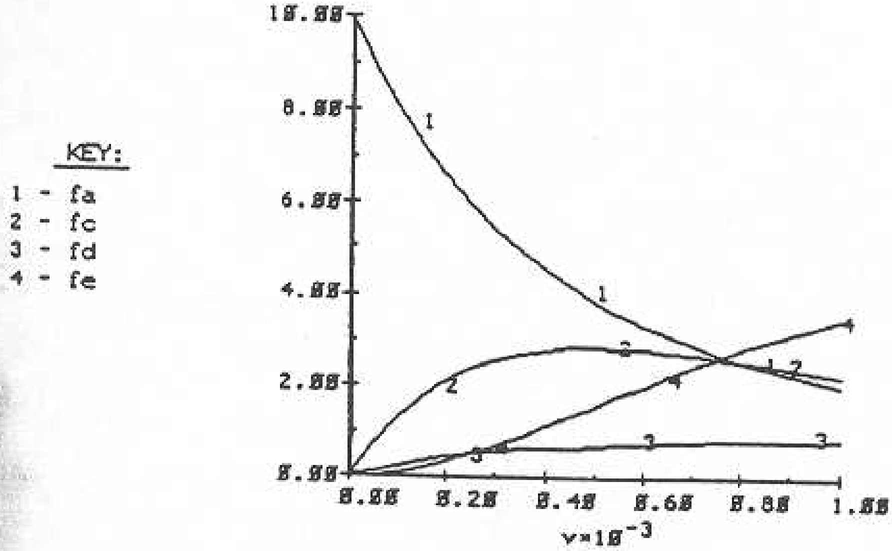
$$\frac{dF_G}{dV} = 1.35 \times 10^{-2}\left(\frac{F_C}{F_T}\right)$$

$$\frac{dF_H}{dV} = 1.35 \times 10^{-2}\left(\frac{F_C}{F_T}\right)$$

$$\frac{dF_C}{dV} = .04\left(\frac{F_A}{F_T}\right)\left(\frac{F_B}{F_T}\right)^{1/2} - 2.4 \times 10^{-2}\left(\frac{F_C}{F_T}\right)$$

```
The equations:
    d(fa)/d(v)=-.04*fa*(fb/ft)**.5/ft-.0135*(fa/ft)**2
    d(fb)/d(v)=-.02*fa*(fb/ft)**.5/ft
    d(fc)/d(v)=.04*fa*(fb/ft)**.5/ft-.024*(fc/ft)
    d(fd)/d(v)=.00675*(fa/ft)**2
    d(fe)/d(v)=.021*(fc/ft)
    d(fg)/d(v)=.0135*(fc/ft)
    d(fh)/d(v)=.0135*(fc/ft)
    ft=fa+fb+fc+fd+fe+fg+fh
Initial values: v0= 0.0, fa0= 10.000, fb0= 5.0000, fc0= 0.0
 fd0= 0.0, fe0= 0.0, fg0= 0.0, fh0= 0.0
Final value:  vf= 1000.0
```

CDP6-I (cont'd)



CDP6-J

Same as 9-14, except $k_5 C_{T0}^2 = 4.5 \times 10^{-6}$

From P9-14

$$A + \frac{1}{2} B \xrightarrow{k_1} C \quad \begin{matrix} \xrightarrow{k_3} E + F\ (2E) \\ \xrightarrow{k_4} G + H \end{matrix}$$

$$A \xrightarrow{k_1} \frac{D}{2}$$

$k_3 C_{T0} = 1.05 \times 10^{-2}$

$k_4 C_{T0} = 1.35 \times 10^{-2}$

$k_3 C_{T0} + k_4 C_{T0} = 2.4 \times 10^{-2}$

$$D + G \rightarrow K + C$$

$$\frac{dF_D}{dV} = .00675 \left(\frac{F_A}{F_T}\right)^2 - .45 \left(\frac{F_D}{F_T}\right)\left(\frac{F_G}{F_T}\right)$$

$$\frac{dF_K}{dV} = .45 \left(\frac{F_D}{F_T}\right)\left(\frac{F_G}{F_T}\right)$$

$$\frac{dF_C}{dV} = .04 \left(\frac{F_A}{F_T}\right)\left(\frac{F_B}{F_T}\right)^{\frac{1}{2}} + .45 \left(\frac{F_D}{F_T}\right)\left(\frac{F_G}{F_T}\right) - 2.4 \times 10^{-2} \left(\frac{F_C}{F_T}\right)$$

$$\frac{dF_G}{dV} = .0135 \left(\frac{F_C}{F_T}\right) - .45 \left(\frac{F_D}{F_T}\right)\left(\frac{F_G}{F_T}\right)$$

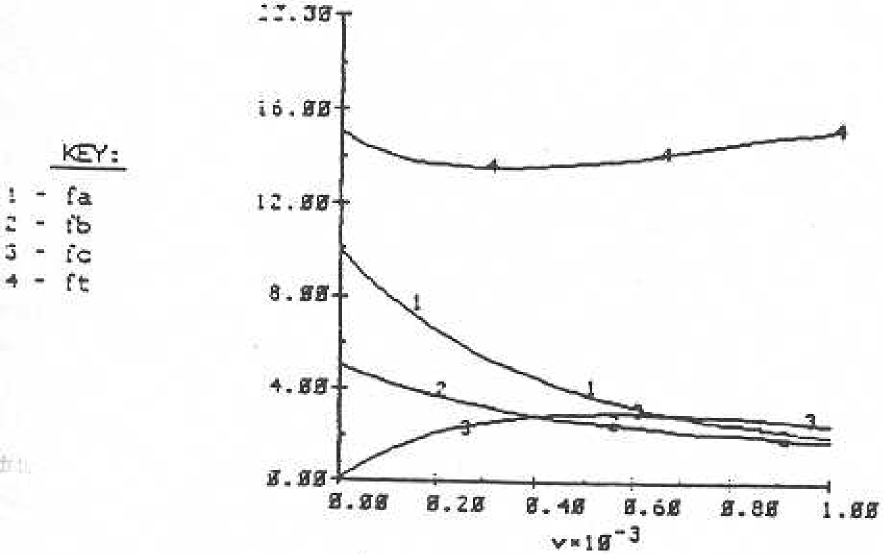
CDP6-J (cont'd)

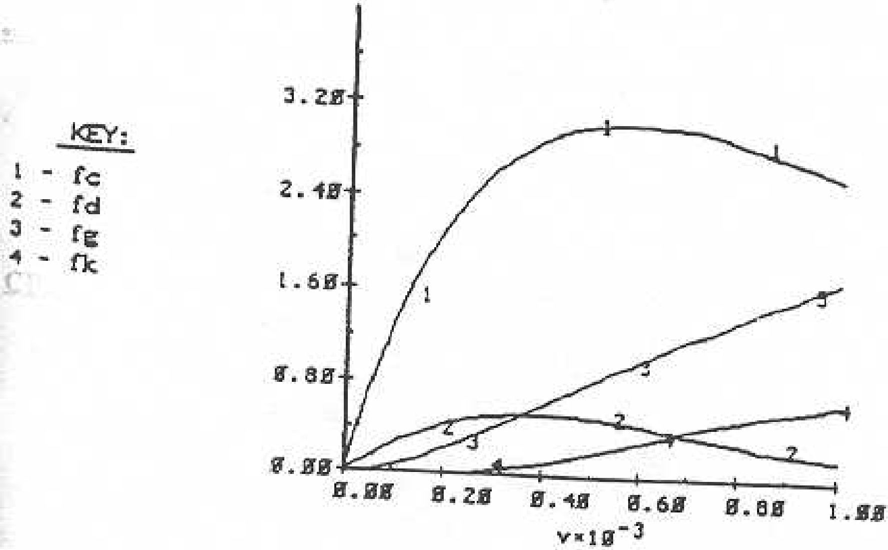
```
 The equations:
     d(fa)/d(v)=-.04*fa*(fb/ft)**.5/ft-.0135*(fa/ft)**2
     d(fb)/d(v)=-.02*fa*(fb/ft)**.5/ft
     d(fc)/d(v)=.04*fa*(fb/ft)**.5/ft-.024*(fc/ft)+p
     d(fd)/d(v)=.00675*(fa/ft)**2-p
     d(fe)/d(v)=.021*(fc/ft)
     d(fg)/d(v)=.0135*(fc/ft)-p
     d(fh)/d(v)=.0135*(fc/ft)
     d(fk)/d(v)=p
     ft=fa+fb+fc+fd+fe+fg+fh+fk
     p=.45*(fd/ft)*(fg/ft)
Initial values: v0= 0.0, fa0= 10.000, fb0= 5.0000, fc0= 0.0
 fd0= 0.0, fe0= 0.0, fg0= 0.0, fh0= 0.0, fk0= 0.0
Final value:  vf= 1000.0

       v               fa              fb              fc              fd
0.0              10.000          5.0000          0.0             0.0
50.000           8.9866          4.6328          0.7047          0.1394
100.00           8.0836          4.3008          1.2854          0.2580
150.00           7.2850          4.0028          1.7540          0.3558
200.00           6.5826          3.7368          2.1248          0.4327
250.00           5.9672          3.5003          2.4128          0.4889
300.00           5.4288          3.2985          2.6318          0.5253
350.00           4.9579          3.1046          2.7941          0.5438
400.00           4.5454          2.9396          2.9101          0.5466
450.00           4.1833          2.7931          2.9880          0.5366
500.00           3.8645          2.6626          3.0347          0.5165

       v               fa              fb              fc              fd
500.00           3.8645          2.6626          3.0347          0.5165
550.00           3.5826          2.5461          3.0555          0.4891
600.00           3.3325          2.4416          3.0549          0.4567
650.00           3.1096          2.3478          3.0366          0.4214
700.00           2.9101          2.2630          3.0036          0.3848
750.00           2.7309          2.1863          2.9585          0.3482
800.00           2.5692          2.1166          2.9035          0.3126
850.00           2.4226          2.0538          2.8406          0.2787
900.00           2.2893          1.9947          2.7713          0.2468
950.00           2.1677          1.9413          2.6972          0.2174
1000.0           2.0563          1.8921          2.6194          0.1906
```

CDP6-J (cont'd)


KEY:
1 - fa
2 - fb
3 - fc
4 - ft
20.00
16.00
12.00
8.00
4.00
0.00
0.00
0.20
0.40
0.60
0.80
1.00
v×10^{-3}
1
2
3
4


KEY:
1 - fc
2 - fd
3 - fg
4 - fk
3.20
2.40
1.60
0.80
0.00
0.00
0.20
0.40
0.60
0.80
1.00
v×10^{-3}
1
2
3
4

CDP6-K

a) Have to determine best temperature, flow rate of propylene and which reactor system. Start with both mole balances:

PBR:

$$\frac{dF_B}{dW} = r_B \qquad \frac{dF_P}{dW} = r_P \qquad \frac{dF_I}{dW} = r_I \qquad \frac{dF_D}{dW} = r_D$$

CSTR:

$$F_{B0} - F_B = -r_B t' \qquad F_{P0} - F_P = -r_P t' \qquad F_I = r_I t'$$

$$F_D = r_D t'$$

Next, do the rate laws:

$$r_B = -k_1 C_B^{.9} C_P \qquad r_P = -k_1 C_B^{.9} C_P - k_2 C_I C_P^{.9} \qquad r_I = k_1 C_B^{.9} C_P - k_2 C_I C_P^{.9}$$

$$r_D = k_2 C_I C_P^{.9}$$

Finally, the stoichiometry:

$$C_j = \frac{F_j}{v_0} \qquad t' = \frac{W}{v_0}$$

To find ideal conditions, use one of the reactors to find the ideal temperature and the ideal entering flow rate of propylene. Like this example using the PBR:

```
6-X
Equations:                                                    Initial value
d(fi)/d(taup)=ri                                              0
d(fp)/d(taup)=rp                                              31
d(fd)/d(taup)=rd                                              0
d(fb)/d(taup)=rb                                              11.6
T=200
k1=3.74e7*exp(-7390/T)
k2=3.7e7*exp(-10000/T)
rd=k2*fi^.5*fp^.9
rb=-k1*fb^.9*fp
rp=-k1*fb^.9*fp-k2*fi^.5*fp^.9
ri=k1*fb^.9*fp-k2*fi^.5*fp^.9
taup0 = 0,   taupf = 1e+09
Variable      Initial value   Maximum value   Minimum value   Final value
taup          0               7.5e+07         0               7.5e+07
fp            31              31              19.4466         19.4466
fi            0               11.5534         0               11.5534
fd            0               2.50903e-05     0               2.50903e-05
fb            11.6            11.6            0.0466102       0.0466102
T             200             200             200             200
k1            3.35498e-09     3.35498e-09     3.35498e-09     3.35498e-09
k2            7.13637e-15     7.13637e-15     7.13637e-15     7.13637e-15
rd            0               3.50827e-13     0               3.50583e-13
rb            -9.44201e-07    -4.13206e-09    -9.44201e-07    -4.13206e-09
ri            9.44201e-07     9.44201e-07     4.13171e-09     4.13171e-09
rp            -9.44201e-07    -4.13241e-09    -9.44201e-07    -4.13241e-09
```

CDP6-K cont'd

The best temperature is 200K and the flow rate should be 31 mol/s or 2678 kg mol/day. The τ' found for the PBR is 7.5*10^{7}. Using the CSTR with the same numbers it is found that the τ' found is 1*10^{12}. So the PBR is better.

```
6-K
Equations:                                            Initial value
f(fb)=fb-fbo-rb*taup                                  0.2
f(fp)=fp-fpo-rp*taup                                  18
f(fi)=ri*taup-fi                                      11
f(fd)=rd*taup-fd                                      0.001
fbo=11.6
taup=1e12
fpo=31
T=200
k1=3.74e4*exp(-7390/T)
k2=3.7e7*exp(-10000/T)
rd=k2*fi^.5*fp^.9
rb=-k1*fb^.9*fp
rp=-k1*fb^.9*fp-k2*fi^.5*fp
ri=k1*fb^.9*fp-k2*fi^.5*fp^.9
```

```
Variable       Value             f()
fb             0.147654          2.29e-15
fp             19.0934           2.787e-15
fi             11.1141           1.01e-15
fd             0.338228          3.347e-17
fbo            11.6
taup           1e+12
fpo            31
T              200
k1             3.35498e-12
k2             7.13637e-15
rb             -1.14523e-11
rd             3.38228e-13
rp             -1.19066e-11
ri             1.11141e-11
```

CDP6-M

$$S_{DU} = \frac{206000\exp\left(-\frac{7610}{T}\right)P_pP_c}{11.7\exp\left(-\frac{1920}{T}\right)P_pP_c}$$

$$= 17606\exp\left(-\frac{5690}{T}\right)$$

Notice the selectivity is completely independent of the pressures of the two reactants, therefore, the reactor could be either a PFR or CSTR without changing the selectivity.

At T = 450°C $\quad S_{DU} = 6.76$

At T = 350°C $\quad S_{DU} = 1.9$

So, the temperature should be at 450°C in order to maximize the selectivity.

CDP6-N

a) To determine which reactions are necessary, make a matrix out of the reactions:

$$\begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & -1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 \end{bmatrix}$$

Reducing it gets this matrix:

$$\begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 & 1 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Therefore reaction 6 can be ignored.

b) 1) In a packed-bed reactor, these are the mole balances:

$$\frac{dF_T}{dW} = r_T$$

$$\frac{dF_M}{dW} = r_M$$

$$\frac{dF_{PX}}{dW} = r_{PX}$$

$$\frac{dF_{MX}}{dW} = r_{MX}$$

$$\frac{dF_{OX}}{dW} = r_{OX}$$

$$\frac{dF_{TMB}}{dW} = r_{TMB}$$

CDP6-N **cont'd**

These are the rate laws needed.

$$r_T = \frac{-k_1 P_T P_M}{Z^2}$$

$$r_M = \frac{-k_1 P_T P_M - k_4 P_M P_{PX} - k_5 P_M P_{MX}}{Z^2}$$

$$r_{PX} = \frac{k_1 P_T P_M - k_2 P_{PX} - k_4 P_M P_{PX}}{Z^2}$$

$$r_{MX} = \frac{k_2 P_{PX} - k_3 P_{MX} - k_5 P_M P_{MX}}{Z^2}$$

$$r_{OX} = \frac{k_3 P_{MX}}{Z^2}$$

$$r_{TMB} = \frac{k_4 P_M P_{PX} + k_5 P_M P_{MX}}{Z^2}$$

Stoichiometry:

$$C_j = \frac{P_j}{RT}$$

$$C_j = C_{T0} \frac{F_j}{F_{T0}}$$

$$P_j = \frac{C_{T0} RT F_j}{F_{T0}} = \frac{P_{T0} F_j}{F_{T0}} = AF_j$$

$$A = \frac{10}{600} = .0167$$

Combining:

$$\frac{dF_T}{dW} = \frac{-k_1 A^2 F_T F_M}{Z^2}$$

$$\frac{dF_M}{dW} = \frac{-k_1 A^2 F_T F_M - k_4 A^2 F_M F_{PX} - k_5 A^2 F_M F_{MX}}{Z^2}$$

$$\frac{dF_{PX}}{dW} = \frac{k_1 A^2 F_T F_M - k_2 A F_{PX} - k_4 A^2 F_M F_{PX}}{Z^2}$$

$$\frac{dF_{MX}}{dW} = \frac{k_2 A F_{PX} - k_3 A F_{MX} - k_5 A^2 F_M F_{MX}}{Z^2}$$

$$\frac{dF_{OX}}{dW} = \frac{k_3 A F_{MX}}{Z^2}$$

$$\frac{dF_{TMB}}{dW} = \frac{k_4 A^2 F_M F_{PX} + k_5 A^2 F_M F_{MX}}{Z^2}$$

Plugging into POLYMATH gets the following graphs:

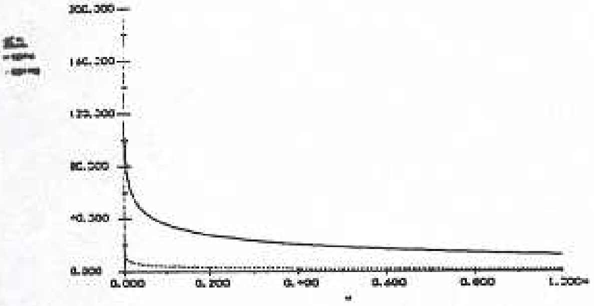
CDP6-N cont'd

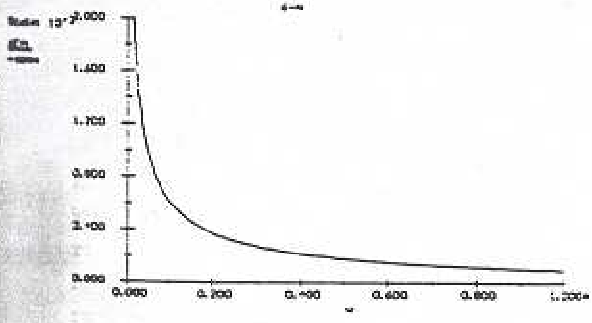
```
6-N
Equations:                                                           Initial value
d(ft)/d(w)=rt                                                        300
d(fm)/d(w)=rm                                                        300
d(fpx)/d(w)=rpx                                                      0
d(fmx)/d(w)=rmx                                                      0
d(fox)/d(w)=rox                                                      0
d(ftmb)/d(w)=rtmb                                                    0
k1=3.9
z=1+3.3*.0167*fpx+13.6*.0167*fmx+33.3*.0167*fox+215*.0167*ft
   mb
k2=.9
k4=1.2
k3=2.3
k5=14.5
rt=-k1*.0167*ft*.0167*fm/z^2
rox=k3*.0167*fmx/z^2
rtmb=(k4*.0167*fm*.0167*fpx+k5*.0167*fm*.0167*fmx)/z^2
rm=(-k1*.0167*ft*.0167*fm-k4*.0167*fm*.0167*fpx-k5*.0167*fm*
    .0167*fmx)/z^2
rpx=(k1*.0167*ft*.0167*fm-k2*.0167*fpx-k4*.0167*fm*.0167*fpx
    )/z^2
rmx=(k2*.0167*fpx-k3*.0167*fmx-k5*.0167*fm*.0167*fmx)/z^2
spox=if(rox>0)then(rpx/rox)else(0)
sptmb=if(rtmb>0)then(rpx/rtmb)else(0)
spmx=if(rmx>0)then(rpx/rmx)else(0)
```

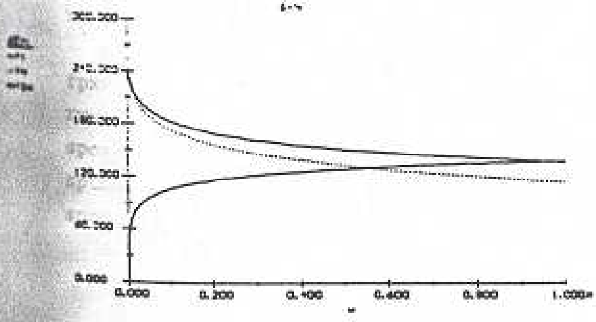
$w_0 = 0,\quad w_f = 10000$

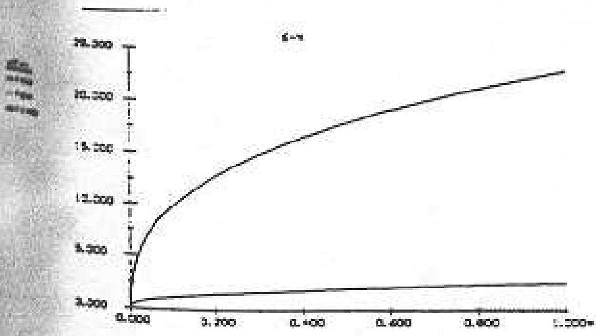
```
6-N
Variable        Initial value   Maximum value   Minimum value   Final value
w               0               10000           0               10000
ft              300             300             136.713         136.713
fm              300             300             113.87          113.87
fpx             0               137.673         0               137.673
fmx             0               1.59862         0               1.59862
fox             0               0.1722          0               0.1722
ftmb            0               22.8432         0               22.8432
k1              3.9             3.9             3.9             3.9
z               1               91.2917         1               91.2917
k2              0.9             0.9             0.9             0.9
k4              1.2             1.2             1.2             1.2
k3              2.3             2.3             2.3             2.3
k5              14.5            14.5            14.5            14.5
rt              -97.8904        -0.00203168     -97.8904        -0.00203168
rox             0               0.000143874     0               1.19763e-05
rtmb            0               0.323931        0               0.000773097
rm              -97.8904        -0.00280478     -97.8904        -0.00280478
rpx             97.8904         97.8904         0.00115388      0.00115388
rmx             0               0.046838        0               9.27257e-05
spox            0               6.55687e+08     0               95.3468
sptmb           0               4332.1          0               1.49254
spmx            0               28964.4         0               12.444
```

CDP6-N cont'd


200.000
160.000
120.000
80.000
40.000
0.000
0.000
0.200
0.400
0.600
0.800
1.000


6-N
10⁻²
2.000
1.600
1.200
0.800
0.400
0.000
0.000
0.200
0.400
0.600
0.800
1.000


6-N
300.000
240.000
180.000
120.000
60.000
0.000
0.000
0.200
0.400
0.600
0.800
1.000


6-N
25.000
20.000
15.000
10.000
5.000
0.000
0.000
0.200
0.400
0.600
0.800
1.000

CDP6-N **cont'd**

2) In a CSTR, these are the mole balances:

$$F_{T0} - F_T = -r_T W$$
$$F_{M0} - F_M = -r_M W$$
$$F_{PX} = r_{PX} W$$
$$F_{MX} = r_{MX} W$$
$$F_{OX} = r_{OX} W$$
$$F_{TMB} = r_{TMB} W$$

The rate laws are the same as the packed-bed and so is the stoichiometry, combine all of those:

$$F_{T0} - F_T = \frac{k_1 A^2 F_T F_M}{Z^2} W$$

$$F_{M0} - F_M = \frac{k_1 A^2 F_T F_M - k_4 A^2 F_M F_{PX} - k_5 A^2 F_M F_{MX}}{Z^2} W$$

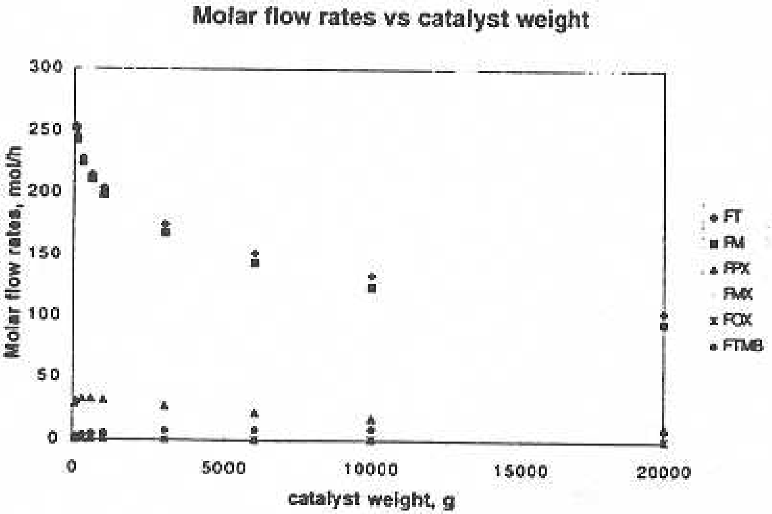
$$F_{PX} = \frac{k_1 A^2 F_T F_M - k_2 A F_{PX} - k_4 A^2 F_M F_{PX}}{Z^2} W$$

$$F_{MX} = \frac{k_2 A F_{PX} - k_3 A F_{MX} - k_5 A^2 F_M F_{MX}}{Z^2} W$$

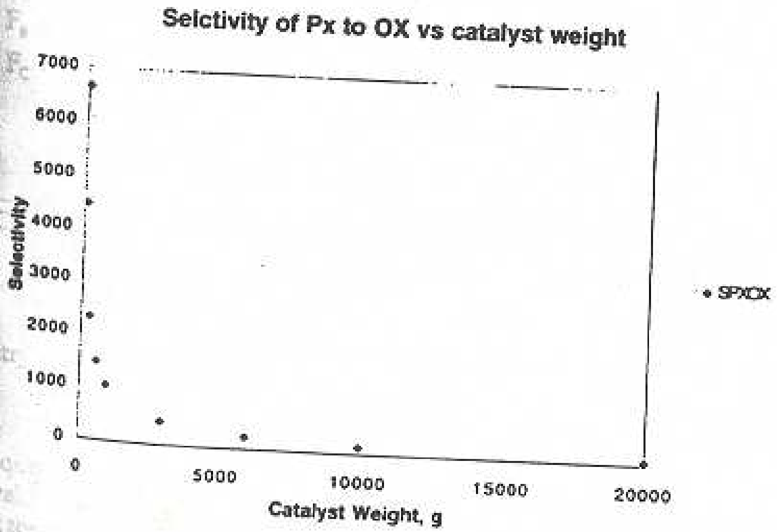
$$F_{OX} = \frac{k_3 A F_{MX}}{Z^2} W$$

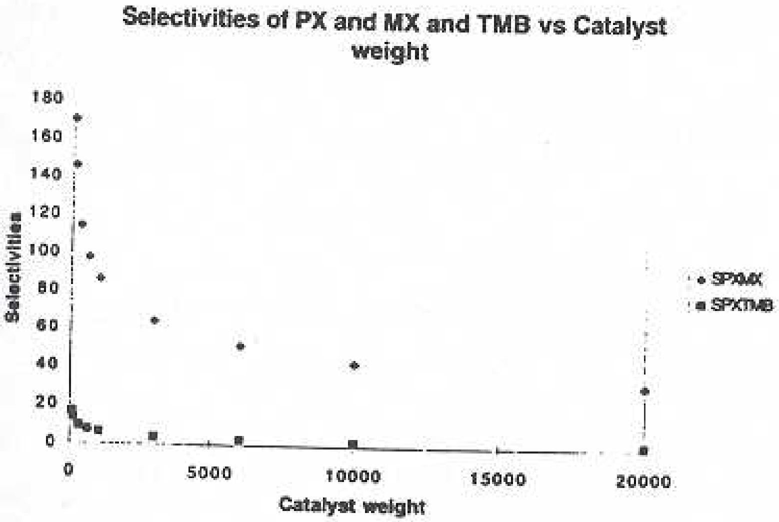
$$F_{TMB} = \frac{k_4 A^2 F_M F_{PX} + k_5 A^2 F_M F_{MX}}{Z^2} W$$

Plugging into POLYMATH gets the following graphs.



```
6-nb2
Equations:                                                          Initial value
f(ft)=ft-fto-rt*w                                                   150
f(fm)=fm-fmo-rm*w                                                   150
f(fpx)=rpx*w-fpx                                                    100
f(fox)=rox*w-fox                                                    50
f(fmx)=rmx*w-fmx                                                    50
f(ftmb)=rtmb*w-ftmb                                                 50
fto=300
w=20000
fmo=300
k1=3.9
z=1+3.3*.0167*fpx+13.6*.0167*fmx+33.3*.0167*fox+215*.0167*ft
  mb
k2=.9
k4=1.2
k3=2.3
k5=14.45
rt=-k1*.0167*ft*.0167*fm/z^2
rox=k3*.0167*fmx/z^2
rtmb=(k4*.0167^2*fm*fpx+k5*.0167^2*fm*fmx)/z^2
rm=(-k1*.0167*fm*.0157*ft-k4*.0167*fm*.0167*fpx-k5*.0167^2*f
  m*fmx)/z^2
rpx=(k1*.0167*ft*.0157*fm-k2*fpx-k4*.0156^2*fm*fpx)/z^2
rmx=(k2*.0157*fpx-k3*.0167*fmx-k5*.0167^2*fm*fmx)/z^2
spox=rpx/rox
sptmb=rpx/rtmb
spmx=rpx/rmx
```





c) Changing the ratio of Toluene to methanol finds the maximum of PX occurs at a ratio of 1.5 to 1. Changing the Concentration of the entering (changing A)stream finds that the concentration o fPX increases as the total concentration increases.

Finding the maximum of MX works the same way and the ratio is 1.61 to 1 and agan higher concentration yields more desired product.

ratio	Fpx
1	139.7
1.06896552	141.6
1.14285714	143.3
1.22222222	144.7
1.30769231	145.72
1.4	146.4
1.5	146.78
1.60869565	146.88

A	Fpx
0.0167	148.78
0.033	151.6
0.05	153.5
0.067	154.4
0.083	155
0.1	155.4
0.117	155.7
0.133	155.9
0.15	156
0.167	156.2
0.183	156.3
0.2	156.3

ratio	Fmx
1	11.8
0.93548387	8.25
1.06896552	17.9
1.14285714	25
1.22222222	30.2
1.30769231	33.6
1.4	35.6
1.5	36.7
1.60869565	37.1
1.72727273	37

A	Fmx
0.0167	37.1
0.033	38.4
0.05	40.1
0.067	40.5
0.083	40.7
0.1	40.8
0.117	40.9
0.133	41
0.15	41

d) Increasing the temperature shows that the ratio to maximize PX gets smaller and is now about 1.14 to 1 at 675°C. Increasing the temperature does the same thing it just makes even more of the product.

T=675	
ratio	Fpx
1	205.1
1.4	203.6
0.71428571	179.2
1.08498552	207.8
1.14285714	209
1.22222222	208.6

A	Fpx
0.0167	208
0.033	210.6
0.05	215.1
0.067	217.7
0.083	219.3
0.1	220.6
0.117	221.5
0.133	222.3
0.15	222.9
0.167	223.4
0.183	223.8
0.2	224.2
0.217	224.5
0.233	224.8
0.25	225.1
0.267	225.3
0.3	225.6
0.333	226
0.367	226.3
0.4	226.5
0.433	226.7
0.467	226.9
0.5	227
0.55	227.3
0.6	227.4
0.7	227.7
0.8	227.89
0.9	228.1
1	228.3

ratio	Fmx
1	21.5
1.08498552	29.6
1.14285714	34.1
1.22222222	35.6
1.30769231	36
1.4	35.7

Similarly, maximizing MX at the new temperature gets a ratio of 1.31 to 1 and again the concentration increases.

e)No solution will be given.

CDP6-O

Mole Balances:

$$F_P = F_{P0} + r_P W \Rightarrow f(C_P) = C_P - C_{P0} - r_P \tau'$$

$$F_O = r_O W \Rightarrow f(C_O) = C_O - r_O \tau'$$

$$F_A = r_A W \Rightarrow f(C_A) = C_A - r_A \tau'$$

$$F_B = r_B W \Rightarrow f(C_B) = C_B - r_B \tau'$$

$$F_C = r_C W \Rightarrow f(C_C) = C_C - r_C \tau'$$

Rate Laws:

$$r_{A1} = \frac{k_1 C_P C_O^{1/2}}{k_a C_{O_2}^{1/2} + (k_1 + \frac{9}{2}k_2 + \frac{3}{4}k_3)C_P}$$

$k_1 = 688e^{-77{,}500/RT}$ $k_2 = 3.5\times10^{-4}e^{-1312/RT}$ $k_3 = 32.8e^{-72{,}630/RT}$ $k_a = 4\times10^{4}e^{-88{,}000/RT}$

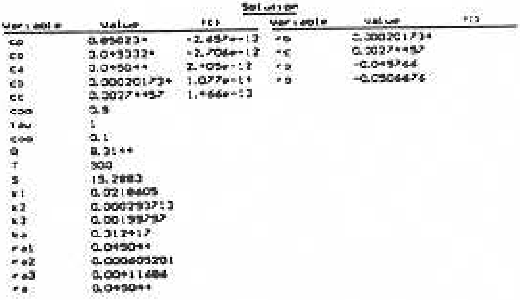
Stoichiometry:

$r_A = r_{A1}$ $r_B = \frac{1}{3}r_{A2}$ $r_C = \frac{2}{3}r_{A3}$ $r_P = -r_{A1} - r_{A2} - r_{A3}$ $r_O = -r_{A1} - \frac{2}{9}r_{A2} - \frac{4}{3}r_{A3}$

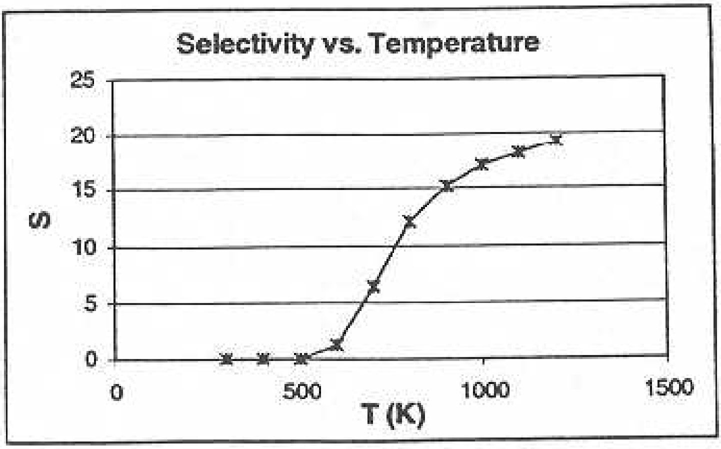
Use these equations in the following POLYMATH program. Vary T and plot the generated values to make the desired graph. Varying the initial concentrations of P and O reveals that the selectivity of acrolein is independent of the feed composition.

CDP6-Q (cont'd)

```
Equations:                                                   Initial value
f(cp)=cp-cpo-rp*tau                                          0.9
f(co)=co-coo-ro*tau                                          0.1
f(ca)=ca-ra*tau                                              0
f(cb)=cb-rb*tau                                              0
f(cc)=cc-rc*tau                                              0
cpo=0.9
tau=1
coo=0.1
R=8.3144
T=900
S=ca/(cb+cc+1e-10)
k1=688*exp(-77500/R/T)
k2=3.5e-4*exp(-1312/R/T)
k3=32.8*exp(-72630/R/T)
ka=4e4*exp(-88000/R/T)
ra1=k1*cp*co**(1/2)/(ka*co**(1/2)+(k1+(9/2)*k2+(3/2)*k3)*
    cp)
ra2=k2*cp*co**(1/2)/(ka*co**(1/2)+(k1+(9/2)*k2+(3/2)*k3)*
    cp)
ra3=k3*cp*co**(1/2)/(ka*co**(1/2)+(k1+(9/2)*k2+(3/2)*k3)*
    cp)
ra=ra1
rb=ra2/3
rc=2/3*ra3
rp=-ra1-ra2-ra3
ro=-ra1-2/9*ra2-4/3*ra3
```



```
                                  Solution
Variable      Value          f()          Variable    Value          f()
cp            0.850234       -2.457e-13   rb          0.000201734
co            0.0493332      -2.706e-12   rc          0.00274457
ca            0.0495044      2.405e-12    rp          -0.049764
cb            0.000201734    1.077e-14    ro          -0.0504476
cc            0.00274457     1.466e-13
cpo           0.9
tau           1
coo           0.1
R             8.3144
T             900
S             15.2883
k1            0.0218405
k2            0.000293713
k3            0.00199797
ka            0.0312417
ra1           0.0495044
ra2           0.000605201
ra3           0.00411686
ra            0.0495044
```



Chapter 7

P7-1. An open-ended problem that requires students to create and original problem and solution.

P7-2. "What if. . ." problem. Part (a) is usually assigned because the student can load the living examples E7-2 directly on to the computer and determine when the PSSH FAILS. Also ask the students to plot the concentration of all intermediates a function of time.

Problems **P7-3**, **P7-4**, **P7-5**, **P7-6**, **P7-7**, and **P7-8**. all involve the PSSH.

P7-3. Is usually assigned in the graduate course.

P7-4. Is the easiest of the PSSH problems. Good reinforcement of PSSH principles.

P7-5. Requires some imagination to realize there is an intermediate NO_3 that is formed.

P7-6. Fairly difficult problem.

P7-7. True problem concerning motor oil degradation. At the undergraduate level only parts **(a)**, **(b)**, and **(c)** are assigned.

P7-8. Just for fun.

Problems **P7-9**, **P7-10**, **P7-11**, **P7-12**, **P7-13**, and **P7-14**. are problems concerning enzymatic reactions.

P7-9. Real data supplied by General Mills. Somewhat open-ended.

P7-10. Good graduate level problem on enzymatic reactions. There is an inconsistency in the journal article.

P7-11. Straight forward problem to calculate V_{max} and K_m.

P7-12. Involves enzyme inhibition. This problem is actually solved on the CD-ROM Professional Book Shelf material.

P7-13. This problem on enzyme substrate inhibition is often assigned because the CSTR has multiple steady states.

P7-14. Fairly straight forward problem to calculate V_{max} and determine which type of enzyme inhibition is occurring.

Problems **P7-15** through **P7-23.** involve polymerization and are currently only assigned at the graduate level. At the undergraduate senior level, one might assigned at the graduate level. At the undergraduate senior level, one might assign **P7-17** and/or **P7-20**. Most problems are quite long.

P7-24. Straight forward reinforcement of Monod kinetics in a batch reactor. Fairly short problem using POLYMATH.

P7-25. A fairly straight forward, but time consuming, problem to plot the data.

P7-26. Straight forward problem using POLYMATH.

P7-27. Very short (Ca. 10 min.) problem.

P7-28. This problem shows an important application of biomass in the petroleum industry. That of bacteria profile modification (BPM). Fairly time consuming yet realistic to plot and analyze all the data.

P7-29. Very short problem to reinforce the principles of Monod kinetics.

P7-30. Fairly straight forward new (1997) problem using POLYMATH. The student should be asked to go beyond what is asked in the problem statement by carrying out a parameter variation and sensitivity analysis.

P7-31. Shows the application of bacteria growth to degrade toxic chemicals. The problem is somewhat open-ended.

P7-32. Straight forward problem using POLYMATH. Could also ask the student to do a sensitivity analysis.

CDP7-A Alternative to **P7-5** and **P7-6**.

CDP7-B Alternative to **P7-6**.

CDP7-C Alternative to **P7-13.**

CDP7-D Fairly straight forward.

CDP7-E Assigned at the graduate level.

CDP7-F Seldom assigned.

CDP7-G Advanced problem on bacterial growth.

CDP7-H Not assigned at undergraduate level.

CDP7-I Assigned every so often.

CDP7-J Fairly straight foward.

Summary

		Assigned	Alternates	Difficulty	Time	Solution Given
	P7-1					No
●	P7-2			SF	70	Partial(a)
●	P7-3	AA	4,5,6	FSF	50	Yes
	P7-4	AA	3,5	SF	40	Yes
●	P7-5	AA	6,7,8,A,B	SF	30	Yes
	P7-6	AA	5,7,8,A,B	FSF	35	Yes
	P7-7	AA	5,6,8,A,B	FSF	70	Yes
	P7-8	AA	5,6,7,A,B	SF	20	Yes
	P7-9	G		MD	60	Yes
	P7-10	G		MD	45	Yes
●	P7-11	AA	14	SF	30	Yes
	P7-12	AA	13,14,C,D	SF	50	Yes
	P7-13	O	12,14,C,D	FSF	45	Yes
	P7-14	O	12,13,C,D	FSF	50	Yes
	P7-15	G	21	SF	45	Yes
	P7-16	G		FSF	75	Yes
	P7-17	G	23,E	MD	90	Yes
	P7-18	G	19,22	MD	90	Yes
	P7-19	G	18,22	MD	60	Yes
	P7-20	G		FSF	60	Yes
	P7-21	G	15	FSF	75	Yes
	P7-22	G	19	MD	90	Yes
	P7-23	G	17	MD	90	Yes
●	P7-24	AA	26,30,32,J	SF	40	Yes
	P7-25	O	28	FSF	60	Yes
	P7-26	AA	24,30,32,J	SF	40	Yes
	P7-27	O	29	SF	40	Yes
	P7-28	I	25	FSF	60	Yes
	P7-29	O	27	SF	40	Yes
	P7-30	AA	24,26,37,J	SF	30	Yes
	P7-31	G		MD	50	Yes
	P7-32	AA	24,26,30,J	FSF	60	Yes
	CDP7-A	AA	5,6,7,8,B	SF	40	Yes
	CDP7-B	AA	5,6,7,8,A	SF	40	Yes
	CDP7-C	AA	12,13,14,D	SF	50	Yes
	CDP7-D	AA	12,13,14,C	FSF	50	Yes
	CDP7-E	G	17,23	MD	60	Yes
	CDP7-F	G		MD	75	Yes
	CDP7-G	O		MD	60	Yes
	CDP7-H	I		MD	70	Yes
	CDP7-I	O		MD	60	Yes
	CDP7-J	AA	24,26,30,32	FSF	45	Yes

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-7

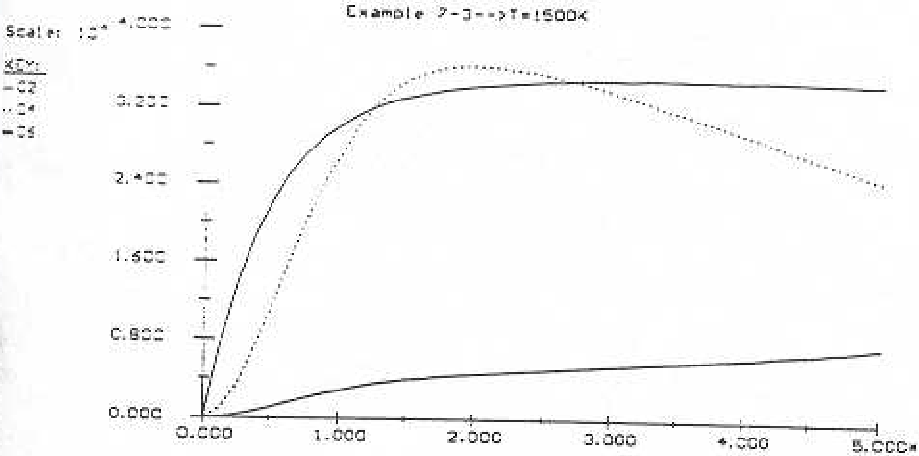
	PSSH	Enzymes	Polymerization	Cell Growth
	2(a),3,4,5,6,7,8	9,10,11,12,13,14	16,17,18,19,20, 21,22,23	24,25,26,27,28
Open-ended	2(a)	10		31
Straight forward	4,7(a),(b),(c)	11		24,29,30
Fairly Straight Forward				
More Difficult				
Parameter Variation				

Chapter 7

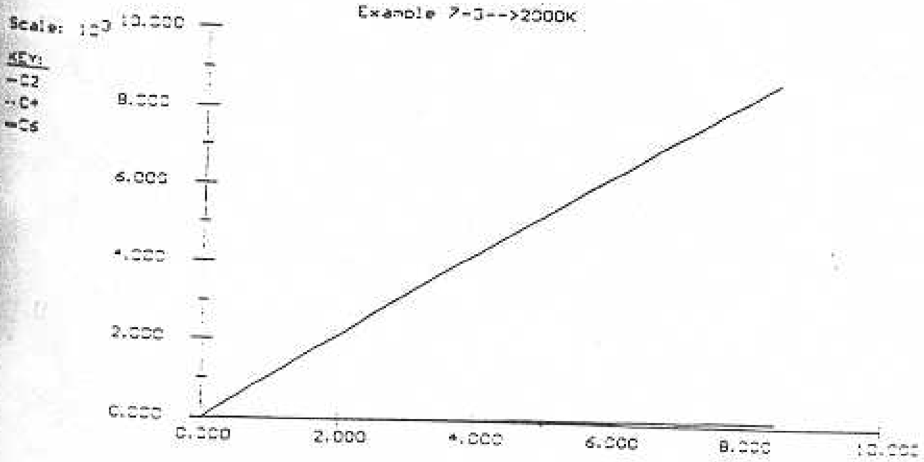
P7-1 No solution will be given.

P7-2

(a) Use the same POLYMATH program as Example 7-2 with the appropriate temperatures. Generate the following graphs:



For T = 1500 K, steady-state is not reached, so PSSH is not valid.



For T = 2000 K, steady-state is not reached, so PSSH is not valid.

P7-3: Burning

$$\left.\begin{array}{l} O_2 \xrightarrow{k_1} 2O\cdot \\ O\cdot + H_2O \xrightarrow{k_2} 2OH\cdot \\ CO\cdot + OH\cdot \xrightarrow{k_3} CO_2 + H\cdot \\ H\cdot + O_2 \xrightarrow{k_4} OH\cdot + O\cdot \end{array}\right\} \quad \text{Burning of Model Compound}$$

$$\left.\begin{array}{l} HCl + H\cdot \xrightarrow{k_5} H_2 + Cl\cdot \\ H\cdot + Cl\cdot \xrightarrow{k_6} HCl \end{array}\right\} \quad \text{Retardation}$$

$$\boxed{-r_{CO} = r_{CO_2} = k_3(CO)(OH\cdot)}$$

$$r_{O\cdot} = 0 = 2k_1(O_2) - k_2(O\cdot)(H_2O) + k_4(H\cdot)(O_2)$$

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 $(O\cdot)$

$$(OH\cdot) = \frac{2k_2(H_2O)\frac{2k_1(O_2) + k_4(H\cdot)(O_2)}{k_2(H_2O)} + k_4(H\cdot)(O_2)}{k_3(CO)}$$

$$(OH\cdot) = \frac{4k_1(O_2) + 3k_4(H\cdot)(O_2)}{k_3(CO)}$$

$$-r_{CO} = r_{CO_2} = k_3(CO)(OH\cdot)$$

$$\boxed{-r_{CO} = 4k_1(O_2) + 3k_4(H\cdot)(O_2)}$$

$$r_{H\cdot} = \overbrace{k_3(CO)(OH\cdot)}^{r_{CO_2}} - k_4(H\cdot)(O_2) - k_5(HCl)(H\cdot) - k_6(Cl\cdot)(H\cdot)$$

$$r_{Cl\cdot} = 0 = k_5(HCl)(H\cdot) - k_6(H\cdot)(Cl\cdot)$$

P7-3 (cont'd)

$$Cl\cdot = \frac{k_5(HCl)}{k_6}$$

$$r_{H\cdot} = 4k_1(O_2) + 3k_4(H\cdot)(O_2) - k_4(H\cdot)(O_2) - 2k_5(HCl)(H\cdot)$$

$$\boxed{r_{H\cdot} = 4k_1(O_2) + 2[k_4(O_2) - k_5(HCl)](H\cdot)}$$

$$r_{H\cdot} = a + b(H\cdot)$$

Constant Volume

$$e^{-bt}\frac{dC_{H}\cdot}{dt} - C_{H}\cdot * b * e^{-bt} = ae^{-bt} \qquad \frac{dC_{H}\cdot}{dt} = a + bC_{H}\cdot$$

Using the integrating factor

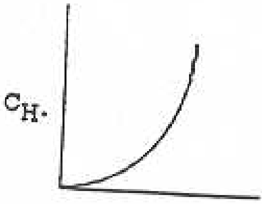
$$\frac{d(e^{-bt}C_{H\cdot})}{dt} = a\,e^{-bt}$$

$$C_{H\cdot} = -\frac{a}{b} + K_1\,e^{bt}$$

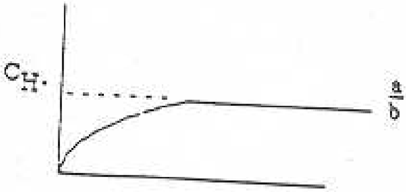
$t = 0 \quad C_{H\cdot} = 0$ therefore $K_1 = \frac{a}{b}$

$$\boxed{C_{H\cdot} = \frac{a}{b}\left[e^{bt} - 1\right]}$$

If $k_4(O_2) > k_5(HCl)$, then "b" is positive



If $k_5(HCl) > k_4(O_2)$, then "b" is negative



P7-3 (cont'd)

$$\frac{dC_{CO}}{dt} = r_{CO} = -\left[4k_1(O_2) + 3k_4(H\cdot)(O_2)\right]$$

$$= -a - p(C_{H\cdot})$$

$$= -a - p\left[\frac{a}{b}e^{bt} - 1\right]$$

$p(C_{H\cdot}) = 3k_4(O_2)C_{H\cdot}$

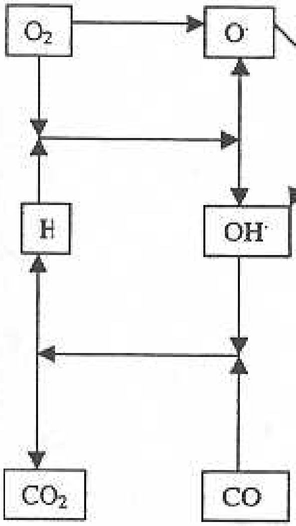
$p = 3k_4(O_2)$

$a = 4k_1(O_2)$

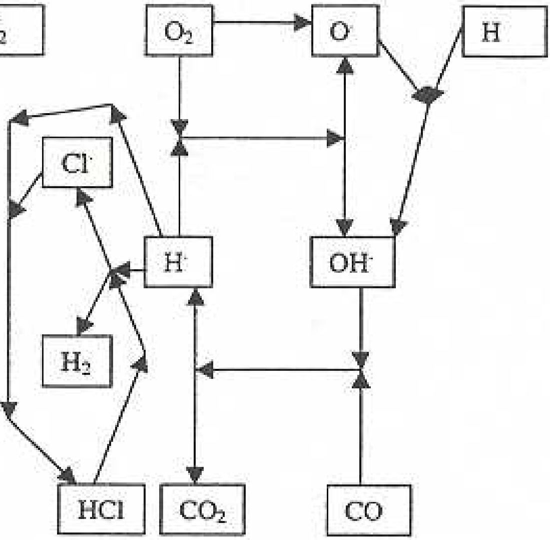
$t = 0 \quad C_{CO} = C_{CO,0}$

$$\boxed{C_{CO} = C_{CO,0} - at - p\frac{a}{b^2}e^{bt} + pt}$$

Reaction Pathway w/o HCL



Reaction Pathway with HCL



P7-4 The reaction sequence is:

$$CH_3CHO \xrightarrow{k_1} CH_3\cdot + CHO\cdot$$

$$CH_3\cdot + CH_3CHO \xrightarrow{k_2} CH_3\cdot + CO + CH_4$$

$$CHO\cdot + CH_3CHO \xrightarrow{k_3} CH_3\cdot + 2CO + H_2$$

$$2CH_3\cdot \xrightarrow{k_4} C_2H_6$$

$r_1 = k_1 C_{AC}$

$r_2 = k_2 C_{AC} C_{CH_3\cdot}$

$r_3 = k_3 C_{CHO\cdot} C_{AC}$

$r_4 = k_4 C_{CH_3\cdot}^2$

P7-4 (cont'd)

$$-r_{AC} = r_1 + r_2 + r_3 = k_1 C_{AC} + k_2 C_{AC} C_{CH_3\cdot} + k_3 C_{AC} C_{CHO\cdot}$$

$$= C_{AC}\left[k_1 + k_2 C_{CH_3\cdot} + k_3 C^2_{CHO\cdot}\right] \qquad (1)$$

Active intermediates: $CH_3\cdot$, $CHO\cdot$

$$-r_{CH_3} = -r_1 + r_2 - r_2 - r_3 + \frac{1}{2} r_4 = 0$$

$$= -k_1 C_{AC} + k_2 C_{AC} C_{CH_3} - k_3 C_{CHO\cdot} C_{AC} - k_2 C_{AC} C_{CH_3\cdot} + \frac{1}{2} k_4 C^2_{CH_3\cdot}$$

$$= -k_1 C_{AC} + k_2 C_{AC} C_{CH_3} - k_3 C_{CHO\cdot} C_{AC} + \frac{1}{2} k_4 C^2_{CH_3\cdot} \qquad (2)$$

$$-r_{CHO\cdot} = -r_1 + r_3 = -k_1 C_{AC} + k_3 C_{CHO\cdot} C_{AC} = 0$$

$$\text{or} = C_{CHO\cdot} = \frac{k_1}{k_3} \qquad (3)$$

Substituting (3) in (2) gives:

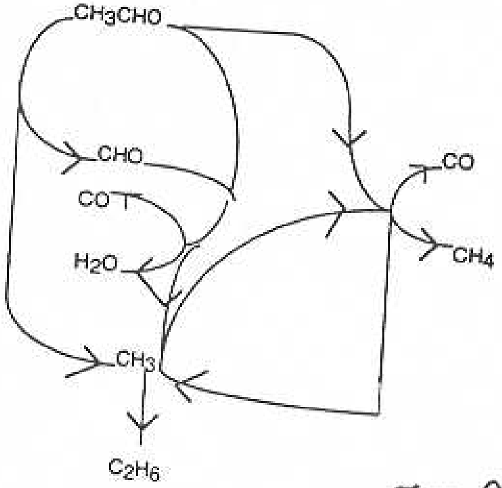
$$\frac{k_4 C^2_{H_3\cdot}}{2} = k_1 C_{AC} + k_3 C_{CHO\cdot} C_{AC} = k_1 C_{AC} + k_1 C_{AC} = 2k_1 C_{AC}$$

$$\text{or } C_{CH_3\cdot} = 2(C_{AC})^{1/2}\left(\frac{k_1}{k_4}\right)^{1/2}$$

$$-r_{AC} = C_{AC}\left[k_1 + 2k_2\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}}(C_{AC})^{\frac{1}{2}} + \frac{k_1^2}{k_3}\right]$$

$$= k_1 C_{AC}\left[1 + \frac{2k_2}{\sqrt{k_1 k_4}}\sqrt{C_{AC}} + \frac{k_1}{k_3}\right]$$

With $\frac{k_2}{\sqrt{k_1 k_4}} >> 1$ or $C_{AC} >> 1$, $-r_{AC} \, \alpha \, (C_{AC})^{3/2}$ as suggested by equation (7-2).



P7-5

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.

$$NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3 \qquad r_1 = k_1[NO][O_2] - k_{-1}[NO_3]$$

$$NO_3 + NO \xrightarrow{k_2} 2NO_2 \qquad r_2 = k_2[NO][NO_3]$$

$$-r_{NO} = -r_1 - r_2$$

$$= -k_1[NO][O_2] + k_{-1}[NO_3] - k_2[NO][NO_3]$$

$$r_{NO_3} = r_1 - r_2$$

$$= k_1[NO][O_2] - k_{-1}[NO_3] - k_2[NO][NO_3]$$

$$[NO_3] = \frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$$

$$-r_{NO} = -k_1[NO][O_2] + (k_{-1} - k_2[NO])\frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$$

$$= \frac{-k_1k_2[NO]^2[O_2] - k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[NO]}$$

$$= \frac{-2k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[NO]}$$

$$k_{-1} >> k_2[NO]$$

$$-r_{NO} = -\frac{2k_1k_2}{k_{-1}}[NO]^2[O_2]$$

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 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:

$$NO + O_2 \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} NO_3 \qquad r_1 = k_1[NO][O_2] - k_{-1}\,NO_3$$

$$NO_3 + NO \xrightarrow{k_2} 2NO_2 \qquad r_2 = k_2[NO][NO_3]$$

$$r_{NO} = -r_1 - r_2 = -k_1[NO][O_2] + k_{-1}[NO_3] - k_2[NO][NO_3]$$

$$-r_{NO_3} \equiv 0 = r_1 - r_2 = k_1[NO][O_2] - k_{-1}[NO_3] - k_2[NO][NO_3]$$

$$\text{or } [NO_3] = \frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}\ ;\ -r_{NO} = -k_1[NO][O_2] + (k_{-1} - k_2[NO])\frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$$

$$r_{NO} = \frac{-k_{-1}k_1[NO][O_2] - k_1k_2[NO]^2[O_2] + k_1k_2[NO][O_2] - k_{-1}k_1[NO]^2[O_2]}{-k_1 + k_2[NO]}$$

$$r_{NO} = \frac{-2k_1k_2[NO]^2[O_2]}{k_1 + k_2[NO]} \quad \text{with } k_{-1} >> k_2[NO],\ r_{NO} = \frac{-2k_1k_2[NO]^2[O_2]}{k_{-1}}$$

If $k_i \,\alpha\, \exp\left(\frac{-E_i}{RT}\right)$ Then for the overall activation energy to be negative,

$$\ln\left(\frac{k_1k_2}{k_{-1}}\right) = \frac{-E_1 + E_2 - E_{-1}}{RT} = E_{OV} < 0 \text{ or } E_1 + E_2 > E_{-1}$$

P7-6 Given decomposition of O^3 in an inert gas:

$$-r_{O_3} = \left[\frac{k[O_3]^2[M]}{[O_2][M] + k^1[O_3]}\right]$$

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:

$$O_3 + O \rightarrow 2O_2$$

$$O_2 + O \rightarrow O_3$$

P7-6 (cont'd)

O_3 and M appear in the numerator. Applying rule 1 of Table 7-1 to O_3: $O_3 \rightarrow O_2 + O\cdot$ If the second and third equations are combined, and M is added to each side of the equation:

$$M + O_3 \underset{k2}{\overset{k1}{\rightleftarrows}} O_2 + O\cdot + M$$

$$O_3 + O\cdot \xrightarrow{k3} 2O_2$$

A mechanism is proposed which satisfies all the rules of thumb:

$$r_{O_3} = -r_1 + r_2 - r_3 = -k_1[M][O_3] + k_2[O_2][O\cdot][M] - k_3[O\cdot][O_3] = 0$$

$$r_{O\cdot} = r_1 - r_2 - r_3 = k_1[M][O_3] - k_2[O_2][O\cdot][M] - k_3[O\cdot][O_3] = 0$$

$$[O\cdot] = \frac{k_1[M][O_3]}{k_2[O_2][M] + k_3[O_3]}$$

$$\text{Then } r_{O_3} = -k_1[M][O_3] + \frac{k_1 k_2 [M]^2 [O_3][O_2] - k_1 k_3 [M][O_3]^2}{k_2[O_2][M] + k_3[O_3]}$$

$$r_{O_3} = \frac{-k_1 k_2 [M]^2 [O_3][O_2] + k_1 k_2 [M]^2 [O_3][O_2] - 2k_1 k_3 [M][O_3]^2}{k_2[O_2][M] + k_3[O_3]}$$

$$r_{O_3} = \frac{\frac{-2k_1 k_3}{k_2}[M][O_3]^2}{[O_2][M] + \frac{k_3}{k_2}[O_3]} \quad \text{with } k = \frac{2k_1 k_3}{k_2} \text{ and } k^1 = \frac{k_3}{k_2}$$

P7-7

$$\left.\begin{array}{l}
\left.\begin{array}{l}
(1)\ I_2 \xrightarrow{k_0} 2I\cdot \\
(2)\ I\cdot + RH \xrightarrow{k_i} R\cdot + HI
\end{array}\right\} \text{INITIATION} \\
\left.\begin{array}{l}
(3)\ R\cdot + O_2 \xrightarrow{k_{p_1}} RO_2\cdot \\
(4)\ RO_2\cdot + RH \xrightarrow{k_{p_2}} ROOH + R\cdot
\end{array}\right\} \text{PROPAGATION} \\
\left.(5)\ RO_2\cdot + RO_2\cdot \xrightarrow{k_t} \text{INACTIVE PRODUCTS}\right\} \text{TERM.}
\end{array}\right\} \begin{array}{l}\text{LOW TEMPERATURES}\\ \text{NO ANTIOXIDANTS}\end{array}$$

$$(6)\ ROOH \xrightarrow{k_{i_3}} RO\cdot + \cdot OH$$

INITIATION
PROPOGATION

HIGHER TEMPERATURES
NO ANTIOXIDANTS

$$(7)\ RO\cdot + RH \xrightarrow{k_{p_4}} ROH + R\cdot$$

$$(8)\ \cdot OH + RH \xrightarrow{k_{p_5}} HOH + R\cdot$$

P7-7 (cont'd)

LOW TEMPERATURES - NO ANTIOXIDANT

$$\frac{d[I\cdot]}{dt} = r_i = 2k_0[I_2] - k_i[I\cdot][RH] \qquad \text{(A)}$$

$$\frac{d[RH]}{dt} = -k_i[I\cdot][RH] - k_{p_2}[RO_2\cdot][RH] \qquad \text{(B)}$$

$$\frac{d[RO_2\cdot]}{dt} = k_{p_1}[R\cdot][O_2] - k_{p_2}[RO_2\cdot][RH] - k_t[RO_2\cdot]^2 \qquad \text{(C)}$$

$$\frac{d[R\cdot]}{dt} = k_i[RH][I\cdot] - k_{p_1}[R\cdot][O_2] + k_{p_2}[RO_2\cdot][RH] \qquad \text{(D)}$$

PSSA . . . . $\frac{d[\text{RADICALS}]}{dt} = 0$

(A) = 0 $\quad r_i = 0 \quad \boxed{[I\cdot] = \frac{2k_0[I_2]}{k_i[RH]}}$

$$\frac{d[R\cdot]}{dt} = 0 = k_i[RH]\underset{\boxed{\frac{2k_0[I_2]}{k_i[RH]}}}{\underset{\uparrow}{[I\cdot]}} - k_{p_1}[R\cdot][O_2] + k_{p_2}[RO_2\cdot][RH]$$

$\boxed{[R\cdot] = \frac{2k_0[I_2] + k_{p_2}[RO_2\cdot][RH]}{k_{p_1}[O_2]}}$: still need to eliminate $[RO_2\cdot]$

$$\frac{d[RO_2\cdot]}{dt} = 0 = k_{p_1}[R\cdot][O_2] - k_{p_2}[RO_2\cdot][RH] - k_t[RO_2\cdot]^2$$

Substitute for $[R\cdot]$:

$$2k_0[I_2] - k_t[RO_2\cdot]^2 = 0$$

$$\boxed{[RO_2\cdot] = \sqrt{\frac{2k_0}{k_t}[I_2]}}$$

Now substitute the expressions for the radicals into $\frac{d[RH]}{dt}$ the expression for the degradation of the oil.

$$\frac{d[RH]}{dt} = -k_i\underset{\underset{[I\cdot]}{\downarrow}}{\left[\frac{2k_0[I_2]}{k_i[RH]}\right]}[RH] - k_{p_2}\left[\frac{2k_0[I_2]}{k_t}\right]^{1/2}[RH]$$

$$= 2k_0[I_2] - \left[\frac{2k_{p_2}^2[k_0]}{k_t}\right]^{1/2}[I_2]^{1/2}[RH]$$

P7-7 (cont'd)

$$\frac{d[R\bullet]}{dt} = k_i[RH][I\bullet] - k_{P_1}[R\bullet][O_2] + k_{P_2}[RO_2\bullet][RH] \quad \text{(same)}$$

$$\frac{d[A\bullet]}{dt} = k_{A1}[AH][RO_2\bullet] - k_{A2}[A\bullet][RO_2\bullet]$$

$$\frac{d[RH]}{dt} = -k_i[I\bullet][RH] - k_{P_2}[RO_2\bullet][RH]$$

Apply PSSH:

$$\frac{d[I\bullet]}{dt} = 0 \qquad \boxed{[I\bullet] = \frac{2k_0[I_2]}{k_i[RH]}}$$

$$\frac{d[A\bullet]}{dt} = 0 \Rightarrow \boxed{[A\bullet] = \frac{k_{A1}[AH]}{k_{A2}}}$$

$$\frac{d[R\bullet]}{dt} = 0 \qquad \boxed{[R\bullet] = \frac{2k_0[I_2] + k_{P_2}[RO_2\bullet][RH]}{k_{P_1}[O_2]}}$$

$$\frac{d[RO_2\bullet]}{dt} \cong 0 \quad 2k_0[I_2] - k_t[RO_2\bullet]^2 - 2(k_{A1}[AH][RO_2\bullet])$$

$$\therefore\ -k_t[RO_2\bullet]^2 - 2k_{A1}[AH][RO_2\bullet] + 2k_0[I_2] = 0$$

$$k_t[RO_2\bullet]^2 + (2k_{A1}[AH])[RO_2\bullet] - 2k_0[I_2] = 0 \qquad \text{Quadradtic in } [RO_2\bullet]$$

$$\boxed{[RO_2\bullet] = \frac{-2k_{A1}[AH] \pm \sqrt{(2k_{A1}[AH])^2 + 8k_t k_0[I_2]}}{2k_t}} \qquad [RO_2\bullet] \text{ MUST be positive}$$

Now (FINALLY!), let's substitute into $\frac{d[RH]}{dt}$:

$$\frac{d[RH]}{dt} = -k_i[I\bullet][RH] - k_{P_2}[RO_2\bullet][RH]$$

$$\boxed{\frac{d[AH]}{dt} = -k_{A1}[AH][RO_2\bullet] = -k_{A1}[AH]\frac{-2k_{A1}[AH] + \sqrt{(2k_{A1}[AH])^2 + 8k_t k_0[I_2]}}{2k_t}}$$

$$\boxed{\frac{d[RH]}{dt} = -2k_0[I_2] - k_{P_2}[RH]\frac{-2k_{A1}[AH] + \sqrt{(2k_{A1}[AH])^2 + 8k_t k_0[I_2]}}{2k_t}}$$

P7-7 (cont'd)

ODE to be solved- low temperatures, no antioxidant:

$$\boxed{-\frac{d[RH]}{dt} = 2k_0[I_2] + \left[\frac{2k_{P_2}^2[k_0]}{k_t}\right]^{1/2}[I_2]^{1/2}[RH]}$$

HIGH TEMPERATURE, NO ANTIOXIDANT

$$\frac{d[RH]}{dt} = -k_i[I\cdot] - k_{P_2}[RO_2\cdot][RH] - k_{P_4}[RO\cdot][RH] - k_{P_5}[OH\cdot][RH]$$

$$\frac{d[I\cdot]}{dt} = 2k_0[I_2] - k_i[RH][I\cdot] \overset{\text{PSSA}}{=} 0 \Rightarrow \boxed{[I\cdot] = \frac{2k_0[I_2]}{k_i[RH]}}$$

$$\frac{d[RO_2\cdot]}{dt} = k_{P_1}[O_2][R\cdot] - k_{P_2}[RO_2\cdot][RH] - k_t[RO_2\cdot]^2$$

$$\frac{d[R\cdot]}{dt} = k_i[I\cdot][RH] - k_{P_1}[R\cdot][O_2] + k_{P_2}[RO_2\cdot][RH] + k_{P_4}[RO\cdot][RH] + k_{P_5}[OH\cdot][RH]$$

$$\frac{d[RO\cdot]}{dt} = k_{i_3}[ROOH] - k_{P_4}[RO\cdot][RH]$$

$$\frac{d[OH\cdot]}{dt} = k_{i_3}[ROOH] - k_{P_5}[OH\cdot][RH]$$

USE PSSA: $\frac{d[X\cdot]}{dt} = 0$

$$\frac{d[RO\cdot]}{dt} = 0 \Rightarrow \boxed{[RO\cdot] = \frac{k_{i_3}[ROOH]}{k_{P_4}[RH]}}$$

$$\frac{d[R\cdot]}{dt} = 0 \Rightarrow [R\cdot] = \frac{k_i[I\cdot][RH] + k_{P_2}[RO_2\cdot][RH] + k_{P_4}[RO\cdot][RH] + k_{P_5}[OH\cdot][RH]}{k_{P_1}[O_2]}$$

$$\frac{d[OH\cdot]}{dt} = 0 \Rightarrow \boxed{[OH\cdot] = \frac{k_{i_3}[ROOH]}{k_{P_5}[RH]}}$$

$$\frac{d[RO_2\cdot]}{dt} = 0 = k_{p_1}[O_2][R\cdot] - k_{p_2}[RO_2\cdot][RH] - k_t[RO\cdot]^2$$

Substitute for [R·]:

$$0 = 2k_0[I_2] + k_{p_4}[OH\cdot][RH] + k_{p_5}[OH\cdot][RH] - k_t[RO\cdot]^2$$

Now substitute for [RO·] and [OH·]:

$$0 = 2k_0[I_2] + k_{i_3}[ROOH] + k_{i_3}[ROOH] - k_t[RO_2\cdot]^2$$

$$[RO_2\cdot] = \sqrt{\frac{2k_0[I_2] + 2k_{i_3}[ROOH]}{k_t}}$$

P7-7 (cont'd)

Now back to the $\frac{d[RH]}{dt}$ equation:

$$\frac{d[RH]}{dt} = -2k_0[I_2] - k_{P_2}[RH]\left[\frac{2k_0[I_2] + 2k_{i_3}[ROOH]}{k_t}\right]^{1/2} - k_{i_3}[ROOH] - k_{i_3}[ROOH]$$

or . . . .

$$\frac{d[RH]}{dt} = -2k_0[I_2] - 2k_{i_3}[ROOH] - k_{P_2}[RH]\left[\frac{2k_0[I_2] + 2k_{i_3}[ROOH]}{k_t}\right]^{1/2}$$

Now let's look at $\frac{d[ROOH]}{dt}$

$$\frac{d[ROOH]}{dt} = k_{P_2}[RO_2\bullet][RH] - k_{i_3}[ROOH]$$

$$\boxed{\frac{d[ROOH]}{dt} = k_{P_2}[RH]\left[\frac{2k_0[I_2] + 2k_{i_3}[ROOH]}{k_t}\right]^{1/2} - k_{i_3}[ROOH]}$$

Remember, we also have:

$$\frac{d[I_2]}{dt} = -k_0[I_2]$$

$$\text{or } [I_2] = [I_2]_0 e^{-k_0 t}$$

Now, let's look at the situation with anti-oxidants present:

LOW TEMPERATURES WITH ANTI-OXIDANTS

Additional reactions:

$$(9) \qquad RO_2\bullet + AH \xrightarrow{k_{A1}} ROOH + A\bullet$$

$$(10) \qquad A\bullet + RO_2\bullet \xrightarrow{k_{A2}} \text{inactive products}$$

Equations:

$$\frac{d[I\cdot]}{dt} = 2k_0[I_2] - k_i[I\cdot][RH]$$

$$\frac{d[RO_2\cdot]}{dt} = k_{P_1}[R\cdot][O_2] - k_{P_2}[RO_2\cdot]^2 - k_{A}[RO_2\cdot][AH] - k_{A_2}[A\cdot][RO_2\cdot]$$

P7-7 (cont'd)

HIGH TEMPERATURES WITH ANTIOXIDANTS

$$\frac{d[I\bullet]}{dt} \cong 0 \Rightarrow \boxed{[I\bullet] = \frac{2k_0[I_2]}{k_i[RH]}}$$

$$\frac{d[RO\bullet]}{dt} \cong 0 = k_{i_3}[ROOH] - k_{p_4}[RO\bullet][RH] \Rightarrow \boxed{[RO\bullet] = \frac{k_{i_3}[ROOH]}{k_{p_4}[RH]}}$$

$$\frac{d[OH\bullet]}{dt} \cong 0 = k_{i_3}[ROOH] - k_{p_5}[RH][OH\bullet] \quad \boxed{[OH\bullet] = \frac{k_{i_3}[ROOH]}{k_{p_5}[RH]}}$$

$$\frac{d[R\bullet]}{dt} = k_i[I\bullet][RH] - k_{p_1}[R\bullet][O_2] + k_{p_2}[RO_2\bullet][RH] + k_{p_4}[RO\bullet][RH] + k_{p_5}[OH\bullet][RH]$$

$$\frac{d[RO_2\bullet]}{dt} = k_{p_1}[O_2][R\bullet] - k_{p_2}[RO_2\bullet][RH] - k_t[RO_2\bullet]^2 - k_{A1}[RO_2\bullet][AH] - k_{A2}[RO_2\bullet][A\bullet]$$

$$\frac{d[A\bullet]}{dt} = k_{A1}[AH][RO_2\bullet] - k_{A2}[RO_2\bullet][A\bullet]$$

Apply PSSA: $\frac{d[R\bullet]}{dt} = 0$

$$\boxed{[R\bullet] = \frac{2k_0[I_2] + k_{p_2}[RO_2\bullet][RH] + k_{p_4}[RO\bullet][RH] + k_{p_5}[OH\bullet][RH]}{k_{p_1}[O_2]}}$$

$$\frac{d[A\bullet]}{dt} = 0 \qquad [A\bullet] = \frac{k_{A1}[AH][RO_2\bullet]}{k_{A2}[RO_2\bullet]} = \boxed{\frac{k_{A1}[AH]}{k_{A2}} = [A\bullet]}$$

Now substitute into $\frac{d[RO_2\bullet]}{dt}$ expression:

$$2k_0[I_2] + k_{p_4}[RO\bullet][RH] + k_{p_5}[OH\bullet][RH] - k_t[RO_2\bullet]^2 - 2(k_{A1}[RO_2\bullet][AH]) = 0$$

$$2k_0[I_2] + 2(k_{i_3}[ROOH]) - k_t[RO_2\bullet]^2 + 2(k_{A1}[RO_2\bullet][AH]) = 0$$

$$k_t[RO_2\bullet]^2 + 2(k_{A1}[RO_2\bullet][AH]) - [2(k_0[I_2] + k_{i_3}[ROOH])] = 0$$

$$[RO_2\bullet] = \frac{-2k_{A1}[AH] \pm \sqrt{4(k_{A1}[AH])^2 + 8k_t[k_0[I_2] + k_{i_3}[ROOH]]} = 0}{2k_t}$$

P7-7 (cont'd)

$$\therefore \boxed{[RO_2\bullet] = \frac{-2k_{A1}[AH] + \sqrt{4(k_{A1}[AH])^2 - 8k_t\{k_0[I_2] + k_{i_3}[ROOH]\}} = 0}{2k_t}}$$

Now finally,

$$\frac{d[RH]}{dt} = -k_i[I\bullet][RH] - k_{P_2}[RO_2\bullet][RH] - k_{P_4}[RO\bullet][RH] - k_{P_3}[OH\bullet][RH]$$

$$\frac{d[RH]}{dt} = -2k_0[I_2] - 2k_{i_3}[ROOH] - k_{P_2}[RH]\left[\frac{-2k_{A1}[AH] + \sqrt{4(k_{A1}[AH])^2 + 8k_t\{k_0[I_2] + k_{i_3}[ROOH]\}}}{2k_t}\right]$$

$$\frac{d[AH]}{dt} = -k_{A1}[AH][RO_2\bullet] = -k_{A1}[AH]\left[\frac{-2k_{A1}[AH] + \sqrt{4(k_{A1}[AH])^2 - 8k_t\{k_0[I_2] + k_{i_3}[ROOH]\}}}{2k_t}\right]$$

$$\frac{d[ROOH]}{dt} = k_{P_2}[RO_2\bullet][RH] - k_{i_3}[ROOH] + k_{A1}[RO_2\bullet][AH]$$

$$\frac{d[ROOH]}{dt} = -k_{i_3}[ROOH] + \{k_{P_2}[RH_2\bullet][RH] + k_{A1}[AH]\}[RO_2\bullet]$$

Finally:

$$\boxed{\frac{d[ROOH]}{dt} = -k_{i_3}[ROOH] + \{k_{P_2}[RH] + k_{A1}[AH]\}\frac{-2k_{A1}[AH] \pm \sqrt{4(k_{A1}[AH])^2 + 8k_t\{k_0[I_2] + k_{i_3}[ROOH}}{2k_t}}$$

P7-8 Given: Illness mechanism

$$H \xrightarrow{k_1} I \qquad r_1 = k_1[H] \qquad \text{(Healthy person gets ill)}$$

$$I + H \xrightarrow{k_2} 2I \qquad r_2 = k_2[H][I] \qquad \text{(healthy person contracts disease from ill person)}$$

$$I \xrightarrow{k_3} H \qquad r_3 = k_3[I] \qquad \text{(Ill person gets well)}$$

$$I \xrightarrow{k_4} D \qquad r_4 = k_4[I] \qquad \text{(Ill person dies)}$$

$$r_D = k_4[I]$$

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 $[I] = \dfrac{k_1[H]}{(k_3 + k_4) - k_2[H]}$

$\therefore\ r_D = \dfrac{k_1 k_4 [H]}{k_3 + k_4 - k_2[H]}$ at $[H] = \dfrac{k_3 + k_4}{k_2}$ the death rate becomes infinite.

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.

P7-9

a) Starting with the design equation for a batch reactor

$$\frac{dC_P}{dt} = r_P$$

$$r_P = kC$$

$$C = (C_{S0} - C_P)\left(1 - \frac{C_P}{1.4}\right)$$

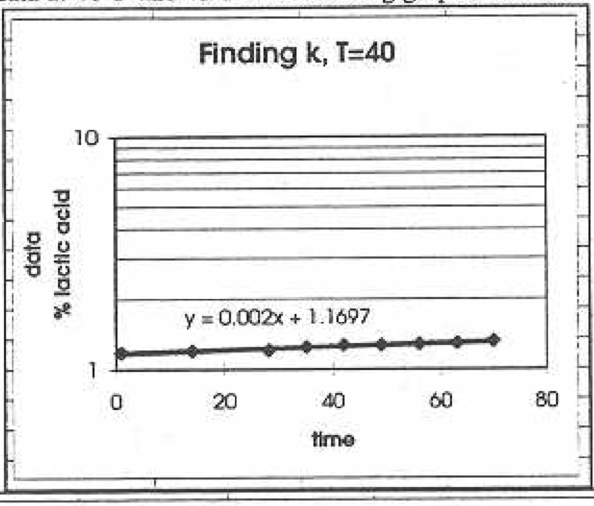
$$\frac{dC_P}{dt} = k\left[C_{S0} - C_P\right]\left[1 - \frac{C_P}{1.4}\right]$$

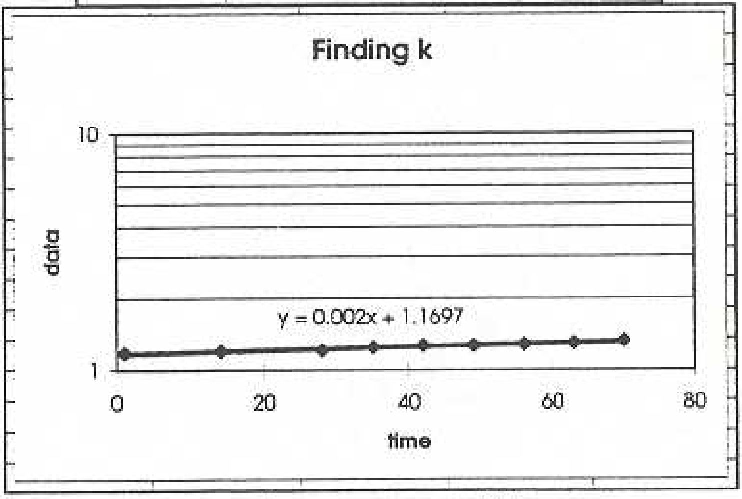
integrating

$$\ln\left(.933\frac{C_P - 1.5}{C_P - 1.4}\right) = 7.14kt + C$$

P7-9 cont'd

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:

$$\ln\left(.933\frac{C_p - 1.5}{C_p - 1.4}\right) = 7.14kt + C$$

$$E = -\frac{R\ln(k_2/k_1)}{1/T_2 - 1/T_1} = 108120\frac{\text{Btu}}{\text{mol}}$$

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 cont'd

c)

$$k_{77} = k_{45}10^\wedge\left(\frac{-E}{2.3R}\left(\frac{1}{536}-\frac{1}{504}\right)\right) = .0023$$

C = 1.211
t = 2 days

d) No solution will be given.

P7-10

Michaelis-Menton Kinetics:

$$-r_s = \frac{V_{max}C_S}{K_m + C_S}$$

$$K_m = 6.2\times10^{-2}\ \text{ml/ml} = 6.2\%$$

$$V_{max} = 5.6\frac{\mu\text{mol}}{\text{ml}\cdot\text{min}} \qquad E = 40\ \text{mg}$$

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:

$$C_T = \frac{\text{density}}{\text{MW}} = \frac{0.9}{300} = 3\times10^{-3}\ \text{mol/ml} = 3\times10^{3}\ \mu\text{mol/ml}$$

$$C_S = C_T C_{S\%}$$

$$\Rightarrow \int_{1.4}^{0.2} -\frac{K_m + C_{S\%}}{C_{S\%}}dC_{S\%} = \int_0^t \frac{V_{max}}{C_T}dt = \int_0^t \frac{5.6\times10^{-3}}{3}dt$$

$$\Rightarrow K_m\ln\left(\frac{1.4}{0.2}\right) + (1.4-0.2) = \frac{5.6\times10^{-3}}{3}t$$

$$\Rightarrow t = \frac{6.2\ln(7)+1.2}{5.6\times10^{-3}/3}\ \text{min} = 7106\ \text{min} = 118.4\ \text{hrs}$$

P7-11

(a) Given: The enzyme catalyzed reaction of the decomposition of hydrogen peroxide. For a batch reactor:

$$\frac{1}{V}\frac{dN_S}{dt} = \frac{dC_S}{-dt} = r_S = \frac{-V_{max}\,C_S}{K_m + C_S} \quad \text{at } t = 0\,,\ C_S = C_{So}$$

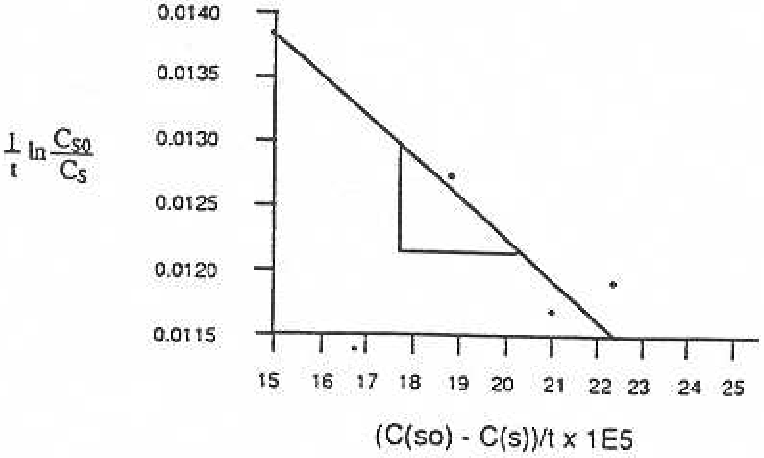
Rearranging and integrating:

$$\int_{C_{So}}^{C_S}\left[\frac{K_m}{C_S} + 1\right]dC_S = -\int_0^t V_{max}\,dt = K_m \ln\frac{C_S}{C_{So}} + C_S - C_{So} = -V_{max}\,t$$

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



$$\text{From the graph, slope} = \frac{.013 - .012}{(17.5 - 20.6) \times 10^{-5}}\left(\frac{\text{min}^{-1}}{\text{g mol l min}^{-1}}\right)$$

$$= \frac{-.001}{-3.1 \times 10^{-5}}\left(\frac{1}{\text{g mol}}\right) = \frac{1}{k_m}$$

$$K_m = .0310 \text{ g mol / l}$$

$$\text{At } \frac{1}{t}\ln\frac{C_{S0}}{C_S} = \frac{.031}{\text{min}}, \quad \frac{C_{S0} - C_S}{t} = \frac{1.75 \times 10^{-4}}{\text{l-min}}\,\text{g mol}$$

$$\therefore \frac{V_{max}}{K_m} = \frac{1}{t}\ln\frac{C_{S0}}{C_S} + \frac{C_{S0} - C_S}{K_m t} = .013 \text{ min}^{-1} + \frac{1.75 \times 10^{-4}}{.0310}\,\frac{\text{g mol/l-min}}{\text{g mol/l}}$$

$$\frac{V_{max}}{K_m} = \left(.013 + 5.64 \times 10^{-3}\right)\text{min}^{-1} = .01865 \text{ min}^{-1}$$

$$V_{max} = \left(.01865 \times \text{min}^{-1}\right)\left(.0310\,\frac{\text{g mol}}{\text{l}}\right) = 5.78 \times 10^{-4}\,\frac{\text{g mol}}{\text{l-min}}$$

(b) $V_{max} \propto [E_0]$. If the enzyme concentration is increased by a factor of three, then

$$V_{max} = 3\left(5.78 * 10^{-4}\,\frac{gmol}{l * \min}\right) = 17.34 * 10^{-4}\,\frac{gmol}{L * \min}$$

$$k_m \ln\frac{C_s}{C_{so}} + C_s - C_{so} = -17.34 * 10^{-4}\,\frac{gmol}{L * \min} * 20 \min = -34.7 * 10^{-4}\,\frac{gmol}{L}$$

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

$$C_S = 0.0092$$

P7-12

$$E + S \overset{k_m}{\Leftrightarrow} E \cdot S \qquad (1)$$

$$E + I \overset{k_i}{\Leftrightarrow} E \cdot I \qquad (2)$$ Competitive Inhibition

$$E \cdot S \overset{k_s}{\rightarrow} E + P \qquad (3)$$

Assuming (1) and (2) to be equilibrium steps:

$$k_m = \frac{[E][S]}{[E \cdot S]} \qquad (4)$$

$$k_i = \frac{[E][I]}{[E \cdot I]} \qquad (5)$$

Rate of production formation: $r_p = k_s[E \cdot S]$ (6)

Combining (4) and (6): $r_p = \dfrac{k_s[E][S]}{k_m}$ (7)

Total enzyme balance: $[E_O] = [E] + [E \cdot S] + [E \cdot I]$ (8)

From (4), (5), and (8): $[E_O] = [E] + \dfrac{[E][S]}{k_m} + \dfrac{[E][I]}{k_i}$ (9)

$$[E] = \frac{[E_O]}{1 + \frac{[S]}{k_m} + \frac{[I]}{k_i}} \qquad (10)$$

Equations (7) and (10) can be combined to give:

$$r_p = \frac{k_s[E_O][S]}{k_m + [S] + \frac{k_m}{k_i}[I]} \qquad (11)$$

Let $V_{max} = k_s[E_O]$ $\qquad r_p = \dfrac{V_{max}[S]}{[S] + k_m\left[1 + \frac{[I]}{k_i}\right]}$

(b) Uncompetitive Inhibition

$$E + S \overset{k_m}{\Leftrightarrow} E \cdot S \qquad (1)$$

$$I + E \cdot S \overset{k_I}{\Leftrightarrow} I \cdot E \cdot S \qquad (2)$$

$$E \cdot S \xrightarrow{k_s} E + P \qquad (3)$$

Assuming (1) and (2) to be equilibrium steps:

$$k_m = \frac{[E][S]}{[E \cdot S]} \qquad (4)$$

$$k_i = \frac{[I][E \cdot S]}{[I \cdot E \cdot S]} \qquad (5)$$

$$r_p = k_s[E \cdot S] \qquad (6)$$

From (4) and (6): $r_p = \frac{k_s}{k_m}[E][S]$ (7)

Total enzyme balance: $[E_O] = [E] + [E \cdot S] + [I \cdot E \cdot S]$ (8)

From (4), (5), and (8): $[E_O] = [E] + \frac{[E][S]}{k_m} + \frac{[I][E][S]}{k_i\, k_m}$ (9)

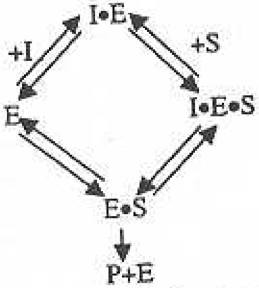
$$\therefore\ [E] = \frac{[E_O]}{1 + \frac{[S]}{k_m} + \frac{[I][S]}{k_i\, k_m}} \qquad (10)$$

From (7) and (10) we get:

$$r_p = \frac{k_s[E_O][S]}{k_m + [S] + \frac{[I][S]}{k_i}} \qquad (11)$$

Let $k_s[E_o] = V_{max}$ $$r_p = \frac{V_{max}[S]}{k_m + [S]\left[1 + \frac{[I]}{k_i}\right]} \qquad (12)$$

(c) Non-competitive Inhibition



Assuming all of the reversible reactions to be equilibrium steps. The inhibitor "I", and the substrate "S" bind at different sites of the enzyme.

$$k_m = \frac{[E][S]}{[E \cdot S]} = \frac{[I \cdot E][S]}{[I \cdot E \cdot S]} \qquad (1)$$

$$k_i = \frac{[E][I]}{[E \cdot I]} = \frac{[E \cdot S][I]}{[E \cdot I \cdot S]} \qquad (2)$$

$$r_p = k_s[E \cdot S] \qquad (3)$$

From (1) and (3): $r_p = \frac{k_s[E \cdot S]}{k_m}$ (4)

Total enzyme balance: $[E_O] = [E] + [E \cdot S] + [I \cdot E] + [I \cdot E \cdot S]$ (5)

$$[E_O] = [E] + \frac{[E][S]}{k_m} + \frac{[I][E]}{k_i} + \frac{[I][E][S]}{k_m\, k_i} \qquad (6)$$

From equations (4) and (6) combined give:

$$r_p = \frac{k_s[E_O][S]}{k_m + [S] + \frac{[I]\, k_m}{k_i} \frac{[I][S]}{k_i}}$$

Let $k_s[E_O] = V_{max}$

$$r_p = \frac{V_{max}[S]}{(k_m + [S])\left(1 + \frac{[I]}{k_i}\right)}$$

P7-13 Given the reaction sequence:

$$E + S \Leftrightarrow E \cdot S$$

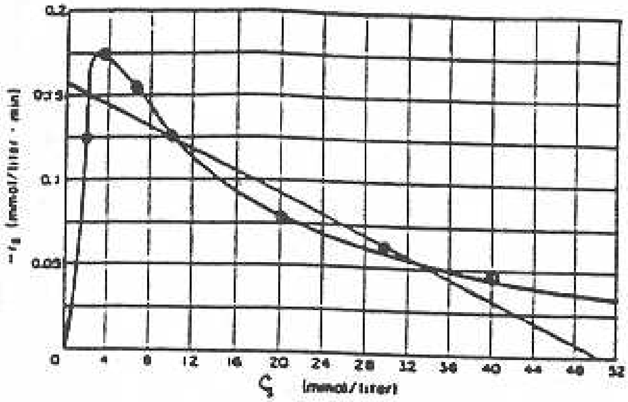
$$E \cdot S + S \Leftrightarrow S \cdot E \cdot S$$

$$E \cdot S \Leftrightarrow E + P$$

The plot of $-r_s$ vs C_s is shown below.

From problem P7-15, 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 $C_s << 1$: $-r_s = k\, C_s\, E_t$ 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.



At $\dfrac{\partial(-r_s)}{\partial C_s} = \dfrac{k\, E_t}{1 + K_1\, C_s + K_2\, C_s^2} - \dfrac{k\, C_s\, E_t\,[K_1 + 2K_2\, C_s]}{(1 + K_1\, C_s + K_2\, C_s^2)^2} = \dfrac{k\, E_t\,(1 - K_2\, C_s^2)}{(1 + K_1\, C_s + K_2\, C_s^2)^2} = 0$

or $C_s^2 = \dfrac{1}{K_2}$ with: $\dfrac{\partial^2(-r_s)}{\partial C_s^2} = \dfrac{-2k\, E_t\, C_s\, K_2}{(1 + K_1\, C_s + K_2\, C_s^2)^2} - \dfrac{2k\, E_t\,(1 - K_2\, C_s^2)(K_1 + 2K_2\, C_s)}{(1 + K_1\, C_s + K_2\, C_s^2)^3}$

$\dfrac{\partial^2(-r_s)}{\partial C_s^2} = \dfrac{2k\, E_t\,[-3K_2\, C_s - K_1 + K_2\, C_s^3]}{(1 + K_1\, C_s + K_2\, C_s^2)^3}$ with $C_s^2 = \dfrac{1}{\sqrt{K_2}}$, the numerator becomes

$2k\, E_t\left[-K_1 - 3\sqrt{K_2} + \dfrac{1}{\sqrt{K_2}}\right] < 0 \;\therefore\;$ $(-r_s)$ goes through a maximum.

This observation also agrees with the above graph

(b) For a CSTR operating with $V = 1000$ l ; $\upsilon_0 = 3.2$ l/min

$\upsilon_0[C_{A0} - C_A] = -r_A V$ or $-r_A = \frac{C_{A0} - C_A}{\tau}$; $\tau = \frac{V}{\upsilon_0} = \frac{1000}{3.2} = 313$ 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:

$$V\frac{dC_S}{dt} = r_S V + C_{S0}\,\upsilon_0 - C_S\,\upsilon_0$$

$$\left.\begin{array}{l} \text{or } \tau\frac{dC_S}{dt} = r_S\tau + C_{S0} - C_S \\ \\ \text{at steady state} \\ \qquad 0 = \bar{r}_S\,\tau + \overline{C}_{S0} + \overline{C}_S \end{array}\right\} \quad \begin{array}{l} \text{Combining} \\ \\ \tau\frac{d\theta_S}{dt} = (r_S - \bar{r}_S)\tau + \theta_{SO} - \theta_S \end{array}$$

Using a Taylor series expansion about $\overline{C}_S$ to linearize $r_S - \bar{r}_S$:

$$r_S - \bar{r}_S = \left(\frac{\partial r_S}{\partial C_S}\right)_{\overline{C}_S}(C_S - \overline{C}_S) = \left(\frac{\partial r_S}{\partial C_S}\right)_{\overline{C}_S}\theta_S \text{ and substituting}$$

$$\bar{v}\frac{d\theta_S}{dt} = \left[\left(\frac{\partial r_S}{\partial C_S}\right)_{\overline{C}_S}\tau - 1\right]\theta_S + \theta_{S0} \quad \text{at } t = 0\,,\ \theta_S = 0$$

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:

At $C_S = 9.4$ m moles/l, $$\left(\frac{\partial(-r_S)}{\partial C_S}\right)_{\bar{C}_S = 9.4} \equiv \frac{\Delta\text{-}r_S}{\Delta C_S} = \frac{0.1425 - 0.1275}{8 - 10} = -\frac{0.150}{2}\ \text{min}^{-1}$$

$$\left(\frac{\partial(-r_S)}{\partial C_S}\right)_{\bar{C}_S} \tau = \left(-\frac{0.150}{2}\ \text{min}^{-1}\right)(313\ \text{min}) = -2.4 < -1$$

∴ the point $C_S = 9.4$, $-r_S = 0.132$ is unstable.

At $C_S = 2.1$ m moles/l, $$\left(\frac{\partial(-r_S)}{\partial C_S}\right)_{\bar{C}_S = 2.1} \equiv \frac{\Delta(-r_S)}{\Delta C_S} = \frac{0.0675 - 0.018}{24 - 44} = -\frac{0.0495}{20}\ \text{min}^{-1}$$

$$\left(\frac{\partial(-r_S)}{\partial C_S}\right)_{\bar{C}_S} \tau = \left(-\frac{0.0495}{2}\ \text{min}^{-1}\right)(313\ \text{min}) = -0.775 > -1 \text{ ; stable}$$

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.

P7-14

Data on Baker's Yeast at 23.4 °C

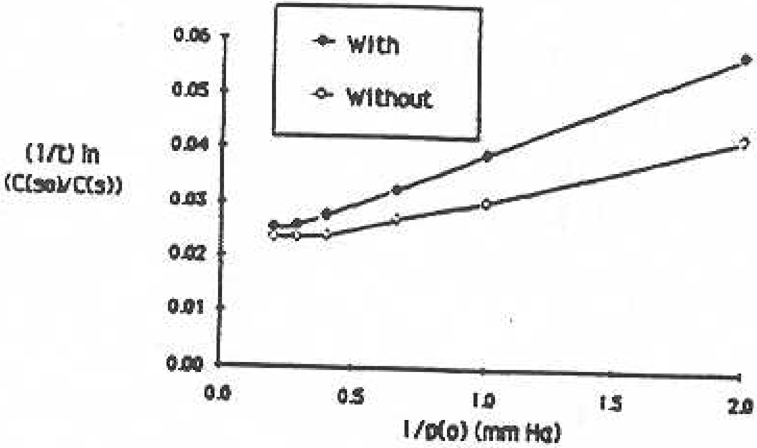
P_{O_2}	Q_{O_2} no sulfanilamide	Q_{O_2} 20 mg sulfanilamide/ml added to medium	$\frac{1}{Q_{O_2}}$ no sulfanilamide	$\frac{1}{P_{O_2}}$	$\frac{1}{Q_{O_2}}$ 20 mg sulfanilamide/ml added to medium
0.0	0.0	0.0	-	-	-
0.5	23.5	17.4	.0425	2.0	.0575
1.0	33.0	25.6	.0303	1.0	.0391
1.5	37.5	30.8	.02666	.66	.03246
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.

P7-14 (cont'd)

$$\therefore \frac{1}{r_p} = \frac{K_m}{V_{max} S} + \frac{1}{V_{max}} = \frac{K_m}{V_{max}}\left(\frac{1}{P_{O_2}}\right) + \frac{1}{V_{max}} = \frac{1}{Q_{O_2}}$$

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 $= 0.019$

$$\therefore V_{max} = 52.63 \frac{\text{ml } O_2}{\text{hr mg cells}}$$

$$K_m = 0.0165 \, V_{max} = (0.0165)(52.63) = 0.8684 \text{ mmHg}$$

(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: $r_p = \dfrac{V_{max} S}{S + K_m\left(1 + \frac{I}{K_I}\right)}$ or $\dfrac{1}{r_p} = \dfrac{K_m\left(1 + \frac{I}{K_I}\right)}{V_{max}}\left(\dfrac{1}{S}\right) + \dfrac{1}{V_{max}}$

In this case, the slope is : $\dfrac{K_m\left(1 + \frac{I}{K_I}\right)}{V_{max}}$ 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: $$r_p = \frac{S\,V_{max}}{K_m + S\left(1 + \frac{I}{K_I}\right)} \quad \text{or} \quad \frac{1}{r_p} = \frac{K_m}{V_{max}}\left(\frac{1}{S}\right) + \frac{1 + \frac{I}{K_I}}{V_{max}}$$

In this case, the slope is the same, but the intercept is $\frac{1 + \frac{I}{K_I}}{V_{max}}$

And for the case of non-competitive inhibition:

$$E + I \Leftrightarrow E \cdot I$$
$$E \cdot I + S \Leftrightarrow I \cdot E \cdot S$$
$$E + S \Leftrightarrow E \cdot S$$
$$I \cdot E \cdot S \Leftrightarrow E \cdot S + I$$
$$E \cdot S \Leftrightarrow P + E$$

$$r_p = \frac{V_{max}\,S}{(S + K_m)\left(1 + \frac{I}{K_I}\right)} \quad \text{or} \quad \frac{1}{r_p} = \frac{1 + \frac{I}{K_I}}{V_{max}} + \frac{1 + \frac{I}{K_I}}{V_{max}}\left(\frac{1}{S}\right)$$

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.

P7-15

(a) No solution will be given.

(b)

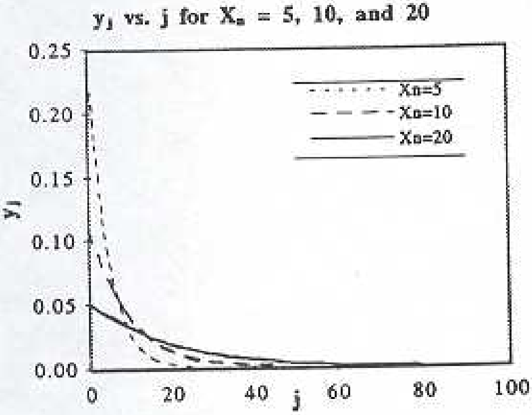
$$y_j = (1-p)p^{j-1} \qquad w_j = j(1-p)^2 p^{j-1}$$

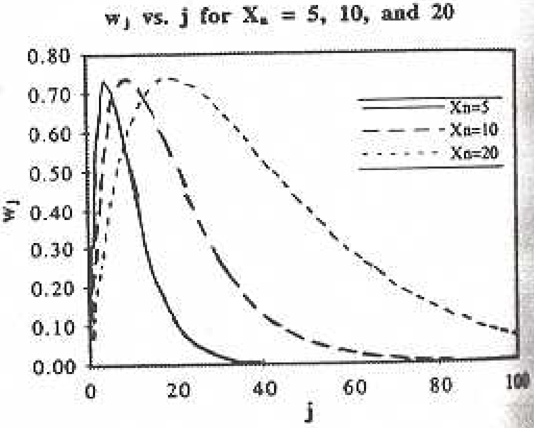
$X_n = \frac{1}{1-p}$ For $X_n = 5$: $p = 0.80$

$X_n = 10$: $p = 0.90$

$X_n = 20$: $p = 0.95$

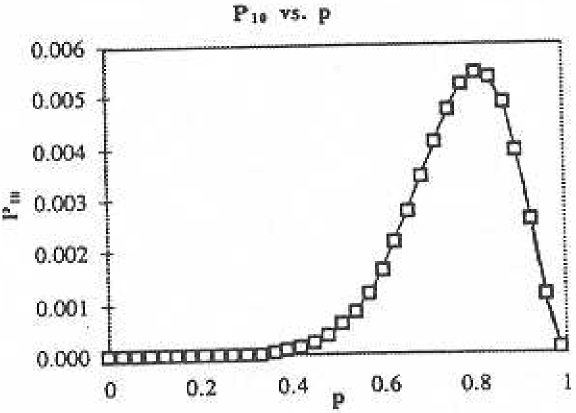
Use these equations to generate the desired graphs:


y_j vs. j for X_n = 5, 10, and 20


w_j vs. j for X_n = 5, 10, and 20

$$P_j = M_o(1-p)^2 p^{j-1} = M_o(1-p)^2 p^9$$

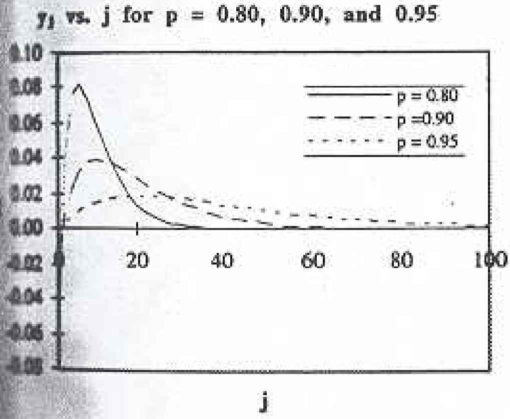
Use the above equation to generate a graph of P_{10} vs. p:

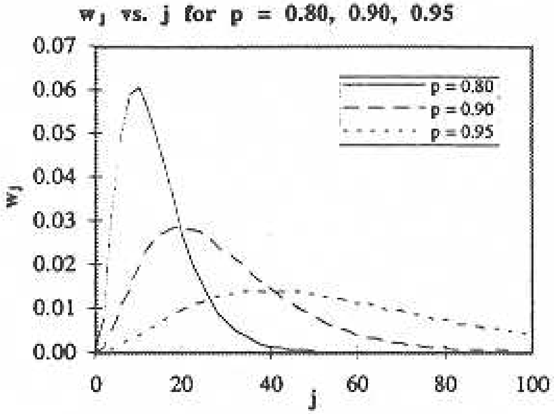

P_{10} vs. p

(c) $y_j = (j-1)(1-p)^2 p^{j-2}$ $\qquad$ $w_j = \frac{1}{2} j(1-p)^3 (j-1) p^{j-2}$

P7-15 (cont'd)

Use these equations to generate graphs of y_j and w_j vs. j.





(d)

$$\overline{M}_n = \mu_n M_M = \frac{M_M}{1-p}$$

$$\overline{M}_w = \mu_w M_M = M_M \frac{1+p}{1-p}$$

$$D = \frac{\mu_w}{\mu_n} = \left(\frac{1+p}{1-p}\right)(1-p) = 1+p$$

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:

$$\overline{M}_n = \frac{104}{1-0.99991} = 1.155\times10^6$$

$$\overline{M}_w = 104\frac{(1+0.99991)}{(1-0.99991)} = 2.311\times10^6$$

$$D = 1+p = 1.99991$$

(e) Mole fraction of polystyrene of chain length 10 (y_{10}).

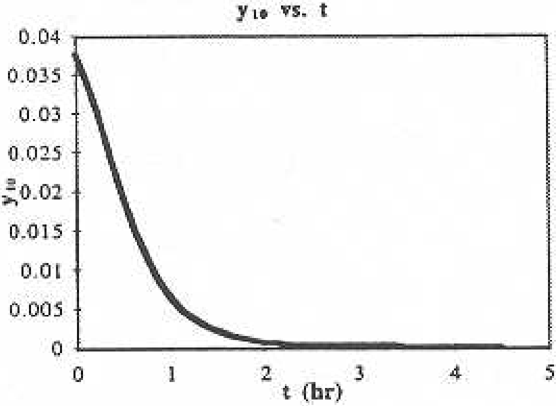
$$I_2 = I_{2o}\exp(-k_o t)$$

$$M = M_o \exp\left[\left(\frac{8k_p^2 f I_{2o}}{k_o k_t}\right)^{1/2}\left(\exp\left(\frac{-k_o t}{2}\right)-1\right)\right]$$

$$p = \beta = \frac{k_p M}{k_p M + k_m M + k_s S + \sqrt{2k_t k_o f(I_2)}}$$

$$y_n = (1-p)p^{n-1} \qquad n = 10$$

Use the above equations to plot y_n vs.t::



P7-16

Reaction

$$R_j + I \xrightarrow{k_n} P_j$$

(a) and (b)

$$\overline{X}_N = \frac{-r_M}{\sum r_j} = \left(\frac{\sum r_j}{-r_M}\right)^{-1}$$

$$\sum r_j = r_i + \sum\left(k_p M\left(R_j - R_{j-1}\right) + (k_a + k_d)R_j \sum R_i k_M M R_j + k_c C R_j + k_s S R_j + k_n I R_j\right)$$

Let $\sum R_j = R^*$

$$\sum r_j = r_i + R^*\left(k_m M + k_s S + k_n I\right)$$

P7-16 (cont'd)

$$\overline{X}_N = \left[\frac{r_i + R^*(k_m M + k_s S + k_n I)}{k_p M R^*}\right]^{-1} = \left[\frac{r_i}{-r_M} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_n I}{k_p M}\right]^{-1}$$

$$\overline{X}_N = \left[\frac{r_i}{r_p} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_n I}{k_p M}\right]^{-1} = \left[\left(\frac{f k_0 k_t}{k_p^2}\right)^{\frac{1}{2}} \frac{I_2^{\frac{1}{2}}}{M} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_n I}{k_p M}\right]^{-1}$$

(c) From the above derivation we know that

$$\frac{1}{\overline{X}_N} = \frac{r_i}{r_p} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_n I}{k_p M}$$

Neglecting the solvent term and rearranging yields:

$$\frac{1}{\overline{X}_N} = \frac{r_i}{-r_M} + \frac{k_m}{k_p} + \frac{k_n I}{k_p M} = \frac{r_i(-r_M)}{(-r_M)^2} + \frac{k_m}{k_p} + \frac{k_n I}{k_p M}$$

Substituting in for $-r_M$ and r_i and simplifying:

$$\frac{1}{\overline{X}_N} = \frac{2k_o f(I_2)/M(-r_M)}{k_p^2(2k_o f(I_2)/k_t)} + \frac{k_m}{k_p} + \frac{k_n I}{k_p M}$$

$$\frac{1}{\overline{X}_N} = \frac{k_t(-r_M)}{k_p^2(M)} + \frac{k_m}{k_p} + \frac{k_n I}{k_p M}$$

(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.

P7-17

a) PFR:

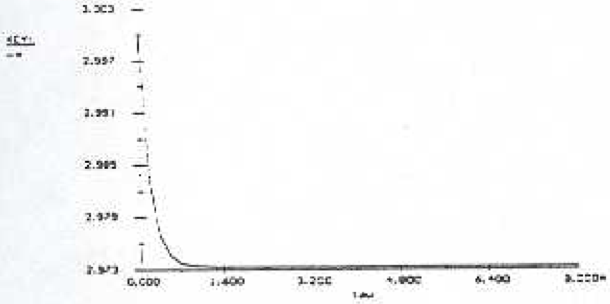
$$\frac{dM}{d\tau} = r_M \qquad \frac{dI_2}{d\tau} = r_{I_2}$$

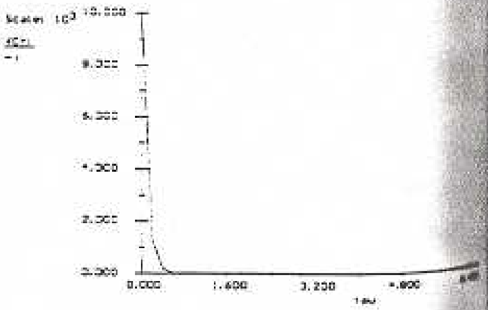
$$r_M = -k_p M \sqrt{\frac{2k_o I_2 f}{k_t}} \qquad r_{I_2} = -k_0 I_2$$

Plug those into POLYMATH to get this graph.

```
Equations:                                    Initial value
d(m)/d(tau)=rm                                3
d(i)/d(tau)=ri                                0.01
kp=10
ko=1e-3
f=.5
kt=5e7
ri=-ko*i
rm=-kp*m*sqrt(2*ko*i*f/kt)
tau0 = 0,   tauf = 79998
```

```
Variable   Initial value   Maximum value   Minimum value   Final value
tau        0               79998           0               79998
m          3               3               2.97129         2.97129
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
```

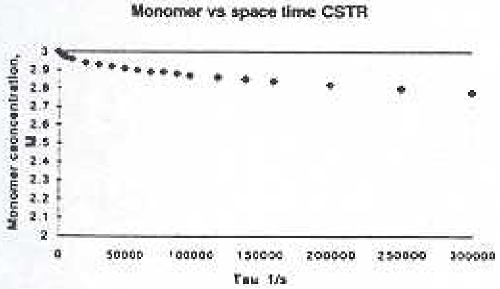


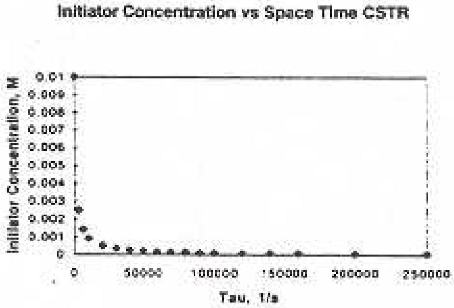


CSTR:

$$M_0 - M = -r_M * \tau \qquad I_{20} - I_2 = -r_{I_2} * \tau$$

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

P7-17 cont'd

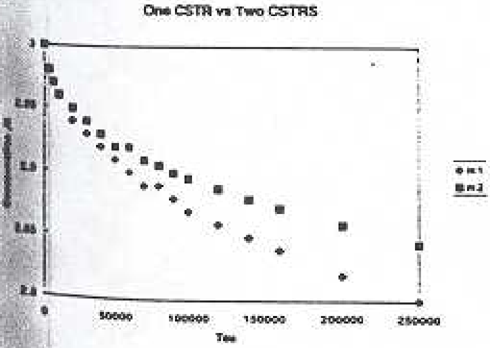
```
Equations:                                   Initial value
f(m)=m-mo-rm*tau                             2.5
f(i)=i-io-ri*tau                             0.001
mo=3
tau=5e11
io=.01
kp=10
ko=1e-3
f=.5
kt=5e7
ri=-ko*i
rm=-kp*m*sqrt(2*ko*i*f/kt)
```

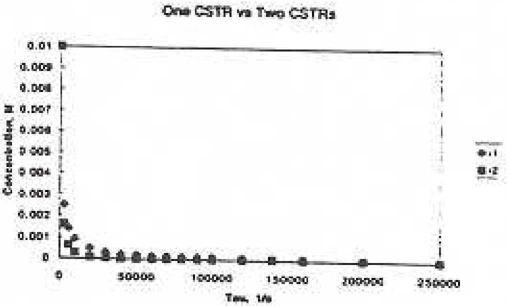
b) For two CSTRs, the design equations change just a bit.

$$M_0 - M_1 = -r_{M_1} * \frac{\tau}{2} \qquad I_{20} - I_{21} = -r_{I_{21}} * \frac{\tau}{2}$$

$$M_1 - M_2 = -r_{M_2} * \frac{\tau}{2} \qquad I_{21} - I_{22} = -r_{I_{22}} * \frac{\tau}{2}$$

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_o 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_t, causes M not to decrease by very much staying very close to 3.

P7-18 No solution will be given

7-19

$$I + M \xrightarrow{k_i} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$-r_I = k_i M I$$

a) Balance on I

$$\tau = \frac{I_0 - I}{-r_I} = \frac{I_0 - I}{k_i M I}$$

$$\Rightarrow I = \frac{I_0}{1 + \tau k_i M}$$

$$-r_M = k_i M I + k_p M \sum_{j=1}^{\infty} R_j$$

$$\text{As} \sum_{j=1}^{\infty} R_j = I_0 - I$$

$$-r_M = k_i M I + k_p M (I_0 - I)$$

Balance on M:

$$\tau = \frac{M_0 - M}{-r_M} = \frac{M_0 - M}{k_i M I + k_p M (I_0 - I)}$$

$$\Rightarrow \tau k_i M I + \tau k_p M (I_0 - I) = M_0 - M$$

$$\Rightarrow \frac{\tau k_i M I_0}{1 + \tau k_i M} + \frac{\tau k_p I_0 M (\tau k_i M)}{1 + \tau k_i M} = M_0 - M$$

$$\Rightarrow \tau k_i I_0 M + \tau^2 k_p k_i I_0 M^2 = (M_0 - M)(1 + \tau k_i M)$$

$$\Rightarrow \tau k_i (1 + \tau k_p I_0) M^2 + (1 + \tau k_i I_0 - \tau k_i M_0) M - M_0 = 0$$

$$\Rightarrow M = \frac{-(1 + \tau k_i I_0 - \tau k_i M_0) + \sqrt{(1 + \tau k_i I_0 - \tau k_i M_0)^2 + 4 * \tau k_i (1 + \tau k_p I_0) M_0}}{2 \tau k_i (1 + \tau k_p I_0)}$$

b) $-r_{R_1} = -k_i M I + k_p M R_1$

Balance on R_1

$$\tau = \frac{0 - R_1}{-k_i M I + k_p M R_1} \Rightarrow R_1 = I \left(\frac{\tau k_i M}{1 + \tau k_p M} \right)$$

$-r_{R_2} = -k_p M R_1 + k_p M R_2$

Balance on R_2

$$\tau = \frac{0 - R_2}{-k_p M R_1 + k_p M R_2} \Rightarrow R_2 = R_1 \left(\frac{\tau k_p M}{1 + \tau k_p M} \right)$$

Similarly,

$$R_3 = R_2 \left(\frac{\tau k_p M}{1 + k_p M \tau} \right)$$

P7-19 cont'd

$$R_j = R_1\left(\frac{\tau k_p M}{1+\tau k_p M}\right)^{j-1}$$

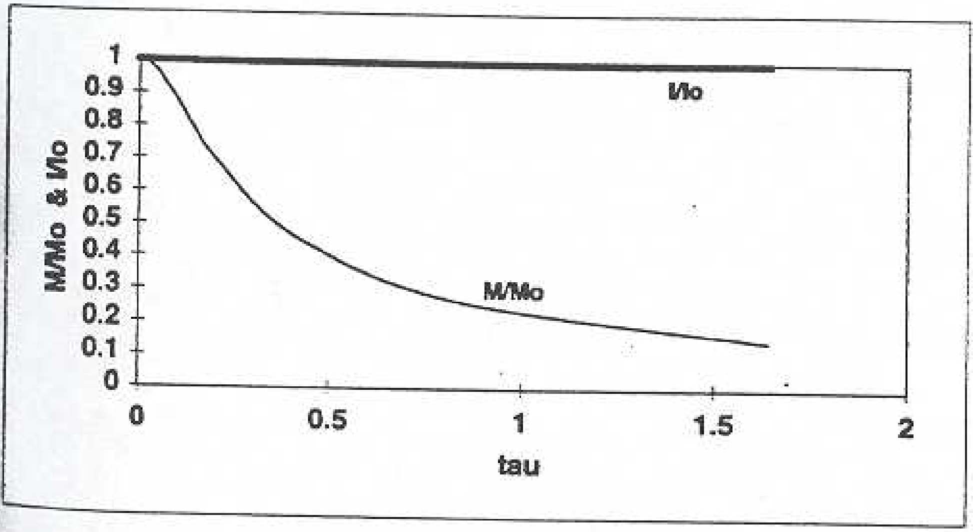
$$R_j = I\left(\frac{\tau k_p M}{1+\tau k_p M}\right)\left(\frac{\tau k_p M}{1+\tau k_p M}\right)^{j-1}$$

$$R_j = \frac{I(\tau k_p M)}{\tau k_p M}\left(\frac{\tau k_p M}{1+\tau k_p M}\right)^{j}$$

$$R_j = \frac{I_0}{1+\tau k_i M}\frac{k_i}{k_p}\left(\frac{\tau k_p M}{1+\tau k_p M}\right)^{j}$$

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)

$$\lambda_0 = \sum_{j=1}^{\infty} R_j = I_0 - I = \frac{\tau k_i M I_0}{1+\tau k_i M}$$

$$\lambda_1 = \sum_{j=1}^{\infty} jR_j = \frac{I_0}{1+\tau k_i M}\frac{k_i}{k_p}\sum_{j=1}^{\infty} j\left(\frac{\tau k_p M}{1+k_p M}\right)^{j}$$

$$= \frac{I_0}{1+\tau k_i M}\frac{k_i}{k_p}\left\{\frac{\left[\tau k_p M/\left(1+\tau k_p M\right)\right]}{\left[1-\frac{\tau k_p M}{\left(1+\tau k_p M\right)}\right]^2}\right\}$$

$$\text{As}\sum_{j=1}^{\infty} j x^j = \frac{x}{(1-x)^2}$$

$$\lambda_1 = \frac{\tau k_i M I_0}{1+\tau k_i M}\left(1+k_p M\right)$$

$$\lambda_2 = \sum_{j=1}^{\infty} j^2 R_j = \frac{I_0}{1+\tau k_i M}\frac{k_i}{k_p}\sum_{j=1}^{\infty} j^2\left(\frac{\tau k_p M}{1+\tau k_p M}\right)^j$$

$$= \frac{I_0}{1+\tau k_i M}\frac{k_i}{k_p}\left\{\frac{\left(\frac{\tau k_p M}{1+\tau k_p M}\right)\left(1+\frac{\tau k_p M}{1+\tau k_p M}\right)}{\left(1-\frac{\tau k_p M}{1+\tau k_p M}\right)^3}\right\}$$

$$As\sum_{j=1}^{\infty} j^2 x^j = \frac{x(1+x)}{(1-x)^3}$$

$$\Rightarrow \lambda_2 = \frac{\tau k_i M I_0}{1+\tau k_i M}\left(1+\tau k_p M\right)\left(1+2\tau k_p M\right)$$

$$\boxed{\begin{aligned} \mu_n &= \frac{\lambda_1}{\lambda_0} = \left(1+\tau k_p M\right) \\ \mu_W &= \frac{\lambda_2}{\lambda_1} = \left(1+2\tau k_p M\right) \\ D &= \frac{\mu_W}{\mu_n} = \frac{1+2\tau k_p M}{1+\tau k_p M} \end{aligned}}$$

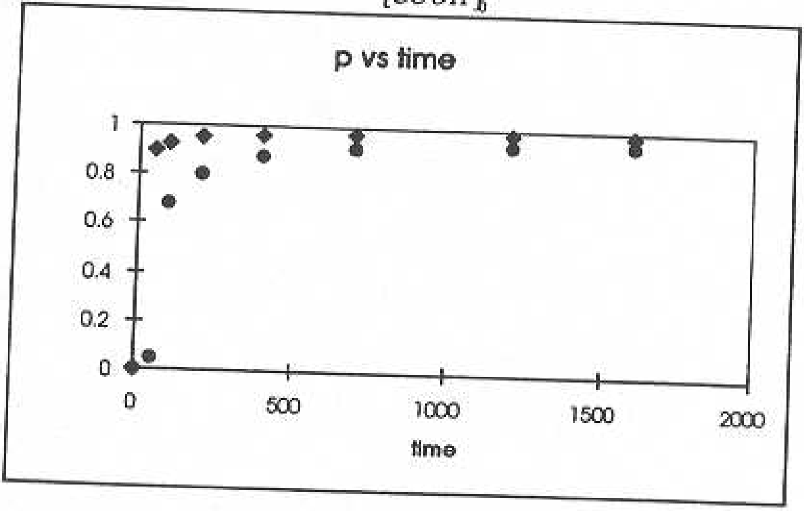
P7-20

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:

$$-\frac{d[COOH]}{dt}=k[COOH][OH][H^+]$$

$$[OH]=[COOH]$$

$$COOH \rightleftarrows COO^- + H^+$$

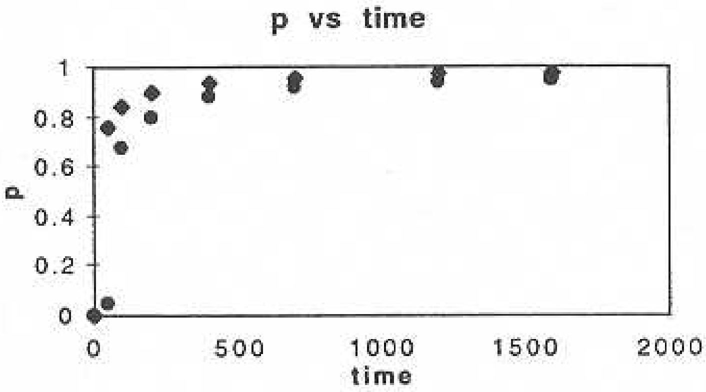
$$K_{eq}=\frac{[COO^-][H^+]}{[COOH]}$$

$$[COO^-]=[H^+]$$

$$[H^+]^2=K_{eq}[COOH]$$

$$-\frac{d[COOH]}{dt}=k[COOH]^{3/2}$$

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.

P7-21 No solution will be given

P7-22

$$I + M \xrightarrow{k_0} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$-\frac{dI}{dt} = k_0 MI = \left(k_p M\right)\frac{k_0 I}{k_p}$$

$$-\frac{dI}{k_p M dt} = \frac{k_0}{k_p} I$$

$$d\theta = k_p M dt$$

$$\frac{dI}{d\theta} = -\frac{k_0}{k_p} I \Rightarrow I = I_0 e^{-\frac{k_0 \theta}{k_p}}$$

$$-\frac{dR_1}{dt} = -k_0 MI + k_p MR_1$$

$$\frac{dR_1}{d\theta} = \frac{k_0}{k_p} I_0 e^{\left(-\frac{k_0}{k_p}\right)\theta} - R_1$$

$$\frac{d\left(e^{\theta} R_1\right)}{d\theta} = \frac{k_0}{k_p} I_0 e^{\left(1-\frac{k_0}{k_p}\right)\theta}$$

$$\Rightarrow R_1 = \frac{k_0}{k_p} \frac{I}{\left(1-\dfrac{k_0}{k_p}\right)}\left[e^{-\frac{k_0 \theta}{k_p}} - e^{-\theta}\right]$$

$$-\frac{dR_2}{dt} = -k_p MR_1 + k_p MR_2$$

$$\Rightarrow \frac{dR_2}{d\theta} = R_1 - R_2$$

$$\Rightarrow \frac{d\left(e^{\theta} R_2\right)}{d\theta} = e^{\theta} R_1 = \frac{k_0 I_0}{k_p - k_0}\left[e^{\left(1-\frac{k_0}{k_p}\right)\theta} - 1\right]$$

$$\Rightarrow R_2 = \frac{k_0 I_0}{k_p\left(1-\dfrac{k_0}{k_p}\right)^2}\left[e^{-\frac{k_0 \theta}{k_p}} - e^{-\theta}\right] - \frac{k_0 I_0 \theta e^{-\frac{k_0}{k_p}}}{k_p - k_0}$$

P7-22

$$\frac{dR_3}{d\theta} = R_2 - R_3$$

$$\Rightarrow \frac{d\left(e^{\theta} R_3\right)}{d\theta} = \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^2}\left[e^{\left(1-\frac{k_0}{k_p}\right)\theta} - 1\right] - \frac{k_0 I_0 \theta}{k_p\left(1-\frac{k_0}{k_p}\right)}$$

$$\Rightarrow R_3 = \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^3}\left[e^{-\frac{k_0}{k_p}\theta} - e^{-\theta}\right] - \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^2}\theta e^{-\theta} - \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)^2}\frac{\theta^2 e^{-\theta}}{2}$$

$$\Rightarrow R_j = \frac{k_0 I_0}{k_p\left(1-\frac{k_0}{k_p}\right)}\left[\frac{e^{-\frac{k_0}{k_p}\theta} - e^{-\theta}}{\left(1-\frac{k_0}{k_p}\right)^{j-1}} - \sum_{i=1}^{j-1}\frac{\theta^i e^{-\theta}}{(i)!\left(1-\frac{k_0}{k_p}\right)^{j-i}}\right]$$

For j>1

P7-23

$$I + M \xrightarrow{k_0} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$\tau = \frac{I_0 - I}{k_0 M I}$$

$$\theta' = k_p M \tau$$

$$\theta' = \frac{k_p\left(I_0 - I\right)}{k_0 I}$$

$$I = \frac{k_p I_0}{k_0\theta' + k_p}$$

$$\tau = \frac{M_0 - M}{k_p M I_0}$$

$$M = \frac{M_0}{k_p I_0 \tau + 1}$$

$$\theta' = \frac{k_p M_0 \tau}{k_p I_0 \tau + 1}$$

$$\tau = \frac{R_1}{k_0 M I - k_p M R_1}$$

$$R_1 = \frac{k_0 I \theta'}{k_p\left(1+\theta'\right)}$$

$$\tau = \frac{R_2}{k_p M R_1 - k_p M R_2}$$

$$R_2 = \frac{R_1\theta'}{1+\theta'} = \frac{k_0 k_p I_0 \theta'^2}{k_p\left(1+\theta'\right)^2\left(k_0\theta' + k_p\right)} = \frac{k_0 I_0 \theta'^2}{\left(1+\theta'\right)^2\left(k_0\theta' + k_p\right)}$$

$$R_j = \frac{k_0 I_0 \left(\dfrac{k_p M_0 \tau}{k_p I_0 \tau + 1}\right)^j}{\left(k_0\theta' + k_p\right)\left(1 + \dfrac{k_p M_0 \tau}{k_p I_0 \tau + 1}\right)^j}$$

P7-24

(1) $$r_g = \overbrace{\mu_{max}\left(1 - \frac{C_C}{C_m}\right)}^{\mu} C_C \qquad \mu_{max} = 0.5 \text{ hr}^{-1} \qquad C_m = 20 \text{ g/dm}^3$$

Substrate in excess

(a) Batch reactor $V = 2 \text{ dm}^3$ (constant)

$$\frac{dC_C}{dt} = r_g \qquad \frac{dC_C}{dt} = \mu_m\left(1 - \frac{C_C}{C_m}\right)C_C$$

$$\frac{dC_C}{dt} = \mu_m\left(C_C - \frac{C_C^2}{C_m}\right)$$

$$\boxed{\frac{dC_C}{dt} = 0.5\text{hr}^{-1}\left(C_C - \frac{C_C^2}{20\text{g/dm}^3}\right) \text{ plot}}$$

$$C_{C0} = \frac{0.4 \text{ g}}{2 \text{ dm}^3} = 0.2 \frac{\text{g}}{\text{dm}^3}$$

(b) $$V\frac{dC_C}{dt} = F(C_{C0} - C_C) + r_g V$$

$$\boxed{\frac{dC_C}{dt} = \frac{F}{V}(C_{C0} - C_C) + r_g} \qquad D = \frac{F}{V}$$

$C_{C0} = 0$ (no cell injunction)

$-D C_C + r_g = 0$

$-DC_C + \mu C_C = 0$

$\therefore D = \mu$

Wash out When $D > \mu$ or

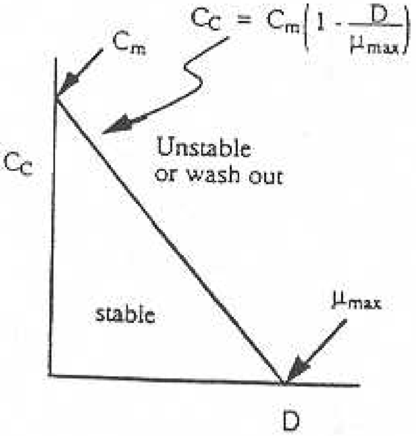
$$D > \mu_{max}\left(1 - \frac{C_C}{C_m}\right)$$

When $D = 0$, $C_C = C_m$

When $C_C = 0$ $D = \mu_{max}$

P7-24 (cont'd)

A plot of C_C vs D gives:



(2)

Let $C = C_C$ and $K = C_m$

$$\frac{dC}{dt} = \mu C\left(1 - \frac{C}{K}\right) \qquad \text{at } t = 0 \text{ , } C = C_0$$

$$\frac{dC}{dt} = \mu\left(C - \frac{C^2}{K}\right)$$

$$\frac{dC}{C^2 - CK} = \frac{-\mu}{K}dt \qquad \frac{dC}{C(C-K)} = \frac{-\mu}{K}dt$$

$$\int_{C_0}^{C}\frac{dC}{C(C-K)} = \int_{C_0}^{C}\left(-\frac{1}{KC} + \frac{1}{K(C-K)}\right)dC$$

$$= -\frac{1}{K}\ln C + \frac{1}{K}\ln(C-K)\Big|_{C=C_0}^{C}$$

$$= \frac{1}{K}\ln\frac{C_0}{C} + \frac{1}{K}\ln\left(\frac{C-K}{C_0-K}\right)$$

$$\frac{1}{K}\left(\frac{C_0(C-K)}{C(C_0-K)}\right) = \frac{-\mu}{K}t$$

$$\therefore \ln\frac{C_0(C-K)}{C(C_0-K)} = -\mu t$$

$$\frac{C_0(C-K)}{C(C_0-K)} = e^{-\mu t}$$

$$\frac{C-K}{CK} = \frac{C_0-K}{C_0 K}e^{-\mu t}$$

P7-24 (cont'd)

$$\frac{C}{CK} - \frac{K}{CK} = \left[\frac{C_0}{C_0 K} - \frac{K}{C_0 K}\right] e^{-\mu t}$$

$$\frac{1}{K} - \frac{1}{C} = \left[\frac{1}{K} - \frac{1}{C_0}\right] e^{-\mu t}$$

$$\frac{1}{C} = \frac{1}{K} + \left[\frac{1}{C_0} - \frac{1}{K}\right] e^{-\mu t}$$

$$\frac{1}{C_C} = \frac{1}{20} + \left(\frac{1}{0.2} - \frac{1}{20}\right) e^{-0.5 t}$$

$$\frac{1}{C_C} = 0.05 + 4.95\, e^{-0.5 t}$$

P7-25

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:

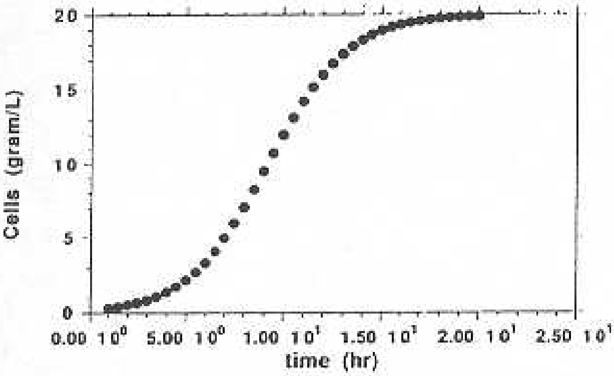
cell + nutrient → more cells + product

(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:

$X = A\, e^{kt}$



P7-25 (cont'd)

where $A = C_{X0}\, e^{-\mu t_{lag}}$

$$\boxed{t_{lag} = \frac{\ln\left(\frac{C_{X0}}{A}\right)}{\mu}}$$

Run 1 (between 15, 20, 30 hrs)

$\mu_{max} = 0.2125\ hr^{-1}$

$A = 7492.6$

$t_{log} = \ln\left(\frac{2.7\times10^4}{7492.6}\right) = 0.21252$

$t_{lag} = 6.0\ hr$

Run 2 (points 10, 15, 20 hrs)

$\mu_{max} = 0.3124\ hr^{-1}$

$A = 5571.7$

$t_{lag} = 5.1\ hr$

(c) Stationary

$t_{stationary}$ between

Time	45 to 55	25 to 15
length of time	10 hr	20 hr

(d) Product start at end of exponential (for both runs)

(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 $D > \mu_{max}$

P7-26 Cell Balance

(a+b) $\frac{dC_C}{dt} = D(C_{C_{IN}} - C_C) + r_g$

$\frac{dC_C}{dt} = 0 \qquad C_{C_{IN}} = 0$

$0 = -DC_C + r_g$

$C_{S0} = 30$

$\mu_{max} = 1.5\ hr^{-1}$

$C_{S_{IN}} = C_{C0} = 0.5\ g/dm^3$

$K_i = 50\ g/dm^3$

$K_S = 1\ g/dm^3$

$D = 0.75$

$Y_{C/S} = 0.08$

P7-26 (cont'd)

$$0 = -DC_C + \left(\frac{\mu_{max} C_S C_C}{K_S + C_S\left(1 + \frac{C_S}{K_I}\right)}\right)$$

$$\boxed{D = \left(\frac{\mu_{max} C_S}{K_S + C_S\left(1 + \frac{C_S}{K_I}\right)}\right)} \qquad D = \left(\frac{1.5\, C_S}{1 + C_S\left(1 + \frac{C_S}{8}\right)}\right)$$

$\boxed{C_S = C_{S0} - y_{S/X} C_C}$ 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

$$D = \left(\frac{1.5\, C_S}{1 + C_S\left(1 + \frac{C_S}{8}\right)}\right) \qquad C_C = (30.0 - C_S)(0.08)$$

(c) IN - OUT + GEN = ACC

$$\frac{dC_C}{dt} = D(C_{C_{IN}} - C_C) + r_g \qquad r_g = \frac{\mu_{max} C_S}{K_S + C_S + \left(1 + \frac{C_S}{K_I}\right)} C_C$$

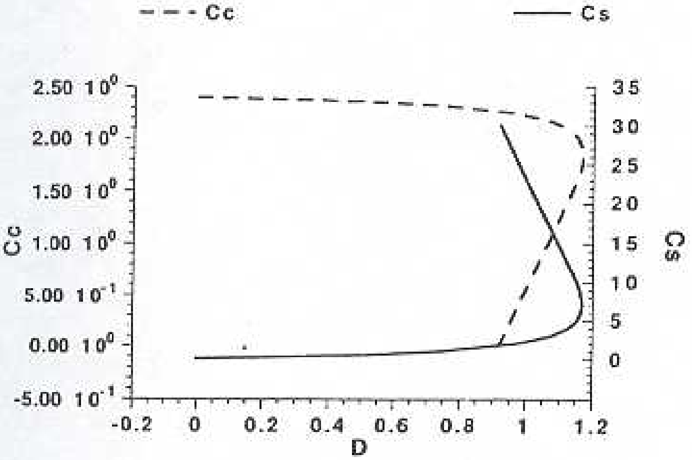
$$\frac{dC_C}{dt} = D(C_{C_{IN}} - C_C) + y_{S/X}\, r_g$$

@ t = 0 $\quad C_{S0} = 30 \quad C_{C0} = 0.5$

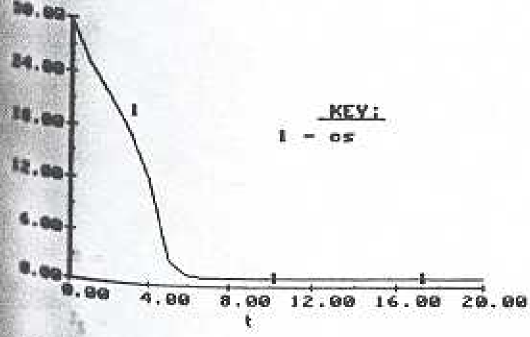
where $\quad D = 0.75 \quad K_I = 50 \quad K_S = 1$

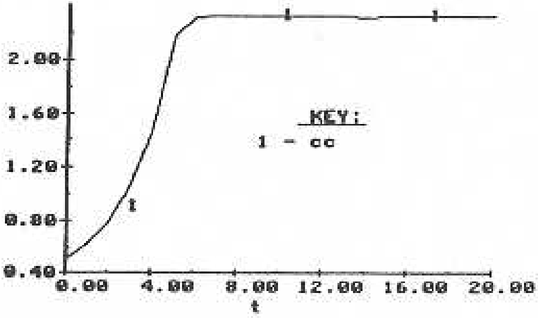
$\mu = 1.5 \quad y_{C/S} = 0.08 \quad C_{S_{IN}} = 30$

P7-26 (cont'd)

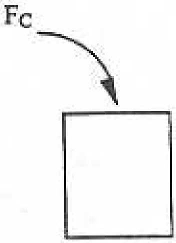


```
The equations:
    d(cc)/d(t)=-d*cc+rg
    d(cs)/d(t)=d*(csin-cs)-rg/ycs
    ki=50
    rg=1.5*cc*cs/(1+cs+cs*cs/ki)
    ycs=0.08
    csin=30
    d=.75
Initial values: t0= 0.0, cc0= 0.5000, cs0= 30.000
Final value:   tf= 20.000
```





P7-27



IN - OUT + GEN = ACC

$$\frac{dN_C}{dt} = F_C + r_g V \qquad r_g = k\,C_C$$

$$\frac{dN_C}{dt} = F_C + k\,C_C\,V \qquad N_C = C_C\,V \qquad \frac{dN_C}{dt} = F_C + k\,N_C$$

$$\frac{dN_C}{dt} - k\,N_C = F_C \qquad N_C = \frac{-F_C}{k} + Ae^{kt} \qquad t = 0,\ N_C = 0,\ A = \frac{F_C}{k}$$

$$\boxed{N_C = \frac{F_C}{K}\left[e^{kt} - 1\right]} \qquad C_C = \frac{N_C}{V_0 + \upsilon_0 t} \qquad N_C = C_C\,(\upsilon_0 t)$$

$$F_C = C_{C0}\,\upsilon_0 \qquad N_C = C_C\,\upsilon_0\,t$$

$$F_C = 0.001\ \text{gm/dm}^3\ \upsilon_0 \qquad N_C = 0.025\ \text{g/dm}^3\,(2\text{hr})\,(\upsilon_0) \qquad = 0.050\ \text{g hr/dm}^3\,(\upsilon_0)$$

$$N_C = \frac{F_C}{k}\left[e^{kt} - 1\right] \qquad 1 = \frac{F_C}{N_C\,k}\left[e^{kt} - 1\right]$$

$$1 = \frac{C_{C0}\,(\upsilon_0)}{C_C\,(\upsilon_0)\,t\,k}\left[e^{kt} - 1\right] \qquad 1 = \frac{C_{C0}}{C_C}\frac{\left[e^{kt} - 1\right]}{kt} \qquad 1 = \frac{0.001\ \text{grn/dm}^3\,(\upsilon_0)}{0.050\ \text{g hr}\,(\upsilon_0)}\left[\frac{e^{kt} - 1}{k}\right]$$

$k = 2.4$ hr

P7-28

Plot log C_C vs t

	Slope μ	Intercept	Time range for curve fit
1	0.39218	1.172×10^7	4 to 8 hr
5	0.79507	1.7953×10^6	5 to 9 hr
10	0.75862	1.8949×10^6	4 to 10 hr
15	0.79157	1.4949×10^6	6 to 9 hr

Slopes = μ $[\text{hrs}]^{-1}$

$$x = x_0\,e^{\mu(t - t_{lag})} \qquad \text{curve fit } x = A\,e^{\mu t}$$

$$A = e^{-\mu t_{lag}} \qquad t_{lag} = \frac{1}{\mu}\ln\left[\frac{x_0}{A}\right]$$

P7-28 (cont'd)

	t_{log} [hr]
1	2.397
5	3.23
10	3.10
15	2.80

C_S (g/l)	μ [hr^{-1}]	t_{lag} [hr]
1	.392	2.4
5	.745	3.2
10	.759	3.1
15	.792	2.8

$$\mu = \mu_{max} \frac{C_S}{K_S + C_S}$$

$$\boxed{\frac{1}{\mu} = \frac{K_S}{\mu_{max}} \frac{1}{C_S} + \frac{1}{\mu_{max}}}$$

Curve fit data to Lineweaver-Burke Equation

int = 1.139 slope = 1.4019

$$\boxed{\begin{aligned} \mu_{max} &= 0.8780 \text{ hr}^{-1} \\ K_S &= 1.23 \text{ g/l} \end{aligned}}$$

Note: curve fits assume constant nutrient concentration in batch reactor.

b) $$\frac{dC_C}{dt} = \mu C_C \left[1 - \frac{(C_C - C_{C0})}{C_{p*}}\right]^n$$

take $\frac{dC_C}{dt} = 0$ stationary phase for n = 1

$$\frac{(C_C - C_{C0})}{C_{p*}} = 1 \qquad C_{p*} = C_C - C_{C0}$$

	C_{p*} [X10^7]	C_{C0} at t_{lag}	$C_C \times 10^{-7}$	Predict
1	45.73	1.172×10^7	46.9	
5	165	1.795×10^6	165	3.5×10^8
10	256	1.895×10^6	256	
15	306	1.4499×10^6	306	

	μ	t_{lag}	C_{p*}	C_C t = 0
1	0.392	2.4	45.7×10^7	3×10^7
5	0.745	3.2	165×10^7	2×10^7
10	0.759	3.1	256×10^7	2×10^7
15	0.792	2.8	306×10^7	1.3×10^7

n = 1.0

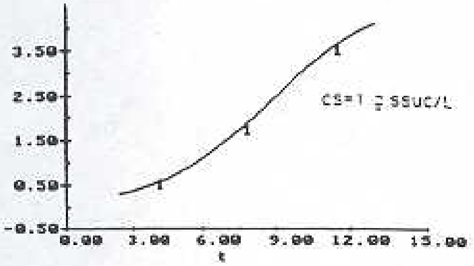
$$r_g = \mu C_C \left[1 - \frac{C_C - C_{C\ t=0}}{C_{p*}}\right]^n$$

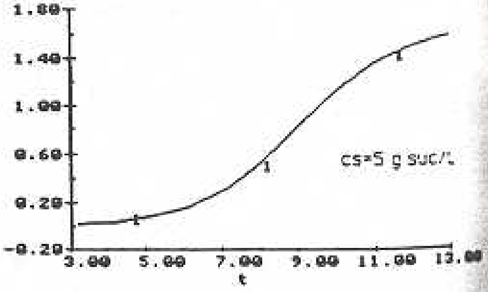
$C_{p*} \cong y_{C/S} (C_{S0})$ n = 1.0 $y_{C/S} = \frac{2.7 \times 10^5 \text{ cell/ml}}{\text{mg suc / L}}$

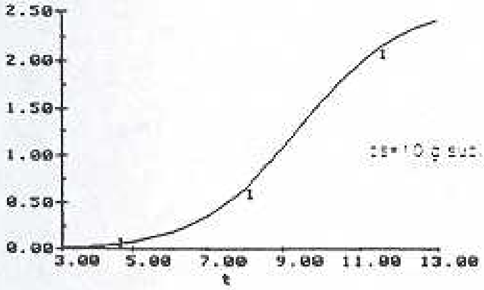
$$r_g = \frac{dC_C}{dt}$$

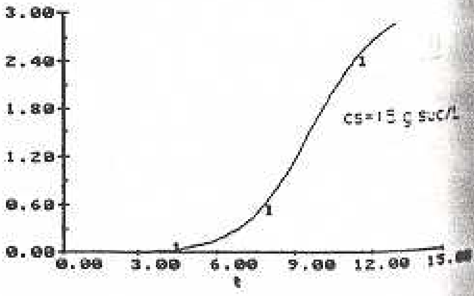
P7-28 (cont'd)

```
The equations:
     d(cc)/d(t)=rg
     mu=0.792
     co=1.33e7
     cstar=306e7
     n=1
     rg=mu*cc*(1-(cc-co)/cstar)**n
Initial values:  t0= 2.8000,  cc0= 1.330×10^7
Final value:   tf= 13.000
```









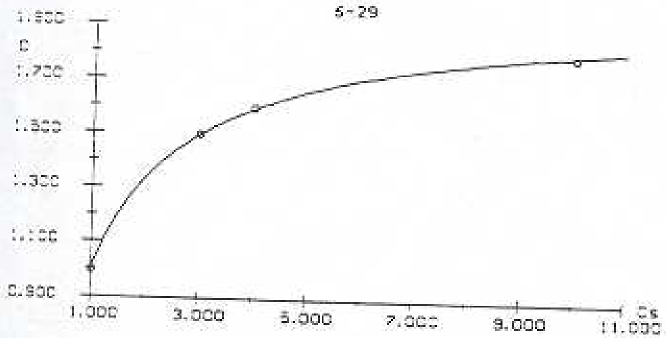
P7-29

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.

P7-29 cont'd



```
Model: C=Cs*mu/(ks+Cs)
mu = 1.98134
ks = 0.972224
2 positive residuals, 2 negative residuals.  Sum of squares = 0.000104625
```

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.

P7-30

The only equation not given is for that of the cells:

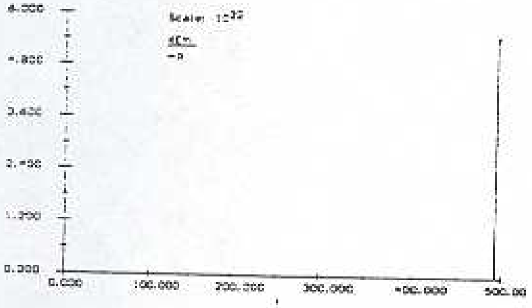
$$\frac{dC}{dt} = rg$$

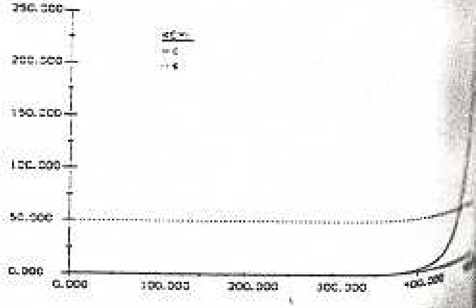
$$rg = \mu C$$

We can then plug into POLYMATH and come up with the following graphs.

P7-30 (cont'd)

```
Equations:                                                    Initial value
d(p)/d(t)=(alp*mu+bet)*x                                      0
d(s)/d(t)=1/yps*(alp*mu+bet)*x                                50
d(c)/d(t)=rg                                                  1e-08
alp=34.5
bet=-.147
yps=1.33
mu0=.25
ks=.018
ksi=11.8
psta=32.4
kpi=.06
so=50
x=(so-s)/so
mu=mu0*(s/(ks+s+s^2/ksi))*(1-p/psta)*exp(-kpi*p)
rg=mu*c
t0 = 0,   tf = 500          Variable     Initial value  Maximum value  Minimum value  Final value
                            t            0              500            0              500
                            p            0              5.46711e-22    0              5.46711e-22
                            s            50             50             50             50
                            c            1e-08          231.597        1e-08          231.597
                            alp          34.5           34.5           34.5           34.5
                            bet          -0.147         -0.147         -0.147         -0.147
                            yps          1.33           1.33           1.33           1.33
                            mu0          0.25           0.25           0.25           0.25
                            ks           0.018          0.018          0.018          0.018
                            ksi          11.8           11.8           11.8           11.8
                            psta         32.4           32.4           32.4           32.4
                            kpi          0.06           0.06           0.06           0.06
                            so           50             50             50             50
                            x            0              0              0              0
                            mu           0.0477313      0.0477313      0.0477313      0.0477313
                            rg           4.77313e-10    11.0544        4.77313e-10    11.0544
```





P7-31 No solution will be given

P7-32

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:                                              Initial value
f(cs)=cs-cso+rp/D                                       4
f(cp)=cp-rp/D                                           2
cso=2
D=50
cc=50
vmax=76
km=.048
cpstar=1.69
rp=vmax*cs/(km+cs)*(1-cp/cpstar)*cc
```

```
                   Solution
Variable           Value            f()
cs                 0.351657         3.222e-15
cp                 1.54834          -3.277e-15
cso                2
D                  50
cc                 50
vmax               76
km                 0.048
cpstar             1.69
rp                 82.4171
```

CDP7-A

Given the reaction

$$2GH_2 \rightarrow 2G = CH_2 + H_2$$

1) $-r_{GH_2} = F(C_{GH}, C_{GH_2})$
2) $-r_{GH_2}$ decreases as C_{GH} increases
3) With no GH, $-r_{GH_2} \alpha C_{GH_2}$
4) With high C_{GH} and low C_{GH_2}, $-r_{GH_2} \alpha C_{GH_2}^2$

A rate law suggested from the observations above is: $-r_{GH_2} = \dfrac{k_1 C_{GH_2}^2}{C_{GH_2} + k_2 C_{GH}}$

This equation suggests the overall reaction mechanism steps:

$$GH_2 + [\ ]^* \rightarrow [\ ]$$

$$GH_2 + [\ ]^* \rightarrow$$

$$GH_2 \rightarrow [\ ]^*$$

Therefore, a mechanism based on the information above is proposed:

$$GH_2 \underset{k-1}{\overset{k1}{\rightleftarrows}} GH + H^* \qquad -r_1 = k_1 C_{GH_2} - k_{-1} C_{GH} C_{H\bullet}$$

$$H^* + GH_2 \xrightarrow{k2} GH + H_2 \qquad -r_2 = k_2 C_{GH_2} C_{H\bullet}$$

$$-r_{GH_2} = k_1 C_{GH_2} - k_{-1} C_{GH} C_{H\bullet} + k_2 C_{H\bullet} C_{GH_2}$$

$$-r_{H\bullet} \equiv 0 = -k_1 C_{GH_2} + k_{-1} C_{GH} C_{H\bullet} + k_2 C_{H\bullet} C_{GH_2}$$

$$\therefore\ C_{H\bullet} = \frac{k_1 C_{GH_2}}{k_{-1} C_{GH} + k_2 C_{GH_2}}$$

$$-r_{GH_2} = k_1 C_{GH_2} + [k_2 C_{GH_2} - k_{-1} C_{GH}]\left[\frac{k_1 C_{GH_2}}{k_{-1} C_{GH} + k_2 C_{GH_2}}\right]$$

$$= \left[\frac{k_1 k_{-1} C_{GH} C_{GH_2} + k_1 k_2 C_{GH_2}^2 + k_1 k_2 C_{GH_2}^2 - k_{-1} C_{GH} k_1 C_{GH_2}}{k_{-1} C_{GH} + k_2 C_{GH_2}}\right]$$

$$-r_{GH_2} = \left[\frac{2k_1 k_2 C_{GH_2}^2}{k_{-1} C_{GH} + k_2 C_{GH_2}}\right]$$

CDP7-B

Given the following reaction scheme:

$$I^- + OCl^- \rightarrow OI^- + Cl^-$$

with the following rate law: $r_{OI^-} = \dfrac{kC_{I^-}C_{OCl^-}}{C_{OH^-}}$

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:

$$-r_{OI} = r_2 = k_{-2}C_{OI^-}C_{H_2O} - k_2C_{HO^-}C_{HOI}$$
$$-r_{HOI} = -r_2 + r_3 = k_2C_{OH^-}C_{HOI} - k_{-2}C_{OI^-}C_{H_2O} - k_3C_{I^-}C_{HOCl} = 0$$
$$k_3C_{I^-}C_{HOCl} = k_2C_{OH^-}C_{HOI} - k_{-2}C_{OI^-}C_{H_2O} = -r_{OI}$$

$$-r_{HOCl} = -r_1 - r_3 = k_1 C_{OH^-} C_{HOCl} - k_{-1} C_{OCl^-} C_{H_2O} + k_3 C_{I^-} C_{HOCl} = 0$$

or $[k_1 C_{OH^-} + k_3 C_{I^-}]\, C_{HOCl} = k_{-1} C_{OCl^-} C_{H_2O}$; i.e., $C_{HOCl} = \dfrac{k_{-1} C_{OCl^-} C_{H_2O}}{k_1 C_{OH^-} + k_3 C_{I^-}}$

Then: $-r_{OI} = \dfrac{k_{-1} k_3 C_{I^-} C_{OCl^-} C_{H_2O}}{k_1 C_{OH^-} + k_3 C_{I^-}}$ is close; with $k_1 \gg k_3$

$$-r_{OI} = \frac{KC_{I^-}C_{OCl^-}}{C_{OH^-}} \quad \text{where } K = \frac{k_{-1}k_3}{k_1}$$

An alternative approach assumes that reaction 1 quickly attains equilibrium, then:

$$C_{HOCl} = \frac{k_{-1}C_{OCl^-}C_{H_2O}}{k_1C_{OH^-}}$$

Then $-r_{OI} = k_3C_{I^-}C_{HOCl} = \left[\dfrac{k_3k_{-1}C_{H_2O}}{k_1}\right]\dfrac{C_{I^-}C_{OCl^-}}{C_{OH^-}}$

These two approaches are basically equivalent

CDP7-C

The following enzymatic reaction

$$E + S \underset{k_2}{\overset{k_1}{\Leftrightarrow}} E \cdot S$$

$$E \cdot S \overset{k_F}{\Leftrightarrow} P + E$$

(a) Non-inhibition:

$$r_P = k_F[E \cdot S]$$

$$r_{E \cdot S} = k_1[E][S] - k_2[E \cdot S] - k_F[E \cdot S]$$

$r_{E \cdot S} = 0$ by the pseudo steady-state hypothesis

$$\therefore [E \cdot S] = \frac{k_1[E][S]}{k_2 + k_F} \quad \text{with } [E_t] = [E] + [E \cdot S]$$

$$[E_t] = [E] + \frac{k_1[E][S]}{k_2 + k_F} = [E]\left\{\frac{k_2 + k_F + k_1[S]}{k_2 + k_F}\right\}$$

$$\text{or } [E] = \frac{[E_t](k_2 + k_F)}{k_2 + k_F + k_1[S]}$$

Expression for r_p now becomes:

$$r_p = k_F[E \bullet S] = \frac{k_F k_1[E][S]}{k_2 + k_F} = \frac{k_1 k_F[S]}{k_2 + k_F}\left[\frac{[E_t](k_2 + k_F)}{k_2 + k_F + k_1[S]}\right]$$

$$r_p = \frac{k_1 k_F[S][E_t]}{k_2 + k_F + k_1[S]}$$

This expression reduces to equation 7-44 of the text.

(b) For competitive product inhibition, reaction scheme is of the form:

$$E + S \underset{k_2}{\overset{k_1}{\Leftrightarrow}} E \cdot S \qquad r_1 = k_1[E][S] - k_2[E \cdot S]$$

$$E + P \underset{k_4}{\overset{k_3}{\Leftrightarrow}} E \cdot P \qquad r_2 = k_3[E][P] - k_4[E \cdot P]$$

$$E \cdot S \overset{k_F}{\rightarrow} P + E \qquad r_3 = k_F[E \cdot S]$$

$$-r_A = r_3 = k_F[E \cdot S]$$

CDP7-C cont'd

$$r_{E\cdot S} = r_1 - r_3 \equiv 0 = k_1[E][S] - k_2[E\cdot S] - k_F[E\cdot S] = 0$$

$$\text{or } [E\cdot S] = \frac{k_1[E][S]}{k_2 + k_F}$$

$$r_{E\cdot P} = r_3 = 0 = k_3[E][P] - k_4[E\cdot P] = 0 \quad \therefore \; [E\cdot P] = \frac{k_3[E][P]}{k_4}$$

Now $\therefore [E_t] = [E] + [E\cdot S] + [E\cdot P]$

$$[E_t] = [E] + \frac{k_1[E][S]}{k_2 + k_F} + \frac{k_3[E][P]}{k_4} = [E]\left\{1 + \frac{k_1[S]}{k_2 + k_F} + \frac{k_3[P]}{k_4}\right\}$$

$$[E_t] = [E]\left\{\frac{k_2 k_4 + k_4 k_F + k_4 k_1[S] + k_2 k_3[P] + k_F k_3[P]}{k_4(k_2 + k_F)}\right\}$$

$$-r_A = k_F[E\cdot S] = \frac{k_1 k_F[E][S]}{k_2 + k_F}$$

$$= \frac{k_1 k_F[S]}{k_2 + k_F}\left\{\frac{k_4(k_2 + k_F)}{k_2 k_4 + k_4 k_F + k_4 k_1[S] + k_2 k_3[P] + k_F k_3[P]}\right\}[E_t]$$

Rearranging $(-r_A)$:

$$-r_A = \frac{k_F[E_t][S]}{[S] + \frac{k_2 + k_F}{k_1}\left\{1 + \frac{k_3[P]}{k_4}\right\}}$$

This expression is similar to Eq 7-67 with K_m replaced by $\frac{k_2 + k_F}{k_1}$, k by k_F, and [I] with [P].

(c) (a) Product inhibition, noncompetitive reaction scheme is:

$$E + S \overset{k_1}{\Leftrightarrow} E\cdot S \qquad (1)$$

$$E + P \overset{k_2}{\Leftrightarrow} E\cdot P \qquad (2)$$

$$E\cdot S + P \overset{k_3}{\rightarrow} E\cdot S\cdot P \qquad (3)$$

Assume reaction (5) controls, then

$$r_1/k_1 \equiv 0,\; r_2/k_2 \equiv 0,\; r_3/k_3 \equiv 0,\; \frac{r_4}{k_4} \equiv 0$$

$$\text{or } [E\cdot S] = K_1[E][S]$$

CDP7-C cont'd

$E \cdot P + S \xrightarrow{k_4} E \cdot S \cdot P$ (4) $[E \cdot P] = K_2[E][P]$

$E \cdot S \xrightarrow{k_5} E + P$ (5) $[E \cdot S \cdot P] = K_3[E \cdot S][P] = K_1K_3[E][S][P]$

$-r_A = k_F[E \cdot S]$

$[E_t] = [E] + [E \cdot S] + [E \cdot P] + [E \cdot S \cdot P]$

$[E_t] = [E] + K_1[E][S] + K_1[E][P] + K_1 K_3[E][S][P]$

or $[E] = \dfrac{[E_t]}{1 + K_1[S] + K_2[P] + K_3[S][P]}$. Then $-r_A = k_F[E \cdot S] = k_F K_1[E][S]$

Now $-r_A = \dfrac{k_F K_1[S][E_t]}{1 + K_1[S] + K_2[P] + K_1 K_3[S][P]}$

This equation is similar to equation 7-86 of the text, with I replaced by P and k_p by k_F.

(b) Product inhibition of the uncompetitive type: Reaction scheme is of the form:

$E + S \underset{k_2}{\overset{k_1}{\Leftrightarrow}} E \cdot S$ $r_1 = k_1[E][S] - k_2[E \cdot S]$

$P + E \cdot S \underset{k_4}{\overset{k_3}{\Leftrightarrow}} E \cdot S \cdot P$ $r_2 = k_3[P][E \cdot S] - k_4[E \cdot S \cdot P]$

$E \cdot S \overset{k_F}{\Leftrightarrow} P + E$ $r_3 = k_F[E \cdot S]$

Rate of formation of P: $r_p = r_3 - r_2$; by pseudo steady-state hypothesis:

$$r_{E \bullet S \bullet P} = r_2 \equiv 0 = k_3[P][E \bullet S] - k_4[E \bullet S \bullet P] \Rightarrow [E \bullet S \bullet P] = \frac{k_3}{k_4}[P][E \bullet S]$$

$$r_{E \bullet S} = r_1 - r_2 - r_3 = r_1 - r_3 \equiv 0 = k_1[E][S] - k_2[E \bullet S] - k_F[E \bullet S] \Rightarrow [E \bullet S] = \frac{k_1[E][S]}{k_2 + k_F}$$

$$[E \bullet S \bullet P] = \frac{k_1 k_3[E][S][P]}{k_4(k_2 + k_F)}; E_t = [E] + [E \bullet S] + [E \bullet S \bullet P]$$

CDP7-C cont'd

$$E_t = [E] + \frac{k_1[E][S]}{k_2 + k_F} + \frac{k_1 k_3 [E][S][P]}{k_4(k_2 + k_F)} = [E]\left\{\frac{k_2 + k_F + k_1[S] + \frac{k_1 k_3}{k_4}[S][P]}{k_2 + k_F}\right\}$$

$$r_p = r_3 = k_F[E \bullet S]$$

$$r_p = \frac{k_F[S][E_t]}{\frac{k_2}{k_1} + \frac{k_F}{k_1} + [S] + \frac{k_3}{k_4}[S][P]}$$

This equation is similar to Eq7-72 of the text, with k_s replaced by k_F, V_{max} by $k_F[E_t]$, $[P]$ by $[I]$, K_m by $\frac{k_2 + k_F}{k_1}$ and K_I by $\frac{k_4}{k_3}$.

CDP7-D

a) Find the equilibrium conversion.

$$K_G = \frac{[E][G]}{[E \cdot S]} \qquad K_F = \frac{[E][F]}{[E \cdot S]}$$

$$[E][G]K_F = [E][F]K_G$$

$$[G] = [G]_0(1 - X_e)$$

$$[F] = [G]_0 X_e$$

$$\frac{X_e}{1 - X_e} = \frac{K_F}{K_G}$$

$$X_e = 0.5$$

b) 60% of $X_e = .3$

Design equation:

$$\frac{dX}{dt} = \frac{-r_G}{C_{G0}}$$

Rate law:

$$-r_G = \frac{E_t((k_3 C_G)/K_G - (k_2 C_F)/K_F)}{1 + (C_G/K_G) + (C_F/K_F)}$$

Stoichiometry:

$$C_G = C_{G0}(1 - X)$$

$$C_F = C_{G0} X$$

$$E = 15$$

Combining and using POLYMATH the answer is 4.4 h.

CDP7-D cont'd

```
Equations:                                            Initial value
d(t)/d(x)=Go/-rg                                      0
Go=2
v=1
E=15
k3=.015
Kg=.15
k2=.015
Kf=.15
cg=Go*(1-x)
cf=Go*x
Ngo=Go/v
rf=E*((k2*cg)/Kg-(k3*cf)/Kf)/(1+cg/Kg+cf/Kf)
rg=-rf
x0 = 0,   xf = 0.3
```

```
7-D
Variable      Initial value   Maximum value   Minimum value   Final value
x             0               0.3             0               0.3
t             0               4.37783         0               4.37783
Go            2               2               2               2
v             1               1               1               1
E             15              15              15              15
k3            0.015           0.015           0.015           0.015
Kg            0.15            0.15            0.15            0.15
k2            0.015           0.015           0.015           0.015
Kf            0.15            0.15            0.15            0.15
cg            2               2               1.4             1.4
cf            0               0.6             0               0.6
Ngo           2               2               2               2
rf            0.209302        0.209302        0.0837209       0.0837209
rg            -0.209302       -0.0837209      -0.209302       -0.0837209
```

c) Use same equations except $E = E_0e^{-0.2t}$.

Using POLYMATH the answer is 10.4 h.

```
Equations:                                            Initial value
d(t)/d(x)=Go/-rg                                      0
Go=2
v=1
E=15*exp(-.2*t)
k3=.015
Kg=.15
k2=.015
Kf=.15
cg=Go*(1-x)
cf=Go*x
Ngo=Go/v
rf=E*((k3*cg)/Kg-(k2*cf)/Kf)/(1+cg/Kg+cf/Kf)
rg=-rf
x0 = 0,   xf = 0.3
```

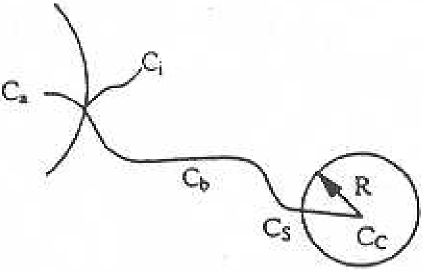
CDP7-D cont'd

```
Variable     Initial value   Maximum value   Minimum value   Final value
x            0               0.3             0               0.3
t            0               10.4199         0               10.4199
Go           2               2               2               2
v            1               1               1               1
B            15              15              1.8665          1.8665
k3           0.015           0.015           0.015           0.015
Xg           0.15            0.15            0.15            0.15
k2           0.015           0.015           0.015           0.015
Xf           0.15            0.15            0.15            0.15
cg           2               2               1.4             1.4
cf           0               0.6             0               0.6
Ngo          2               2               2               2
rf           0.209302        0.209302        0.0104177       0.0104177
rg           -0.209302       -0.0104177      -0.209302       -0.0104177
```

A conversion of 0.3 will be achieved quicker if a bigger K_f is used. A larger K_G will have the opposite effect and the conversion will be achieved at a slower rate. The value of k_2 has the same effect as K_f and k_3 has a similar effect to K_G.

CDP7-E No solution will be given

CDP7-F



(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:

$$\begin{aligned} R_{O_2} &= k_l a_b (C_i - C_b) \\ &= k_l a_b C_C (C_b - C_s) \\ &= \frac{\eta}{y_{O_2}} k C_S C_C \end{aligned}$$

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 $\eta \to 1$ 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:

$$\frac{1}{k_C a_C} = \alpha_2 d_p^b \qquad 1.5 \le b \le 2$$

$$R_C = y_{O_2} C_i\left[\frac{1}{k_l a_b} + \frac{1}{C_C}\left(\alpha_1 d_p + y_{O_2} \alpha_2 d_p^b\right)\right]^{-1}$$

CDP7-F (cont'd)

$$R_C = y_{O_2} C_i \left[\frac{1}{k_l a_b} + \frac{1}{C_C} \left(\alpha_1' C_C^{1/3} + \alpha_2' C_C^{b/3} \right) \right]^{-1}$$

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:

$$\mu \left(\text{hr}^{-1} \right) = \mu m \left(\frac{C_N}{K_N + C_N} \right) \left(\frac{C_0}{K_0 + C_0} \right)$$

$$R_C = \mu C_C$$

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:

$$\frac{C_0}{K_0 + C_0} = \frac{C_0}{K_0}$$

This implies that the consumption of oxygen is diffusion limited inside the pellet, i.e., that the Thiele modulus is large $(\phi > 1)$ (See Ref. 1, p.396). In order to check this (and to find the effectiveness factor) we calculate the Thiele modulus. For a first-order reaction in a biological pellet:

$$\phi = \frac{R}{3}\sqrt{\frac{\mu_{max}\, \rho_0}{y_{O_2}\, K_0\, D_0^{eff}}}$$

maximum specific growth rate $= \mu_{max} = 0.3\ hr^{-1} = 8.3 \times 10^{-5}\ s^{-1}$

yield coefficient: $Y_{O_2} = 1.5 \frac{g\ cell}{g\ O_2}$

Monod constant: $K_0 = 3.2 \times 10^{-7} \frac{g\ O_2}{cm^3}$

Effective diffusity: $D_0^{eff} = 1 \times 10^{-5} \frac{cm^2}{s}$

Pellet radius: $R = 0.01\ cm$

Cell density in pellet: $\rho_0 = f_{cell}\, \rho_{cell} = 0.5\left(\frac{300\ g}{l}\right)\left(\frac{l}{10^3\ cm^3}\right)$

$$= 0.15\ g/cm^3$$

$$\phi = 5.4$$

For a first-order reaction, the effectiveness factor is:

$$\eta = \frac{3}{\phi^2}(\phi \cosh \phi - 1)$$

$$\eta = 0.45$$

Reaction rate constant:

$$k = \frac{\mu_{max}}{K_s} = \frac{8.3 \times 10^{-5}\ s^{-1}}{3.2 \times 10^{-4} \frac{gO_2}{l}} = 0.26 \frac{l}{gO_2\ s}$$

Finally, assume an initial cell concentration of 0.25 g cell/l, the cell concentration equation now becomes:

$$\frac{(C_C - 0.25)\frac{g\ cell}{l}}{3.67 \times 10^{-2}\ s^{-1}} + \left[\frac{1.5 \frac{g\ cell}{gO_2}}{(0.45)\left(0.26 \frac{l}{gO_2\ s}\right)}\right] \ln 4C_C = \left(1.5 \frac{g\ cell}{gO_2}\right)\left(7.7 \times 10^{-3} \frac{g\ O_2}{l}\right) t$$

$$27.25\ (C_C - 0.25) + 12.8 \ln 4C_C = 0.012\ t$$

Clearly, mass transfer from the gas to the liquid phase and internal diffusion play important roles in determining the cell growth rate.

CDP7-F (cont'd)

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%?

$$k_l a_2 = k_l a_1 \left(1.5^{0.95}\right)$$

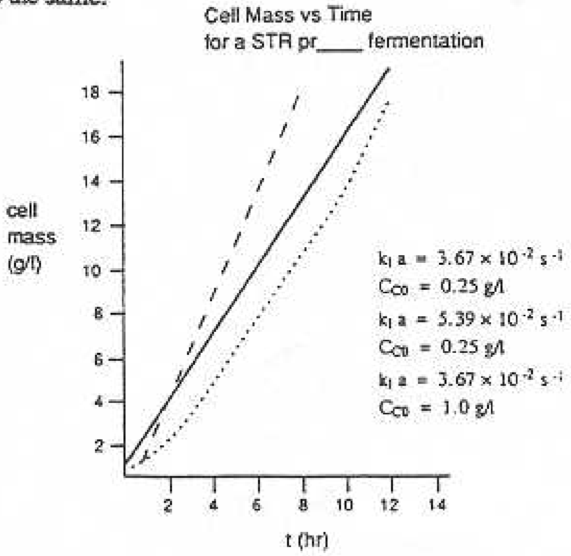
$$= \left(3.67 \times 10^{-2}\right) s^{-1} \left(1.5^{0.95}\right)$$

$$= \left(5.39 \times 10^{-2}\right) s^{-1}$$ (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?

$C_{C0} = 1.0$ g/l (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-G

$r_B = \mu_{max} C_B$

$r_A = ka\, C_A C_B$

$-r_{ad} = kd\, C_A$ $\qquad D = F/V$

Baterial balance:

$$\frac{dC_B}{dt} = D(C_{Bin} - C_B) + \mu_{max} C_B - \frac{k_a C_A C_B}{y_{A/B}}$$

Amoeba Balance

$$\frac{dC_A}{dt} = D(C_{Ain} - C_A) + k_a C_A C_B - k_d C_A$$

steady state $\quad \frac{dC_A}{dt} = \frac{dC_B}{dt} = 0 \qquad C_{B_{IN}} = 0 \quad C_{A_{IN}} = 0$

$$DC_B = \mu_{max} C_B - \frac{k_a C_A C_B}{y_{A/B}} \qquad (1)$$

$$DC_A = k_a C_A C_B - k_d C_A \qquad (2)$$

To rectify the contamination problem, have D high enough to wash out amoebas but not bacteria.

wish $C_A = 0$

$$\boxed{C_B = \frac{D + k_d}{k_a}} \qquad \boxed{C_A = \frac{D - \mu_{max}}{k_a} y_{A/B}}$$

CDP7-G (cont'd)

for $C_A = 0$ $\quad D = \mu_{max}$ $\quad$ No amoebas after reaching steady state.

$$C_B = \frac{\mu_{max} + k_d}{k_a} = \frac{0.5 + 0.01}{0.5} = 0.22\ \frac{g}{dm^3}$$ final bacterial concentration when $C_A = 0$

b) $C_{B_{IN}} = 0 \quad C_{A_{IN}} = 0$ then Bacteria and Amoeba Balance becomes

$$\boxed{\begin{aligned} \frac{dC_B}{dt} &= (\mu_{max} - D)\,C_B - \left(\frac{k_a C_A C_B}{y_{A/B}}\right) \\ \frac{dC_A}{dt} &= k_a C_A C_B - (D + k_d)\,C_A \end{aligned}}$$

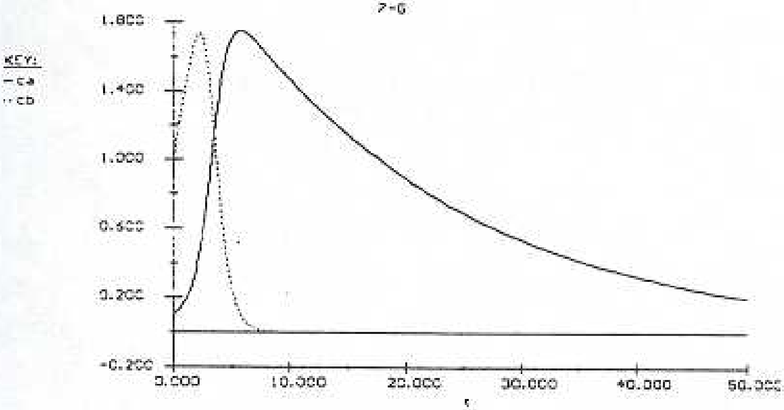
$\mu_{max} = 0.5\ hr^{-1}$ $\qquad k_d = 0.01$

$D = 0.04\ hr^{-1}$ $\qquad y_{A/B} = 0.5$

$k_a = 0.5$ $\qquad C_{A0} = 0.1$

$C_{B0} = 1.0$ $\quad \}$ at $t = 0$

```
7-G
Equations:                                                  Initial value
d(cb)/d(t)=(.5-d)*cb-.5/.5*ca*cb                            1
d(ca)/d(t)=.5*ca*cb-(d+.01)*ca                              0.1
d=.04
t0 = 0,   tf = 50
```



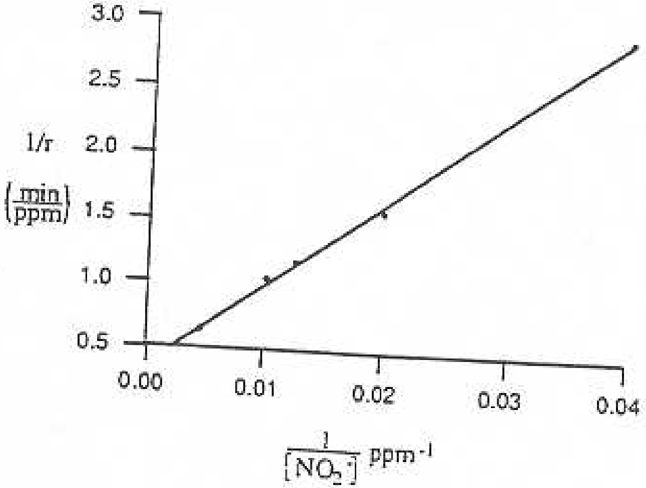
CDP7-H No solution will be given

CDP7-I

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, $V_{max} = \frac{1}{\text{intercept}} = 2.73\ \frac{\text{ppm}}{\text{min}}$

$\therefore\ K_m = 165$ ppm

Next, need conversion as a function of time.

Design equation: $N_{S0}\frac{dX}{dt} = -r_S V$

CDP7-I (cont'd)

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

$$S_0 = 0.25\left(\frac{mol}{l}\right)\left(46\frac{g}{mol}\right)\left(\frac{1000\ mg}{g}\right)\left(\frac{1\ ppm}{mg/l}\right) = 11{,}500\ ppm$$

Iteration to find the conversion obtained after 68 hrs gives: $X = 0.930$

The $[NO_2^-]$ level is: $(1 - 0.930)(11{,}500\ ppm) = 805\ ppm$

Since t, K_m, and S_0 are fixed by the system, the change must be made in V_{max}.

Desired conversion: $$X = 1 - \frac{500}{11{,}500} = .9565$$

$$\therefore\ \text{Desired } V_{max} = \frac{11{,}500(.9565) - 165\ln(1 - .9565)}{4080} = 2.823\ \frac{ppm}{min}$$

Since $V_{max}\ \alpha\ [E_t]$, increasing the concentration of whole cells in the emulsion will increase

$$V_{max}: \left(\frac{2.823}{273}\right) 50\ \frac{mg\ cells}{ml\ emulsion} = 51.7\ \frac{mg\ cells}{ml\ emulsion}.$$

Therefore, increasing the cell loading to 52 $\frac{mg\ cells}{ml\ emulsion}$ would results in a level of $[NO_2^-] <$ 500 ppm after 68 hours.

CDP7-J

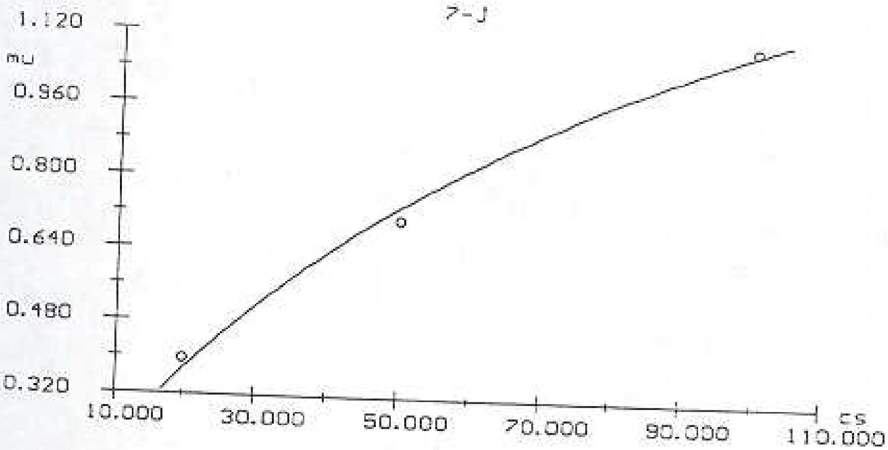
a)Find the μ value by dividing r_g by C_c.

μ	C_s
1.1	100
.71	50
.4	20

CDP7-J (cont'd)

Using POLYMATH, find the values for μ_{max} and K_S.

They are: $\mu_{max} = 2.1$
$K_S = 92.2$



```
Model: mu=mumax*cs/(ks+cs)
mumax = 2.09665
ks = 92.2253
2 positive residuals, 1 negative residuals.  Sum of squares = 0.00151407
```

b) Using the equation :

$$V = \frac{m_p}{Y_{P/C} r_g}$$

$$Y_{P/C} = \frac{Y_{P/S}}{Y_{C/S}} = .11$$

$$C_S = C_{S0} - C_C Y_{C/S} = 77.8$$

$$r_g = \frac{\mu_{max} C_S C_C}{K_S + C_S} = 19$$

$$V = 9.57 dm^3$$

Chapter 8

P8-1. An open-ended problem that requires students to create and original problem and solution.

P8-2. "What if. . ." problem. Many good extensions of the **Living Example** problems. Choose one or two parts **(c)** through **(k)** and alternate parts assigned form year to year. Part **(d)** is the easiest.

P8-3. Actual case history. This problem is continued in Chapter 9, **P9-3**. The point of this problem is to calculate the conditions at the time the CSTR feed was shut off. Fairly straight forward. The students have to use the enthalpy balance that includes phase change.

P8-4. Very good California problem. It takes some time for the students to realize that there is essentially complete conversion ($X=1$) and that work is done on the system.

P8-5. This problem concerns a liquid phase reaction carried out adiabatically. Parts **(a)** through **(d)** are straight forward and reinforce the principle of non-isothermal reactor design. Part **(e)** asks for a sensitivity analysis (i.e. parameter variation).

P8-6. This problems concerns an adiabatic gas phase reaction. The students sometimes forget that the gas phase reaction the concentration is a function of temperature. Overall this is a very straight forward problem.

P8-7. This problem extends **P8-6** to include pressure drop. Very straight forward using POLYMATH. However, one may run into trouble during the integration if α is to large and have to use the POLYMATH stiff algorithm.

P8-8. This problem encompasses all the facets of non-isothermal PBR and CSTRs with heat exchange. Fairly straight forward with POLYMATH and reinforces the concepts. This problem can be alternated form year to year with **P8-9, P8-12,** and **P8-15.**

P8-9. Same comments as for **P8-8** except it does not have any CSTR calculations. Alternate with **P8-8, P8-12,** and **P8-15.**

P8-10. This problem shows the competing effects of adding an inert to an endothermic reaction. The students are asked to find the concentration (flow rate) of inert that maximizes the conversion. A straight forward problem. That can be alternated with **P8-23.**

P8-11. This problem requires the student to apply the energy balance to a membrane reactor. The student will have to derive the necessary relationships from first principles because there are not formulas given for membrane reactors with heat effects in the book.

P8-12. Same comments as for **P8-8** except there are no CSTR calculations. Alternate with **P8-8**, **P8-9**, and **P8-15**.

P8-13. Straight forward problem involving reactor staging.

P8-14. No calculations are required in this somewhat complex problem on reactor staging.

P8-15. Same comments as for **P8-8**, however, even though this reaction is reversible, the problem is fairly straight forward.

P8-16. This problem is a very slightly more difficult problem on reactor staging than **P8-13**, yet is reasonably straight forward.

P8-17. This is a straight forward problem on multiple steady states. Alternate to **P8-20**, **P8-21**, and **P8-22**.

P8-18. This problem is usually assigned at the graduate level.

P8-19. Problem involving calculating the conditions for the reaction to RUNAWAY.

P8-20. Same comments as **P8-17**. Alternate to **P8-17**, **P8-21**, and **P8-22**.

P8-21. Same comments as **P8-17**. Alternate to **P8-17**, P8-20, and **P8-22**.

P8-22. This problem is the most often problem assigned of the multiple steady state problems.

P8-23. Find the optimum feed rate of inerts for **Living Example 8-7**. Similar to **P8-10**.

P8-24. Derivation of energy balance to include radial temperature gradients. Assigned only at the graduate level.

Problems **P8-25** through **P8-27** concern using **Living Example Problem E8-10** to study different effects and conditions for the SO_2 oxidation.

Problems **P8-28** through **P8-32** involve multiple reactions with heat effects. In my mind these problems are one of the pinnacles, if not *the* pinnacle of an undergraduate course in chemical reaction engineering.

P8-28. This problem concerns series reaction with heat effects in a CSTR. The instruction could extend the problem statement in the text to ask the students to carry out a parameter sensitivity. E.g. increase/decrease/ E_1 and E_2. This problem could be alternated with **P8-31**, which involves parallel reactions.

P8-29. Encompasses all the aspects of multiple reactions with heat effect. Fairly straight forward problem with POLYMATH.

P8-30. This problem on the production of styrene is almost always assigned. It encompasses all the facets of multiple reactions with heat effects. The students will be able to find an optimum inlet temperature and an optimum inert flow rate. Double or triple credit is often assigned for this problem.

P8-31. Parallel reactions with heat effects in a CSTR. Quite straight forward using the POLYMATH non-linear equation solver.

P8-32. *<Prof. Fogler: Anything going here?>*

CDP8-A Very straight forward.

CDP8-B Assigned at graduate level.

CDP8-C Assigned at graduate level.

CDP8-D Assigned at graduate level.

CDP8-E Continuation of problems **P8-26** and **P8-27**.

CDP8-F Continuation of problems **P8-26** and **P8-27**.

CDP8-G Continuation of problems **P8-26** and **P8-27**.

CDP8-H Straight forward problem of parallel reactions H with heat effects.

CDP8-I Alternative to problems **P8-20**, **P8-21**, **P8-22**, **CDP8-?**, and **CDP8-N**.

CDP8-J Straight forward problem of series reactions with heat effects.

CDP8-K No so straight forward of multiple reaction with heat effects.

CDP8-L More complicated version of Problems **P8-20**, **P8-21**, and **P8-22**.

CDP8-M Alternative to **P8-20**, **P8-21**, and **P8-22**.

CDP8-N More complicated version of **P8-20**, **P8-21**, and **P8-22**.

CDP8-O Straight forward problem of multiple reactions O with heat effects.

CDP8-P Straight forward alternative to **P8-6**.

		Assigned	Alternates	Difficulty	Time	Solution Given
	P8-1				–	No
●	P8-2				120	No
●	P8-3			FSF	45	Yes
●	P8-4			FSF	30	Yes
●	P8-5	AA	6,J,N	SF	75	Yes
	P8-6	AA	5,J,N	SF	50	Yes
	P8-7	O		SF	30	Yes
●	P8-8	AA	9,12	SF	75	Yes
	P8-9	AA	8,12	SF	60	Yes
●	P8-10		23	SF	60	Yes
	P8-11	G		MD	75	Yes
	P8-12	AA	8,9	FSF	60	Yes
●	P8-13	AA	14,15,16	SF	45	Yes
	P8-14	AA	13,15,16	MD	60	Yes
	P8-15	AA	13,14,16	FSF	70	Yes
	P8-16	AA	13,14,15	SF	45	Yes
	P8-17	AA	20,21,22,L	SF	60	Yes
	P8-18	G		MD	75	Yes
	P8-19	O/G		MD	60	Yes
	P8-20	AA	17,21,22,D,L,I	SF	95	Yes
●	P8-21	AA	17,20,22,D,L,I	SF	60	Yes
	P8-22	AA	17,20,21,D,L,I	FSF	75	Yes
	P8-23	O	10	SF	75	Yes
	P8-24	G		MD	120	No
●	P8-25	G		MD	90	Yes
	P8-26	I	27,E,F,G	MD	90	Yes
	P8-27	I	26,E,F,G	MD	75	Yes
	P8-28	I/G	29,30,31,H	MD	75	Yes
	P8-29	AA	28,30,31,H	MD	60	Yes
●	P8-30	AA	28,29,31,H	MD	100	Yes
●	P8-31	O	28,29,30,H	MD	60	Yes
	P8-32				60	Yes
	CDP8-A			FSF	75	Yes
	CDP8-B	G	C	MD	45	Yes
	CDP8-C	G	B	FSF	45	Yes
	CDP8-D	I/G	17,20,21,22,L,I	MD	60	Yes
	CDP8-E	I/G	26,27,F,G	MD	60	Yes
	CDP8-F	I/G	26,27,E,G	MD	60	Yes
	CDP8-G	I/G	26,27,E,F	MD	60	Yes
	CDP8-H	I	28,29,30,31	MD	45	Yes
	CDP8-I	I	17,20,21,22,D,L	FSF	45	Yes
	CDP8-J	I	5,8,G	FSF	40	Yes
	CDP8-K	G	28,29,30,31,H,I	MD	75	Yes
	CDP8-L	G/O	17,20,21,22,D,I	MD	120	Yes
	CDP8-M	AA	5,6,J,P	SF	45	Yes
	CDP8-N	I	17,20,21,22,D,I,L	MD	60	Yes

CDP8-O	AA	29,30,31,H,I,J	MD	75	Yes
CDP8-P	O	5,6,J,N	FSF	75	Yes

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.

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

Summary Table Ch-8

	PFR	PBR	CSTR	Membrane	Staging	MSS	Multiple Reaction
Adiabatic	2(e),5(a), 6(a),10,23		3,5(a,d) 6(b)	11	13,14,16	17,20,21, 22	28,31,3
Non adiabatic	15	7,8,12,26, 27	4,8(c), 15(c),19				28,30
Straight forward	5(a,c),6(a)	8(a),12(a)	5(a,d), 6(b),8(c)		13 16	20 21	30(a,b,c
Parameter variation	2(c,d,g,h,i) 5(b,e),8(e) 9(b,c), 10(c),12(d)		12(j)				

Chapter 8

P8-1 No solution will be given.

P8-2 No solution will be given.

P8-3

Part I: Find reactor temperature at steady state (prior to shut down).

Let M: mass of NH_4NO_3 in reactor
F_{A0}: lbs/hr NH_4NO_3 fed to reactor

Mass balance: $F_{A0} - F_{A0}(1-X) = -r_AV = kM$.

$$X = \frac{k(T)M}{F_{A0}}$$

Energy balance:

$$-F_{A0}\Sigma\theta_i[H_{io} - H_i(T)] + F_{A0}X\Delta H_{Rxn}(T) + F_{A0}(1-X)\Delta H_{VA} = 0$$

where $H_i(T)$ is the enthalpy of i at the phase and 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:

$$NH_4NO_3(l) \rightarrow 2H_2O(g) + N_2O(g)$$

$$A \rightarrow 2B + C$$

The last term $F_{A_0}(1-X)\Delta H_{VA}$ accounts for the unreacted NH_4NO_3, which exits as vapor rather than liquid. Now, we can make some substitutions

$$\theta_B = \frac{0.17}{0.83}\ ,\ \theta_A = 1\ ;\ \theta_C = 0$$

Heat capacity of A is given, and the enthalpy change for water 200°F (l)→ 500°F (g) is also given. So, after dividing out F_{AO}, we obtain:

$$C_{pA}(T-200) + \theta_B\left[H_B(500°F) - H_B(200°F) + C_{pB}(T-500)\right]$$
$$+ \Delta H_{Rxn}X + (1-X)\Delta H_{VA} = 0$$

The previous equation assumes that (1) Heat capacities are constant over a reasonable temperature range, and (2) the phase change NH_4NO_3 (aqueous) → NH_4NO_3 (liquid) is isenthalpic. In addition, we must account for the effect of the temperature dependence of ΔH_{Rxn}

P8-3 cont'd

$$\Delta H_{Rxn}(T) = \Delta H_{Rxn}(T_r) + (T-T_r)\left[\frac{44}{80}C_{p_C} + \frac{36}{80}C_{p_B} - C_{p_A}\right] = \Delta H_{Rxn}(T_r) + (T-T_r)\,\Delta C_p$$

Let $\Delta H_W = H_B(500) - H_B(200)$, we have:

$$C_{p_A}(T-200) + \theta_B\left(\Delta H_W + C_{p_B}(T-500)\right) + X\left[\Delta H_{Rxn} + \Delta C_p(T-500)\right]$$
$$+ (1-X)\,\Delta H_{V_A} = 0$$

or: $T\left\{C_{p_A} + \theta_B C_{p_B}\right\} + \left[-C_{p_A}(200) + \theta_B\left(\Delta H_w - 500C_{p_B}\right)\right]$

$$+ X\left[\Delta H_{Rxn} + \Delta C_p(T-500)\right] + (1-X)\,\Delta H_{V_A} = 0$$

Numerical substitution with.

$$k(560) = 5.03;\ k(510) = 0.53$$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \rightarrow \frac{E_A}{R} = -\ln\left(\frac{k_2}{k_1}\right)\left[\frac{1}{T_2} - \frac{1}{T_1}\right]^{-1}$$

$$\frac{E_A}{R} = -\ln\left(\frac{5.03}{0.53}\right)\left[\frac{1}{560 + 459.67} - \frac{1}{510 + 459.67}\right]^{-1} = 44499$$

$$A_O = k_1 \exp\left(\frac{E_A}{RT_1}\right) = 4.51424 \times 10^{19}$$

$C_{p_A} = 0.38\ \frac{\text{Btu}}{\text{lb} \cdot \text{R}}$; $C_{p_B} = 0.466$ (P = 1 atm over 450 - 500°F Himmelblau)

$C_{p_C} = 0.2521\ \frac{\text{Btu}}{\text{lb} \cdot \text{R}}$ (Himmelblau, App. E, over 230-265°C)

$$\theta_B = \frac{0.17}{0.83} = 0.205$$

$$\Delta H_w = 1034\ \frac{\text{Btu}}{\text{lb}}$$

$$F_{A0} = 257.3\ \frac{\text{lb } NH_4NO_3}{\text{hr}}$$

$$\Delta C_p = \frac{44.02}{80.05}(0.2521) + \frac{36.03}{80.05}(0.466) - 0.38 = -0.0316\ \frac{\text{Btu}}{\text{lb} \cdot \text{R}}$$

$$\Delta H_{Rxn} = -336\ \frac{\text{Btu}}{\text{lb } NH_4NO_3}$$

$$\Delta H_{V_A} = C_{p_A}(410 - T)$$

Substituting all of this into the mass and energy balances:

P8-3 cont'd

mass balance: $X = \dfrac{4.51 \times 10^{19} \exp\left(\dfrac{-44499.4}{T + 459.67}\right) M}{257.3}$

Energy balance:

$$0 = 0.48\ T + 88.21 + X(-320.20 - 0.03\ T) + (1 - X)(155.80 - 0.38T)$$

Assume X = 0.96 and M = 500. From mass balance:

$$T = \left[\ln\left[\frac{XF_{A0}}{M_{A0}}\right] / E_A\right]^{-1} - 459.67$$

$$T = 510°F$$

P8-4 Given: The endothermic liquid phase elementary reaction

$$A + B \rightarrow 2C$$

Feed	A	B	C
F_{io} ; $\left(\frac{\text{lb mole}}{\text{hr}}\right)$	10	10	0.0
T_{io} , (°F)	80	80	--
$\tilde{C}_{P_{io}}$, $\left(\frac{\text{Btu}}{\text{lb mole °F}}\right)$	51	44	47.5
MW , $\left(\frac{\text{lb}}{\text{lb mole}}\right)$	128	94	222
ρ_i , $\left(\frac{\text{lb}}{\text{ft}^3}\right)$	63	67.2	65

ΔH_R = 20.000 Btu/lbmole. A = constant

Energy balance with work term included is:

$$\frac{\dot{Q} - \dot{W}_s}{F_{A0}} - X_A\ \Delta H_R = \Sigma\theta_i\ \tilde{C}_{P_i}[T - T_o]\ ;$$

$$\theta_A = 1,\ \theta_B = \frac{F_{B0}}{F_{A0}} = \frac{10}{10} = 1,\ X_{AF} = 1$$

$$\dot{Q} = UA\ (T_S - T)$$

Substituting into energy balance,

P8-4 cont'd

See page no. 444 eqn 8.51

$$UA(T_S - T) - W_S - F_{A0}\Delta H_R X_{AF} = F_{A0}[C_{pA} + C_{pB}][T - T_o] \text{, or}$$

$$UA(T_S - T_O) - \dot{W}_S - F_{A0}\Delta H_R = \{F_{A0}[C_{pA} + C_{pB}] + UA\}[T - T_o] \text{, or}$$

$$T = T_o + \frac{UA(T_S - T_o) - \dot{W}_S - F_{A0}\Delta H_R}{F_{A0}[C_{pA} + C_{pB}] + UA}$$

$$-W_S = 25\ \text{hp} \times \frac{2545\ \text{Btu}}{\text{hp}\cdot\text{hr}} = 63{,}525\ \frac{\text{Btu}}{\text{hr}}$$

$$T = 80^\circ\text{F} + \frac{150\ \frac{\text{Btu}}{\text{hr ft}^2\ ^\circ\text{F}} \times 10\ \text{ft}^2 (365.9 - T)^\circ\text{F} + 63{,}625\ \frac{\text{Btu}}{\text{hr}} - 10\ \frac{\text{lb mol}}{\text{hr}} \times \frac{20{,}000\ \text{Btu}}{\text{lb mol}}}{10\ \frac{\text{lb mol}}{\text{hr}}[51 + 44]\ \frac{\text{Btu}}{\text{lb mol}\ ^\circ\text{F}} + 150\ \frac{\text{Btu}}{\text{hr ft}^2\ ^\circ\text{F}} \times 10\ \text{ft}^2}$$

$$T = 199\ ^\circ\text{F}$$

P8-5

$$A + B \rightarrow C$$

1) $V_{PFR} = F_{A0}\int \frac{dX}{-r_A}$, $\quad V_{CSTR} = \frac{F_{A0}}{-r_A}$

2) $-r_A = k\,C_A\,C_B$, $\quad k = k(300)\,e^{\frac{E}{R}\left(\frac{1}{300} - \frac{1}{T}\right)}$

3) Liquid Phase $\quad C_A = C_{A0}(1-X)$

$C_{A0} = C_{B0}$ $\quad C_B = C_{A0}(1-X)$

4) Adiabatic

$$T = T_o + \frac{X(-\Delta H_R(T_o))}{\Sigma\Phi_i\,\tilde{C}_{P_i} + X\Delta\tilde{C}_P}$$

A) $\Delta C_p = C_{pC} - C_{pB} - C_{pA} = 30 - 15 - 15 = 0$

$\Delta H_R(T) = H_C - H_B - H_A = (-41{,}000) - (-15{,}000) - (-20{,}000)$

B) $\Delta H_R(T) = -6{,}000$ cal/mole A

C) $\Sigma\theta_i\,\tilde{C}_{P_i} = C_{pA} + \theta_B C_{pB} = C_{pA} + C_{pB} = 15 + 15 = 30$ cal/mol · K

$$T = 300 + \frac{6000\,X}{30} = 300 + 200\,X$$

$$\boxed{T = 300 + 200\,X}$$

P8-5 cont'd

5) $-r_A = k\,C_{A0}^2(1-X)^2$

$-r_A = 10^{-2}\,k\,(1-X)^2$

6) Parameter Evaluation

A) CSTR $X = 0.85$ $T = 300 + 170 = 470$

$k = 4.31, \quad k\,C_{A0}^2 = 0.0431$

$$-r_A = (.0431)(.15)^2 = 9.71 \times 10^{-4}\,\frac{\text{mol}}{\text{dm}^3\cdot\text{s}}$$

$$V = \frac{F_{A0}X}{-r_A} = \frac{C_{A0}V_0X}{-r_A} = \frac{(0.1)(2)(.85)}{9.71 \times 10^{-4}}$$

$$\boxed{V = 175\ \text{dm}^3}$$

B) PFR

X	T	k	$-r_A \times 10^4$	$\frac{F_{A0}}{-r_A}$
0	300	0.01	1	$f_0 = 2000$
.2	340	.072	4.6	$f_1 = 435$
.4	380	.34	12.3	$f_2 = 163$
.6	420	1.21	19.3	$f_3 = 103$
.8	460	3.42	13.7	$f_4 = 146$
.85	470	4.31	9.71	$f_5 = 206$

$$V = \frac{h}{3}[f_0 + 4f_1 + 2f_2 + 4f_3 + f_4] + \frac{h}{2}[f_4 + f_5]$$

$$= \frac{0.2}{3}[2000 + 4(435) + 2(163) + (103) + 146] + \frac{.05}{2}[146 + 206]$$

$$= \frac{0.2}{3}[2000 + 1740 + 326 + 412 + 146] + \frac{.05}{2}[146 + 206]$$

$$V = 308. + 8.8 = 317\ \text{dm}^3$$

b) $$T = T_o + \frac{(-\Delta H_R)X}{\Sigma\,\theta_i\,C_{P_i}}$$

$550 = T_o + 200$

$$\boxed{T_o = 350}$$

P8-5 cont'd

c) POLYMATH

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$r_A = -k\,C_A^2$$

$$\frac{dT}{dV} = (r_A)(\Delta H_R)/(C_{pA} + C_{pB})/F_{A0}$$

$$\Delta H_R = -6{,}000$$

$$k = 0.01 \exp\left[5032.7\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

$$C_A = 0.1\,(1-X)$$

$$F_{A0} = 0.2$$

d) POLYMATH CSTR

$$F(X) = 500 - \frac{.2X}{-r_A}$$

$$r_A = -.01\,k\,(1-X)^2$$

$$k = 0.01 \exp\left[5033\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

$$F(T) = 300 + 200X - T$$

$X = .9$, $T = 480$, $k = 5.4$

Polymath $X = .9211$ $T = 484.21$

e) Making $E = 1000$, causes the conversion to decrease and the profile will be a straight line for the same volume. Making $E = 30000$ cause X to go to completion at a volume of only about 60 dm^3. Making $\Delta H_R = -2000$ decreases the conversion and makes the profile a straight line. Making $\Delta H_R = -25000$ also causes the reaction to go to completion in a volume of only 45 dm^3.

f) To find T_r, the following must be true:

$$T_r - T_c = \frac{RT_r^2}{E}$$

So:

$$T_c = \frac{T_0 + \kappa T_A}{1+\kappa} = \frac{300 + 3*300}{1+3} = 300$$

$$\frac{1.987}{10000} T_r^2 - T + 300 > 0$$

$$T_r > 320.4K$$

P8-6

$$\frac{dX}{dW} = -r_A'/F_{A0}$$

$$\frac{dT}{dW} = \frac{r_A' \, \Delta H_R}{F_{A0} \, C_{pA}}$$

neglect pressure drop , $\varepsilon = 1.0$

$$r_A = -k\, C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{T_o}{T} = -\, k\, C_{A0} \frac{(1-X)}{(1+X)} \left(\frac{450}{T}\right) .$$

$$C_{A0} = \frac{y_{A0}\, P_o}{RT_o} = \frac{(1)(10)}{(0.082)(450)} = 0.271 \, \frac{mol}{dm^3}$$

$$F_{A0} = \upsilon_o \, C_{A0} = \left(\frac{20 \, dm^3}{s}\right)\left(0.271 \, \frac{mol}{dm^3}\right) = 5.42 \, \frac{mol}{s}$$

$$E = \frac{31.4 \, kJ}{mol} \quad , \quad \frac{E}{R} = 3776.6$$

$$k = (.133) \exp\left[3776.6 \left(\left(\frac{1}{450}\right) - \left(\frac{1}{T}\right)\right)\right]$$

$$\Delta C_p = 15 + 25 - 40 = 0$$

$$\Delta H_R = -40 + -50 - (-70) = -20 \, \frac{kJ}{mol}$$

Since the reaction is adiabatic, we could solve the energy balance to give

$$\boxed{T = T_o - \frac{\Delta H_R(T_o)\, X}{\Sigma \theta_i \, \tilde{C}_{p_i} + X \Delta C_p}}$$

P8-6 cont'd

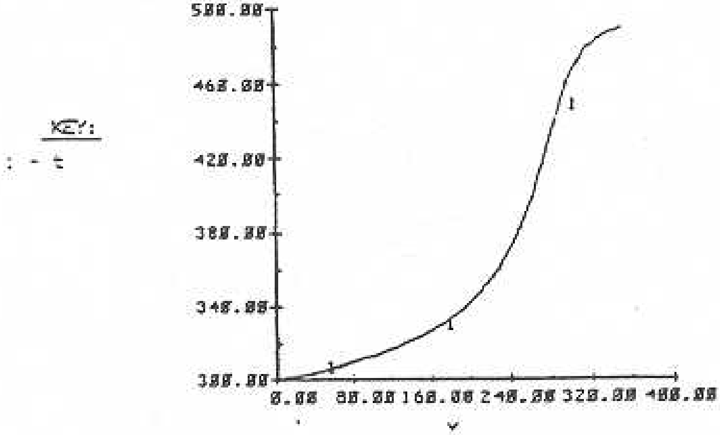
$$T = T_o - \frac{\Delta H_R X}{C_{pA}}$$

$$T = 450 - \frac{(-20{,}000)X}{40}$$

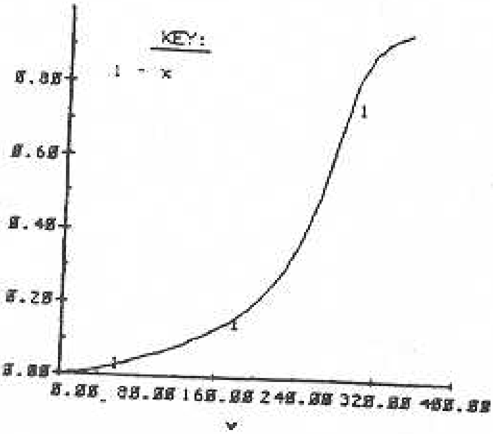
$$\boxed{T = 450 + 500\,X}$$

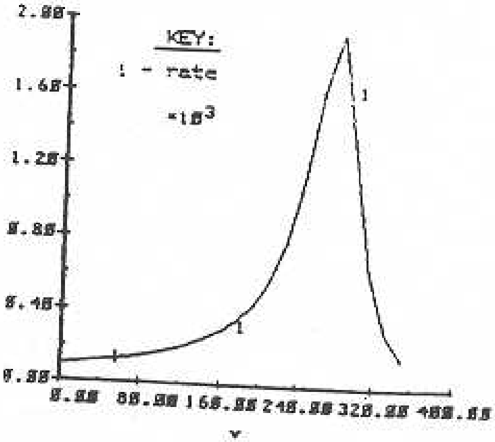
See POLYMATH Program Below

```
                                   Problem

The equations:
     d(x)/d(v)=-ra/fa0
     d(t)/d(v)=ra*dh/(cpa+cpb)/fa0
     k=.01*exp(5032.7*(1/300-1/t))
     ca0=.1
     ca=ca0*(1-x)
     ra=-k*ca**2
     dh=-6000
     cpa=15
     cpb=15
     fa0=.2
     rate=-ra
Initial values: v0= 0.0, x0= 0.0, t0= 300.00
Final value:  vf= 250.00
```



P8-6 cont'd





b) Fluidized bed CSTR

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

$$-r'_A = k\, C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{T_o}{T}$$

$$k = (.133)\exp\left[3776.6\left(\left(\frac{1}{450}\right)-\left(\frac{1}{T}\right)\right)\right]$$

Adiabatic with $\dot{W}_s = 0$

$$\boxed{T = T_o - \frac{\Delta H_R(T_o)\,X}{\Sigma\theta_i\,\tilde{C}_{p_i} + X\Delta C_p}}$$

$\Delta H_R\ (T_R) = -20{,}000$ kJ/mol

$\Delta C_p = 0$, Pure A fed

$$T = T_o + \frac{(-\Delta H_R(T_R))\,X}{C_{PA}} = 450 + \frac{(-(-20{,}000))X}{40}$$

$$\boxed{T = 450 + 500\,X}$$

when $X = .8$, $T = 850$

P8-6 cont'd

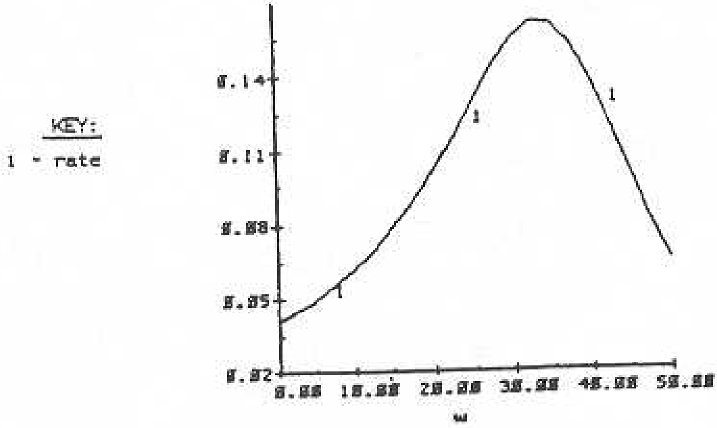
$$k = (.133)\exp\left[3776\left(\frac{1}{450} - \frac{1}{850}\right)\right]$$

$$k = 6.9 \quad , \quad \varepsilon = 1$$

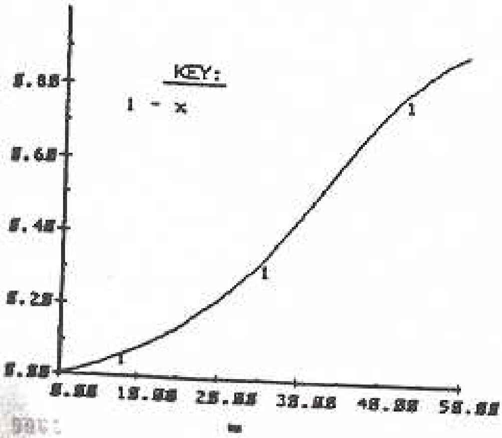
$$-r_A' = 6.9\,(0.271)\frac{(1-.8)}{(1+.8)}\;\frac{450}{850} = \frac{0.11\text{ mol}}{\text{kg cat}\cdot\text{s}}$$

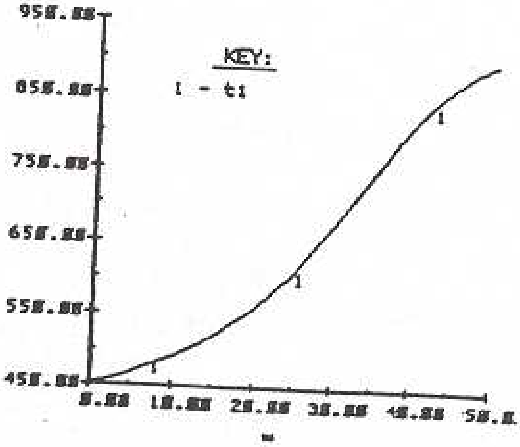
$$\boxed{W = \frac{(5.42\text{ mol/s})(.8)}{.11\text{ mol/kg cat}\cdot\text{s}} = 39.4\text{ kg cat}}$$

```
                                problem 8-6

The equations:
     d(x)/d(w)=-ra/fa0
     t1=450+500*x
     k=.133*exp(3776.6*((1/450)-(1/t1)))
     ca0=.271
     ca=ca0*(1-x)*(450/t1)/(1+x)
     ra=-k*ca
     fa0=5.42
     dhr=-20000
     cpa=40
     rate=-ra
Initial values: w0= 0.0, x0= 0.0
Final value:  wf= 50.000
```



P8-6 cont'd





P8-7

$$\frac{dX}{dW} = \frac{-r'_A}{F_{AO}}$$

$$\frac{dT}{dW} = \frac{r_A(\Delta H_R)}{F_{AO}C_{pA}}$$

or since reaction is adiabatic with $\dot{W}_S = 0$ we could use

$$T = 450 + 500\,X$$

$$-r'_A = k\,C_{A0}\frac{(1-X)}{(1+X)}\left(\frac{450}{T}\right)y$$

where $y = P/P_o$

Then

$$\frac{dy}{dW} = -\frac{\alpha\,(1+\varepsilon X)(T/T_o)}{2y} = -\frac{\alpha\,(1+X)}{2y}\left(\frac{T}{450}\right)$$

$$k = \left(\frac{0.133}{s}\right)\exp\left[3776.6\left(\left(\frac{1}{450}\right)-\left(\frac{1}{T}\right)\right)\right].$$

See POLYMATH Program $-r'_A = k\,C_{A0} = 0.27\ \frac{mol}{dm^3}$, $F_{A0} = 5.42\ \frac{mol}{s}$, $\alpha = 0.019\ kg^{-1}$

p8-7 cont'd

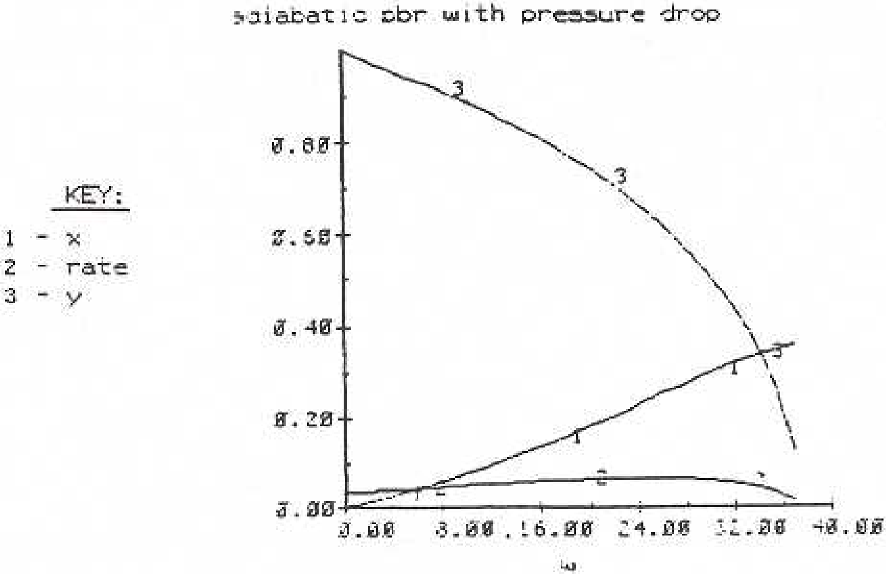
adiabatic pbr with pressure drop

The equations:

```
    d(x)/d(w)=-ra/fa0
    d(t1)/d(w)=ra*dhr/(fa0*cpa)
    d(y)/d(w)=-(1+x)*(t1/450)*alpha/(2*y)
    k=.133*exp(3776.6*((1/450)-(1/t1)))
    ca0=.271
    ca=ca0*(1-x)*(450/t1)/(1+x)*y
    ra=-k*ca
    fa0=5.42
    dhr=-20000
    cpa=40
    rate=-ra
    alpha=.019
```

Initial values: $w_0 = 0.0$, $x_0 = 0.0$, $t1_0 = 450.00$, $y_0 = 1.0000$

Final value: $w_f = 37.000$



p8-7 cont'd

```
                         adiabatic por

                      Integration Results

      w            x            t1           rate            y
  0.0          0.0          450.00        0.0360        1.0000
  1.5000       0.0101       455.05        0.0378        0.9856
  3.0000       0.0207       460.34        0.0396        0.9707
  4.5000       0.0318       465.89        0.0416        0.9552
  6.0000       0.0434       471.71        0.0436        0.9392
  7.5000       0.0556       477.81        0.0457        0.9224
  9.0000       0.0684       484.20        0.0478        0.9049
  10.500       0.0818       490.89        0.0500        0.8866
  12.000       0.0958       497.89        0.0523        0.8674
  13.500       0.1104       505.20        0.0545        0.8472
  15.000       0.1256       512.82        0.0567        0.8259

      w            x            t1           rate            y
  15.000       0.1256       512.82        0.0567        0.8259
  16.500       0.1415       520.74        0.0589        0.8035
  18.000       0.1579       528.96        0.0609        0.7797
  19.500       0.1749       537.44        0.0626        0.7544
  21.000       0.1923       546.16        0.0641        0.7275
  22.500       0.2102       555.08        0.0653        0.6986
  24.000       0.2283       564.14        0.0659        0.6676
  25.500       0.2465       573.26        0.0659        0.6341
  27.000       0.2647       582.36        0.0652        0.5976
  28.500       0.2825       591.27        0.0634        0.5566
  30.000       0.2997       599.86        0.0606        0.5109
```

p8-7 cont'd

adiabatic pbr

Integration Results

w	x	t1	rate	y
30.000	0.2997	599.86	0.0606	0.5109
30.300	0.3031	601.53	0.0599	0.5012
30.600	0.3064	603.19	0.0591	0.4912
30.900	0.3096	604.82	0.0583	0.4810
31.200	0.3128	606.42	0.0574	0.4705
31.500	0.3160	608.00	0.0564	0.4597
31.800	0.3191	609.56	0.0554	0.4486
32.100	0.3222	611.09	0.0544	0.4372
32.400	0.3252	612.58	0.0532	0.4254
32.700	0.3281	614.05	0.0520	0.4132
33.000	0.3310	615.48	0.0507	0.4006
33.300	0.3337	616.87	0.0493	0.3875
33.600	0.3364	618.22	0.0478	0.3739
33.900	0.3391	619.53	0.0462	0.3598
34.200	0.3416	620.80	0.0445	0.3450
34.500	0.3440	622.02	0.0427	0.3295
34.800	0.3464	623.19	0.0408	0.3132
35.100	0.3486	624.30	0.0387	0.2960
35.400	0.3507	625.36	0.0364	0.2777
35.700	0.3527	626.35	0.0340	0.2581
36.000	0.3546	627.27	0.0313	0.2369

w	x	t1	rate	y
36.000	0.3546	627.27	0.0313	0.2369
36.075	0.3550	627.49	0.0305	0.2311
36.150	0.3554	627.70	0.0298	0.2253
36.225	0.3558	627.90	0.0290	0.2193
36.300	0.3562	628.10	0.0282	0.2131
36.375	0.3566	628.30	0.0274	0.2067
36.450	0.3570	628.48	0.0265	0.2001
36.525	0.3573	628.67	0.0256	0.1933
36.600	0.3577	628.84	0.0247	0.1862
36.675	0.3580	629.01	0.0238	0.1789
36.750	0.3584	629.17	0.0228	0.1713
36.825	0.3587	629.33	0.0217	0.1633
36.900	0.3590	629.48	0.0206	0.1549
36.975	0.3592	629.62	0.0194	0.1460
37.050	0.3595	629.75	0.0182	0.1366
37.125	0.3598	629.87	0.0168	0.1264
37.200	0.3600	629.99	0.0154	0.1155
37.275	0.3602	630.09	0.0138	0.1034
37.350	0.3604	630.18	0.0120	0.0898
37.425	0.3605	630.26	0.987×10^{-2}	0.0740
37.500	0.3607	630.32	0.701×10^{-2}	0.0526

P8-8 Same as 8-6 except for the energy balance

$$\frac{dX}{dW} = -r_A'/F_{A0}$$

$$\frac{dT}{dW} = \frac{\left[(U_a/\rho_C)(T_a-T) + (r_A')(\Delta H_R)\right]}{F_{A0}\,\Sigma\,\theta_i\,C_{P_i}}$$

$$\frac{dT}{dW} = \frac{\left[(U_a/\rho_C)(T_a-T) + (r_A')(\Delta H_R)\right]}{F_{A0}\,C_{pA}}$$

$U_a/\rho_C = 0.8$ J/s · kg cat · K

$T_a = 323$ K

Other variables the same P8-6

For Parts (a), (b), and (c)

$$r_A = -k\,C_{A0}\frac{(1-X)}{(1+X)}\left(\frac{450}{T}\right)$$

For Part (d)

$$r_A = -k\,C_{A0}\frac{(1-X)}{(1+X)}\frac{450}{T} + \frac{k_r\,C_{A0}^2\,X^2}{(1+X)^2}\left(\frac{450}{T}\right)^2$$

This system of equations must be solved numerically. See POLYMATH Program and results.

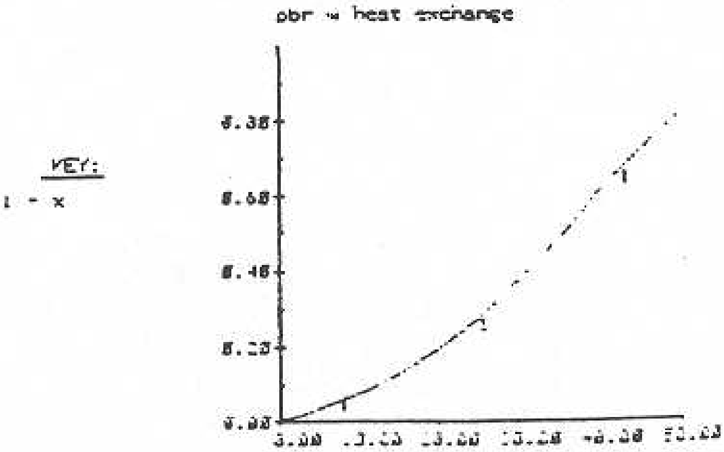
(a)
```
                              pbr w heat exchange
The equations:
      d(x)/d(w)=-ra/fa0
      d(t1)/d(w)=(ua*(ta-t1)+ra*dhr)/(fa0*cpa)
      k=.133*exp(3776.6*((1/450)-(1/t1)))
      ca0=.271
      ca=ca0*(1-x)*(450/t1)/(1+x)
      ra=-k*ca
      fa0=5.42
      dhr=-20000
      cpa=40
      rate=-ra
      ua=.3
      ta=323
Initial values: w0= 0.0, x0= 0.0, t10= 450.00
Final value:  wf= 50.000
```

P8-8 cont'd

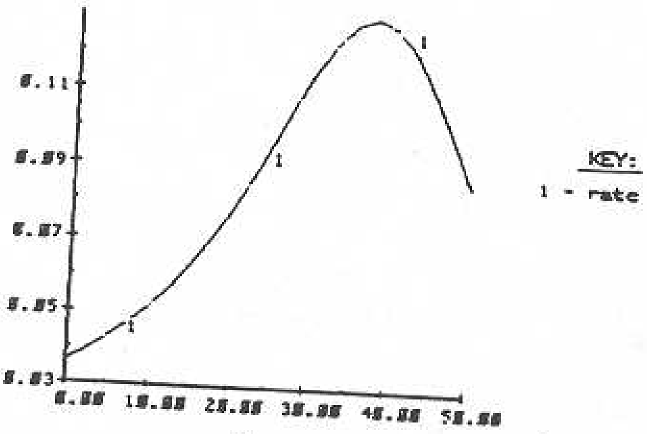
```
                         Integration Results

           w              x              t1              rate
     0.0            0.0            450.00           0.0360
     2.5000         0.0170         457.30           0.0392
     5.0000         0.0355         465.20           0.0420
     7.5000         0.0556         474.05           0.0469
     10.000         0.0783         483.95           0.0516
     12.500         0.1034         494.93           0.0571
     15.000         0.1311         507.15           0.0633
     17.500         0.1618         520.77           0.0703
     20.000         0.1961         535.90           0.0782
     22.500         0.2341         552.95           0.0869
     25.000         0.2763         571.84           0.0962
```

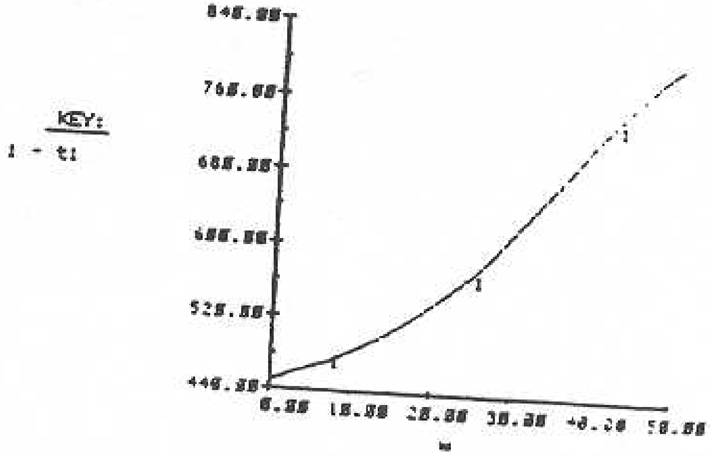
```
                          pbr w heat exchange

                         Integration Results

           w              x              t1              rate
     25.000         0.2763         571.84           0.0962
     27.500         0.3223         592.73           0.1057
     30.000         0.3737         615.50           0.1140
     32.500         0.4285         640.10           0.1226
     35.000         0.4865         666.10           0.1281
     37.500         0.5459         692.50           0.1301
     40.000         0.6050         719.04           0.1280
     42.500         0.6635         744.14           0.1216
     45.000         0.7174         767.11           0.1117
     47.500         0.7662         787.30           0.0994
     50.000         0.8089         804.31           0.0859
```

(a)



P8-8 cont'd





P8-8 (b) Conversion as a function of entering temperature.

T_o = 400 X = .22

T_o = 410 X = .30

T_o = 420 X = .42

T_o = 430 X = .56

T_o = 440 X = .70

T_o = 450 X = .81

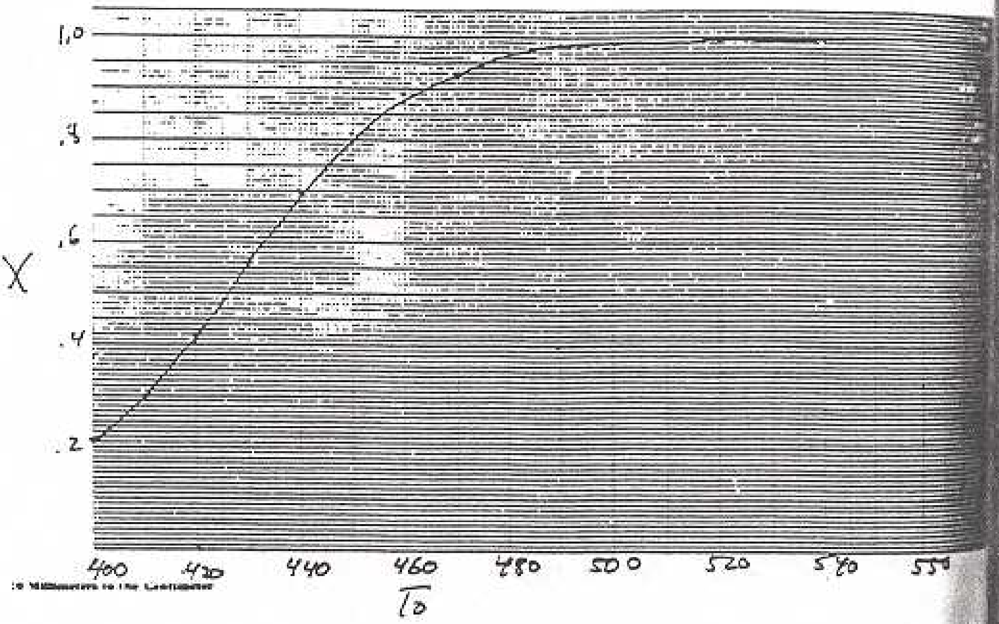
T_o = 460 X = .88

T_o = 470 X = .925

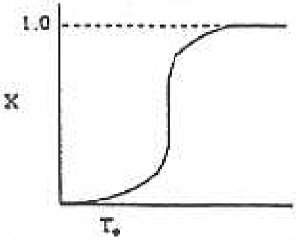
T_o = 500 X = .979

T_o = 550 X = .996

P8-8 cont'd



Because the activation energy and heat of reaction are not particulary large there is not a particularly large jump in temperature with entering temperature. For large E and ΔH_R one might find.



P8-8 (c)

$$UA(T_a - T) - F_{A0}\sum \theta_i \tilde{C}_{Pi}(T - T_0) - F_{A0}X(\Delta H_R) = 0$$

$$UA(T_a - T) - F_{A0}C_{pA}(T - T_0) - F_{A0}X(\Delta H_R) = 0$$

$$500(323 - T) - 5.42(40)(T - 450) - 5.42(0.8)(20000) = 0$$

$$T = 482.9$$

$$W = 655.9$$

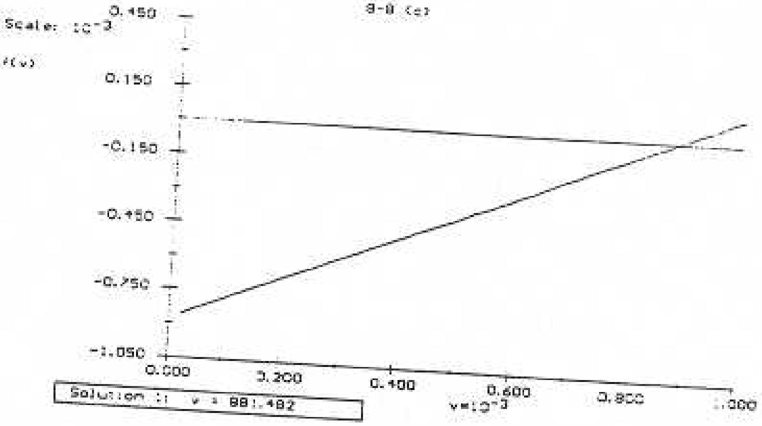
P8-8 cont'd

CSTR

(c) The equations:

```
f(v)=v-fa0*x/(-ra)
t=482.9
k=.133*exp(3776.6*(1/450-1/t))
ca0=.271
x=.8
ra=-k*ca0*(1-x)*450/(t*(1+x))
fa0=5.42
```

Search range: v_{min}= 20.000, v_{max}= 1000.0



P8-8 cont'd

P8-8 (d) Repeat Part 8-8(a) for W = 80 kg and assuming a reversible reaction with a reverse specific reaction rate of

$$k_r = 0.2\exp\left(\frac{E}{R}\left[\frac{1}{450}-\frac{1}{T}\right]\right)\left(\frac{dm^6}{kgcat*mol*s}\right), E = 51.4\frac{kJ}{mol}$$

```
                 for w heat exchange and reverse rxn

The equations:
     d(x)/d(w)=-ra/5.42
     d(t1)/d(w)=(ua*(ta-t1)+ra*dhr)/(5.42*cpa)
     k=.133*exp(3776.6*((1/450)-(1/t1)))
     ca0=.271
     ca=ca0*(1-x)*(450/t1)/(1+x)
     kr=.2*exp(6185.3*((1/450)-(1/t1)))
     ra=-k*ca+kr*(ca0*x*(450/t1)/(1+x))**2
     dhr=-20000
     cpa=40
     rate=-ra
     ua=.8
     ta=323
Initial values: w0= 0.0, x0= 0.0, t10= 450.00
Final value:  wf= 50.000


                       Integration Results

          w              x              rate            t1
     25.000         0.2681           0.0869         567.83
     27.500         0.3007           0.0907         585.83
     30.000         0.3507           0.0917         604.39
     32.500         0.3928           0.0889         622.79
     35.000         0.4324           0.0820         639.73
     37.500         0.4680           0.0719         654.54
     40.000         0.4934           0.0601         666.66
     42.500         0.5234           0.0481         675.90
     45.000         0.5430           0.0374         682.44
     47.500         0.5581           0.0285         686.65
     50.000         0.5696           0.0216         689.02
```

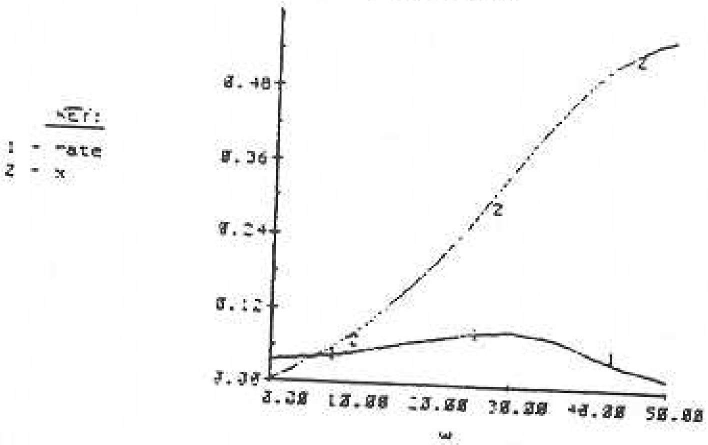
P8-8 cont'd

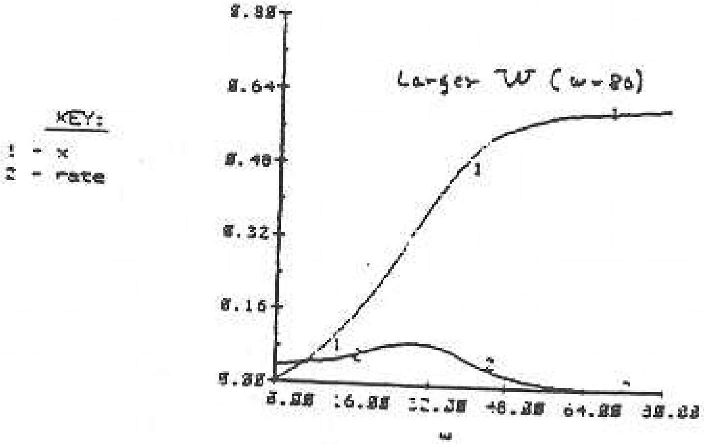
cbr w heat exchange

Integration Results

w	x	rate	T1
0.0	0.0	0.0360	450.00
2.5000	0.0170	0.0392	457.30
5.0000	0.0255	0.0423	465.23
7.5000	0.0554	0.0468	474.03
10.000	0.0777	0.0513	493.66
12.500	0.1025	0.0565	494.55
15.000	0.1299	0.0623	506.59
17.500	0.1600	0.0685	519.92
20.000	0.1931	0.0750	534.56
22.500	0.2292	0.0814	550.53
25.000	0.2631	0.0869	567.83

cbr w heat exchange





P8-8 cont'd

e) The lower Ua/ρ_b is the higher the temperature gets and the bigger the conversion gets. For example when the quantity equals 0.1, X = 0.9 and T = 891K. When the quantity equals 20, X = 0.06 and T = 326.7K. As for the ambient temperature change, in a northern state in the winter, (T_a = 266K), the conversion falls to .78 and the temperature falls to 778K. In the summer (T = 305K), the conversion is at 0.8 while the temperature of the reactor goes to 797.1K. As you can see the ambient temperature of the seasons does not change the usefulness of the reactor that much.

f) If pressure drop were included the combined temperature and pressure might make the reactor unuseable as it might build up too much.

g) No solution will be given.

P8-9

$$2A \longrightarrow B$$

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:

$$\frac{dT}{dV} = \frac{Ua(T_A - T) + (-r_A)(-\Delta H_{RX})}{F_{A0}C_{pA}}$$

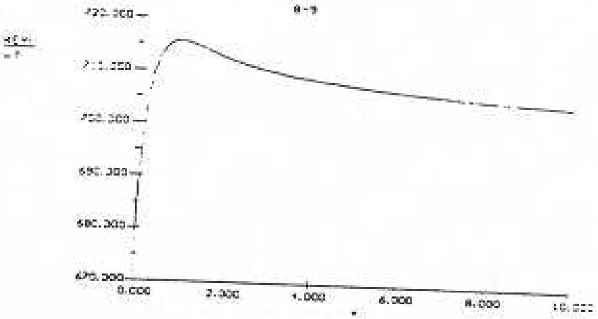
$$\frac{dT}{dV} = \frac{5(700-T) + (231 + .012(T-298))(-r_A)}{5 * .122}$$

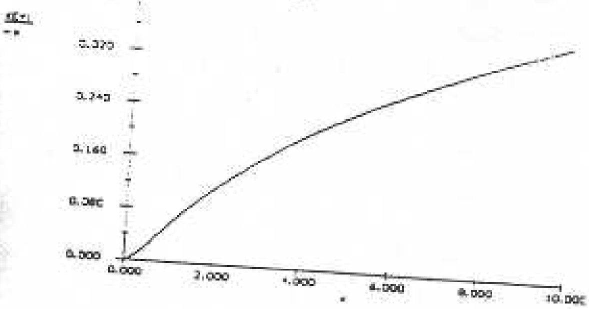
Plugging those into POLYMATH gets the following program and the following graphs. The conversion achieved is 0.36.

```
8-9
                                                              Initial value
Equations:
d(T)/d(v)=(Ua*(Ta-T)+(-ra)*(-Dhr))/(fao*cpa)                  675
d(x)/d(v)=-ra/fao                                             0
fao=5
Ua=5
Ta=700
Dhr=-231-.012*(T-298)
cpa=.1222
k=1.48e11*exp(-19124/T)
cao=1
ca=cao*(1-x)
ra=-k*ca^2
v0 = 0,   vf = 10
```

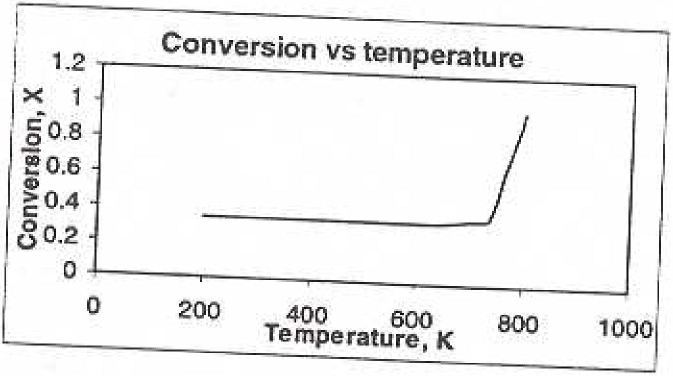
P8-9 cont'd

```
8-9
Variable     Initial value  Maximum value  Minimum value  Final valu
v            0              10             0              10
T            675            715.56         675            704.769
X            0              0.358088       0              0.358088
Fao          5              5              5              5
Ua           5              5              5              5
Ta           700            700            700            700
Dhr          -235.524       -235.524       -236.011       -235.881
cpa          0.1222         0.1222         0.1222         0.1222
k            0.0734336      0.365882       0.0734336      0.243008
cao          1              1              1              1
ca           1              1              0.641912       0.641912
ra           -0.0734336     -0.0734336     -0.333621      -0.100132
```





b) Using the same POLYMATH program we were able to change the entering temperature and come up with this graph.



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.

P8-9 cont'd

```
8-9
Variable      Initial value  Maximum value  Minimum value  Final value
v             0              10             0              10
T             675            758.054        675            712.267
x             0              0.486285       0              0.486285
fao           5              5              5              5
Ua            5              5              5              5
Ta            708.2          708.2          708.3          708.2
Dhr           -235.524       -235.524       -236.521       -235.971
cpa           0.1222         0.1222         0.1222         0.1222
k             0.0734336      1.63679        0.0734336      0.32335
cao           1              1              1              1
ca            1              1              0.513715       0.513715
ra            -0.0734336     -0.(   .36     -1.07779       -0.0853333
```

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.

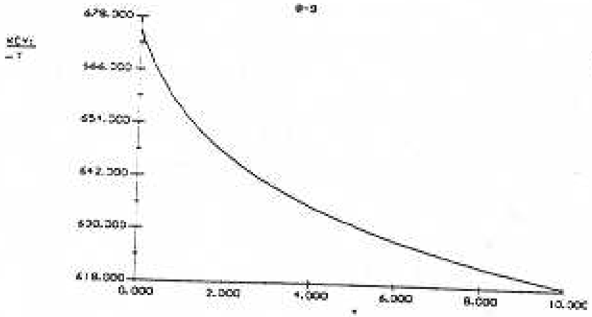
$$T = \frac{T_0 C_{pA} - 231X - 3.576X}{C_{pA} - 0.012X}$$

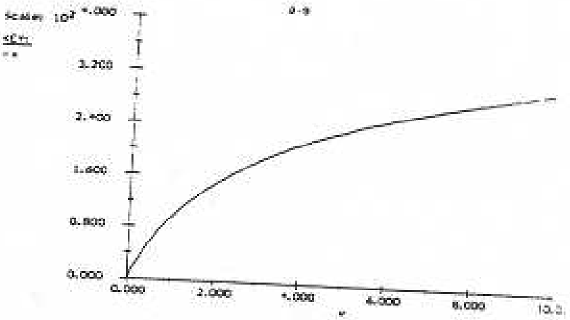
Plugging that into POLYMATH gets the following program and graphs.

```
8-9
Equations:                                         Initial value
d(x)/d(v)=-ra/fao                                  0
Ua=5
fao=5
Ta=708.3
cpa=.1222
cao=1
To=675
ca=cao*(1-x)
T=(To*cpa-231*x-3.576*x)/(cpa-.012*x)
k=1.48e11*exp(-19124/T)
Dhr=-231-.012*(T-298)
ra=-k*ca^2
v0 = 0,    vf = 10
```

```
8-9
Variable      Initial value  Maximum value  Minimum value  Final valu
v             0              10             0              10
x             0              0.0304837      0              0.0304837
Ua            5              5              5              5
fao           5              5              5              5
Ta            708.3          708.3          708.3          708.3
cpa           0.1222         0.1222         0.1222         0.1222
cao           1              1              1              1
To            675            675            675            675
ca            1              1              0.969516       0.969516
T             675            675            618.334        618.334
k             0.0734336      0.0734336      0.0054738      0.0054738
Dhr           -235.524       -234.844       -235.524       -234.844
ra            -0.0734336     -0.00514516    -0.0734336     -0.005145
```

P8-9 **cont'd**





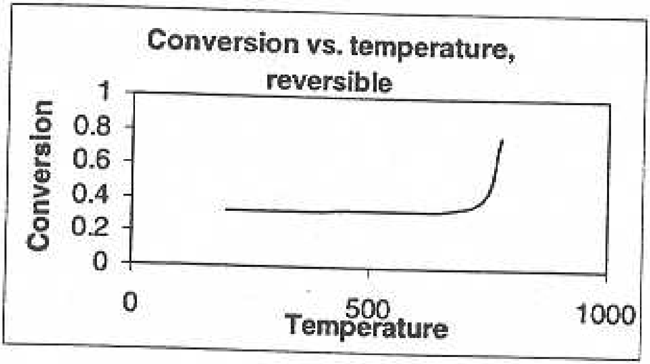
e) When it becomes reversible with inerts the two equations that change are the rate law and the energy balance.

$$-r_A = k\left(C_A^2 - \frac{C_B}{K}\right)$$

$$\frac{dT}{dV} = \frac{Ua(T_A - T) + (-r_A)(-\Delta H_R)}{F_{A0}(C_{pA} + \Theta_I C_{pI})}$$

$$K = 100000 \exp\left[\frac{\Delta H_R}{R}\left(\frac{1}{675} - \frac{1}{T}\right)\right]$$

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.

f) No solution will be given.

P8-10

a)

$$C_A = C_T \frac{F_A}{F_T}$$

$$\theta = \frac{F_I}{F_A}$$

$$C_T = C_A + C_I$$

$$F_T = F_A + F_I$$

$$\frac{1}{C_A} = \frac{1}{C_A + C_I} \frac{F_I + F_A}{F_A}$$

$$\frac{1}{C_A} = \frac{1}{C_A + C_I} (\theta_I + 1)$$

$$C_A = \frac{C_A + \frac{P_I}{RT}}{(\theta_I + 1)}$$

where $\theta_I = \frac{F_I}{F_A}$

b) Mole balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A$$

$$k = \exp(34.4 - 34.222 / T)$$

$$\varepsilon = \frac{1}{\theta_I + 1}$$

$$C_A = C_{A0} \frac{1 - X}{1 + \varepsilon X}$$

$$-r_A = k\left(\frac{\frac{C_{A0} + C_I}{\theta_I + 1}(1 - X)}{1 + \left(\frac{1}{\theta_I + 1}\right)X} \right)$$

$$T = \frac{X(-80000) + C_{pA}T_0 + \theta_I C_{pI} T_0}{C_{pA} + \theta_I C_{pI} T_o}$$

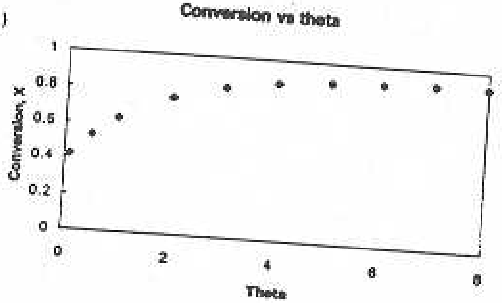
Plugging into POLYMATH gives the following.

P8-10 cont'd

```
8-10
Equations:                                                  Initial value
d(x)/d(v)=-ra/fao                                           0
cao=.022
fao=10
theta=.1
cio=2/.082/1100
T=(x*-80000+170*1100+theta*200*1100)/(170+theta*200)
k=exp(34.34-34222/T)
ra=-k*((cao+cio)/(theta+1))*(1-x)/(1+x/(theta+1))
v0 = 0,   vf = 500
```

8-10

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	500	0	500
x	0	0.420529	0	0.420529
cao	0.022	0.022	0.022	0.022
fao	10	10	10	10
theta	0.1	0.1	0.1	0.1
cio	0.0221729	0.0221729	0.0221729	0.0221729
T	1100	1100	922.935	922.935
k	25.2567	25.2567	0.0646006	0.0646006
ra	-1.01424	-0.0010875	-1.01424	-0.0010875



c) There is a maximum at about a theta of 8. This is due to the fact that there is so much more inert in the reactor than reactants.

d) Increasing the temperature by 200k causes the reaction to go to completion at a very low theta. Decreasing the temperature has the opposite effect and the conversion will drop dramatically.

e) No solution will be given.

P8-11

a) Start with the complete energy balance:

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s - \sum_{i=1}^{n} E_i F_i \big|_{in} - \sum_{i=1}^{n} E_i F_i \big|_{out} - \sum_{i=1}^{n} R_i V E_i \big|_{out}$$

The following simplifications can be made:

1) It is at steady-state.
2) In part a, there is no heat added or taken away.
3) There is no shaft work.

That leaves us with the following:

$$0 = -\sum_{i=1}^{n} E_i F_i \big|_{in} - \sum_{i=1}^{n} E_i F_i \big|_{out} - \sum_{i=1}^{n} R_i V E_i \big|_{out}$$

P8-11 cont'd

Evaluating the energy terms:

$$\text{In}: H_{A0}F_{A0} + H_{B0}F_{B0} + H_{C0}F_{C0}$$

$$\text{Out}: H_A(F_A + R_AV) + H_B(F_B + R_BV) + H_C(F_C + R_CV)$$

Simplifying again:

$$-F_{A0}\left[(H_{A0} - H_A) + (H_{B0} - H_B)\theta_B + (H_{C0} - H_C)\theta_C\right] - \Delta H_{RX}F_{A0}X - \Delta H_{Rx}R_BV = 0$$

$$-F_{A0}\sum_{i=1}^{n}\theta_iC_{pi}(T - T_i) - F_{A0}X\left[\Delta H_{RX}(T) + \int_{T_R}^{T}\Delta C_p dT\right] - \sum_{i=1}^{n}R_iV\left[\Delta H_{RX}(T) + \int_{T_R}^{T}\Delta C_p dT\right] = 0$$

Differentiating with respect to V with $\Delta C_p = 0$:

$$-F_{A0}\sum_{i=1}^{n}\theta_iC_p\frac{dT}{dV} - F_{A0}\frac{dX}{dV}(\Delta H_{Rx}(T)) - \sum_{i=1}^{n}R_i[\Delta H_{rX}(T)]$$

$$\frac{dT}{dV} = \frac{F_{A0}(-r_A)[\Delta H_{rX}(T)] + \sum_{i=1}^{n}R_i[\Delta H_{rX}(T)]}{F_{A0}\sum_{i=1}^{n}\theta_iC_p}$$

Combine that with the following mole balances and rate law:

$$\frac{dF_A}{dV} = r_A \qquad \frac{dF_B}{dV} = -r_A \qquad \frac{dF_C}{dV} = -r_A - k_CC_C$$

$$-r_A = kC_A$$

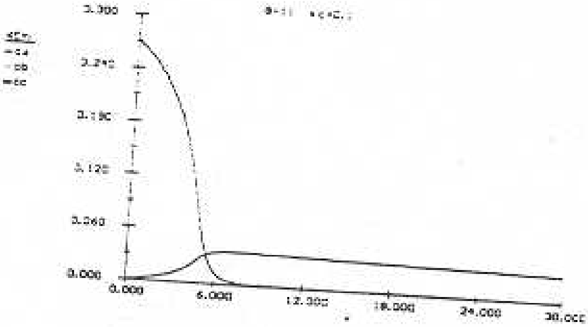
$$C_A = C_{T0}\frac{F_A}{F_T}\frac{T_0}{T} \qquad C_B = C_{T0}\frac{F_B}{F_T}\frac{T_0}{T} \qquad C_C = C_{T0}\frac{F_C}{F_T}\frac{T_0}{T}$$

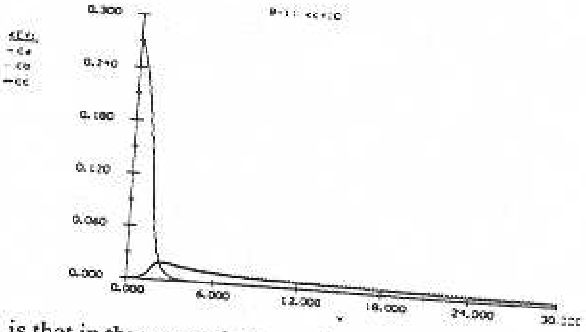
Plug them into POLYMATH and get the following program and graphs for different values of k_c.

```
                                                                   Initial value
Equations:
d(fb)/d(v)=-ra                                                     0
d(fa)/d(v)=ra                                                      5.42
d(fc)/d(v)=-ra-kc*cc                                               0
d(T)/d(v)=(fao*(-ra)*(-Dhr1)+Rc*(-Dhr1))/(fao*cpa)                 450
kc=10
Dhr1=-20000
cpa=40
To=450
E=31400
R=8.31
cto=10/(.082*To)
k=.133*exp(E/R*(1/450-1/T))
fao=cto*20
ft=fao
cc=cto*fc/ft*To/T
ca=cto*fa/ft*To/T
cb=cto*fb/ft*To/T
Rc=kc*cc
ra=-k*ca
v0 = 0,   vf = 30
```

```
Variable   Initial value   Maximum value   Minimum value   Final value
v          0               30              0               30
fb         0               5.42            0               5.42
fa         5.42            5.42            7.38118e-14     7.38118e-14
fc         0               4.13013         0               1.01336
T          450             3566.51         450             3566.51
kc         10              10              10              10
Dhr1       -20000          -20000          -20000          -20000
cpa        40              40              40              40
To         450             450             450             450
E          31400           31400           31400           31400
R          8.31            8.31            8.31            8.31
cto        0.271003        0.271003        0.271003        0.271003
k          0.133           204.379         0.133           204.379
fao        5.42005         5.42005         5.42005         5.42005
ft         5.42005         5.42005         5.42005         5.42005
cc         0               0.0307012       0               0.00639295
ca         0.271           0.271           4.65656e-16     4.65656e-16
cb         0               0.0171587       0               0.0341931
Rc         0               0.307012        0               0.0639295
ra         -0.036043       -9.51704e-14    -2.53479        -9.51704e-14
```

P8-11 cont'd





b) The only difference in B is that in the energy balance a heat term is added:

$$\frac{dT}{dV}=\frac{Ua(T_a-T)+F_{A0}(-r_A)[\Delta H_{rX}(T)]+\sum_{i=1}^{n}R_i[\Delta H_{rX}(T)]}{F_{A0}\sum_{i=1}^{n}\theta_i C_p}$$

Plug this into POLYMATH and the following program and graphs are generated:

P8-11 cont'd

Equations:	Initial value
d(fb)/d(v)=-ra	0
d(fa)/d(v)=ra	5.42
d(fc)/d(v)=-ra-kc*cc	0
d(T)/d(v)=(Ua*(Ta-T)+fao*(-ra)*(-Dhr1)+Rc*(-Dhr1))/(fao*cpa)	450

kc=.1

Dhr1=-20000

cpa=40

To=450

E=31400

R=8.31

Ua=.8

Ta=323

cto=10/(.082*To)

k=.133*exp(E/R*(1/450-1/T))

fao=cto*20

ft=fao

cc=cto*fc/ft*To/T

ca=cto*fa/ft*To/T

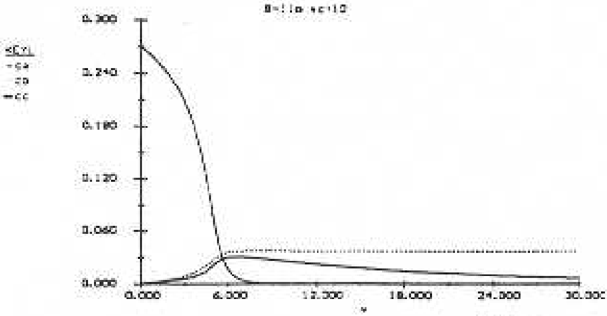
cb=cto*fb/ft*To/T

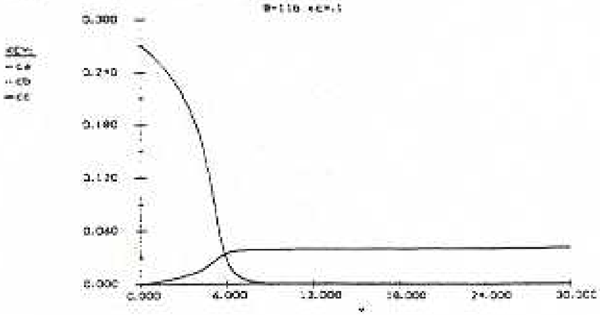
Rc=kc*cc

ra=-k*ca

$v_0 = 0, \quad v_f = 30$

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	30	0	30
fb	0	5.42	0	5.42
fa	5.42	5.42	2.2186e-13	2.2186e-13
fc	0	5.38912	0	5.31801
T	450	3107.16	450	2924.6
kc	0.1	0.1	0.1	0.1
Dhr1	-20000	-20000	-20000	-20000
cpa	40	40	40	40
To	450	450	450	450
E	31400	31400	31400	31400
R	8.31	8.31	8.31	8.31
Ua	0.8	0.8	0.8	0.8
Ta	323	323	323	323
cto	0.271003	0.271003	0.271003	0.271003
k	0.133	174.749	0.133	161.975
fao	5.42005	5.42005	5.42005	5.42005
ft	5.42005	5.42005	5.42005	5.42005
cc	0	0.0409133	0	0.0409133
ca	0.271	0.271	1.70684e-15	1.70684e-15
cb	0	0.0416979	0	0.0416979
Rc	0	0.00409133	0	0.00409133
ra	-0.036043	-2.76466e-13	-2.45733	-2.76466e-13





8-12

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: $C_A=C_{A0}\left(\frac{1-X}{1+X}\right)\left(\frac{T}{T_0}\right)y$

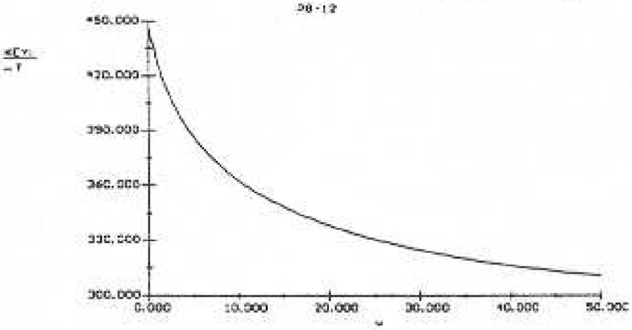
Evaluating the parameters: $k=\exp\left[\frac{E}{R}\left(\frac{1}{450}-\frac{1}{T}\right)\right]=\exp\left[3776.76\left(\frac{1}{450}-\frac{1}{T}\right)\right]$

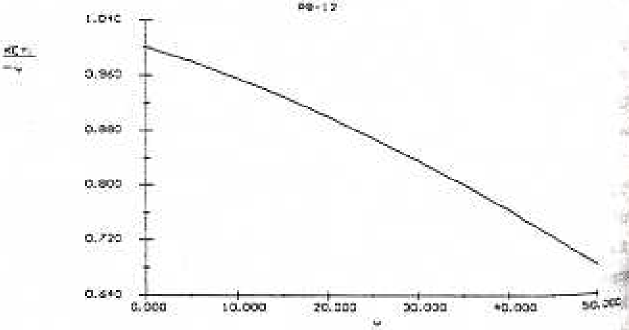
Plugging these equations into POLYMATH we get the following plots.

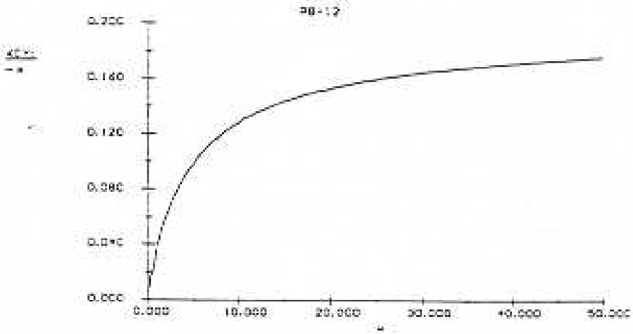
```
Equations:                                                   Initial value
d(y)/d(w)=-a/(2*y)*(To/T)*(1+x)                              1
d(T)/d(w)=(U*(Ta-T)-ra*dh)/fao/cpa                           450
d(x)/d(w)=-ra/fao                                            0
U=5
a=0.007
To=450
Ta=300
dh=-20000
fao=5
cpa=40
k=exp(3776.76*(1/450-1/T))
cao=0.25
ca=cao*((1-x)/(1+x))*(T/450)*y
ra=-k*ca
w0 = 0,    wf = 50
```

P8-12 (cont'd)

```
Variable       Initial value  Maximum value  Minimum value  Final value
w              0              50             0              50
y              1              1              0.682386       0.682386
T              450            450            310.691        310.691
x              0              0.175758       0              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
dh             -20000         -20000         -20000         -20000
fao            5              5              5              5
cpa            40             40             40             40
k              1              1              0.0232094      0.0232094
cao            0.25           0.25           0.25           0.25
ca             0.25           0.25           0.0825702      0.0825702
ra             -0.25          -0.0019164     -0.25          -0.0019164
```







P8-12

(b) From the POLYMATH summary table it is apparent that the maximum value for $-r_A$ occurs at the beginning of the reactor.

(c) The maximum value for the temperature also occurs at the beginning of the reaction.

d) Doubling the heat-transfer coefficient causes a decrease in both the temperature, conversion and the pressure drop. Halving the heat-transfer coefficient cause an increase in temperature, conversion and pressure drop.

P8-13

$$K_C = \frac{C_C C_D}{C_A C_B} = \frac{X_e^2}{(1-X_e)^2}$$

$$\sqrt{K_C} = \frac{X_e}{1-X_e} \quad \text{or} \quad X_e = \frac{\sqrt{K_C}}{1+\sqrt{K_C}}$$

POLYMATH

$$f(X_e) = X_e - (1-X_e)\sqrt{K_C}$$

$$K_C = 500{,}000 \exp\left[\frac{-30{,}000}{1.987}\left(\frac{1}{323} - \frac{1}{T}\right)\right]$$

T	X_e	T	X_e
300	1.000	440	0.585
320	0.999	460	0.40
340	0.995	480	0.26
360	0.984	500	0.1529
380	0.895	520	0.091
400	0.887	540	0.057
420	0.76	560	0.035

P8-13 cont'd

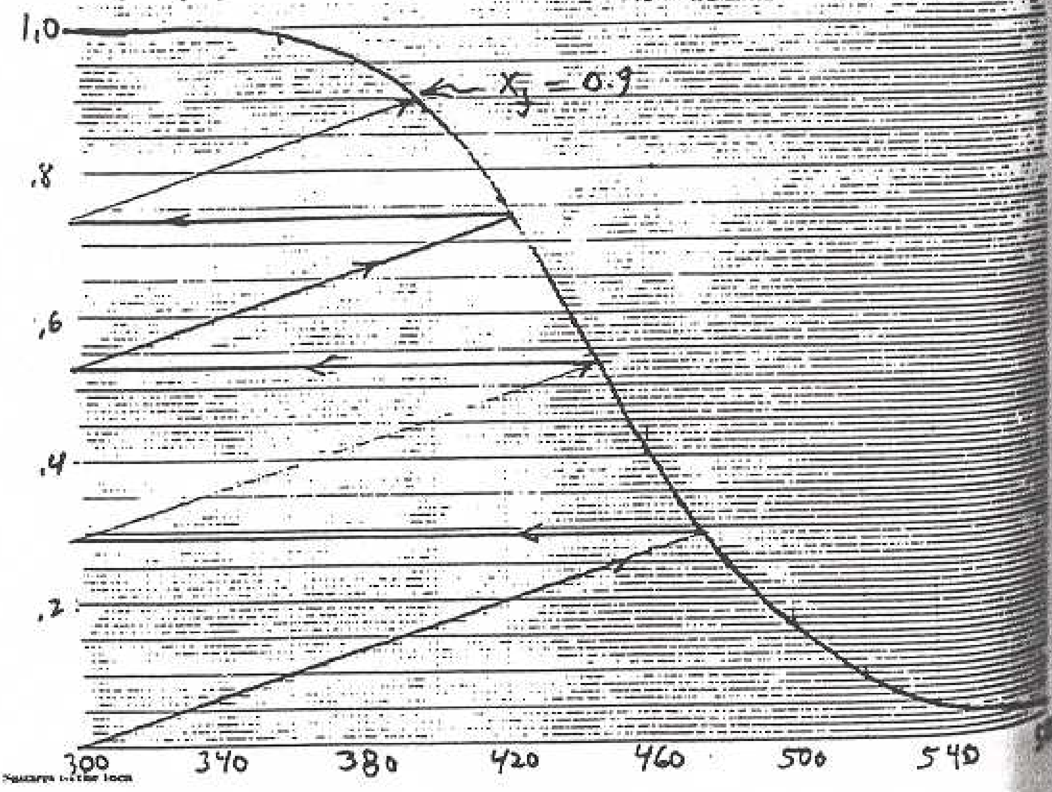
$$T = T_o - \frac{\Delta H_R X}{C_{P_A} + C_{P_B}} = 300 - \frac{(-30,000)}{(25 + 25)} X = 300 + \frac{30,000}{50} X$$

$$T = 300 + 600\,X$$

$$X = \frac{T - 300}{600}$$

*

```
The equations:
     f(x)=x-(1-x)*k**.5
     k0=500000
     t=390
     e=exp(-30000*(1/323-1/t))
     k=k0*e
Search range: xmin= 0.0, xmax= 1.0000
```



P8-14 For first reactor

$$K_C = \frac{X_{e1}}{1-X_{e1}} \quad \text{or} \quad X_{e1} = \frac{K_C}{1+K_C}$$

For 2nd reactor

$$K_C = \frac{\theta_{B2} + X_{e2}}{1-X_{e2}} \quad \text{or} \quad X_{e2} = \frac{K_C - \theta_{B2}}{1+K_C}$$

For 3rd reactor

$$K_C = \frac{\theta_{B3} + X_{e3}}{1-X_{e3}} \quad \text{or} \quad X_{e3} = \frac{K_C - \theta_{B3}}{1+K_C}$$

1st reactor: in first reactor $X_e = 0.2$

Therefore $F_B = F_{A01}(.2)$

2nd reactor: moles of A entering the 2nd reactor: $F_{A02} = 2F_{A01} - F_{A01}\,(.2) = 1.8\,F_{A01}$

$$\theta_{B2} = \frac{.2F_{A01}}{1.8F_{A0}} = 0.11$$

$$-F_{A02}\,\Sigma\, C_{P_i}\theta_i\,(T-T_o) + F_{A02}X\,(-\Delta H_R) = 0$$

$$X = \frac{\left(C_{pA} + \theta_B C_{pB}\right)(T-T_o)}{-\Delta H_R}$$

Slope is now negative

3rd reactor

Say $X_{e2} = 0.3$

$$\theta_B = (0.2F_{A01}) + .3F_{A02} = F_{A01}(.2 + (.3)(1.8))$$

$$F_{A03} = F_{A01} + F_{A02}\,(1-X_{e2}) = F_{A01} + 1.8F_{A01}\,(1-X_{e2}) = 1 + 1.8(1-.3)F_{A01}$$

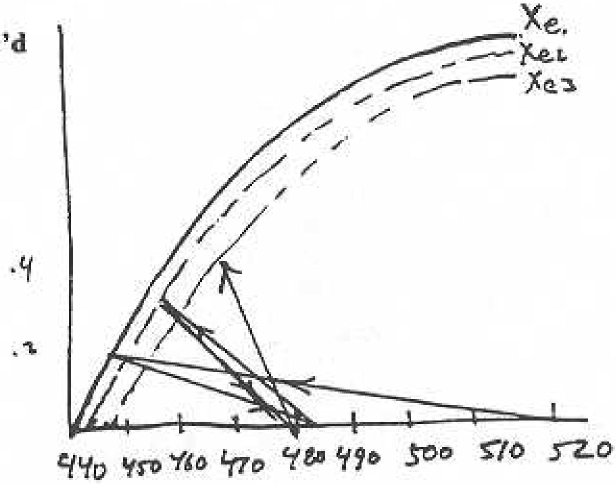
$$F_{A03} = 2.26\,F_{A01}$$

B. Feed to reactor 3

$$F_{B3} = 2F_{A01} + .3F_{A02} = (.2 + (.3)(1.8))\,F_{A01} = .07F_{A01}$$

$$\theta_{B3} = \frac{0.74}{2.26}$$

P8-14 cont'd



Feed temperature to reactor 2 is $\dfrac{520 + 450}{2} = 485$

Feed temperature to reactor 3 is $\dfrac{2 \cdot 460 + 520}{3} = 480$

$X_{final} = (.4)$

$$\text{Moles of B} = (.2F_{A01}) + .3F_{A02} + .4F_{A03} = F_{A01}\,(.2 + .54 + (.4)(2.26)) = 1.64\,F_{A01}$$

$$X = \frac{F_B}{3F_{A01}} = 0.54$$

P8-15 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.

$T_O = 77°C = 350°K$

$Y_{A0} = Y_{B0} = 0.5$

$$C_{A0} = \frac{Y_{A0}P_O}{RT_O} = \frac{(0.5)\,(5.74\text{ atm.})}{\left(0.082\,\frac{1\text{ atm}}{\text{g mol°K}}\right)(350°K)} = 0.1\text{ gmol/l}$$

P8-15 **cont'd**

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:

$\Delta H_R(T_R) = 2H_C - H_A - H_B = 2(-45{,}000) + 40{,}000 + 30{,}000 = -20{,}000$ J/mole

$\Delta C_p \quad = 2C_{pc} - C_{pA} - C_{pB} = 2(20) - 25 - 15 = 0$

So $\Delta H_R(T)$ = constant = -20,000 J/mole

$$K_C = K_{C1} \exp\left[\frac{\Delta H_R}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \qquad (2)$$

$$\therefore \quad K_C = 25{,}000 \exp\left[\frac{-20{,}000}{8.314}\left(\frac{1}{298} - \frac{1}{T}\right)\right]$$

$$K_C = 25{,}000 \exp\left[-2405.6\left(\frac{1}{298} - \frac{1}{T}\right)\right] \qquad (3)$$

k and K_C can be calculated by equation (1) and (3) if T is given.

$$K_C = \frac{C_C^2}{C_A C_B}$$

$C_A = C_{A0}(1 - X)\,f$

$C_B = C_{A0}(1 - X)\,f \qquad$ where $f = \frac{T_O}{T}$

$C_C = 2C_{A0}\,X\,f$

P8-15 cont'd

Substitute C_A, C_B, and C_C into K_C

$$K_C = \frac{4C_{A0}^2 X^2 f^2}{C_{A0}^2 (1-X)^2 f^2} = \frac{4X^2}{(1-X)^2} \tag{4}$$

$$\therefore \sqrt{K_C} = \frac{2X}{1-X} \quad \text{or} \quad X_{eg} = \frac{\sqrt{K_C}}{2+\sqrt{K_C}} \tag{5}$$

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:

$$-X\,\Delta H_R = \Sigma\, \theta_i\, C_{P_i} (T - T_O) \tag{6}$$

$$\theta_A = \theta_B = 1 \;,\; \theta_C = 0 \;,\; T_O = 350\text{K}$$

Substitute : $+20{,}000X = (25+15)(T-350) \Rightarrow T = 500X + 350$

$$\text{or} \quad X = 0.002\,(T - 350) \tag{7}$$

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: $\quad V = F_{A0}\displaystyle\int \frac{dX}{-r_A}$ (8)

Rate law: $-r_A = k\left[C_A C_B - \dfrac{C_C^2}{K_C}\right]$

$$-r_A = k\, C_{A0}^2 f^2 \left[(1-X)^2 - \frac{(2X)^2}{K_C}\right] \tag{9}$$

$$\text{So } V = \frac{F_{A0}}{C_{A0}^2}\int_0^{0.7} \frac{dX}{kf^2\left[(1-X)^2 - \frac{4X^2}{K_C}\right]} = \frac{1200}{(0.1)^2}\int_0^{0.7} f(X)\,dX$$

$$V = 1.2\times 10^5 \int_0^{0.7} f(X)\,dX \quad \text{where } f(X) = \frac{1}{kf^2\left[(1-X)^2 - \frac{4X^2}{K_C}\right]} \tag{10}$$

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}

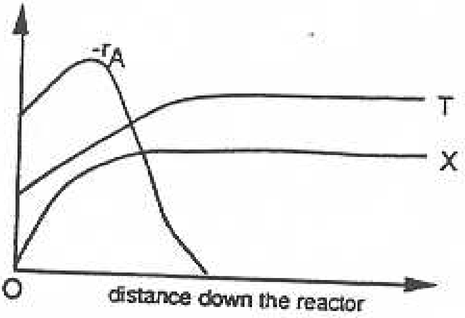
The integral can be evaluated using Simpson's rule for the first six segments and trapeziodal rule for the last segment.

$$I = \int_0^{0.7} f(X)\,dX \cong \frac{0.1}{3}\left[0.0323 + 4\left(2.58\times10^{-3}\right) + 2\left(3.98\times10^{-4}\right) + 4\left(9.89\times10^{-5}\right) + 2\left(3.53\times10^{-5}\right) + 4\left(1.70\times10^{-5}\right) + 1.08\times10^{-5}\right] + \frac{0.1}{2}\left[1.08\times10^{-5} + 4.98\times10^{-6}\right]$$

$I = 1.5 \times 10^{-3}$

$V_{PFR} = \left(1.2 \times 10^{5}\right)\left(1.5 \times 10^{-3}\right) = 180\ \text{L}$

(b) Exothermic, adiabatic



(c) CSTR design equation: $V = \dfrac{F_{A0}X_A}{-r_A}$

$$V = \frac{F_{A0}X}{kC_{A0}^2 f^2\left[(1-X)^2 - \dfrac{4X^2}{K_C}\right]}$$

P8-15 cont'd

$$\frac{X}{k\,f^2\left[(1-X)^2 - \frac{4X^2}{K_C}\right]} = \frac{1500\text{L} \times (0.1)^2\left(\frac{\text{mol}}{\text{l}}\right)^2}{1200\,\frac{\text{mol}}{\text{min}}} = 0.0125$$

$$(1-X)^2 - \frac{4X^2}{K_C} = 80\,\frac{X}{f^2\,k}$$

$$1 - 2X + X^2 - \frac{4X^2}{K_C} = \frac{80X}{f^2 k}$$

$$\left(1 - \frac{4}{K_C}\right)X^2 - \left(2 + \frac{80}{f^2\,k}\right)X + 1 = 0$$

Let $b_1 = 1 - \frac{4}{K_C}$ and $b_2 = 2 + \frac{80}{f^2\,k}$ (11)

$$\Rightarrow X = \frac{b_2 \pm \sqrt{b_2^2 - 4b_1}}{2b_2} \qquad (12)$$

Nonadiabatic energy balance:

$$\frac{-UA}{F_{A0}}(T - T_A) - X\Delta H_R = \Sigma\,\theta_i\,C_{P_i}(T - T_O)$$

$$\frac{-10\,\frac{W}{m^2\,K} \times 2}{1200\,\frac{\text{mol}}{\text{min}}} \times \frac{1\text{kW}}{1000\text{W}} \times \frac{1\text{hr}}{60\text{min}} \times \frac{3.6 \times 10^6\ \text{J}}{1\text{KW.hr}}(T - 290) + 20000X = 40(T - 350)$$

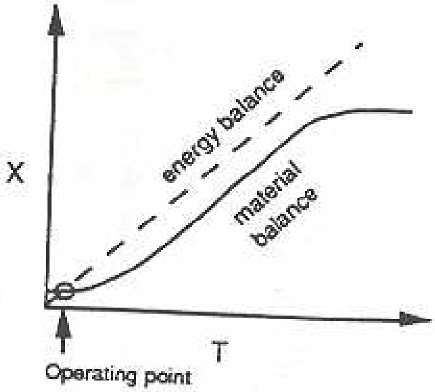
$$-T + 290 + 20{,}000X = 40T - 14{,}000$$

$$T = 348.5 + 487.8\,X \qquad (13)$$

So the procedure to calculate X is as follows:

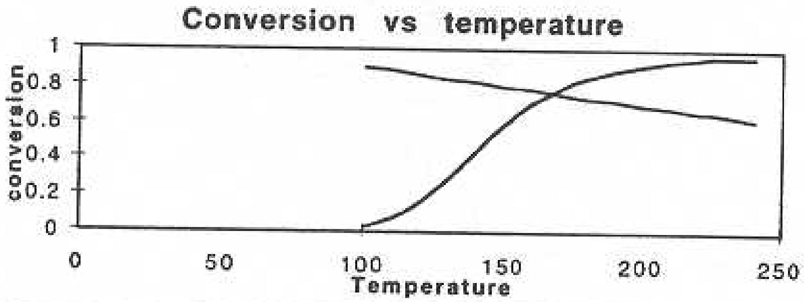
1. Choose increments in T and calculate X as a function of T from equation (13). This is the value given by energy balance.
2. Choose increments in T and calculate b_1 and b_2 from equation (11). (K_C and k can be calculated from equation (3) and c1) respectively.)
3. Calculate X, discarding $X > 1$ 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:

P8-15 cont'd



The actual calculation gives: X = 0 which is the conversion in CSTR.

d) The same equations can be used except that ΔH_{rx} = 20000 and T_0 = 550K. The following graph shows the equilibrium conversion for this case.

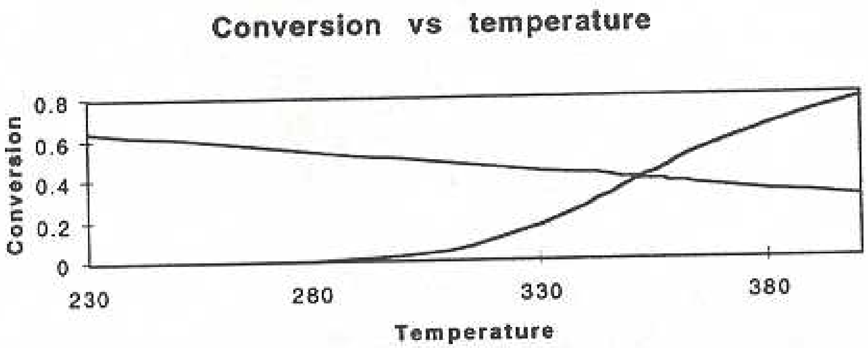


The following POLYMATH program gives the PFR volume necessary to get a conversion of .65.

```
Equations:                                               Initial value
d(x)/d(v)=-ra/fao                                        0
fao=1200
T=-500*x+550
cao=.064
To=550
k=.035*exp(8419.5*(1/273-1/T))
Kc=25000*exp(2405.6*(1/298-1/T))
f=To/T
ca=cao*(1-x)*f        Variable   Initial value   Maximum value   Minimum value   Final value
cb=cao*(1-x)*f        v          0               1e+08           0               1e+08
cc=2*cao*x*f          x          0               0.649546        0               0.649546
ra=-k*(ca*cb-cc^2/Kc) fao        1200            1200            1200            1200
v0 = 0.   vf = 1e+08  T          550             550             225.227         225.227
                      cao        0.064           0.064           0.064           0.064
                      To         550             550             550             550
                      k          194867          194867          5.04735e-05     5.04735e-05
                      Kc         1.00983e+06     1.00983e+06     1841.48         1841.48
                      f          1               2.44198         1               2.44198
                      ca         0.064           0.064           0.0547713       0.0547713
                      cb         0.064           0.064           0.0547713       0.0547713
                      cc         0               0.203031        0               0.203031
                      ra         -798.173        -1.50285e-07    -798.173        -1.50285e-07
```

P8-15 cont'd

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.

P8-16

First, we must determine a relationship between the change in T and the change in X.

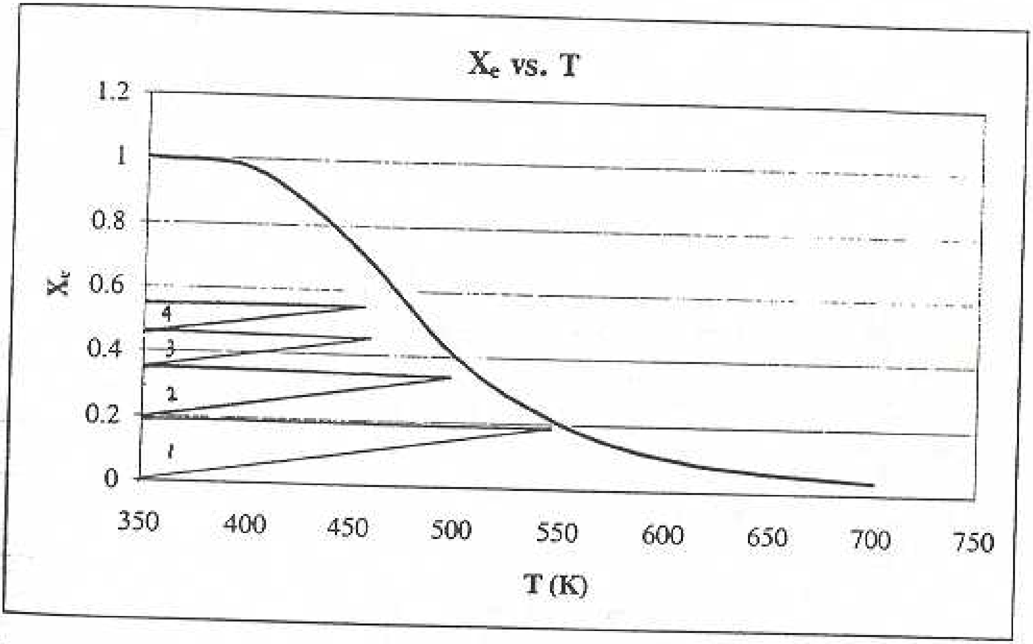
Energy Balance: $$\frac{dT}{dW} = \frac{UA(T_a - T) + (-r_A)(-\Delta H_R)}{F_{Ao}\left[C_{pA} + \Theta_B C_{pB} + X\Delta\Delta_p\right]} = \frac{(-r_A)(-\Delta H_R)}{F_{Ao}\left[C_{pA} + C_{pB}\right]}$$

Mole Balance: $$\frac{dX}{dW} = \frac{-r_A}{F_{Ao}}$$

Combine: $$\frac{\frac{dT}{dW}}{\frac{dX}{dW}} = \frac{dT}{dX} = \frac{-\Delta H_R}{C_{pA} + \Theta_B C_{pB} + \Theta_I C_{pI}} = \frac{10{,}000}{2+5+2(1.5)} = 1{,}000$$

$$\frac{dT}{dX} = 1{,}000$$

After determining this relationship, graph the data given in the problem statement as X_e vs. T. From this graph we can determine the number of reactors required to achieve any exit conversion.



From this it can be seen that it would require 4 reactors in series to achieve 55% (>50%) overall conversion. To achieve 95% conversion would require large numbers of reactors in series. This would be of concern because with each reactor the change in pressure increases, which can cause instability.

P8-17

(a)

$$G(T) = \Delta H_R X$$

$$X = \frac{\tau k}{1+\tau k} \qquad k = 6.6\times10^{-3}\exp\left[\frac{E}{R}\left(\frac{1}{350}-\frac{1}{T}\right)\right]$$

$$R(T) = C_{po}(1+\kappa)(T-T_c)$$

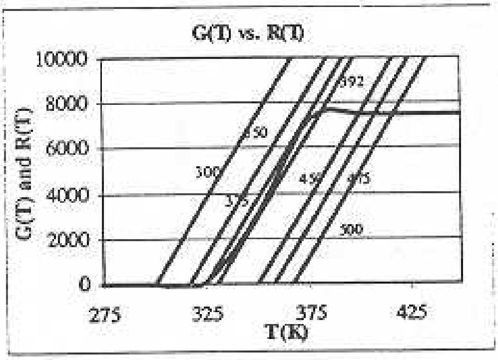
$$C_{po} = \sum \Theta_i C_{pi} = \Theta_A C_{PA} + \Theta_I C_{pI} = 20+30=50 \qquad \kappa = \frac{UA}{C_{po}F_{Ao}} = \frac{8000}{(50)(80)} = 2$$

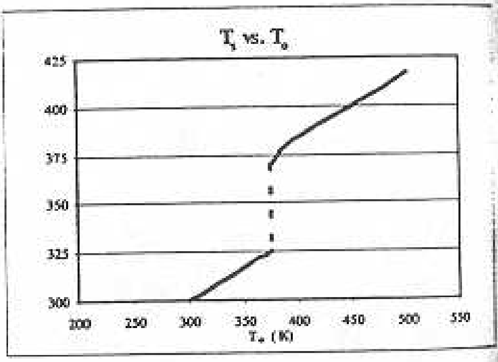
$$T_c = \frac{T_o F_{Ao} C_{po} + UAT_a}{UA + C_{po}F_{Ao}} = \frac{\kappa T_a + T_o}{1+\kappa} = \frac{(2)(300)+450}{1+2} = 350$$

To find the steady-state T, we must set G(T) = R(T). This can be done either graphically or using the solver in Excel. We find that for T_o = 450 K, the steady-state temperature is 358 K.

P8-17 (cont'd)

(b)
First, we must plot G(T) and R(T) for many different T_o's on the same plot. From this we generate data that we use to plot T_s vs. T_o.





(c) For high conversion the feed stream must be preheated to at least 390 K (117°C). At this temperature, X = 0.98 and T = 380 K (107°C) in the CSTR. Any feed temperature above this point will provide higher conversions.

(d) For a temperature of 375 K, the conversion is 0.968.

(e) The inlet extinction temperature is 375 K (102°C).

P8-18

a) P8-6 is adiabatic so the radial reactor has no effect on it.

b)

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A$$

$$C_A = C_{A0}\frac{1-X}{1+X}\frac{T_0}{T}y$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y}$$

$$\frac{dT}{dW} = \frac{U(r)\frac{2h}{\rho}(T_A - T) + (-r_A)(-\Delta H_R)}{F_{A0}C_{pA}}$$

$$U = U(r_0)\left(\frac{r_0}{r}\right)^{.5}\left(\frac{T}{T_0}\right)^{.5}$$

P8-18 (cont'd)

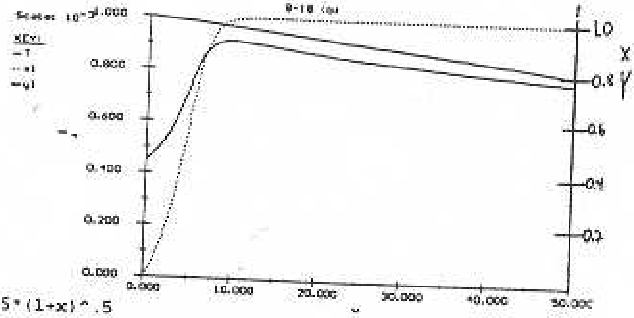
Since h and ρ are unknown, we will assume that they are both equal to one. We will also assume that r varies as $W^{.5}$ varies.
so:

$$\frac{dT}{dW}=\frac{U(r)(T_A-T)+(-r_A)(-\Delta H_R)}{F_{A0}C_{pA}}$$

$$U=U(r_0)\left(\frac{W_0^{.5}}{W}\right)^{.5}\left(\frac{T}{T_0}\right)^{.5}$$

Plugging those into POLYMATH gets the following graph.

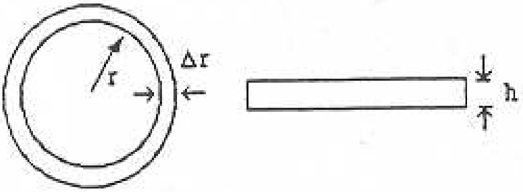
```
Equations:                                             Initial value
d(y)/d(w)=-alp/(2*y)                                   1
d(x)/d(w)=-ra/fao                                      0
d(T)/d(w)=(U*(Ta-T)+(-ra)*(-Dhrl))/(fao*40)            450
fao=5
alp=.007
Ta=300
Dhrl=-20000
wo=.01
To=450
e=31400
R=8.413
cao=9.22/(.082*450)
x1=1000*x
y1=1000*y
U=5*(wo^.5/w^.5)^.5*(T/To)^.5*y^.5*(1+x)^.5
k=exp(e/R*(1/450-1/T))
ca=cao*(1-x)*To/T
cc=2*x*cao*To/T
Kc=25000*exp(Dhrl/R*(1/298-1/T))
cb=ca
ra=-k*(ca*cb-cc^2/Kc)
```



```
Variable   Initial value   Maximum value   Minimum value   Final value
w          0.01            50              0.01            50
y          1               1               0.806269        0.806269
x          0               1               0               1
T          450             908.457         450             775.478
fao        5               5               5               5
alp        0.007           0.007           0.007           0.007
Ta         300             300             300             300
Dhrl       -20000          -20000          -20000          -20000
wo         0.01            0.01            0.01            0.01
To         450             450             450             450
e          31400           31400           31400           31400
R          8.413           8.413           8.413           8.413
cao        0.249864        0.249864        0.249864        0.249864
x1         0               1000            0               1000
y1         1000            1000            806.269         806.269
U          5               5               0.991339        0.991339
ca         0.1             0.1             0.021683        0.021683
cc         0               0.144234        0               0.144234
Kc         7530.55         7530.55         4276.15         4916.65
cb         0.1             0.1             0.021683        0.021683
ra         -0.310572       -0.0543463      -1.28948        -0.0543463
```

P8-18 (cont'd)

(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 $\Delta r \to 0$

$$\frac{dF_A}{dr} = (r_A)2\pi\rho r h$$

$$F_A = F_{AO}(1-X_A) \Rightarrow \frac{dF_A}{dr} = -F_{AO}\frac{dX_A}{dr}$$

$$\text{so: } \frac{dX_A}{dr} = \frac{-2\pi r h \rho (r_A)}{F_{AO}} \qquad (1)$$

$$\text{or: } \frac{dX_A}{dW} = -\frac{r_A}{F_{AO}} \qquad (2)$$

Assuming pressure drop is negligible. The rate equation is:

$$-r_A = k\left(\frac{P_{SO_2}}{P_{SO_3}}\right)^{1/2}\left[P_{O_2} - \left(\frac{P_{SO_3}}{K_p P_{SO_2}}\right)^2\right]$$

The stoichiometry : $SO_2 + \frac{1}{2}O_2 \Leftrightarrow SO_3$

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

$$\delta = -0.5,\ y_{AO} = 0.11 \therefore \varepsilon = y_{AO}\delta = -0.055\ ;\ \theta_C = 0\ ;\ \theta_B = \frac{10}{11} = 0.91$$

$$P_{SO_2} = P_{SO_{2,0}}\frac{1-X_A}{1+\varepsilon X_A}\ ;\ P_{SO_3} = P_{SO_{2,0}}\frac{X_A}{1+\varepsilon X_A}\ ;\ P_{O_2} = P_{SO_{2,0}}\frac{(0.91-0.5X_A)}{1+\varepsilon X_A}$$

$$\text{Then: } -r_A = k(t)\left(\frac{1-X_A}{X_A}\right)^{1/2}\left[P_{SO_{2,0}}\left(\frac{0.91-0.5X_A}{1-0.055X_A}\right) - \frac{X_A^2}{(1-X_A)^2 K_p^2}\right] \qquad (3)$$

P8-18 (cont'd)

Equation (3) is true for $X_A < 0.05$

for $X_A \geq 0.05$

$$-r_A = k(t)\,(4.35)\left[0.22\left(\frac{0.91-0.025}{1-0.055(0.05)}\right) - \frac{0.0025}{(1-0.05)^2 K_p^2}\right]$$

$$-r_A = k(t)\left[0.848 - \frac{0.01205}{K_p^2}\right] \tag{4}$$

Energy balance:

$$F_{AO}\left(\Sigma\theta_i\, C_{p_i} + X\,\Delta C_p\right)T|_r - F_{AO}\left(\Sigma\theta_i\, C_{p_i} + \Delta C_p\, X\right)T|_{r+\Delta r}$$
$$+\, r_A\,\Delta W\left(\Delta H_R\right) - (2)\left(\Delta A\right)U(r)\;(T-T_A) = 0$$

or: $$F_{AO}\left(\Sigma\theta_i\, C_{p_i} + X\,\Delta C_p\right)T|_r - F_{AO}\left(\Sigma\theta_i\, C_{p_i} + \Delta C_p\, X\right)T|_{r+\Delta r}$$
$$+\, r_A\, 2\pi r h\rho\left(\Delta H_R\right)\Delta r - (2)\left(2\pi r\,\Delta r\right)U(r)\;(T-T_A) = 0$$

Taking the limit as $\Delta r \to 0$:

$$F_{AO}\left(\Sigma\theta_i\, C_{p_i} + X\,\Delta C_p\right)\frac{dT}{dr} = -U(r)\,4\pi r\,(T-T_A) + (-r_A)\left(-\Delta H_R\right)2\pi r h\rho$$

Rearranging:

$$\frac{dT}{dr} = \frac{-U(r)\,4\pi r\,(T-T_A) + (-r_A)\left(-\Delta H_R\right)2\pi r h\rho}{F_{AO}\left(\Sigma\theta_i\, C_{P_i} + X\,\Delta C_P\right)} \tag{5}$$

or: $$\frac{dT}{dW} = \frac{-U(r)\frac{2h}{\rho}(T-T_A) + (-r_A)\left(-\Delta H_R\right)}{F_{AO}\left(\Sigma\theta_i\, C_{P_i} + X\,\Delta C_P\right)} \tag{6}$$

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:

$$K_P = \exp\left[\frac{42{,}311}{RT} - 11.24\right]\left(K_P \text{ in atm}^{-1/2}\ ,\ T \text{ in } ^\circ R\right) \tag{7}$$

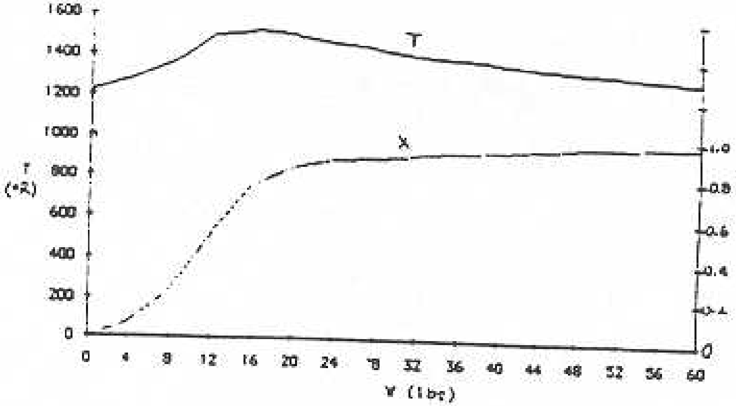
$$k = \exp\left[\frac{-176{,}008}{T} - 110.1\ln T + 912.84\right] \tag{8}$$

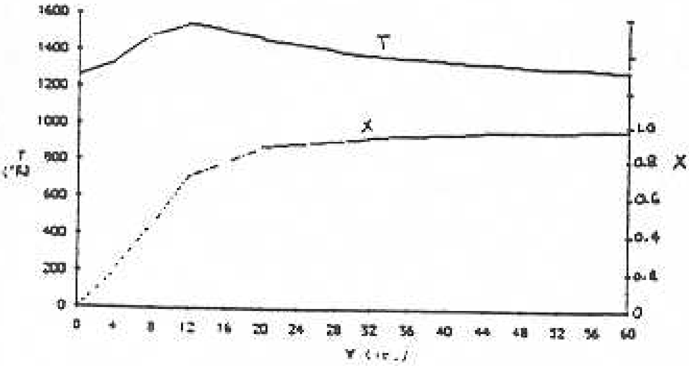
$$\Delta H_R(T) = -42{,}471 - (1.563)(T-1260) + \left(1.36\times10^{-3}\right)\left(\frac{T^2-1260^2}{2}\right)$$
$$-\left(2.459\times10^{-7}\right)\left(\frac{T^3-1260^3}{3}\right) \text{ where } \Delta H_R \text{ in } \frac{\text{Btu}}{\text{lbmole}} \tag{9}$$

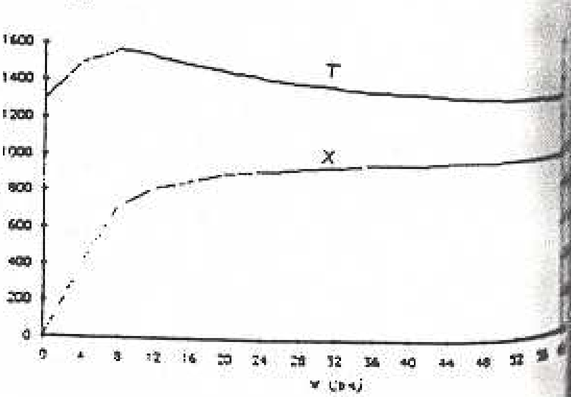
P8-18 (cont'd)

$$\Sigma\theta_i C_{p_i} = 57.23 + 0.014T - 1.788 \times 10^{-6} T^2 \tag{10}$$

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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d)

$$\frac{dX}{dr} = \frac{-2\pi rh\rho(-r_A)}{F_{A0}}$$

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

$$C_A = C_B = C_{A0}(1-X)\frac{T_0}{T}$$

P8-18 (cont'd)

$$C_C = 2C_{A0}X\frac{T_0}{T}$$

$$\frac{dT}{dr} = \frac{U(r)4\pi r(T_A - T) + (-r_A)(-\Delta H_{R1})}{F_{A0}(C_{pA} + C_{pB})}$$

$$U = U(r_0)\left(\frac{r_0}{r}\right)^{.5}\left(\frac{T}{T_0}\right)^{.5}$$

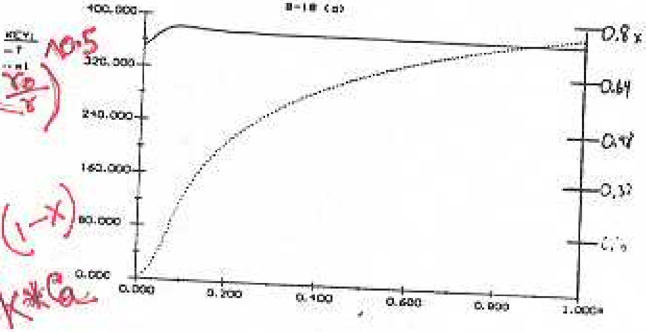
Plug those into POLYMATH to generate this graph of temperature and conversion as a function of radius.

```
Equations:
d(x)/d(r)=-2*3.1416*h*(ra)/fao
d(T)/d(r)=(U*4*3.1415*r*(Ta-T)+(-ra)*(-Dhr1))/(fao*(cpa+c
   pb))
Ta=373
Dhr1=-20000
fao=1200
cpa=25
cpb=15
h=.5
ro=.5
To=350
E=70000
R=8.31
cao=.1
U=33.3*(ro/r)^.5*(T/To)^.5
k=.035*exp(E/R*(1/273-1/T))
ca=cao*(1-x)/(1+x)*(To/T)*y
ra=-k*ca
w0 = 0.01,          wf = 50
```

Ta
Dhr1
fao
Cpa
Cpb
h=0.5
ro
To
E=70000
R
Cao

```
Variable      Initial value   Maximum value   Minimum value   Final value
r             0.5             1000            0.5             1000
x             0               0.768838        0               0.768833
T             350             381.395         350             373.135
Ta            373             373             373             373
Dhr1          -20000          -20000          -20000          -20000
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             70000           70000           70000           70000
R             8.31            8.31            8.31            8.31
cao           0.1             0.1             0.1             0.1
U             33.3            33.3            0.768826        0.768826
k             31.0572         225.061         31.0572         138.105
```

$U = 33.3 * \left(\frac{r_0}{r}\right)^{0.5}$



K

$C_a = C_{a0}(1-x)$

$r_a = -K * C_a$

$W_0 = 0.01$

$W_f = 50$

P8-19

The energy balance for a CSTR:

$$-F_{A0}X\Delta H_{Rx}(T)=F_{A0}\left[\sum\theta_i\tilde{C}_{pi}(T-T_0)+\frac{UA}{F_{A0}}(T-T_a)\right]$$

$$F_{A0}X=-r_AV$$

C_{pS} is independent of temperature so:

$$C_{p0}(T-T_0)=C_{pS}$$

$$G(T)=(-\Delta H_{Rx})\left(\frac{-r_AV}{F_{A0}}\right)$$

$$R(T)=F_{A0}C_{pS}+UAT_r-UAT$$

So taking the derivative of those with respect to temperature we get:

$$\frac{dR(T)}{dT}=UA$$

$$\frac{dG(T)}{dT}=\frac{-\Delta H_{Rx}}{F_{A0}}\frac{d(-r_A)}{dT}$$

where

$$\frac{d(-r_A)}{dT}=\frac{E}{RT^2}(-r_A)$$

Set those two equations equal to each other and then divide the energy balance by the resulting equation and the following is found.

$$\ln\frac{1.421}{1.127}=\left[\frac{E}{R}\left(\frac{323-313}{323*313}\right)\right]$$

$$E=19474$$

$$\frac{F_{A0}C_{pS}}{UA}+(T_r-T_a)>\frac{RT_r^2}{E}$$ and it will be a runaway reaction.

$$\frac{90000\text{g/min}*4\text{J/g}*1\text{min}/60\text{ s}}{120J/s*m^2*K*A}+(358-273)>\frac{8.314*358^2}{19474}$$

$$6000+10200>6566*A$$

$A<2.5m^2$ for it to be a runaway.

P8-20

a) $A \rightleftarrows B$

Mole balance: $V = \dfrac{F_{A0}x}{-r_A} = \dfrac{v_0 C_{A0} x}{k\left[C_A - C_B / K_e\right]}$

$$\left(\frac{v}{v_0}\right)k\left[(1-x) - x/K_e\right]$$

$$x\left[1 + \tau k\left(1 + 1/K_e\right)\right] = \tau k$$

$$x = \frac{\tau k}{1 + \tau k\left(1 + 1/K_e\right)}$$

$$G(T) = \left(-\Delta H_{Rx}\right)x = 80000 * x$$

$k = 1\ \text{min}^{-1}$ $\tau = 10$ min. $K_e = 100$

$$x = \frac{10}{1 + 10(1.01)} = .901$$

$$G(400) = 72080 \quad \text{cal/mol}$$

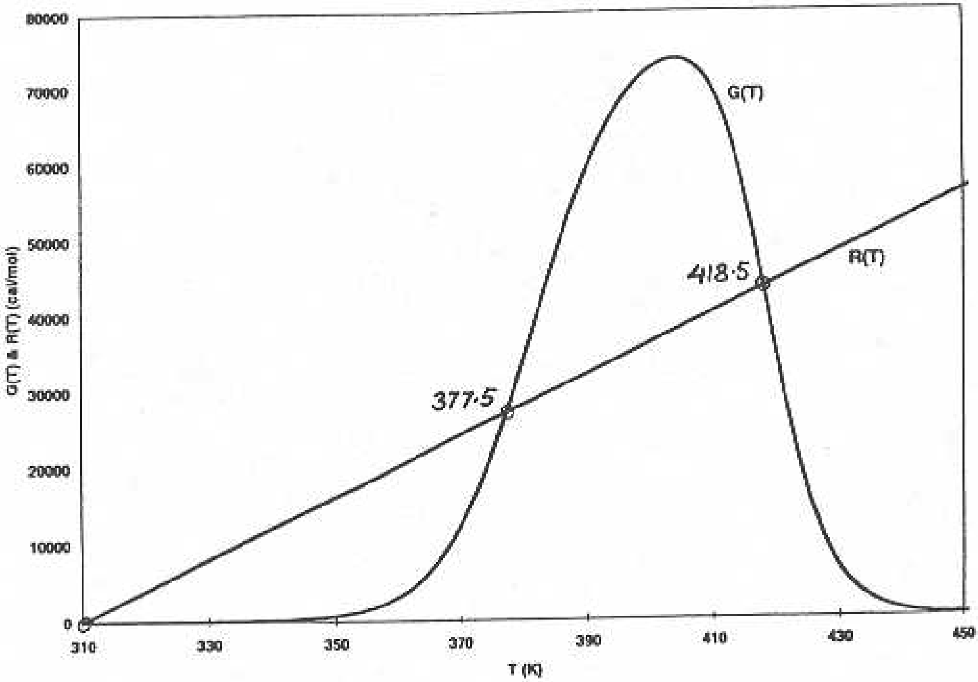
b) $\kappa = \dfrac{UA}{F_{A0}C_{pA}} = \dfrac{3600}{10 * 40} = 9$

$$R(T) = C_{pA}(1+\kappa)(T - T_c) = 400(T - T_c)$$

$$T_c = \frac{T_0 + \kappa T_a}{1+\kappa} = \frac{310 + 9 * 310}{1+9} = 310$$

$$R(T) = 400(T - 310)$$

The following plot gives the steady state temperatures of 310, 377.5 and 418.5 K.



c) 310K and 418.5 K are locally stable steady-state points.

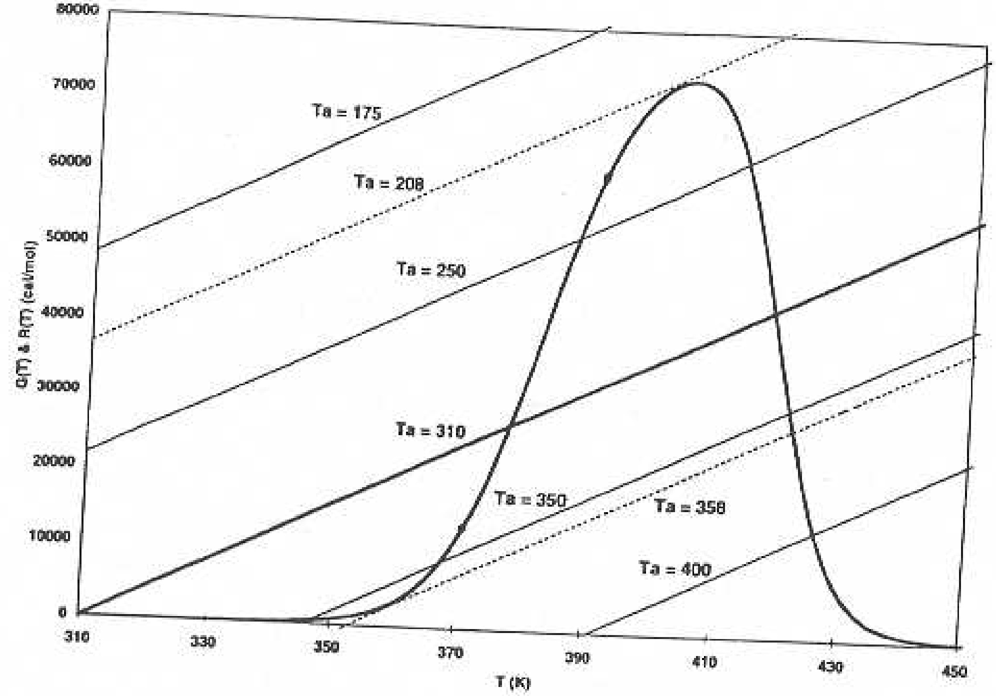
d)

$$R(418.5) = 400(418.5 - 310) = 43400$$

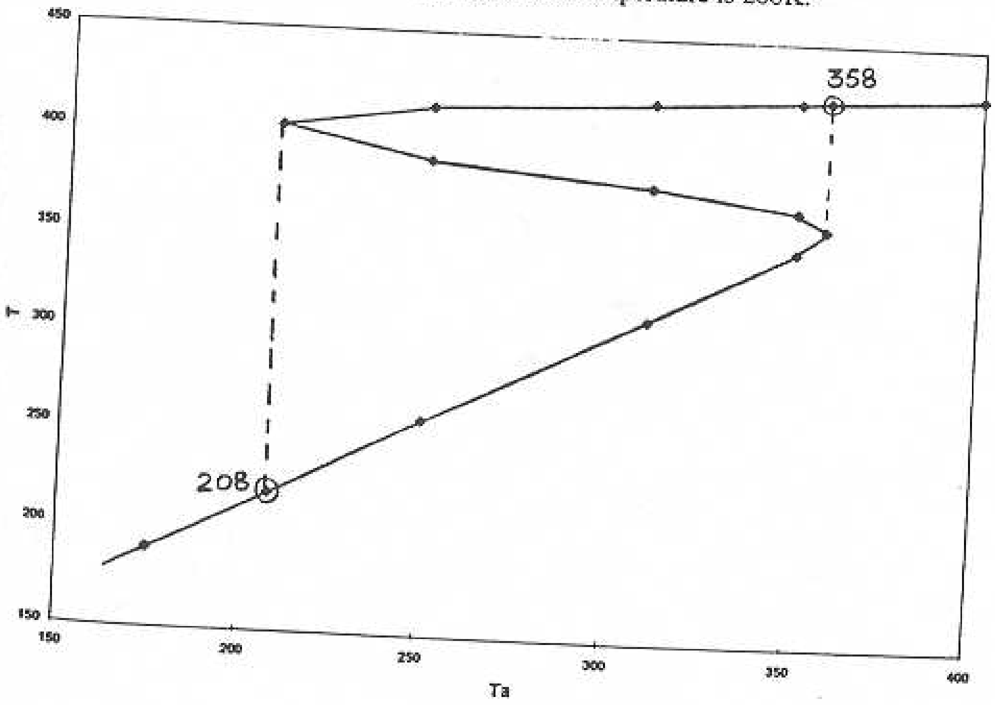
$$G(418.5) = 43400 = 80000 * x$$

$$x = \frac{43400}{80000} = .54$$

e) This plot shows T_a varied.

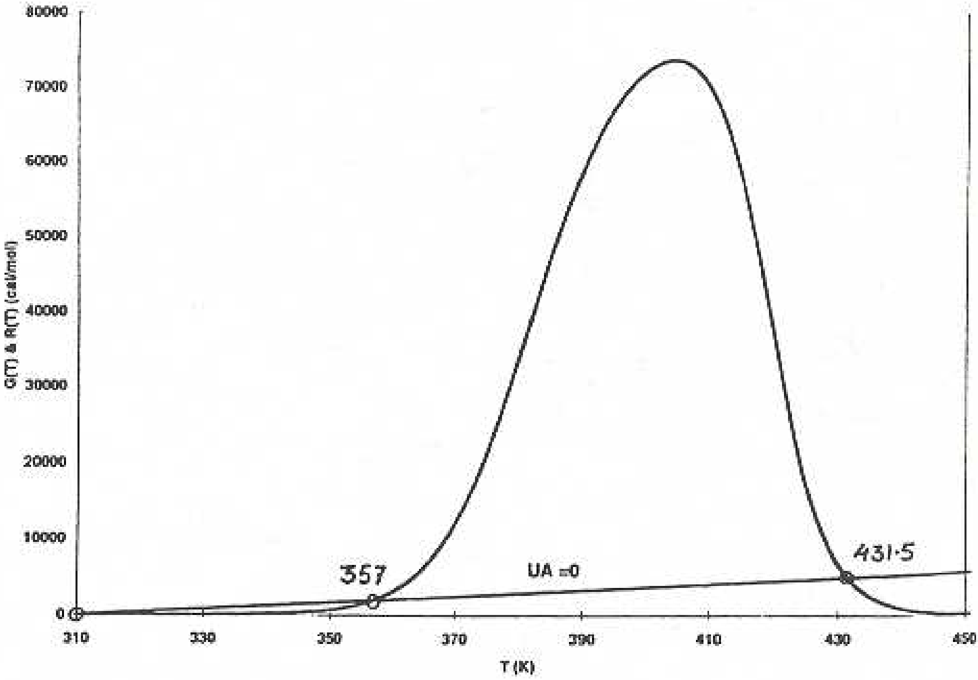


This plot shows the way to find the ignition and extinction temperatures. The ignition temperature is 358 K. The extinction temperature is 208K.



P8-20 cont'd

f) This plot shows what happens if the heat exchanger quits. The upper steady-state temperature now becomes 431.5 K.



g) No solution will be given.

8-21 Given the first order, irreversible, liquid phase reaction:

$$A \rightarrow B$$

Jacketed CSTR $UA = 1.0\ \text{cal/min.}\ ^\circ C$

$T_A = 100\ ^\circ C$

Pure A feed: $F_{A0} = 0.5$ g mole/min : $C_{pA} = C_{pB}\ 2\ \frac{\text{cal}}{\text{g mole}\ ^\circ C}$; $\Delta C_p = C_{pB} - C_{pA} = 0$

$\Delta H_R = -200\ \frac{\text{cal}}{\text{g mole A}} = \text{constant}$

Design equation: $V = \frac{F_{A0} X}{-r_A}$

Rate Law: $-r_A = k\, C_A$

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

Energy balance: $-UA(T - T_A) - F_{A0} X (\Delta H_R) = F_{A0} \Sigma \theta_i C_{pi} (T - T_0)$

$$V = \frac{F_{A0} X}{-r_A} = \frac{F_{A0} X}{k\, C_{A0}(1 - X)} = \frac{\upsilon_0}{k(1 - X)} \tag{1}$$

Simplification of equation (1) with $\tau = \frac{V}{\upsilon_0}$ gives

$$X = \frac{\tau k}{1 + \tau k} = \frac{1}{1 + \frac{1}{\tau k}} \tag{2}$$

The equation for heat generation curve is:

$$Q_g = F_{A0} X(-\Delta H_R) = \frac{F_{A0}(-\Delta H_R)}{1 + \frac{1}{\tau k}} \tag{3}$$

This is the curve plotted in the problem statement. From equation (3) we can get:

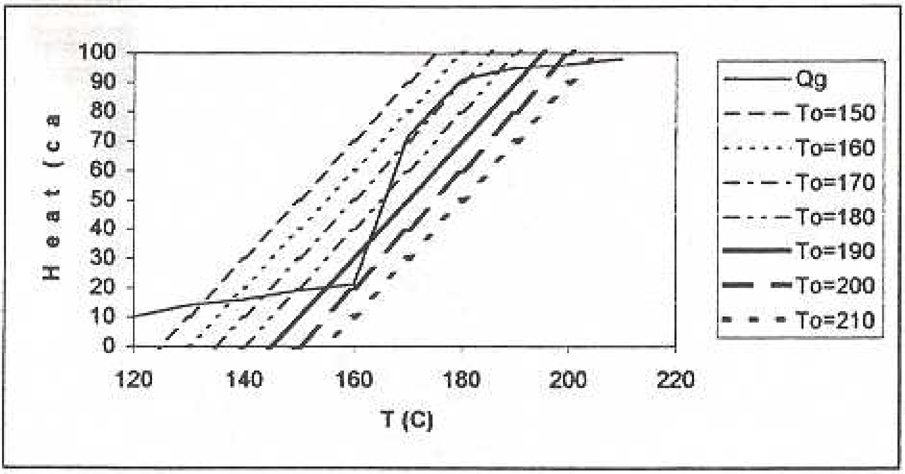
$$X = \frac{Q_g}{F_{A0}(-\Delta H_R)} = \frac{Q_g}{(0.5)(200)} = \frac{Q_g}{100} \tag{4}$$

The equation for heat removal curve is:

$$Q_R = F_{A0} C_{pA}(T - T_0) + UA(T - T_A) = (0.5)(2)(T - T_0) + (1.0)(T - 100)$$

$$Q_R = 2T - T_0 - 100 \tag{5}$$

Plot this along with the heat generation curve for various T_0. This is shown in Figure P8-22-1.



The intersection between Q_g and Q_R can be used to prepare the ignition - extinction curve shown in figure P8-22-2. The values for T_S as a function of inlet temperature, T_0, are tabulated below.

T_0 (°C)	T_S (°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

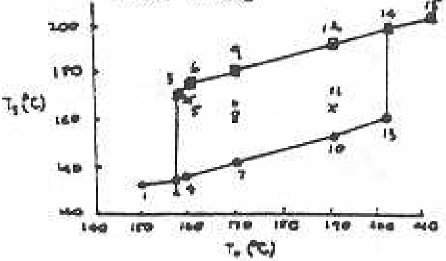


FIGURE P8-22-2

a) To obtain high conversion, the reactor must operate at or beyond point 14 in figure P-22-2. So the minimum inlet temperature for high conversion is $T_0 \geq 202$ °C .

b) The temperature of the fluid in the reactor corresponding to temperature in part 1 is $T_s \geq 199$ °C (point 14 in figure P8-22-2).

c) The inlet temperature of the fluid is $T_0 = 202 + 5 = 207$ °C . This will be somewhere between points 14 and 15 in figure P8-22-2. Once the fluid is cooled from this temperature, it will follow the line formed by points 15, 14, 12, 9, etc.. Now $T_0 = 207 - 10 = 197$ °C. From figure P8-22-2, $T_s = 195.5$ °C. From equation (5),

P8-21 (cont'd)

$Q_R = 2*196.5 - 197 - 100 = 96 cal/\min.$. Now since at intersection point

$Q_R = Q_g$., so Q_g = 96 cal/mon. From equation (4): $X = \dfrac{Q_g}{100} = 0.96$

d) Extinction temperature is the temperature corresponding to point 3 in figure P-22-2:
Text = 157 °C.

e) No solution will be given

P8-22

$$F_{AO} X = -r_A V = k\, C_{AO}\left(1-\left(1+\frac{1}{K_e}\right)X\right)V = C_{AO}\, \upsilon_o\, X$$

$$\tau = \frac{V}{V_0}$$

$$\tau k\left(1-\frac{(K_e+1)}{K_e}X\right) = X$$

$$\frac{\tau k}{1+\tau k\dfrac{(K_e+1)}{K_e}} = X$$

$$\frac{\tau k}{1+\tau k\left[\dfrac{K_e+1}{k_e}\right]} = X$$

$$G(T) = \frac{(-r_A)(-\Delta H)}{F_{AO}} = X\,(-\Delta H_R) = 80{,}000\, X$$

$$R(T) = C_{pA}\,(1+K)\,[T-T_c]$$

$$T_c = \frac{T_o + K\,T_A}{1+K},\; K = \frac{UA}{F_{A0}\, C_{pA}} = \frac{2000}{(10)(40)} = 5$$

⊛ X = tau*k [

$$T_c = \frac{300+(5)(313)}{6} = 311$$

$$R(T) = (40)(1+5)(T-311) = 240\,[T-311]$$

$$k = .001\exp\left(\frac{150{,}000}{8.31}\left(\frac{1}{373}-\frac{1}{T}\right)\right) = 0.001\exp\left[18.051\left(\frac{1}{373}-\frac{1}{T}\right)\right]$$

$$K = 100.0\exp\left(\frac{80{,}000}{8.31}\left(\frac{1}{350}-\frac{1}{T}\right)\right) = 100\exp\left[9{,}267\left(\frac{1}{350}-\frac{1}{T}\right)\right]$$

```
Multiple Steady States
Equations:
d(T)/d(z)=2
tau=100
k=0.001*exp(18051*(1/373-1/T))
ke=100*exp(-9267*(1/350-1/T))
To=300
Ta=313
Tc=(To+5*Ta)/6
X=tau*k/(1+tau*k*(1+ke)/ke)
r=240*(T-Tc)
g=80000*X
z0 = 0,  zf = 100
```

z→tau = 100

T0 = 300
Ta = 313

⊛

X

Tc

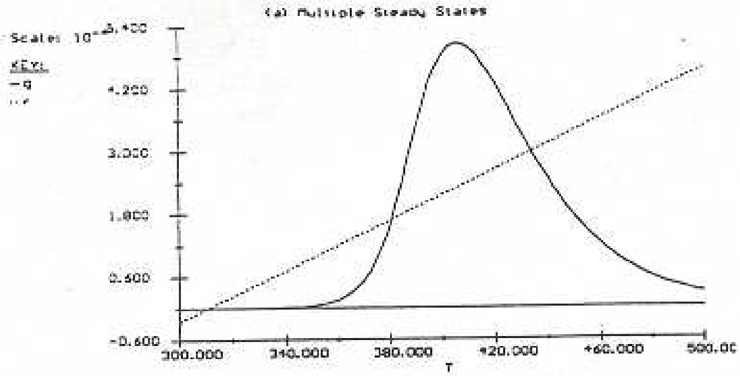
g

R

z=0
=100

```
Variable      Initial value   Maximum value   Minimum value   Final valu
z             0               100             0               100
T             300             500             300             500
tau           100             100             100             100
k             7.68763e-09     217.968         7.68763e-09     217.968
ke            8250.49         8250.49         0.0355089       0.0355089
To            300             300             300             300
Ta            313             313             313             313
Tc            310.833         310.833         310.833         310.833
X             7.68762e-07     0.631768        7.68762e-07     0.0342912
r             -2600           45400           -2600           45400
g             0.061501        50541.4         0.061501        2743.29
```

P8-22 (cont'd)



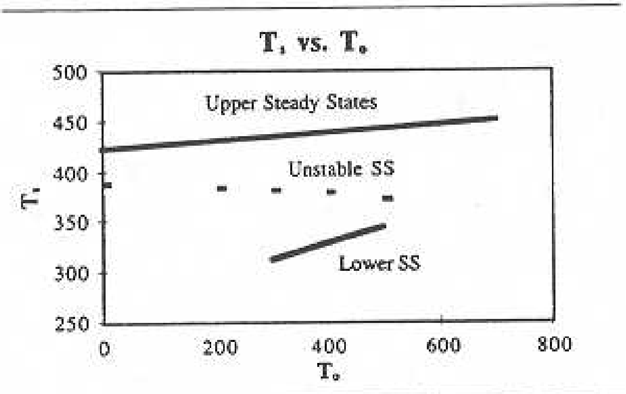
(b) Vary T_s to determine the effect on the number of steady states:

For $T_s > 367$, there is only one steady-state.

For $300 < T_s < 367$, there are three.

For $T_s < 300$, there are only two.

(c) Vary T_o and record all T_s's. Use these data to generate a plot of T_s vs. T_o. From this graph determine the ignition and extinction temperatures.



From this it is apparent that the extinction temperature is 235° F and the ignition temperature is 562°F.

(d) For $K_e = \infty$,

$$X = \frac{\tau k}{1 + \tau k\left(\frac{\infty + 1}{\infty}\right)} = \frac{\tau k}{1 + \tau k}$$

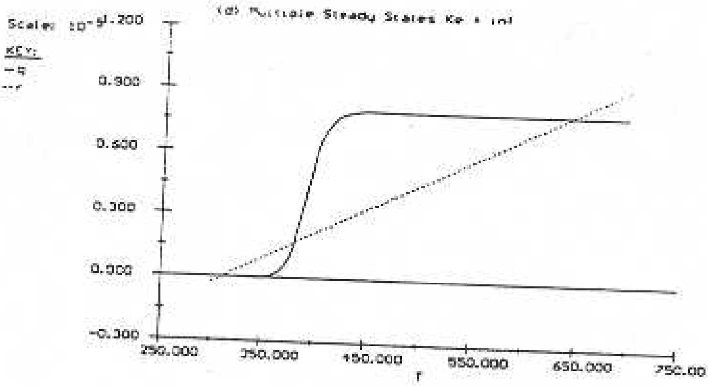
$$= \frac{\tau k}{1 + \tau k\left[\frac{k_e + 1}{k_e}\right]}$$

$$= \frac{\tau k}{1 + \tau k\left[1 + \frac{1}{k_e}\right]} \xrightarrow{k_e \to \infty} \frac{\tau k}{1 + \tau k}$$

Use the same POLYMATH program, but with this new equation for X, to produce the desired graphs.

P8-22 (cont'd)

```
(d) Multiple Steady States Ke = inf
Equations:                            Variable   Initial value  Maximum value  Minimum value  Final value
d(T)/d(z)=2                           z          0              200            0              200
tau=100                               T          300            700            300            700
k=0.001*exp(18051*(1/373-1/T))        tau        100            100            100            100
ke=100*exp(-9267*(1/350-1/T))         k          7.68763e-09    6.57775e+06    7.68763e-09    6.57775e+06
To=300                                ke         8250.49        8250.49        0.000178058    0.000178058
Ta=313                                To         300            300            300            300
Tc=(To+5*Ta)/6                        Ta         313            313            313            313
X=tau*k/(1+tau*k)                     Tc         310.833        310.833        310.833        310.833
r=240*(T-Tc)                          X          7.68762e-07    1              7.68762e-07    1
g=80000*X                             r          -2600          93400          -2600          93400
f=g-r                                 g          0.061501       80000          0.061501       80000
z0 = 0,   zf = 200                    f          2600.06        50510.4        -13400         -13400
```



Repeat parts (b) and (c) for this new situation:

By varying T_a, the following data were obtained:

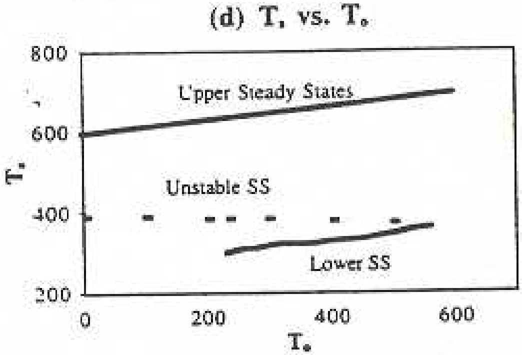
For $T_a > 367$, there is 1 steady state.

For $367 > T_a > 60$, there are three steady states.

For $T_a < 60$, there is only one steady state.

For $T_a = 367$ and 60, there are two steady states.

By varying T_o, the following graph was generated:


(d) T, vs. T₀

From this we can see that the extinction temperature is 235°F and the ignition temperature is 562°F. Note that these are the same values as above.

P8-23

(a)

Initial Calculations:

For 1 inch schedule 40 pipe, D = 1.049 in = 0.0266 m

$$V = \pi D^2 L = \pi(0.0266\text{ m})^2(10\text{ m}) = 0.0223\text{ m}^3$$

$$F_{Ao} = (6000\text{ kg/hr})\left(\frac{1000\text{ g}}{\text{kg}}\right)\left(\frac{1\text{ mol}}{58\text{g}}\right)\left(\frac{1\text{ hr}}{3600\text{s}}\right) = 28.736\text{ mol/s}$$

Dividing this into 1000 tubes, $F_{Ao} = 0.0287$ mol/s

To develop our Design Equation, we must use the data given in Example 8-7.

Mole Balance: $\dfrac{dX}{dV} = \dfrac{-r_A}{F_{A0}}$

Rate Law: $-r_A = kC_A$

Stoichiometry: $C_A = \dfrac{C_{Ao}(1-X)T_o}{(1+\varepsilon X)T}$ $\qquad \varepsilon = y_{Ao}\delta = y_{Ao}$

$$C_{Ao} = \frac{P_o}{RT_o}y_{Ao} = 57.276y_{Ao}$$

$$y_{Ao} = \frac{F_{Ao}}{F_{To}} = \frac{F_{Ao}}{F_{Ao} + F_{N_2o}} = \frac{F_{Ao}}{F_{Ao} + \Theta_{N_2}F_{Ao}} = \frac{F_{Ao}}{\Theta_{N_2}(1+F_{Ao})}$$

P8-23 (cont'd)

Energy Balance : $$\frac{dT}{dV} = \frac{-r_A\left(-\Delta H_{Rx}\right)}{F_{Ao}\left(C_{pA} + \Theta_{N_2} C_{pN_2} + X\Delta C_p\right)}$$

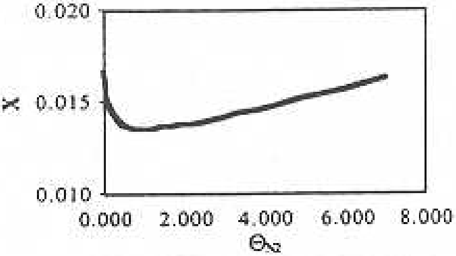
$$-\Delta H_{Rx} = 80{,}770 + 6.8\left(T - T_R\right) - 5.75\times10^{-3}\left(T^2 - T_R^2\right) - 1.27\times10^{-6}\left(T^3 - T_R^3\right)$$

$C_{pN_2} = 4.19(6.50 + 0.001T)$ $\qquad$ $C_{pA} = 26.63 + 0.183T + 45.86\times10^{-6}T^2$

$\Delta C_p = 6.8 - 11.5\times10^{-3}T - 3.81\times10^{-6}T^2$

Use these equations in POLYMATH. Vary F_{N2o}, while keeping F_{To} constant to generate a graph of X vs. Θ_{N2}:

X vs. Θ_{N2} with Constant Flow Rate



```
P8-23 (a)  Constant Flow Rate
Equations:                                                Initial value
d(T)/d(V)=-ra*delh/(fao*(cpa+thetan*cpn+X*delcp))         1050
d(X)/d(V)=-ra/fao                                         0
k=8.2e14*exp(-34222/T)
cpa=26.63+0.183*T+45.86e-6*T**2
cpn=4.19*(6.50+0.001*T)
delcp=6.8-11.5e-3*T-3.81e-6*T**2
fn=0.0286
To=1050
Tr=298
delh=80770+6.8*(T-Tr)-5.75*(T**2-Tr**2)-1.27e-6*(T**3-Tr*
  *3)
fao=0.0287-fn
thetan=fn/fao
yao=fao/thetan/(fao+1)
cao=57.276*yao
ca=cao*(1-X)*To/(1+yao*X)/T
```

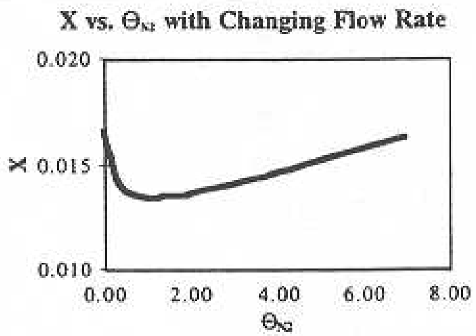
→ k → Cpa → CpN2 → delCp → fn → T → Tr → delh → fao → thetan → Yao → Cao → Ca

```
Variable         Initial value   Maximum value   Minimum value   Final value
V                0               0.0223          0               0.0223
T                1050            1050            1037.34         1037.34
X                0               0.0207844       0               0.0207844
k                5.74279         5.74279         3.85847         3.85847
cpa              269.341         269.341         265.813         265.813
cpn              31.6345         31.6345         31.5815         31.5815
delcp            -9.47552        -9.22931        -9.47552        -9.22931
fn               0.0286          0.0286          0.0286          0.0286
To               1050            1050            1050            1050
Tr               298             298             298             298
delh             -5.7443e-06     -5.59243e-06    -5.7443e-06     -5.59243e-06
fao              0.0001          0.0001          0.0001          0.0001
thetan           286             286             286             286
yao              3.49615e-07     3.49615e-07     3.49615e-07     3.49615e-07
cao              2.00246e-05     2.00246e-05     2.00246e-05     2.00246e-05
ca               2.00246e-05     2.00246e-05     1.98476e-05     1.98476e-05
```

P8-23 (cont'd)

(b)

Use the same equations in POLYMATH, but this time vary F_{N2o} while keeping F_{Ao} constant, allowing the overall flow rate (F_{To}) to change.



```
P8-23 (b)  Changing Flow Rate
Equations:                                                Initial value
d(T)/d(V)=-ra*delh/(fao*(cpa+thetan*cpn+X*delcp))         1050
d(X)/d(V)=-ra/fao                                         0
k=8.2e14*exp(-34222/T)
fao=0.0287
cpa=26.63+0.183*T+45.86e-6*T**2
cpn=4.19*(6.50+0.001*T)
delcp=6.8-11.5e-3*T-3.81e-6*T**2
fn=0.01144
To=1050
Tr=298
delh=80770+6.8*(T-Tr)-5.75*(T**2-Tr**2)-1.27e-6*(T**3-Tr*
   *3)
thetan=fn/fao
yao=fao/thetan/(fao+1)
cao=57.276*yao
ca=cao*(1-X)*To/(1+yao*X)/T
ra=-k*ca
V0 = 0,    Vf = 0.0223
```

```
Variable     Initial value  Maximum value  Minimum value  Final value
V            0              0.0223         0              0.0223
T            1050           1050           828.919        828.919
X            0              0.0134562      0              0.0134562
k            5.74279        5.74279        0.000963674    0.000963674
fao          0.0287         0.0287         0.0287         0.0287
cpa          269.341        269.341        209.833        209.833
cpn          31.6345        31.6345        30.7082        30.7082
delcp        -9.47552       -5.35045       -9.47552       -5.35045
fn           0.0287         0.0287         0.0287         0.0287
To           1050           1050           1050           1050
Tr           298            298            298            298
delh         -5.7443e+06    -3.35655e+06   -5.7443e-06    -3.35655e-06
thetan       1              1              1              1
yao          0.0278993      0.0278993      0.0278993      0.0278993
cao          1.59796        1.59796        1.59796        1.59796
ca           1.59796        1.99616        1.59796        1.99616
```

P8-24 No solution will be given.

P8-25

a) $A + B \longrightarrow C$ Liquid phase

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_AC_B$$

$$k = .01 * \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{300}\right)\right)$$

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

The energy balance is next.

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_R)}{F_{A0}\left[C_{pA} + C_{pB}\right]}$$

$$a = \frac{4}{D}$$

$$assume\ D = 4$$

$$U = \frac{5J}{m^2Ks}\left(\frac{1cal}{4.1841J}\right)\left(\frac{1m^2}{10^2dm^2}\right) = .0120\frac{cal}{dm^2Ks}$$

Plug those into POLYMATH to come up with these two graphs of conversion and temperature.

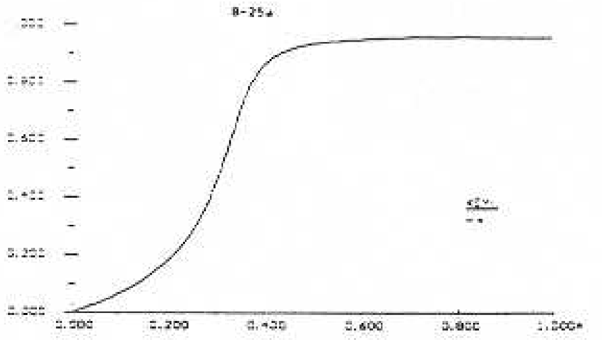
```
Equations:                                                      Initial value
d(x)/d(v)=-ra/fao                                               0
d(T)/d(v)=(U*a*(Ta-T)+(-ra)*(-Dhr1))/(fao*(cpa+cpb))            300
U=.0120
a=1
Ta=300
Dhr1=-6000
fao=.2
cpa=15
cpb=15
E=10000
R=1.987
cao=.1
ca=cao*(1-x)
cb=cao*(1-x)
k=.01*exp(-E/R*(1/T-1/300))
ra=-k*ca*cb
v0 = 0,    vf = 1000
```

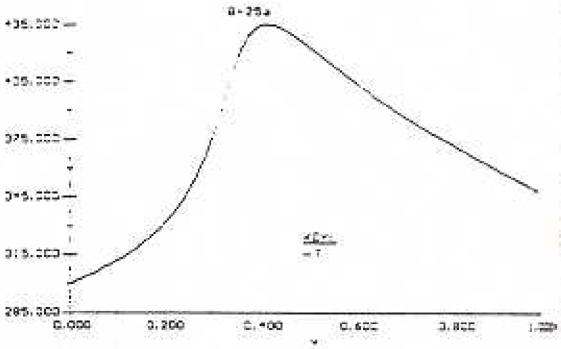
E = 10000

R=1.987

```
Variable        Initial value  Maximum value  Minimum value  Final value
v               0              1000           0              1000
x               0              0.962152       0              0.962152
T               300            434.882        300            346.181
U               0.012          0.012          0.012          0.012
a               1              1              1              1
Ta              300            300            300            300
Dhr1            -6000          -6000          -6000          -6000
fao             0.2            0.2            0.2            0.2
cpa             15             15             15             15
cpb             15             15             15             15
E               10000          10000          10000          10000
R               1.987          1.987          1.987          1.987
cao             0.1            0.1            0.1            0.1
ca              0.1            0.1            0.00378482     0.00378482
cb              0.1            0.1            0.00378482     0.00378482
k               0.01           1.81836        0.01           0.1319
```

P8-25 cont'd





b) Gas-phase reaction

$$A \longrightarrow B + C$$

The design equation for a PBR is then:

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A$$

$$C_A = \frac{C_{A0}(1-X)}{1+X}\frac{T_0}{T}$$

$$k = .133 * \exp\left(\frac{E}{R}\left(\frac{1}{450} - \frac{1}{T}\right)\right)$$

$$C_{A0} = \frac{P}{RT} = \frac{10}{(0.082)(450)} = .27\frac{mol}{dm^3}$$

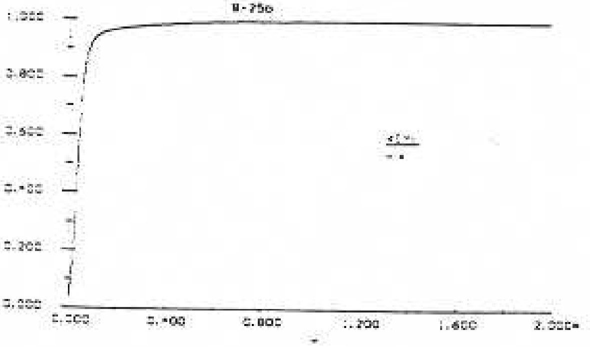
Then the energy balance:

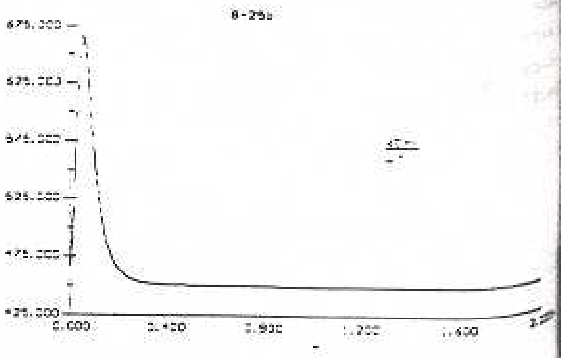
$$\frac{dT}{dW} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_R)}{F_{A0} * C_{pA}}$$

$$\Delta H_R = -40 - 50 + 70 = -20 kJ/mol$$

$$U = 5$$

Plug those into POLYMATH gives the following graphs:





P8-25 cont'd

```
8-25b
Equations:                                                   Initial value
d(x)/d(w)=-ra/fao                                            0
d(T)/d(w)=(U*a*(Ta-T)+(-ra)*(-Dhr))/(fao*cpa)                450
U=5
a=1
Ta=450
Dhr=-20000
fao=5.4
cpa=40
E=31400
R=8.3144
cao=.27
To=450
ca=(cao*(1-x)*To)/((1+x)*T)
k=.133*exp(E/R*(1/450-1/T))
ra=-k*ca
w0 = 0,    wf = 2000
```

```
8-25b
Variable      Initial value  Maximum value  Minimum value  Final value
w             0              2000           0              2000
x             0              0.999924       0              0.999924
T             450            665.963        450            450.006
U             5              5              5              5
a             1              1              1              1
Ta            450            450            450            450
Dhr           -20000         -20000         -20000         -20000
fao           5.4            5.4            5.4            5.4
cpa           40             40             40             40
E             31400          31400          31400          31400
R             8.3144         8.3144         8.3144         8.3144
cao           0.27           0.27           0.27           0.27
To            450            450            450            450
ca            0.27           0.27           1.02394e-05    1.02394e-05
k             0.133          2.0221         0.133          0.133016
ra            -0.03591       -1.362e-06     -0.093202      -1.362e-06
```

c) Gas-phase

$$A + B \rightleftarrows C$$

Use the design equation:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = k\left[C_A C_B - \frac{C_C^2}{K_e}\right]$$

$$C_A = C_{A0}(1-X)\frac{T_0}{T}$$

$$C_B = C_{A0}(1-X)\frac{T_0}{T}$$

$$C_C = 2C_{A0}X\frac{T_0}{T}$$

$$k = .035 * \exp\left[\frac{E}{R}\left(\frac{1}{273} - \frac{1}{T}\right)\right]$$

$$K_e = 25000 * \exp\left[\frac{\Delta H_R}{R}\left(\frac{1}{298} - \frac{1}{T}\right)\right]$$

$$C_T = \frac{P}{RT} = \frac{580.5}{(8.309)(350)} = .2$$

$$C_A = .5 * .2 = .1$$

P8-25 cont'd

Then use the energy balance:

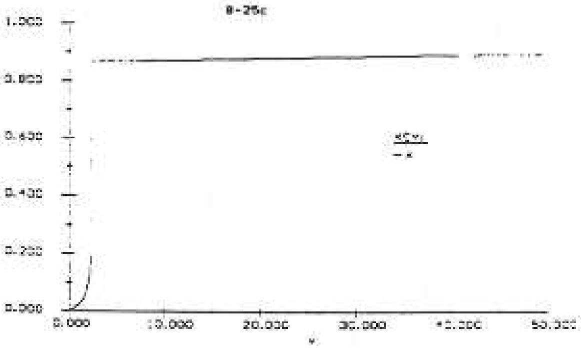
$$\frac{dT}{dV}=\frac{Ua(T_a-T)+(-r_A)(-\Delta H_R)}{F_{A0}(C_{pA}+C_{pB})}$$

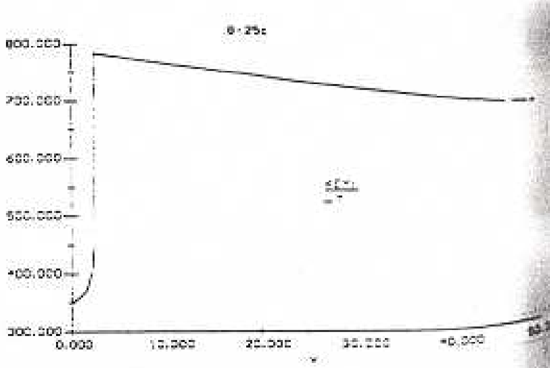
$$\Delta H_R=-90+40+30=-20$$

Plug those into POLYMATH and get the following graphs.

```
8-25c
Equations:                                                    Initial value
d(x)/d(v)=-ra/fao                                             0
d(T)/d(v)=(U*a*(Ta-T)+(-ra)*(-Dhr1))/(fao*(cpa+cpb+Dcp))      350
U=5
a=1
Ta=350
Dhr1=-20000
fao=20
cpa=25
cpb=15
Dcp=0
E=70000
R=8.3144
cao=.1
To=350
k=.035*exp(E/R*(1/273-1/T))
ca=cao*(1-x)*To/T
cc=2*cao*x*To/T
K=25000*exp(Dhr1/R*(1/298-1/T))
cb=ca
ra=-k*(ca*cb-cc^2/K)
v0 = 0,   vf = 50
```

```
Variable     Initial value  Maximum value  Minimum value  Final value
v            0              50             0              50
x            0              0.890645       0              0.890645
T            350            782.841        350            682.116
U            5              5              5              5
a            1              1              1              1
Ta           350            350            350            350
Dhr1         -20000         -20000         -20000         -20000
fao          20             20             20             20
cpa          25             25             25             25
cpb          15             15             15             15
Dcp          0              0              0              0
E            70000          70000          70000          70000
R            8.3144         8.3144         8.3144         8.3144
cao          0.1            0.1            0.1            0.1
To           350            350            350            350
k            30.9458        1.84821e+07    30.9458        3.7762e+06
ca           0 1            0.1            0.00561108     0.00561108
cc           0              0.0913997      0              0.0913997
K            7535.33        7535.33        168.568        265.357
cb           0.1            0.1            0.00561108     0.00561108
ra           -0.309458      -0.00928109    -1059.19       -0.00928109
```





P8-26 The results of the computer program are presented below:

Tabulation of Results

$T_0 = 1360$			$T_0 = 1370$		
X	T	Z	X	T	Z
0.050	1386.4	219.6	0.050	1396.3	99.4
0.100	1412.7	252.8	0.100	1422.6	114.9
0.150	1438.9	259.2	0.150	1448.9	117.9
0.200	1465.1	260.4	0.200	1475.0	118.5
0.250	1491.2	260.6	0.250	1501.2	118.7
0.300	1517.3	260.6	0.300	1527.2	118.7
0.350	1543.3	260.6	0.350	1553.2	118.7
0.400	1569.2	260.6	0.400	1579.1	118.7
0.450	1595.1	260.6	0.450	1605.0	118.7
0.500	1620.9	260.6	0.500	1630.8	118.7
0.525	1633.8	260.6	0.524	1643.2	118.7
0.533	1637.9	260.6			

```
C W=CATALYST WEIGHT                    AC=CROSS SECTIONAL AREA
C R=REACTION RATE                      AKI=SPECIFIC REACTION RATE
C T=TEMPERATURE                        AKE=EQUILIBRIUM CONSTANT
C X=CONVERSION                         DX=INCREMENT IN CONVERSION
C Z=DISTANCE DOWN THE REACTOR RHO=BULK DENSITY
C FAO=ENTERING MOLAR FLOW RATE OF A
C PFREQ=PRINTING FREQUENCY
      INTEGER PFREQ
      WRITE (5,10)
   10 FORMAT('ENTER VALUES OF TO,FAO,AC,RHO,DX,PFREQ SEPARATED BY COMMAS'/
     1        'EXAMPLE'/' 1370.,.00306,.196,152.,.001,25.')
      READ (5,20) TO, FAO, AC, RHO, DX, PFREQ
   20 FORMAT(5F10.5,I5)
      WRITE (6,30)
   30 FORMAT('1',9X,'TO',16X,'FAO',12X,'AC',11X,'RHO',14X,'DX'/)
      WRITE (6,40) TO  FAO, AC, RHO, DX
   40 FORMAT(5X,5F15.5//)
      WRITE (6,50)
   50 FORMAT(5X,'X',14X,'T',14X,'AKI',12X,'AKE',12X,'R',14X,'W',14X,'Z'/
     1        )
      XI = 0.0
      X = 0.0
      W = 0.0
      IFREQ = -1
   60 CONTINUE
C CALCULATE ADIABATIC TEMPERATURE
      T = (43260.*X + 77.3*TO) / (1.8*X + 77.3)
C  CALCULATE SPECIFIC REACTION RATE & EQUILIBRIUM CONSTANT AT THIS
C TEMPERATURE
      AKI = EXP(92.5 - 149750./T)
      AKE = EXP(42300./T - 24.2 + 0.17*ALOG(T))
C C ALCULATE RATE OF REACTION
      IF  (X .GT. 0.05) GO TO 70
      R = AKI * (0.4292 - 0.01176/AKE)
      GO TO 80
   70 R = AKI * SQRT((1. - X)/X) * ((.91 - .5*X)/(9.1 - .5*X) - (X/(1. -
     1 X))**2./AKE)
C CALCULATE THE CATALYST WEIGHT AND REACTOR LENGTH
C NECESSARY TO ACHIEVE THIS CONVERSION.
   80 W = W + FAO * (X - XI) / R
      Z = W / RHO / AC
      IFREQ = IFREQ + 1
      IF  (IFREQ .NE. PFREQ) GO TO 95
      IFREQ = 0
      WRITE (6,90) X, T, AKI, AKE, R, W, Z
   90 FORMAT(1X,1P7E15.5)
C CHECK TO SEE IF EQUILIBRIUM HAS BEEN REACHED
   95 IF  (R .LE. 0.0) GO TO 100
C INCREMENT X AND THEN REPEAT THE CALCULATIONS AS NECESSARY
      XI = X
      X = X + DX
      GO TO 60
  100 WRITE(6,90) X, T, AKI, AKE, R, W, Z
      END
```

P8-26 (cont'd)

$T_0 = 1375$

X	T	Z
0.050	1401.3	67.15
0.100	1427.6	77.79
0.150	1453.9	79.92
0.200	1480.0	80.34
0.250	1506.1	80.42
0.300	1532.2	80.44
0.350	1558.2	80.45
0.400	1584.1	80.45
0.450	1609.9	80.45
0.500	1635.8	80.45
0.520	1646.1	80.45

$T_0 = 1380$

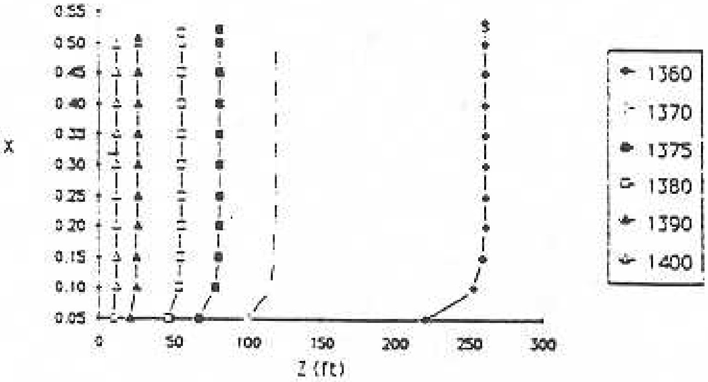
X	T	Z
0.050	1406.3	45.49
0.100	1432.6	52.82
0.150	1458.9	54.31
0.200	1485.0	54.60
0.250	1511.1	54.66
0.300	1537.1	54.68
0.350	1563.1	54.68
0.400	1589.0	54.68
0.450	1614.9	54.68
0.500	1640.7	54.68
0.515	1648.4	54.68

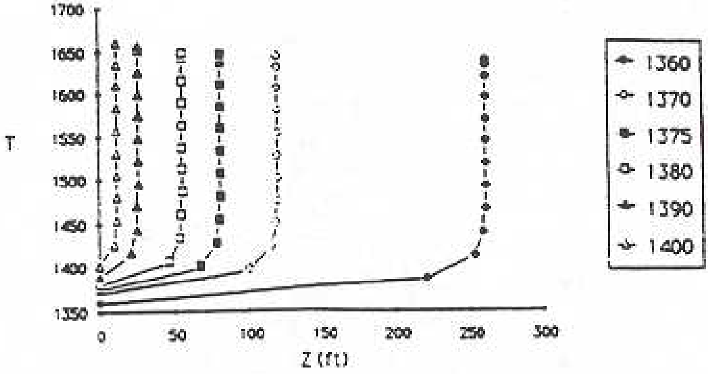
$T_0 = 1390$

X	T	Z
0.050	1416.3	21.06
0.100	1442.6	24.56
0.150	1468.8	25.29
0.200	1494.9	25.43
0.250	1521.0	25.46
0.300	1547.1	25.47
0.350	1573.0	25.47
0.400	1598.9	25.47
0.450	1624.8	25.47
0.500	1650.6	25.47
0.506	1653.7	25.47

$T_0 = 1400$

X	T	Z
0.050	1426.3	9.8
0.100	1452.6	11.5
0.150	1478.8	11.9
0.200	1504.9	12.0
0.250	1530.9	12.0
0.300	1557.0	12.0
0.350	1583.0	12.0
0.400	1608.9	12.0
0.450	1634.7	12.0
0.497	1659.0	12.0





Comments:
- X and T increase with Z
- Exothermic
- Reaction front increases for decreasing T_0

From data

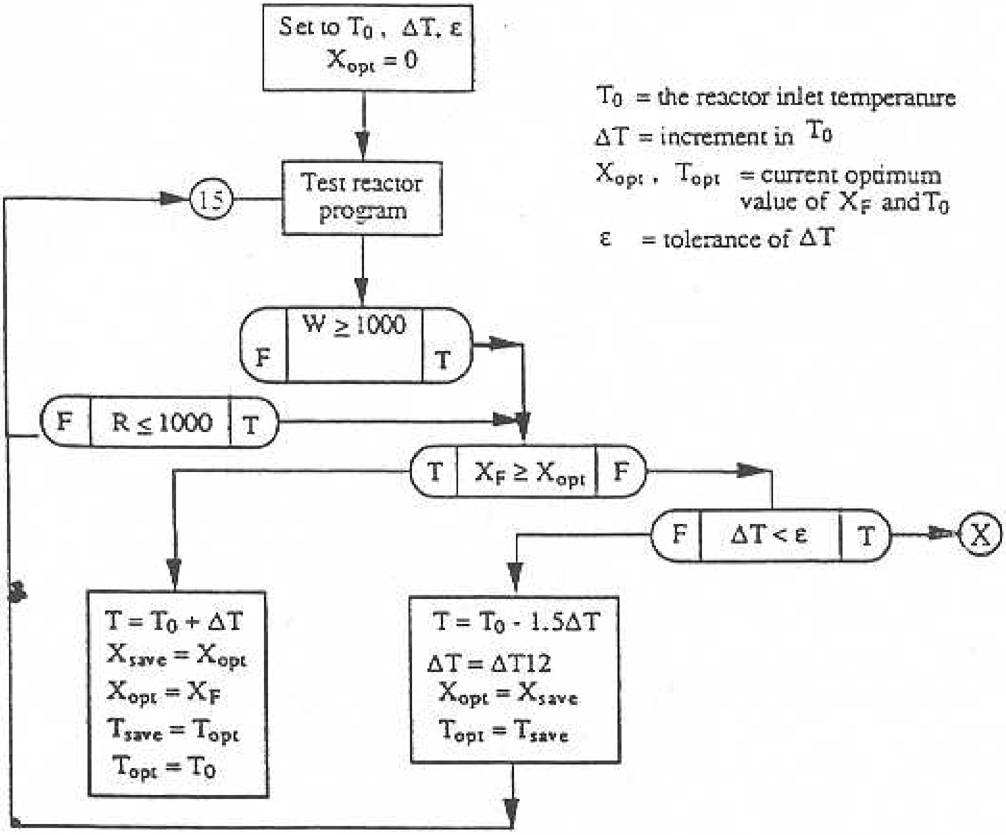
Reaction front (ft)	T_0 (°K)	X (final)
37834.60	1300	0.589
260.60	1360	0.533
118.70	1370	0.524
80.45	1375	0.520
54.68	1380	0.515
25.47	1390	0.506
12.00	1400	0.497
5.72	1410	0.488
2.75	1420	0.479
2.62×10^{-5}	1600	0.324

To obtain "best" T_0, we would have to examine conversion, reaction front and catalyst weight, then weigh these factors to find the one where all is satisfied to a good extent.

P8-27 Because the reaction is exothermic, the final equilibrium conversion will decrease in temperature. So long as X_F, the final conversion for a reactor with W = 1000lb, is much less than X_e, the equilibrium conversion at the outlet, an increase in T_0 should increase X_F at the point where $X_F = X_e$, however, any increase in temperature should decrease X_F. It appears, therefore, that a unique maximum conversion for X_F with respect to T exist and may be found by starting with a low value of T_0 and increase T_0 until X_F no longer increases.

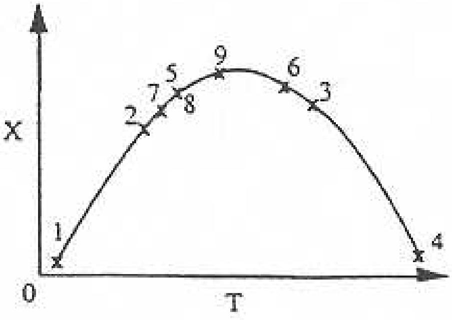
First, an additional exist statement to the program should be added so that computation ceases when W ≥ 1000 lb. Proposed modifications to the program are shown below.

P8-27 (cont'd)



T_0 = the reactor inlet temperature
ΔT = increment in T_0
X_{opt}, T_{opt} = current optimum value of X_F and T_0
ε = tolerance of ΔT

In this scheme, T_0 is increased as long as X_F is increased. The maximum value of X_F is set at X_{opt} if X_F is greater than the previously calculated value of X_F. Once $X_{opt} > X_F$, T_0 is incremented to a value below the current optimum point, ΔT is decreased and T_{opt} and X_{opt} are reset. The process continues with T_0 jumping past the previously calculated T_{opt} until ΔT is decremented below some tolerance ε. This process is illustrated below with the points numbered in sequential order. Note that part 5 and 8 are one and the same sequences of calculations of proposed program.



P8-28

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:

$$C_i = \frac{F_i}{v_0}\frac{T}{T_0}$$

$$F_B = 10F_C$$

$$.5 = \frac{.05 - F_A}{0.5}$$

$$F_A = .025$$

$$11F_C = .025$$

$$F_C = .023 \qquad \mathrm{F_B} = .023$$

From this we can use two of the mole balances to solve for T

$$\frac{F_{A0} - F_A}{k_1 F_A} = \frac{F_c}{k_2 F_B}$$

$$\frac{1}{A_1 e^{-E/RT}} = \frac{0.1}{A_2 e^{-E/RT}}$$

$$T = 269°F$$

Knowing the temperature we can then solve for the Volume:

$$V = \frac{F_B v_0}{k_1 F_A - k_2 F_B}\frac{T_0}{T} = 11.9\,ft^3$$

We then need the energy balance:

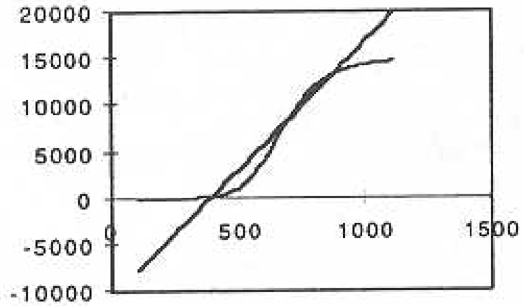
$$UA(T_a - T) - F_{A0}C_{pa}(T - T_0) + V\left[(\Delta H_{R1})(r_{1A}) + \Delta H_{R2}(r_{2B})\right] = 0$$

Solve for A and we get:

$A = 399\ \text{ft}^2$

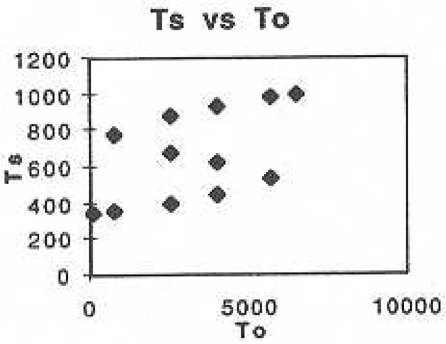
d) In order to get multiple steady-states, the kappa, tau and feed temperature had to be changed. $\kappa = 0.1$, $\tau = 0.0005$ and T_0 would be changed around.

This first graph is G(T), R(T) vs T at $T_0 = 2000$ °F



As can be seen there are three steady-states.

The next graph is of T_s vs. T_0.



P8-29

$$B \rightleftarrows A \longrightarrow C$$

Mole Balances: $\frac{dF_A}{dW} = r_A \qquad \frac{dF_B}{dW} = r_B \qquad \frac{dF_C}{dW} = r_C$

Rate laws:

$$r_A = -r_{2B} + r_{1A} + r_{3A}$$
$$r_B = -r_{1A} + r_{2B}$$
$$r_C = -r_{3A}$$
$$-r_{1A} = k_1 C_A$$
$$-r_{2B} = k_2 C_B$$
$$-r_{3A} = k_3 C_C$$

Stoichiometry:

$$C_A = C_T \frac{F_A}{F_T}\frac{T_0}{T} \qquad C_B = C_T \frac{F_B}{F_T}\frac{T_0}{T}$$

Energy Balance:

$$\frac{dT}{dW} = \frac{Ua(T_A - T) + (-r_{1A})(-\Delta H_{R1A}) + (-r_{2B})(-\Delta H_{R2B}) + (-r_{3A})(-\Delta H_{R3A})}{F_A C_{pA} + F_B C_{pC} + F_C C_{pC}}$$

$$\frac{dT}{dW} = \frac{16(500 - T) + 1800(-r_{1A}) - 1800(-r_{2B}) + 1100(-r_{3A})}{100(F_A + F_B + F_C)}$$

Evaluate the parameters.

$$k_1 = 0.5\exp[2(1 - 320/T)]$$

$$k_2 = \frac{k_1}{K_C}$$

$$k_3 = 0.005\exp[4.6(1 - 460/T)]$$

$$K_C = 10\exp[4.8(430/T - 1.5)]$$

Plug those into POLYMATH and the following program is created.

```
                                                                        Initial value
Equations:
d(fb)/d(w)=rb                                                           1
d(fa)/d(w)=ra                                                           1
d(fc)/d(w)=rc                                                           0
d(T)/d(w)=(Ua*(Ta-T)+(-r1a)*(-Dhr1a)+(-r2b)*(Dhr1a)+(-r3a)*(            330
    -Dhr3a))/(fa*cpa+fb*cpb+fc*cpc)
Ua=16
Ta=500
Dhr1a=-1800
Dhr3a=-1100
cpa=100
cpb=100
cpc=100
k1=.5*exp(2*(1-320/T))
```

P8-29 cont'd

```
k3=.005*exp(4.6*(1-(460/T)))
ct=2
ft=2
To=330
Kc=10*exp(4.8*(430/T-1.5))
k2=k1/Kc
ca=ct*fa/ft*To/T
cb=ct*fb/ft*To/T
r1a=-k1*ca
r3a=-k3*ca
rc=-r3a
r2b=-k2*cb
rb=-r1a+r2b
ra=-r2b+r1a+r3a
w0 = 0,   wf = 100
```

```
Variable    Initial value    Maximum value    Minimum value    Final value
w           0                100              0                100
fb          1                1.37086          0.48269          0.48269
fa          1                1.23955          0.627195         1.04039
fc          0                0.476925         0                0.476925
T           330              500.098          330              500.098
Ua          16               16               16               16
Ta          500              500              500              500
Dhr1a       -1800            -1800            -1800            -1800
Dhr3a       -1100            -1100            -1100            -1100
cpa         100              100              100              100
cpb         100              100              100              100
cpc         100              100              100              100
k1          0.53124          1.02747          0.53124          1.02747
k3          0.000816537      0.00723019       0.000816537      0.00723019
ct          2                2                2                2
ft          2                2                2                2
To          330              330              330              330
Kc          3.88503          3.88503          0.462911         0.462911
k2          0.13674          2.21959          0.13674          2.21959
ca          1                1                0.566569         0.68652
cb          1                1.25646          0.318513         0.318513
r1a         -0.53124         -0.360779        -0.834834        -0.705382
r3a         -0.000816537     -0.000755951     -0.00565343      -0.00496367
rc          0.000816537      0.00565343       0.000755951      0.00496367
r2b         -0.13674         -0.13674         -0.839884        -0.706969
rb          0.3945           0.3945           -0.0583793       -0.0015878
ra          -0.395316        0.0570191        -0.395316        -0.00337587
```

a) As seen in the above table, the lowest concentration of o-xylene (A) = .57mol/dm^3

b) The maximum concentration of m-xylene (B) = 1.26 mol/dm^3

c) The maximum concentration of o-xylene = 1 mol/dm^3

d) The same equations are used except that $F_{B0} = 0$. The following table is generated.

P8-29 cont'd

```
Variable     Initial value   Maximum value   Minimum value   Final value
w            0               100             0               100
fa           2               2               0.746157        1.03729
fb           0               1.24923         0               0.481236
fc           0               0.481477        0               0.481477
T            330             500.102         330             500.102
Ua           16              16              16              16
Ta           500             500             500             500
Dhr1a        -1800           -1800           -1800           -1800
Dhr3a        -1100           -1100           -1100           -1100
cpa          100             100             100             100
cpb          100             100             100             100
cpc          100             100             100             100
k1           0.53124         1.02748         0.53124         1.02748
k3           0.000816537     0.00723042      0.000816537     0.00723042
ct           2               2               2               2
ft           2               2               2               2
To           330             330             330             330
Kc           3.88503         3.88503         0.462896        0.462896
k2           0.13674         2.21969         0.13674         2.21969
ca           2               2               0.642753        0.68447
cb           0               1.08752         0               0.317551
r1a          -1.06248        -0.444729       -1.06248        -0.703282
r3a          -0.00163307     -0.00116466     -0.00565086     -0.00494901
rc           0.00163307      0.00565086      0.00116466      0.00494901
r2b          -0              -0              -0.839501       -0.704864
rb           1.06248         1.06248         -0.0496506      -0.00158212
ra           -1.06411        0.0478847       -1.06411        -0.00336689
```

The lowest concentration of o-xylene = 0.64 mol/dm^3. The highest concentration of m-xylene = 1.09 mol/dm^3. The maximum concentration of o-xylene = 2 mol/dm^3.

e) Decreasing the heat of reaction of reaction 1 slightly decreases the amount of B 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.

P8-30

$$A \leftrightarrow B + C$$

$$A \rightarrow D + E$$

$$A + C \rightarrow F + G$$

We want the exiting flow rates of B, D, and F

P8-30 **cont'd**

Start with mole balances 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:

$$r_A = -r_{1S} - r_{2B} - r_{3T} \qquad r_B = r_{1S}$$

$$r_C = r_{1S} - r_{3T} \qquad r_D = r_{2B}$$

$$r_E = r_{2B} \qquad r_F = r_{3T}$$

$$r_F = r_{3T}$$

$$r_{1S} = \rho(1-\phi)\exp\left(-0.08539 - \frac{10925}{T}\right)\left(P_A - \frac{P_B P_C}{K}\right)$$

$$r_{2B} = \rho(1-\phi)\exp\left(13.2392 - \frac{25000}{T}\right)P_A$$

$$r_{3T} = \rho(1-\phi)\exp\left(0.2961 - \frac{11000}{T}\right)P_A P_C$$

Stoichiometry:

$$P_A = \frac{F_A}{F_T} P_{T0}$$

$$P_B = \frac{F_B}{F_T} P_{T0}$$

$$P_C = \frac{F_C}{F_T} P_{T0}$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_F + F_G + F_I$$

$$F_I = \text{steamratio} * .00344$$

Energy balance:

$$\frac{dT}{dV} = \frac{-(r_{1S} * \Delta H_{R1A} + r_{2B} * \Delta H_{R2A} + r_{3T} * \Delta H_{R3A})}{F_A * 299 + F_B * 273 + F_C * 30 + F_D * 201 + F_E * 90 + F_F * 249 + F_G * 68 + F_I * 40}$$

Evaluate the parameters:

$$\Delta H_{R1A} = 118{,}000$$

$$\Delta H_{R2A} = 105{,}200$$

$$\Delta H_{R3A} = -53{,}900$$

P8-30 cont'd

$$K_{p1} = \exp(b_1 + \frac{b_2}{T} + b_3 \ln(T) + [(b_4 T + b_5)T + b_6]T)$$

a) Now plugging into POLYMATH with a initial temperature of 800 K we get the following program and answer.

$F_B = 0.000898$ kmol/s $\quad F_D = 1.07*10^{-5}$ kmol/s $\quad F_F = 3.59*10^{-5}$ kmol/s

```
8-30
Equations:                                                                Initial value
d(fa)/d(v)=ra                                                             0.00344
d(fb)/d(v)=rb                                                             0
d(fc)/d(v)=rc                                                             0
d(fd)/d(v)=rd                                                             0
d(fe)/d(v)=re                                                             0
d(ff)/d(v)=rf                                                             0
d(fg)/d(v)=rg                                                             0
d(T)/d(v)=-(r1s*H1a+r2b*H2a+r3t*H3a)/(fa*299+fb*273+fc*30                 800
   +fd*201+fe*90+ff*68+fi*40)
H1a=118000
H2a=105200
H3a=-53900
p=2137
phi=.4
K1=exp(-17.34-1.302e4/T+5.051*ln(T)+((-2.314e-10*T+1.302e
   -6)*T+-4.931e-3)*T)
sr=14.5
fi=sr*.00344
ft=fa+fb+fc+fd+fe+ff+fg+fi
Pa=fa/ft*2.4
Pb=fb/ft*2.4
Pc=fc/ft*2.4
r2b=p*(1-phi)*exp(13.2392-25000/T)*Pa
rd=r2b
re=r2b
r3t=p*(1-phi)*exp(.2961-11000/T)*Pa*Pc
rf=r3t
rg=r3t
r1s=p*(1-phi)*exp(-.08539-10925/T)*(Pa-Pb*Pc/K1)
rb=r1s
rc=r1s-r3t
ra=-r1s-r2b-r3t
v0 = 0,   vf = 10
```

P8-30 cont'd

```
8-30
Variable          Initial value   Maximum value   Minimum value   Final value
v                 0               10              0               10
fa                0.00344         0.00344         0.00249597      0.00249597
fb                0               0.000897375     0               0.000897375
fc                0               0.000861498     0               0.000861498
fd                0               1.07785e-05     0               1.07785e-05
fe                0               1.07785e-05     0               1.07785e-05
ff                0               3.58772e-05     0               3.58772e-05
fg                0               3.58772e-05     0               3.58772e-05
T                 800             800             765.237         765.237
H1a               118000          118000          118000          118000
H2a               105200          105200          105200          105200
H3a               -53900          -53900          -53900          -53900
p                 2137            2137            2137            2137
phi               0.4             0.4             0.4             0.4
K1                0.0459123       0.0459123       0.0196554       0.0196554
sr                14.5            14.5            14.5            14.5
fi                0.04988         0.04988         0.04988         0.04988
ft                0.05332         0.0542282       0.05332         0.0542282
Pa                0.154839        0.154839        0.110465        0.110465
Pb                0               0.0397155       0               0.0397155
Pc                0               0.0381277       0               0.0381277
r2b               2.99119e-06     2.99119e-06     5.16009e-07     5.16009e-07
rd                2.99119e-06     2.99119e-06     5.16009e-07     5.16009e-07
re                2.99119e-06     2.99119e-06     5.16009e-07     5.16009e-07
r3t               0               4.19563e-06     0               4.15139e-06
rf                0               4.19563e-06     0               4.15139e-06
rg                0               4.19563e-06     0               4.15139e-06
r1s               0.000213755     0.000213755     2.48131e-05     2.48131e-05
rb                0.000213755     0.000213755     2.48131e-05     2.48131e-05
rc                0.000213755     0.000213755     2.06617e-05     2.06617e-05
ra                -0.000216746    -2.94805e-05    -0.000216746    -2.94805e-05
```

P8-30 cont'd

b) $T_0 = 930$ K

$F_B = 0.00194$ kmol/s $F_D = 0.000217$ kmol/s $F_F = 0.000204$ kmol/s

```
8-30
Variable        Initial value   Maximum value   Minimum value   Final value
v               0               10              0               10
fa              0.00344         0.00344         0.00108529      0.00108529
fb              0               0.00193494      0               0.00193494
fc              0               0.00174035      0               0.00173155
fd              0               0.000216382     0               0.000216382
fe              0               0.000216382     0               0.000216382
ff              0               0.000203387     0               0.000203387
fg              0               0.000203387     0               0.000203387
T               930             930             850.383         850.383
H1a             118000          118000          118000          118000
H2a             105200          105200          105200          105200
H3a             -53900          -53900          -53900          -53900
P               2137            2137            2137            2137
phi             0.4             0.4             0.4             0.4
K1              0.630438        0.630438        0.13914         0.13914
sr              14.5            14.5            14.5            14.5
fi              0.04988         0.04988         0.04988         0.04988
ft              0.05332         0.0554713       0.05332         0.0554713
Pa              0.154839        0.154839        0.0469559       0.0469559
Pb              0               0.0837162       0               0.0837162
Pc              0               0.0753373       0               0.0749166
r2b             0.000236028     0.000236028     5.77759e-06     5.77759e-06
rd              0.000236028     0.000236028     5.77759e-06     5.77759e-06
re              0.000236028     0.000236028     5.77759e-06     5.77759e-06
r3t             0               3.10453e-05     0               1.46241e-05
rf              0               3.10453e-05     0               1.46241e-05
rg              0               3.10453e-05     0               1.46241e-05
r1s             0.00144198      0.00144198      5.83176e-06     5.83176e-06
rb              0.00144198      0.00144198      5.83176e-06     5.83176e-06
rc              0.00144198      0.00144198      -8.79236e-06    -8.79236e-06
ra              -0.001678       -2.62335e-05    -0.001678       -2.62335e-05
```

c) $T_0 = 1100$ K

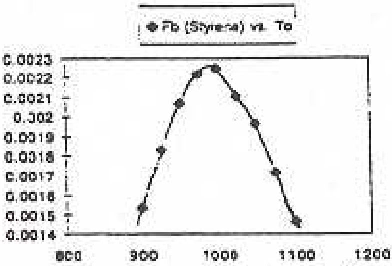
$F_B = 0.00165$ kmol/s $F_D = 0.00161$ kmol/s $F_F = 0.000127$ kmol/s

```
8-30
Variable        Initial value   Maximum value   Minimum value   Final value
v               0               10              0               10
fa              0.00344         0.00344         5.15006e-05     5.15006e-05
fb              0               0.00174939      0               0.0016543
fc              0               0.00164874      0               0.00152682
fd              0               0.00160673      0               0.00160673
fe              0               0.00160673      0               0.00160673
ff              0               0.00012747      0               0.00012747
fg              0               0.00012747      0               0.00012747
```

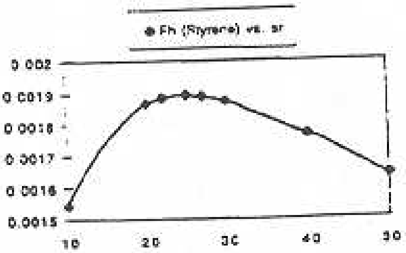
P8-30 cont'd

```
T        1100           1100           980.458        981.412
H1a      118000         118000         118000         118000
H2a      105200         105200         105200         105200
H3a      -53900         -53900         -53900         -53900
p        2137           2137           2137           2137
phi      0.4            0.4            0.4            0.4
K1       7.68635        7.68635        1.44882        1.47059
sr       14.5           14.5           14.5           14.5
fi       0.04988        0.04988        0.04988        0.04988
ft       0.05332        0.0565888      0.05332        0.056581·
Pa       0.154839       0.154839       0.00218451     0.00218451
Pb       0              0.0742133      0              0.0701703
Pc       0              0.0699522      0              0.0647634
r2b,     0.015039       0.015039       1.3615e-05     1.3615e-05
rd       0.015039       0.015039       1.3615e-05     1.3615e-05
re       0.015039       0.015039       1.3615e-05     1.3615e-05
r3t      0              0.000115069    0              3.30759e-06
rf       0              0.000115069    0              3.30759e-06
rg       0              0.000115069    0              3.30759e-06
r1s      0.00885966     0.00885966     -1.63841e-05   -1.56075e-05
rb       0.00885966     0.00885966     -1.63841e-05   -1.56075e-05
rc       0.00885966     0.00885966     -2.01381e-05   -1.8915e-05
ra       -0.0238986     -1.3151e-06    -0.0238986     -1.3151e-06
```

d) Plotting the production of styrene as a function of T_0 gives the following graph. The temperature that is ideal is 995K



e) Plotting the production of styrene as a function of the steam ratio gives the following graph and the ratio that is the ideal is 25:1.



f) No solution will be given

g) No solution will be given.

P8-31

Mole balances

$$V=\frac{v_0(C_{A0}-C_A)}{-r_A} \qquad V=\frac{v_o(C_{B0}-C_B)}{-r_B}$$

$$V=\frac{v_0C_D}{r_D} \qquad V=\frac{v_0C_U}{r_U}$$

Rate laws:

$$-r_A=k_1C_A+k_2C_B \qquad r_D=k_1C_A$$

$$-r_B=k_1C_A+k_2C_B \qquad r_U=k_2C_B$$

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.

```
Equations:                                         Initial value
f(ca)=tau*ra+cao-ca                                0.0017
f(cb)=tau*rb+cbo-cb                                0.0017
f(cd)=cd-tau*rd                                    0.0072
f(cu)=cu-tau*ru                                    0.0012
f(V)=171000/(20190*ca+6660*cb)-V                   3794
cao=.01
cbo=.01
vo=6000
k1=6.73
k2=1.11
tau=V/vo
rd=k1*ca
ru=k2*cb
ra=-k1*ca-k2*ca
rb=ra
```

P8-31 cont'd

```
                        8-31
                      Solution
Variable          Value              f()
ca                0.00167821         -3.12e-18
cb                0.00167821         -3.12e-18
cd                0.00714358         -2.158e-18
cu                0.00117821         -3.686e-19
V                 3794.94            -8.531e-13
cao               0.01
cbo               0.01
vo                6000
k1                6.73
k2                1.11
tau               0.63249
rd                0.0112944
ru                0.00186282
ra                -0.0131572
rb                -0.0131572
```

a) $C_U = .0012$
$C_D = .0072$

b) $V = 3794\ dm^3$

c) No solution will be given.

P8-32

Mole balances:

$$V = \frac{(C_{A0} - C_A)v_o}{-r_A} \qquad \mathrm{V} = \frac{\mathrm{v}_0 C_B}{r_B}$$

This solution only uses one CSTR, if there is more than one CSTR, then the mole balances would both look like the first one.

Rate law:

$$-r_A = k_1 C_A \qquad r_B = k_1 C_A - k_2 C_B$$

Energy balance:

$$T = \frac{100f(T_a) + F_{A0}C_{pA}T_0 + (-\Delta H_{rx1})(-r_a V) + (-\Delta H_{rx2})(-r_B V)}{100f + F_{A0}C_{pA}}$$

Evaluate the parameters:

$$k_1 = 0.3\exp\left[7000\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

$$k_2 = 0.03\exp\left[7000\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

POLYMATH

```
8-32
Equations:                                                   Initial value
f(ca)=ca-cao-tau*ra                                          2
f(cb)=cb-tau*rb                                              2
f(T)=(100*f*Ta+fao*cpa*To+V*(Dhr1*ra+Dhr2*rb))/(100*f+fao    300
   *cpa)-T
cao=5
tau=6
f=0
Ta=273
cpa=20
To=273
V=4
Dhr1=10000
Dhr2=-10000
k1=.3*exp(7000*(1/300-1/T))
k2=.03*exp(7000*(1/300-1/T))
ra=-k1*ca
rb=k1*ca-k2*cb
vo=V/tau
fao=cao*vo
```

P8-32 cont'd

```
                         8-32
                       Solution
Variable              Value              f()
-------------------------------------------------
 ca                  4.89538            2.971e-13
 cb                  0.104393          -2.962e-13
 T                   252.099           -5.929e-11
 cao                 5
 tau                 6
 f                   0
 Ta                  273
 cpa                 20
 To                  273
 V                   4
 Dhr1                10000
 Dhr2                -10000
 k1                  0.00356174
 k2                  0.000356174
 ra                  -0.0174361
 rb                  0.0173989
 vo                  0.666667
 fao                 3.33333
```

From POLYMATH we see that we get a $C_B = 0.104$ mol/dm^3 and a $v_0 = 0.67$ dm^3/min. This gives us a $F_B = .06968$ mol/min which is also 100 mol/day. The parameters that work for this are as follows:

$T_0 = 273$K
$v_0 = 0.67$ dm^3/min
$V = 4$ dm^3
$f = 0$
$C_{A0} = 0$

CDP8-A

a) The first task is to find the equilibrium conversion. We need to use the following equations:

$$K_c = \frac{C_B^2}{C_A} = \frac{\dfrac{4C_{A0}^2X_e^2}{(1+\varepsilon X_e)^2}\left(\dfrac{T_0}{T}\right)^2}{\dfrac{C_{A0}(1-X_e)}{(1+\varepsilon X_e)}}$$

$$X_e^2(\varepsilon K_c T + 4C_{A0}T_0) - \varepsilon T K_c X_e - T K_c = 0$$

$$X_e = \frac{\varepsilon T K_c - \sqrt{(\varepsilon T K_c)^2 - 4(\varepsilon K_c T + 4C_{A0}T_0)TK_c}}{2(\varepsilon K_c T + 4C_{A0}T_0)}$$

$$X_{eb} = \frac{C_{pA}(T-T_0) + 0.2 * C_{pI}(T-T_0)}{-\Delta H_{rx} - \Delta C_p(T-T_R)}$$

Then K changes with temperature so we need to come up with that equation:

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H_{rx} + \Delta C_p(T-T_R)}{RT^2}$$

$$\ln K_c = \ln K_p - \ln T - \ln R$$

POLYMATH

```
8-A1
Equations:                                                                  Initial value
d(lnkp)/d(T)=(Dhrxl+Dcp*(T-Tr))/(R*T^2)                                     18.98
cao=.5
Dhrxl=-75000
Dcp=8
Tr=300
R=8.314
cpa=12
To=300
cpi=15
eps=.8
kc=exp(lnkp-ln(T)-ln(R))
Xe=(eps*T*kc+sqrt(eps*T*kc+4*(eps*kc*T+4*cao*To)*T*kc))/(
    2*(eps*kc*T+4*cao*To))
xeb=(cpa*(T-To)+.2*cpi*(T-To))/(-Dhrxl-Dcp*(T-Tr))
```

T_0 = 300, T_f = 642.3

```
8-A1
Variable        Initial value  Maximum value  Minimum value  Final value
T               300            642.3          300            642.3
lnkp            18.98          18.98          3.17469        3.17469
cao             0.5            0.5            0.5            0.5
Dhrx1           -75000         -75000         -75000         -75000
Dcp             8              8              8              8
Tr              300            300            300            300
R               8.314          8.314          8.314          8.314
cpa             12             12             12             12
To              300            300            300            300
cpi             15             15             15             15
eps             0.8            0.8            0.8            0.8
kc              70142          70142          0.0044792      0.0044792
Xe              1.618          1.618          0.0710356      0.0710356
xeb             0              0.0710543      0              0.0710543
```

We find that the equilibrium conversion is 0.071

$X = 0.0568$

To find the volume neccessary we can then use the algorithm starting with the mole balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

Rate law:

$$-r_A = k\left(C_A - \frac{C_B^2}{K_c}\right)$$

Stoichiometry:

$$C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X}\frac{T_0}{T} \qquad C_B = \frac{2C_{A0}X}{1+\varepsilon X}\frac{T_0}{T}$$

Energy balance:

$$T = \frac{X\left[-\Delta H^\circ_{rx} + \Delta C_p T_R\right] + C_{pA}T_0 + \theta_I C_{pI} T_0}{C_{pA} + \theta_I C_{pI} + X\Delta C_p}$$

Evaluate the parameters:

$$\ln\frac{0.217}{0.324} = \frac{E}{R}\left(\frac{1}{340} - \frac{1}{300}\right)$$

CDP8-A cont'd

$$\frac{E}{R} = 1022.16$$

$$k = 0.217 * \exp\left[1022.16\left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

$$\Delta C_p = 2C_{pB} - C_{pA} = 8 J/molK$$

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_{rx} + \Delta C_p (T - T_R)}{RT^2}$$

$$\int_{K_{pR}}^{K_{p2}} d \ln K_p = \int_{T_R}^{T} \frac{\Delta H_{rx} + \Delta C_p (T - T_R)}{RT^2} dT$$

$$\ln \frac{K_{p2}}{K_{pR}} = -\left[\frac{\Delta H_{rx} - \Delta C_p (T_R)}{R}\right]\left[\frac{1}{T} - \frac{1}{T_R}\right] + \frac{\Delta C_p}{R} \ln \frac{T}{T_R}$$

$$\text{But } K_p = \frac{P_B^2}{P_A} = \frac{C_B^2 (RT)^2}{C_A (RT)} = K_C RT \Rightarrow \ln K_p = \ln K_C + \ln T + \ln R$$

$$\therefore \ln\left(\frac{K_{C2}}{K_{CR}}\right) = \frac{\ln K_{P2}}{\ln K_{PR}} - \ln \frac{T}{T_R} = -\left[\frac{\Delta H_R - \Delta C_p T_R}{R}\right]\left[\frac{1}{T} - \frac{1}{300}\right] + \left[\frac{8}{8.314} - 1\right] \ln \frac{T}{300}$$

$$\ln\left(\frac{K_{C2}}{70000}\right) = -\left[\frac{-75000 - 8 * 300}{8.314}\right]\left[\frac{1}{T} - \frac{1}{300}\right] + \left[\frac{8}{8.314} - 1\right] \ln \frac{T}{300}$$

$$K_{C2} = 70000 \exp\left[9309.6\left(\frac{T_R - T}{T_R T}\right) - 0.0378 \ln \frac{T}{T_R}\right]$$

POLYMATH

```
8-A(a)
Equations:                                                    Initial value
d(v)/d(x)=fao/-ra                                             0
vo=100
cao=.5
eps=.8
To=300
Tr=300
Dhrx1=-75000
cpa=12
cpi=15
cpb=10
l=v/(3.1416*.25^2)
x1=600*x
fao=vo*cao
Dcp=2*cpb-cpa
T=(x*(-Dhrx1+x*Dcp*Tr)+cpa*To+.2*cpi*To)/(cpa+.2*cpi+x*Dc
   p)
```

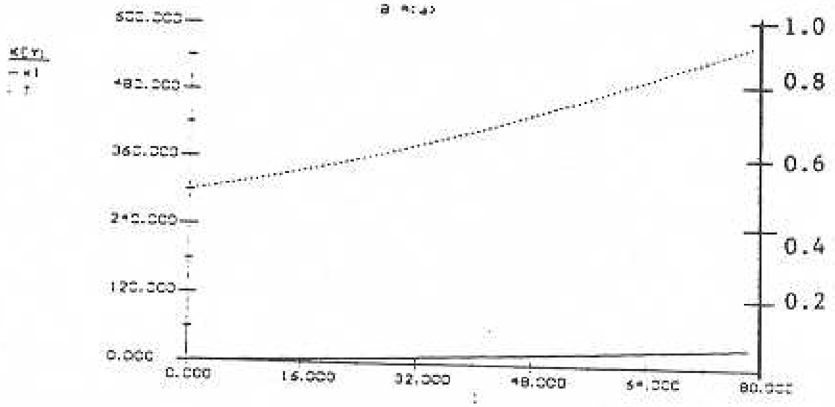
CDP8-A cont'd

```
k=.217*exp(1022.16*(1/300-1/T))
Kc=70000*exp(9309.6*(Tr-T)/(Tr*T)-0.0378*ln(T/Tr))
ca=(cao*(1-x)*To)/((1+eps*x)*T)
cb=(2*cao*x*To)/((1+eps*x)*T)
ra=-k*(ca-cb^2/Kc)
x0 = 0,   xf = 0.057
```

```
8-A(a)
Variable    Initial value  Maximum value  Minimum value  Final value
x           0              0.057          0              0.057
v           0              15.4136        0              15.4136
vo          100            100            100            100
cao         0.5            0.5            0.5            0.5
eps         0.8            0.8            0.8            0.8
To          300            300            300            300
Tr          300            300            300            300
Dhrx1       -75000         -75000         -75000         -75000
cpa         12             12             12             12
cpi         15             15             15             15
cpb         10             10             10             10
l           0              78.5007        0              78.5007
x1          0              34.2           0              34.2
fao         50             50             50             50
Dcp         8              8              8              8
T           300            568.245        300            568.245
k           0.217          1.08387        0.217          1.08387
Kc          70000          70000          0.0296935      0.0296935
ca          0.5            0.5            0.238068       0.238068
cb          0              0.0287803      0              0.0287803
ra          -0.1085        -0.1085        -0.239856      -0.227801
```

We find that the volume neccessary is 15.4 dm³.

b) This graph shows conversion and temperature as a function of length.



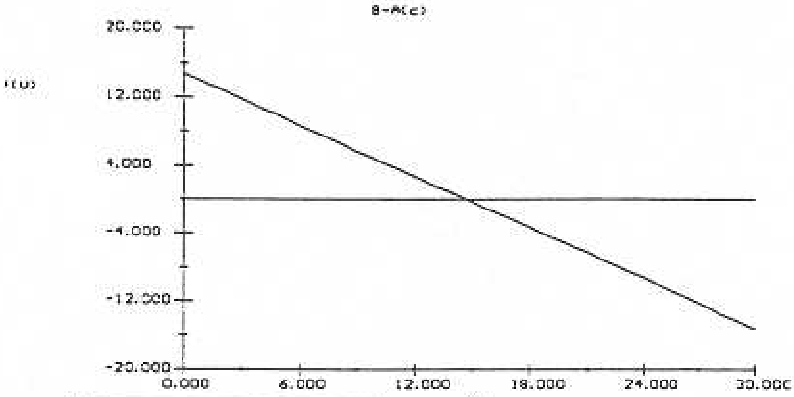
CDP8-A cont'd

c) In a CSTR all that will change is the mole balance:

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

POLYMATH

```
8-A(c)
Equations:
f(V)=fao*x/-ra-V
x=.06
To=300
cao=.5
vo=100
eps=.8
Tr=300
Dhrx=-75000
cpi=15
cpa=12
cpb=10
fao=cao*vo
Dcp=2*cpb-cpa
T=(x*(-Dhrx+Dcp*Tr)+.2*cpi*To+cpa*To)/(cpa+.2*cpi+x*Dcp)
k=.217*exp(1022.16*(1/300-1/T))
Kc=70000*exp(9306*(Tr-T)/(Tr*T)-.0378*ln(T/Tr))
ca=cao*(1-x)*To/((1+eps*x)*T)
cb=2*cao*x*To/((1+eps*x)*T)
ra=-k*(ca-cb^2/Kc)
Vmin = 0,   Vmax = 30
```



Solution 1:   V = 14.7769

CDP8-A cont'd

We find that the volume necessary is 14.8 dm^3.

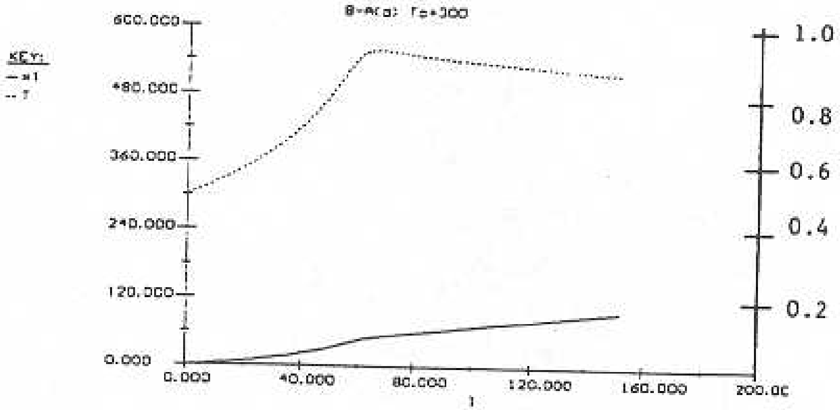
d) The only thing that changes is the energy balance from part (a):

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_R - \Delta Cp(T - T_R))}{F_{A0}(C_{pA} + 0.2C_{pI} + X\Delta C_p)}$$

$$a = \frac{2\pi r l}{\pi r^2 l} = \frac{2}{r} = \frac{2}{.25} = 8$$

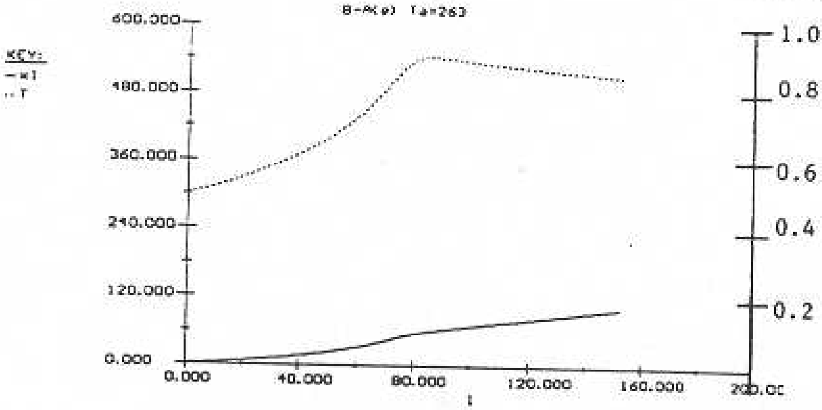
POLYMATH gives us the following graphs.

```
8-A(d)
Equations:                                                              Initial value
d(T)/d(v)=(U*a*(Ta-T)+(-ra)*(-Dhrx-Dcp*(T-Tr)))/(fao*(cpa              300
    +.2*cpi+x*Dcp))
d(x)/d(v)=-ra/fao                                                       0
k=.217*exp(1022.16*(1/300-1/T))
U=10
a=8
Ta=300
Dhrx=-75000
Dcp=8
Tr=300
cpa=12
cpi=15
vo=100
cao=.5
eps=.8
To=300
x1=x*600
l=v/(3.1416*.25^2)
Kc=70000*exp(9309.6*(Tr-T)/(Tr*T)-.0378*ln(T/Tr))
fao=cao*vo
ca=cao*(1-x)*T/((1+eps*x)*To)
cb=2*cao*x*T/((1+eps*x)*To)
ra=-k*(ca-cb^2/Kc)
v0 = 0,    vf = 30
```

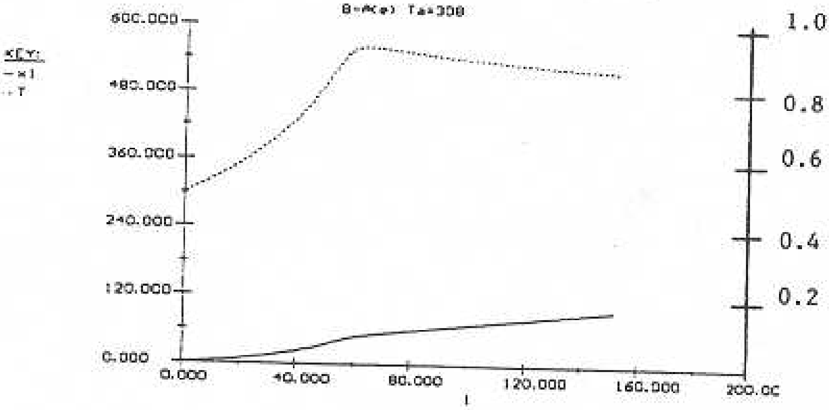


CDP8-A cont'd

e) For winter operation assume a temperature of -10°C. This is the graph:

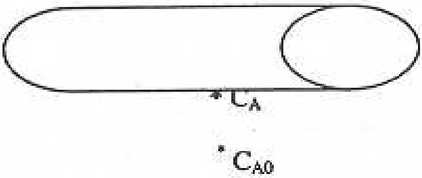


For summer operation assume a temperature of 35°C This is the graph.



CDP8-B

A → products
$$-r_A'' = \frac{k_1 C_A}{(k_2 + k_3 C_A)^2} \frac{gmol}{cm^2 s}$$



a)

$$Sh = \frac{k_L D}{D_{AB}} = 0.4 \mathrm{Re}^{0.4} Sc^{1/3} = 0.4 \mathrm{Re}^{0.4} Sc^{1/3}$$

Convective diffusive flux

$$J_D = k_L (C_{A0} - C_A) = \frac{ShD_{AB}}{D} (C_{A0} - C_A)$$

Reaction Rate/Area

$$J_R = -r_A'' = \frac{k_1 C_A}{(k_2 + k_3 C_A)^2}$$

At steady state:

$$J_D = J_R$$
$$\frac{ShD_{AB}}{D} (C_{A0} - C_A) = \frac{k_1 C_A}{(k_2 + k_3 C_A)^2} \tag{1}$$

At Bifurcation point,

$$\left.\frac{\partial J_D}{\partial C_A}\right|_{C_A^*} = \left.\frac{\partial J_R}{\partial C_A}\right|_{C_{A^*}}$$
$$-\frac{ShD_{AB}}{D} = \frac{k_1}{(k_2 + k_3 C_A^*)^2} \left[1 - \frac{2C_A^* k_3}{k_2 + k_3 C_A^*}\right] \tag{α}$$
$$-\frac{ShD_{Ab}}{D} = \frac{k_1 (k_2 - k_3 C_A^*)}{(k_2 + k_3 C_A^*)^3}$$

$$\frac{k_1 C_A^*}{\left(k_2+k_3 C_A^*\right)^2}=-\frac{ShD_{AB}}{D}\frac{\left(k_2+k_3 C_A^*\right)}{\left(k_2-k_3 C_A^*\right)}C_A^*$$

Substituting this in (1), at steady state:

$$\frac{ShD_{AB}}{D}\left(C_{A0}-C_A^*\right)=-\frac{ShD_{AB}}{D}\left(\frac{k_2+k_3 C_A^*}{k_2-k_3 C_A^*}\right)C_A^*$$
$$\left(C_{A0}-C_A^*\right)\left(k_2-k_3 C_A^*\right)=-\left(k_2+k_3 C_A^*\right)C_A^*$$
$$k_2 C_{A0}-\left(k_2+k_3 C_{A0}\right)C_A^*+k_3 C_A^{*2}=-k_2 C_A^*-k_3 C_A^{*2}$$
$$2k_3 C_A^{*2}-k_3 C_{A0} C_A^*+k_2 C_{A0}=0 \qquad (2)$$

For equation (2) having real solution:

$$\left(-k_3 C_{A0}\right)^2-4*2k_3*k_2 C_{A0}\geq 0$$
$$k_3^2 C_{A0}^2-8\left(k_3 C_{A0}\right)k_2\geq 0$$
$$k_3 C_{A0}\left(k_3 C_{A0}-8k_2\right)\geq 0$$

As $k_3 C_{A0}>0$

$C_{A0}>\frac{8k_2}{k_3}$ Condition for having M.S.S

Lowest $C_{A0}=\frac{8k_2}{k_3}=\frac{8*2}{2000}=8*10^{-3}\frac{gmol}{cm^3}$

b) At bifurcation point both roots of equation (2) for C^* coincide for this

$$C_{A0}=\frac{8k_2}{k_3}$$
$$C_A^*=-\frac{\left(-k_3 C_{A0}\right)}{2k_3}=\frac{C_{A0}}{2}$$

Substituting this in equation (1)

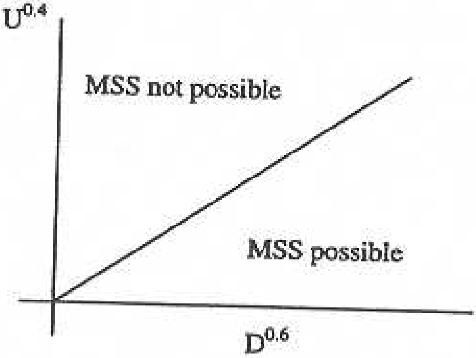
$$\frac{ShD_{AB}}{D}\left(C_{A0}-\frac{C_{A0}}{2}\right)=\frac{k_1C_{A0/2}}{\left(k_2+k_3C_{A0}/2\right)^2}$$

$$\frac{0.4\,\mathrm{Re}^{0.4}\,Sc^{1/3}D_{AB}}{D}=\frac{k_1}{k_2+k_3\dfrac{4k_2}{k_3}}$$

$$\frac{U^{0.4}}{D^{0.6}}=\frac{k_1\nu^{0.4}}{2k_2D_{AB}Sc^{1/3}}$$

c)

$$\frac{U^{0.4}}{D^{0.6}}=\frac{432(0.1)^{0.4}}{2*2*0.1*1^{1/3}}$$
$$=430$$
$$U=\left[430*0.025^{0.6}\right]^{1/0.4}$$
$$=15152\frac{cm}{s}$$



I)

$$-r_A = kC_A \tag{1}$$

Plugging that into the CSTR mole balance and writing as a function of C_A.

$$F(C_A) = \frac{C_A}{\tau} - \frac{C_{A0}}{\tau} + kC_A$$
$$F(y) = \alpha C_A - \beta + G(C_A) \tag{2}$$

Taking the derivative of that:

$$\left.\frac{dF}{dC_A}\right|_{C_A^*} = \frac{1}{\tau} + k = 0 \tag{3}$$

There is no point where this is true so this will not have multiple steady-states.

II) $$-r_A = \frac{kC_A}{1+KC_A} \tag{4}$$

Plugging that into the CSTR mole balance and writing as a function of C_A:

$$F(C_A) = \frac{C_A}{\tau} - \frac{C_{A0}}{\tau} + \frac{kC_A}{1+KC_A} \tag{5}$$

Taking the derivative of that:

$$\left.\frac{dF}{dC_A}\right|_{C_A^*} = \frac{1}{\tau} + \frac{k}{\left(1+KC_A^*\right)^2} = 0 \tag{6}$$

There is no point where this is true so this will not have MSS.

III) $$-r_A = \frac{kC_A}{(1+KC_A)^3} \tag{7}$$

Plugging into the CSTR mole balance and writing as a function of C_A:

$$F(C_A) = \frac{C_A}{\tau} - \frac{C_{A0}}{\tau} + \frac{kC_A}{\left(1+KC_A\right)^3} = 0 \tag{8}$$

Taking the derivative of this:

$$\left.\frac{dF}{dC_A}\right|_{C_A^*} = \frac{1}{\tau} + \frac{k - 2kKC_A^*}{(1+KC_A)^4} = 0 \qquad (9)$$

Combining the last two equations we come up with:

$$3KC_A^{*2} - 2KC_{A0}C_A^* + C_{A0} = 0$$
$$C_A^* = \frac{2KC_{A0} \pm \sqrt{4KC_{A0}(KC_{A0} - 3)}}{6K} \qquad (10)\&(11)$$

From this we can see that $KC_{A0} > 3$ for this to be true. Next taking equation (9) we find that:

$$\frac{1}{\tau k} = \frac{2KC_A^* - 1}{\left(1 + KC_A^*\right)^4} \qquad (12)$$

We see that the left side has a maximum so to determine where it is we take the derivative and solve for where it equals zero.

$$\frac{6K - 6K^2C_A^*}{\left(1 + KC_A^*\right)^5} = 0 \qquad (13)$$
$$C_A^* = \frac{1}{K} \qquad (14)$$

Plugging that back into equation (12):

$$\frac{1}{\tau k} = \frac{1}{16} \qquad (15)$$

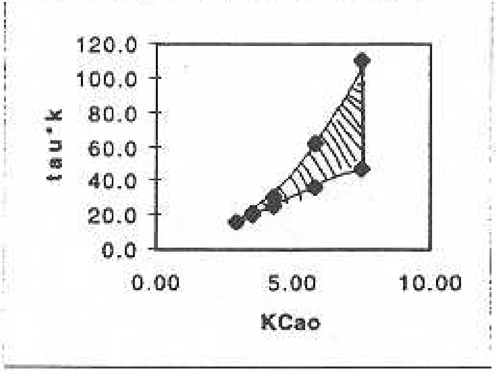
τk cannot be under 16. Now taking $y = C_A/C_{A0}$ and plug into equations (10 and (8) we come up with the following equations:

$$KC_{A0} = \frac{1}{y(2 - 3y)} \qquad (16)$$
$$\tau k = \frac{(1 - y)(1 + KC_{A0}y)^3}{y} \qquad (17)$$

We can then come up with the following table and graph:

CDP8-C cont'd

y	KCao	τk
0.075	7.51	47.1
0.1	5.88	36.1
0.15	4.30	25.2
0.2	3.57	20.2
0.32	3.00	16.0
0.467	3.57	21.7
0.5165	4.30	31.2
0.5666	5.88	62.1
0.5916	7.51	111.2



▨ = MSS

CDP8-D

The rate law is:

$$-r_A = \frac{kC_AC_B}{1+KC_A} \tag{1}$$

Plugging that into the mole balance for a CSTR:

$$F(C_A) = \frac{C_A}{\tau} - \frac{C_{A0}}{\tau} + \frac{kC_AC_B}{1+KC_A} = 0 \tag{2}$$

For multiple steady-states to occur equation (2) must be true as well as this equation:

CDP8-D cont'd

$$\left.\frac{dF}{dC_A}\right|_{C_A^*} = \frac{1}{\tau} + \frac{kC_B}{(1+KC_A)^2} = 0$$

There is no quantity of C_A where this is true so there are no regions where multiple steady-state occurs.

CDP8-E

Energy balance over system from Z = 0 to any Z

$$Q - XF_{A0}\left[\Delta H_R^0(T_R) + \int_{T_R}^{T} \Delta C_p dT\right] = \left[F_{A0}\sum\theta_i \int_{T_i}^{T} C_{pi} dT\right]$$

Energy balance over system from Z = 0 to dZ

$$\dot{Q} - \frac{d\dot{Q}}{dZ} - X F_{A0}\left\{\Delta H_R^0(T_R) + \int_{T_R}^{T} \Delta C_p\, dT\right\} - \frac{d}{dZ}\left\{X F_{A0}\left[\Delta H_R^0(T_R) + \int_{T_R}^{T} \Delta C_p\, dT\right]\right\}$$

$$= F_{A0}\,\Sigma\theta_i \int_{T_i}^{T_R} C_{pi}\, dT + \frac{d}{dZ}\left[F_{A0}\,\Sigma\theta_i \int_{T_i}^{T_R} C_{pi}\, dT\right]$$

Subtracting

$$\frac{d\dot{Q}}{dZ} - \frac{d}{dZ}\left[X F_{A0}\left\{\Delta H_R^0(T_R) + \int_{T_R}^{T} \Delta C_p\, dT\right\}\right] = \frac{d}{dZ}\left[F_{A0}\,\Sigma\theta_i \int_{T_i}^{T_R} C_{pi}\, dT\right]$$

But $\frac{d}{dZ}\left[F_{A0}\,\Sigma\theta_i \int_{T_i}^{T} C_{pi}\, dT\right] = F_{A0}\,\Sigma\theta_i\, C_{pi}\frac{dT}{dZ}$; $\frac{d}{dZ}\int_{T_R}^{T} \Delta C_p\, dT = \Delta C_p \frac{dT}{dZ}$

and $\frac{d\dot{Q}}{dZ} = UA\,(T_A - T)$

Energy balance becomes:

$$UA\,(T_A - T) - F_{A0}\left[X\,\Delta H_R^0(T_R) + \Delta C_p(T - T_R)\right]\frac{dX}{dZ} - X F_{A0}\,\Delta C_p \frac{dT}{dZ} = F_{A0}\,\Sigma\theta_i\, C_{pi}\frac{dT}{dZ}$$

or $$\frac{dT}{dZ} = \frac{UA\,(T - T_A) - F_{A0}\left[X\,\Delta H_R^0(T_R) + \Delta C_p(T - T_R)\right]}{F_{A0}\left(\Sigma\theta_i\, C_{pi} + X\Delta C_p\right)}\ \frac{dX}{dZ}$$

Material balance for $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

CDP8-E cont'd

$$F_{A0}dX_A = (-r_A)dW, \quad -r_A = k_1\sqrt{\frac{P_{SO_2}}{P_{SO_3}}}\left[P_{O_2} - \frac{P_{SO_3}^2}{K_P P_{SO_2}^2}\right]$$

with $y_{SO_2} = y_A = 0.11$, $y_{O_2} = 0.1$ and $y_I = 0.79$; $\delta = 1-1-\frac{1}{2} = -\frac{1}{2}$

$\theta_A = 1.0$, $\theta_{O_2} = \frac{0.10}{0.11} = 0.91$ and $\theta_I = \frac{0.79}{0.11} = 7.17$; $P_0 = 1$ atm

$$P_{SO_2} = C_{SO_2}RT = \frac{RTC_{A0}(1-X)}{1+\varepsilon X} = \frac{P_{A0}(1-X)}{1+\varepsilon X} = \frac{y_{A0}P_0(1-X)}{1+\varepsilon X}$$

$$P_{O_2} = C_{O_2}RT = C_{A0}RT\left[\frac{\theta_{O_2} - 0.5X}{1+\varepsilon X}\right] = \frac{y_{A0}P_0(\theta_{O_2} - 0.5X)}{1+\varepsilon X}$$

$$P_{SO_3} = C_{SO_3}RT = \frac{C_{A0}RTX}{1+\varepsilon X} = \frac{y_{A0}P_0X}{1+\varepsilon X}$$

$$-r_A = k_1\left[\frac{\frac{y_{A0}P_0(1-X)}{1+\varepsilon X}}{\frac{y_{A0}P_0X}{1+\varepsilon X}}\right]^{\frac{1}{2}}\left[\frac{y_{A0}P_0(\theta_{O_2} - 0.5X)}{1+\varepsilon X} - \frac{\left(\frac{y_{A0}P_0X}{1+\varepsilon X}\right)^2}{K_p\left[\frac{y_{A0}P_0(1-X)}{1+\varepsilon X}\right]^2}\right]$$

$$-r_A = k_1\left[\frac{1-X}{X}\right]^{\frac{1}{2}}\left[\frac{y_{A0}P_0(\theta_{O_2} - 0.5X)}{1+\varepsilon X} - \frac{X^2}{K_p(1-X)^2}\right]$$

Now $dW = \rho_B\frac{\pi D^2}{4}dZ$

$$\therefore \frac{dX}{dZ} = \frac{-r_A}{F_{A0}}\rho_B\frac{\pi D^2}{4} = \frac{k_1\rho_B\pi D^2}{4F_{A0}}\left(\frac{1-X}{X}\right)^{\frac{1}{2}}\left[\frac{y_{A0}P_0(\theta_{O_2} - 0.5X)}{1+\varepsilon X} - \frac{X^2}{K_p(1-X)^2}\right]$$

With $\rho_B = 150\ \frac{\text{lb}}{\text{ft}^3}$; $D = 1$ ft ; $\frac{\rho_B\pi D^2}{4} = \frac{(150)(\pi)(1)}{4} = 117.8\ \frac{\text{lb}}{\text{ft}}$

$\varepsilon = y_{A0}\delta = (0.11)(-0.5) = -0.055$; $y_{A0}P_0 = 0.11$ atm

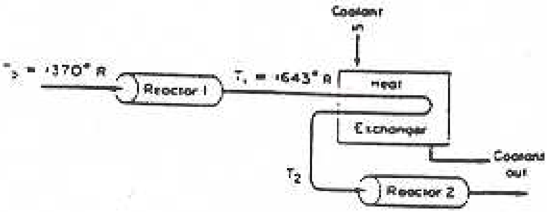
$$\therefore \frac{dX}{dZ} = \frac{117.8\,k_1}{F_{A0}}\left(\frac{1-X}{X}\right)^{\frac{1}{2}}\left[\frac{0.11(\theta_{O_2} - 0.5X)}{1-0.055X} - \frac{X^2}{K_P(1-X)^2}\right]$$

$$= \frac{117.8\,k_1}{F_{A0}}\left(\frac{1-X}{X}\right)^{\frac{1}{2}}\left[\frac{0.11(0.91 - 0.5X)}{1-0.055X} - \frac{X^2}{K_P(1-X)^2}\right]$$

The equation in the text program calculating the adiabatic temperature has to be replaced by the energy balance. T must now be calculated by a different formula, similar to that for X. If the Euler's method of solving differential equations is used, the expressions of $\frac{dT}{dZ}$ should follow that for $\frac{dX}{dZ}$, since the value of $\frac{dX}{dZ}$ is necessary for its calculation. After each step, the new value of T may be obtained from the equation.

$$T_{new} = T_{old} + \left(\frac{dT}{dZ}\right)_{T_{old}}\Delta Z$$

CDP8-F cont'd



Conditions on reactor 1 are fixed; therefore, the outlet conversion, X_{F1}, from the first reactor is determined. This value is used as a an entrance condition for reactor 2. The overall conversion can then be maximized in a procedure identical to that outline in problem P-8.

CDP8-G

a) Assuming that there is an unique cost optimum with respect to the inlet temperature T_2, a routine similar to that outlined in P8-8 and modified as suggested in P8-10(a) can be used. First, the conditional statement cutting off reactor calculations when W exceeds 1000 lb. should be discarded and / or modified such that the reactor calculations cease when X_{F2} exceeds 0.95. Instead of maximizing conversion, a routine similar to that shown in P8-8 minimizing the total cost function can be implemented.

b) This problem appears to be a two-variable optimization. Energy balance can be used to characterize the steam conditions, i.e., $\phi(0, T_0, T_p, X_F) = 0$. By the overall energy balance on system. (Here ϕ is represented in the form

$$T_F = \frac{43.620\ X_F + 77.3\ T_0}{1.8\ X_F + 77.3} = 0\ ,$$

which is an adiabatic energy balance between any T_0 and T_F, given any conversion X_F. Also by an energy balance over the heat exchanger and reactor 2, $\phi(0, T_0, X_1, T_2) = 0$. Since there are three pieces of process equipment, there are three independent energy balances. From this system, the unknowns are: T_F, X_1, T_2, T_0 and T_1. Therefore, any two of the variables must be set to characterize the system. An optimum subroutine could be devised using a method such as that of the steepest ascent to minimize process costs.

CDP8-H

Find temperature where the concentration of B is the greatest.

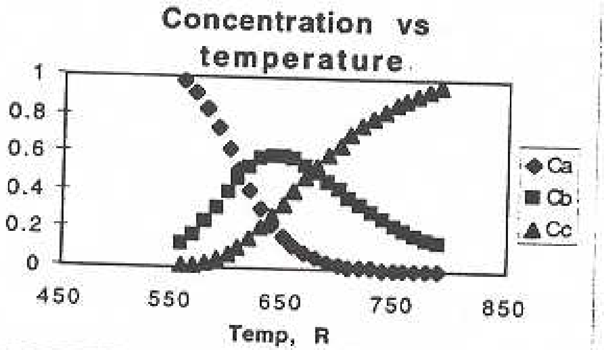
$$\tau = \frac{C_{A0} - C_A}{k_1 C_A + k_2 C_A}$$

$$\tau = \frac{C_B}{k_1 C_A} \qquad \tau = \frac{C_C}{k_2 C_A}$$

$$k_1 = 3\times 10^8 e^{-(27000/(R*T))}$$

$$k_2 = 2\times 10^{14} e^{-(45000/(R*T))}$$

Then graphing those as a function of temperature gives the following graph where the maximum of B occurs at 643°R of 185°F.



Once the temperature is found use the energy balance to determine the area of the heating coil.

$$A = \frac{F_{A0}C_{pA}T_0 + (-\Delta H_{RX1})(-r_{A1}V) + (-\Delta H_{RX2})(-r_{A2}V) - F_{A0}C_{pA}T}{UT - UT_A}$$

$$= \frac{90*.8*130 + 15000*.199183*.199868*30 - 25000*.10106*.199868*30 - 90*.8*184}{.111*184 - .111*212} = 361\,ft^2$$

CDP8-I

Find the maximum of G(T)
From 8-20

$$X = \frac{\tau k}{1 + \tau k\left(1 + \frac{1}{K}\right)}$$

$$G(T) = (-\Delta H_{RX})X = 80000 * X$$

$$k = e^{-(20000*(1/T - 1/400))}$$

CDP8-I cont'd

$$K = 100e^{(80000/R*(1/400-1/T))}$$

T	k	K	X	G
396	0.6034751	276.40849	0.85519442	68415.5532
398	0.777823	165.831208	0.8813724	70509.7923
400	1	100	0.9009009	72072.0721
402	1.28242936	60.6065371	0.91367851	73094.2808
402.5	1.36418749	53.5164184	0.91575967	73260.7736
403	1.45093538	47.2703356	0.91736725	73389.3801
403.5	1.54296375	41.7660986	0.9184818	73478.5441
404	1.64057945	36.9140939	0.91908048	73526.4385
404.5	1.7441063	32.6357129	0.91913688	73530.9504
405	1.85388595	28.8619781	0.91862084	73489.6672
405.5	1.97027887	25.5323441	0.91749833	73399.8661
406	2.09366529	22.5936505	0.91573134	73258.5069
408	2.66550133	13.8953936	0.90132096	72105.6766
410	3.38553585	8.58647606	0.87260063	69808.0502
412	4.29010273	5.33075524	0.82583193	66066.5542

The maximum X value occurs at 404.5 K and the G value is 73530.

Find where R(T) equals G(T)

$$R(T) = C_{pA}(1+\kappa)(T - T_C)$$

$$T_C = \frac{T_0 + \kappa T_a}{1+\kappa} = \frac{310 + \kappa * 310}{1+\kappa} = 310$$

Solving R(T) for κ, κ = 18.45

$$\kappa = \frac{UA}{F_{A0}C_{pA}}$$

$$UA = 7380$$

CDP8-J

a) Starting with the mole balance in a "fluidized bed"

$$W = \frac{v_0(C_{A0} - C_A)}{-r_A}$$

$$\theta = \frac{W}{v_0}$$

$$\theta = \frac{C_{A0} - C_A}{k_1 C_A}$$

$$\theta = \frac{C_{A0} - C_A}{k_1 C_{A0}(1-\alpha_p)}$$

$$1 - \alpha_p = \frac{\alpha_p}{k\theta}$$

$$\alpha_p = \frac{k_1\theta}{1+k_1\theta}$$

Using the mole balance on p

$$\theta = \frac{C_p}{k_1C_A - k_2C_p}$$

$$C_p = \alpha_p\theta_pC_{A0}$$

$$\theta = \frac{\alpha_p\theta_pC_{A0}}{k_1C_{A0}\left(1-\alpha_p\right) - \alpha_p\theta_pC_{A0}k_2}$$

$$\theta k_1C_{A0} - \theta k_1C_{A0}\alpha_p - \theta\alpha_p\theta_pC_{A0}k_2 = \alpha_p\theta_pC_{A0}$$

$$\theta k_1 - \theta k_1\alpha_p = \theta\alpha_p\theta_pk_2 + \alpha_p\theta_p$$

$$\theta_p = \frac{\theta k_1\left(1-\frac{k_1\theta}{1+k_1\theta}\right)}{\frac{k_1\theta}{1+k_1\theta}\left(1+\theta k_2\right)}$$

Finally:

$$\theta = \frac{C_p}{k_1C_A - k_2C_p}$$

$$C_p = C_{A0}\eta$$

$$\theta = \frac{C_{A0}\eta}{k_1C_{A0}\left(1-\alpha_p\right) - k_2C_{A0}\eta}$$

$$k_1\theta\left(1-\alpha_p\right) - k_2\theta\eta = \eta$$

$$\eta = \frac{k_1\theta\left(1-\frac{k_1\theta}{1+k_1\theta}\right)}{1+k_2\theta}$$

c) We need equations for the two k's and the equation to find a. Every other quantity or equation is known.

CDP8-J **cont'd**

$$k_1 = 5.33 * 10^{15} * \exp\left[\frac{43900}{1.987}\left(\frac{1}{423} - \frac{1}{T}\right)\right]$$

T in K

$$k_2 = 2.65 * 10^{5} * \exp\left[\frac{20414}{1.987}\left(\frac{1}{423} - \frac{1}{T}\right)\right]$$

$$a = \frac{\frac{C_{A0}}{\theta} C_{pA}(T - T_0) - (-k_1 C_{A0}(1 - \alpha_p) * -449000) - ((k_1 C_{A0}(1 - \alpha_p) - k_2 C_{A0}\eta) * (-784000}{U(T_a - T)}$$

Where T is in °C. We then get this table where with these equations and the temperatures given we find the θ where the concentration of P is maximized.

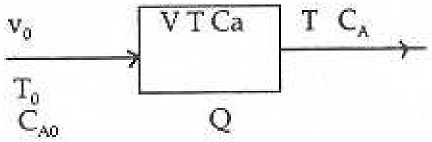
T	k1	k2	α	η	a	Cp
331	3.3252E+22	383868745	1	0.5714367	1.53251186	0.00025486
365	2.3357E+23	950289557	1	0.35414693	1488.271	0.00015795
423	4.185E+24	3636190933	1	0.11194938	1642.11894	4.9929E-05

θ
1.95E-09

d) No solution will be given.

e) No solution will be given.

CDP8-L



Assummed
ρ, C_p, ΔH constant

Mole Balance:

$$v_0 C_{A0} - vC_A + \frac{V}{v_0} r_A = \frac{V}{v_0}\frac{dC_A}{dt}$$

Let $C_A = C_{A0}(1-X_A)$; $\tau = \frac{V}{v_0}$; $r = -\frac{r_A}{C_{A0}}$; $\theta = \frac{t}{\tau}$

giving $\frac{dX_A}{d\theta} = -X_A + \tau v = F(X_{A,T})$

Rate equation:

$$-r_A = kC_A = kC_{A0}(1-X_A)$$

$$k = k_{30}\exp\left[-\frac{19870}{1.987}\left(\frac{1}{T} - \frac{1}{303.2}\right)\right]$$

$$r = k(1-X_A)$$

Energy balance:

$$\dot{Q} - \dot{W}_s + v_0\rho C_p(T_0 - T) + \Delta H * r_A * V = V\rho C_p\frac{dT}{dt} - V\frac{dP}{dt}$$

$$Q = 0;\ W = 0;\ \frac{dP}{dt} = 0$$

$$T_0 - T + \frac{\Delta H}{\rho C_p} r_A \frac{V}{v_0} = \frac{V}{v_0}\rho C_p\frac{dT}{dt}$$

$$J = -\frac{\Delta H_r C_{A0}}{\rho C_p}$$

$$\frac{dT}{d\theta} = T_0 - T + \tau J r = G(X_A, T)$$

a) τ for extinction and ignition -C_{A0} = 5 gmol/dm^3

$$J = -\frac{(-15120)(5)}{(.9)(1.21)(1000)} = 70K$$

$k_{30} = 1.0\ \text{min}^{-1}$ $\qquad$ $T_0 = 293.2K$

CDP8-L cont'd

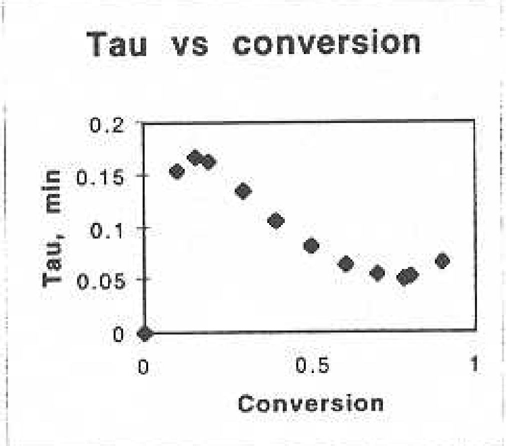
Relations become:

$$-X_A + \tau r = 0$$

$$T_0 - T + \tau J r = 0$$

Energy balance becomes: $T_0 - T + JX_A$

$$\tau = \frac{X_A}{r(X_A, T)} = \frac{X_A}{k_{30}(1-X_A)\exp\left[-10^4\left(\frac{1}{T_0 + JX_A} - \frac{1}{303.2}\right)\right]}$$



Could do numerically, but not difficult analytically. IG/ER points are where:

$$\frac{d\tau}{dX_A} = 0$$

$$\ln\tau = \ln X_A - \ln(1-X_A) + 10^4\left(\frac{1}{T_0 + JX_A} - \frac{1}{303.2}\right) - \ln k_{30}$$

$$\frac{d}{dX_A}\ln\tau = \frac{1}{X_A} - \frac{1}{1-X_A} - \frac{10^4 J}{(T_0 + JX_A)^2} = 0$$

$$f(X_A) = \frac{1}{X_A} - \frac{1}{1-X_A} - \frac{7\times10^5}{(293.2+70X_A)^2} = 0$$

Roots are: $X_A = 0.1567, 0.7881$

Giving $\tau = 0.16728, 0.05163$

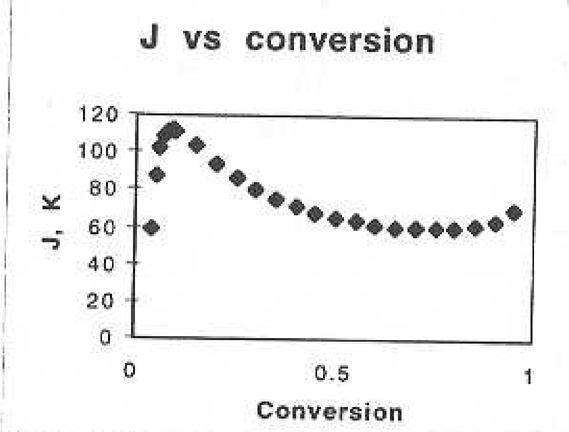
nction curve and ignition-T_0 = 20°C, τ = 0.1 min.

ly in J. Need to find J limits.

$$= \frac{1}{303.2} + 10_{-4}\ln\left(\frac{k_{30}\tau(1-X_A)}{X_A}\right)$$

$$T_0 + JX_A = \frac{1}{\frac{1}{303.2} + 10^{-4}\ln\left(\frac{k_{30}\tau(1-X_A)}{X_A}\right)}$$

$$J = \frac{1}{X_A}\left[\frac{303.2}{1+0.03032\ln\left(\frac{k_{30}\tau(1-X_A)}{X_A}\right)} - T_0\right]$$



To find the analytical solution:

$$\frac{d}{dX_A}\ln J = 0$$

and solve: $X_A = 0.0921, \quad 0.7437$
$J = 110.01, \quad 59.812$ K
$C_{A0} = 7.8579, \quad 4.2723$ gmol/l

c) T_0 for extinction and ignition $\tau = 0.1$ min $C_{A0} = 5$
Similar procedure. T_0 only enters in energy balance

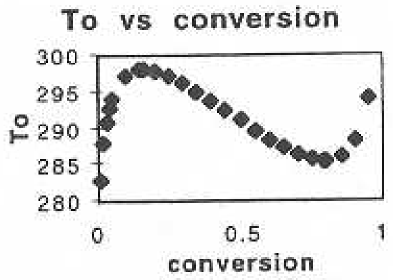
$$T_0 = \frac{303.2}{\left[1-0.03022\ln\left(\frac{k_{30}\tau(1-X_A)}{X_A}\right)\right]} - JX_A$$

$$\frac{dT_0}{dX_A} = \frac{303.2(.03032)\left[\frac{1}{1-X_A}+\frac{1}{X_A}\right]}{\left[1-0.03022\ln\left(\frac{k_{30}\tau(1-X_A)}{X_A}\right)\right]^2} - 70 = 0$$

(very similar to J case) in fact, identical! Except that J is fixed and T_0 varies

CDP8-L cont'd

Plot of T_0 vs X_A:



Roots are: $X_A = 0.1636, \quad 0.7902$

Giving $T_0 = 298.04, \quad 285.37$

[All roots are found with POLYMATH]

2)

a) $F = 0, G = 0$

$$F = 0 \qquad G = 0$$

$$-X_A + \tau r = 0 \qquad T_0 - T + J\tau r = 0$$

$$-X_A + \tau k(1 - X_A) = 0 \qquad T_0 - T + \tau J k(1 - X_A) = 0$$

$$X_A = \frac{k\tau}{1 + k\tau} \qquad X_A = \frac{T_0 - T}{\tau J k} + 1$$

$$k = k_{30} \exp\left[-10^4\left(\frac{1}{T} - \frac{1}{303.2}\right)\right]$$

Plot attached. Solve simultaneously for X_A and T for $t = 0.1$ min, $k_{30} = 1$ min^{-1}, J = 70 K, and T_0 = 293.2 K.

Solve above equations simultaneously to find stable and unstable points

$$f(X_A, T) = -X_A + \tau k(1 - X_A) = 0$$

$$g(X_A, T) = T_0 - T + \tau J k(1 - X_A) = 0$$

Use POLYMATH to find the roots of the equations.

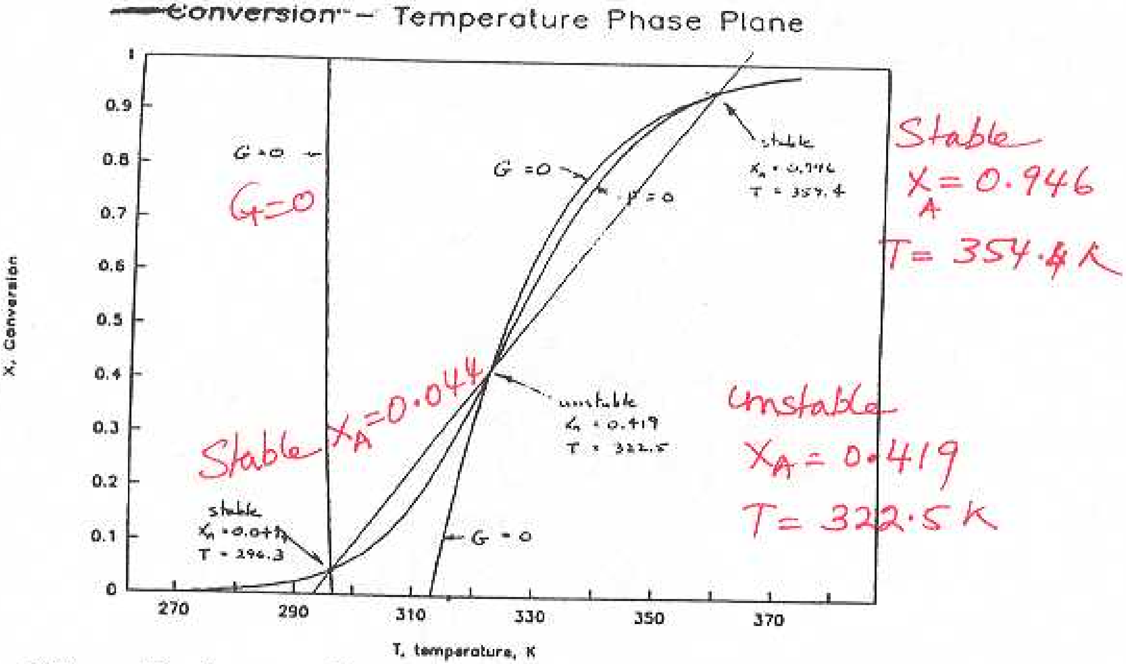
CDP8-L cont'd

```
Equations:                                    Initial value
f(x)=-x+tau*k*(1-x)                           0.9455
f(T)=To-T+tau*J*k*(1-x)                       359.39
tau=.1
k=1*exp(-1e4*(1/T-1/303.2))
To=293
J=70
```

Roots are:

	X_A	T	
1	.00444	296.31	Stable
2	.4186	322.5	Unstable
3	.9455	359.39	Stable

This graph is also made from the equations showing the intersection of the two equations.

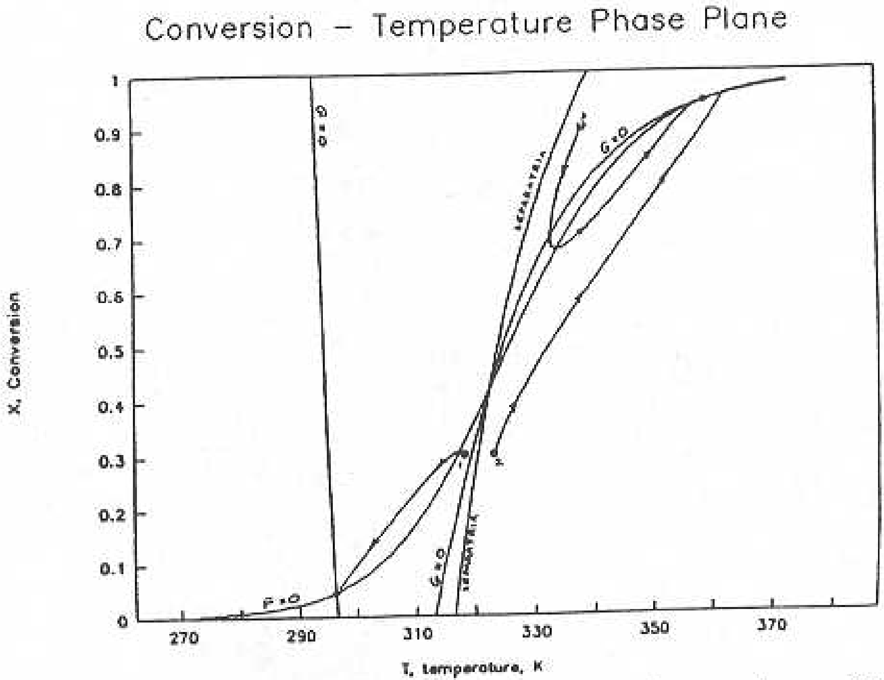


c) Separatrix-shown on Phase-Plane plot.
Found by solving:

$$\frac{dT}{dX} = \frac{G}{T} = \frac{(293.2 - T) + 0.1(70)k(1-X)}{-X + 0.1k(1-X)}$$

for various initial conditions at X = 0 or 1, until trajectory went toward unstable point. Trials and errors were:

$X_i = 0, X_f = 0.414$		$X_i = 1, X_f = .424$	
T_i	T_f	T_i	T_f
317.2	327.2	337.2	318.1
316.2	318.2	337.4	318.3
316.7	324.5	339	320.6
316.6	324.2	340.4	315.4
316.5	322.4	339.5	322.5



R.L. Carr

Solution is unstable near (0.4186, 322.5), but integrations went smoothly except for one case.

POLYMATH will only intergrate from lower to higher X, so equation was rewritten with γ = 1-X, as

$$\frac{dT}{d\gamma} = -\frac{293.2 - T + .1(70)k\gamma}{-(1-\gamma) + 0.1k\gamma}$$

d) Phase and time trajectories

The equations

$$\frac{dX}{d\theta} = -X + 0.1k(1-X)$$

$$\frac{dT}{d\theta} = 293.2 - T + 0.1(70)k(1-X)$$

were solved simultaneously with POLYMATH for the three cases.

Time responses are attatched.

Discussion:

Case 1:(45°C, 0.3):Reaction "extinguishes" after a momentary increases in conversion.

CFP8-L cont'd

Case 2:(50°C, 0.3): Reaction "ignites". T and X overshoot slightly. Final stabilization is rapid becasue of the high temperature (and hence k).

Case 3:(65°C, 0.9):Reactor "ignites" after significant dips in T and X. Reactant had to build up some before reaction could begin to raise temperature.

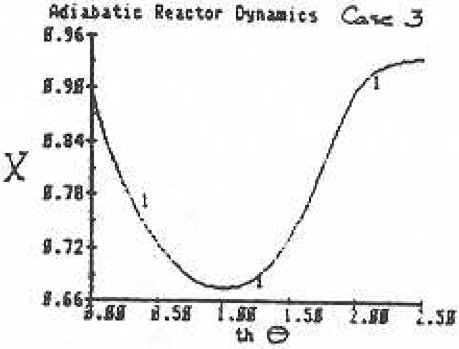
Time Trajectories

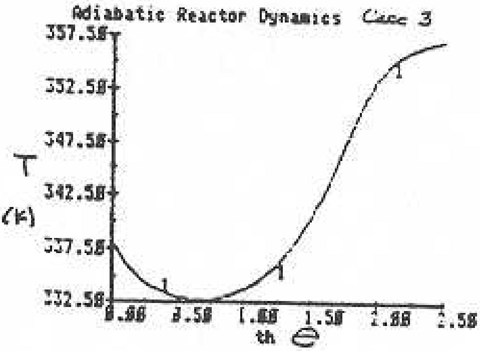
Case 3

Case 3 Adiabatic Reactor Dynamics

Integration Results

θ	X	T
0.0	0.9000	338.20
0.1250	0.8367	335.88
0.2500	0.7894	334.44
0.3750	0.7529	333.53
0.5000	0.7246	333.00
0.6250	0.7032	332.79
0.7500	0.6879	332.85
0.8750	0.6785	333.19
1.0000	0.6748	333.81
1.1250	0.6773	334.77
1.2500	0.6867	336.11
1.3750	0.7039	337.93
1.5000	0.7305	340.35
1.6250	0.7674	343.37
1.7500	0.8131	346.99
1.8750	0.8604	350.67
2.0000	0.8973	353.57
2.1250	0.9182	355.32
2.2500	0.9279	356.25
2.3750	0.9324	356.79
2.5000	0.9349	357.16





Separatrix

Upper

Integration Results

T	1−X
339.50	0.0
338.18	0.0288
336.93	0.0576
335.75	0.0864
334.63	0.1152
333.56	0.1440
332.55	0.1728
331.60	0.2016
330.69	0.2304
329.83	0.2592
329.02	0.2880
328.24	0.3168
327.49	0.3456
326.79	0.3744
326.11	0.4032
325.46	0.4320
324.83	0.4608
324.24	0.4896
323.66	0.5184
323.09	0.5472
322.50	0.5760

Lower

Integration Results

X	T
0.0	316.50
0.0207	316.74
0.0414	316.99
0.0621	317.25
0.0828	317.50
0.1035	317.76
0.1242	318.03
0.1449	318.30
0.1656	318.58
0.1863	318.86
0.2070	319.15
0.2277	319.45
0.2484	319.75
0.2691	320.06
0.2898	320.37
0.3105	320.69
0.3312	321.02
0.3519	321.36
0.3726	321.70
0.3933	322.05
0.4140	322.40

R.L. Curl 10-30-90

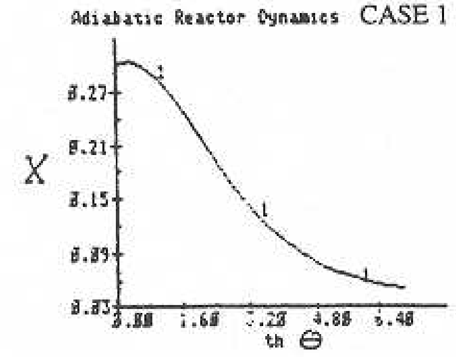
Time Trajectories

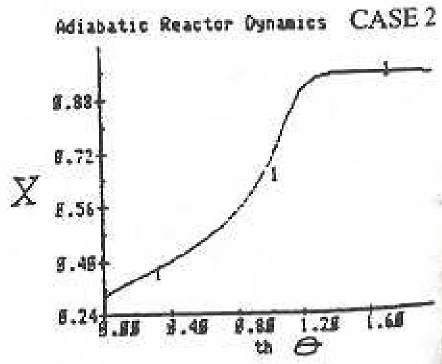
Case 1

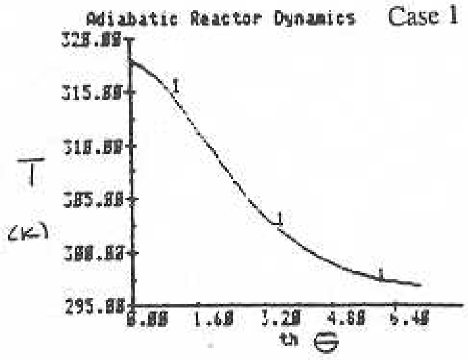
```
Case 1 Adiabatic Reactor Dynamics
              Integration Results
    θ                 X            T
  0.0              0.3000       318.20
  0.3500           0.3049       317.37
  0.7000           0.2993       316.14
  1.0500           0.2653       314.57
  1.4000           0.2652       312.75
  1.7500           0.2413       310.78
  2.1000           0.2158       308.79
  2.4500           0.1905       306.88
  2.8000           0.1669       305.13
  3.1500           0.1457       303.57
  3.5000           0.1272       302.23
  3.8500           0.1116       301.09
  4.2000           0.0985       300.15
  4.5500           0.0877       299.32
  4.9000           0.0789       298.75
  5.2500           0.0713       298.23
  5.6000           0.0661       297.84
  5.9500           0.0616       297.52
  6.3000           0.0580       297.26
  6.6500           0.0551       297.06
  7.0000           0.0528       296.90
```

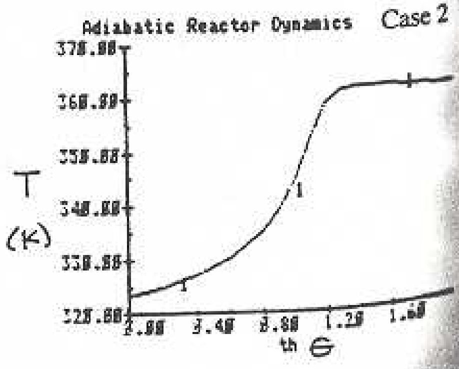
Case 2

```
Case 2 Adiabatic Reactor Dynamics
              Integration Results
    θ                 X            T
  0.0              0.3000       323.20
  0.1000           0.3230       324.01
  0.2000           0.3479       324.92
  0.3000           0.3727       325.96
  0.4000           0.3991       327.17
  0.5000           0.4280       328.62
  0.6000           0.4607       330.39
  0.7000           0.4995       332.63
  0.8000           0.5475       335.57
  0.9000           0.6101       339.57
  1.0000           0.6950       345.16
  1.1000           0.8053       352.56
  1.2000           0.9053       359.28
  1.3000           0.9437       361.71
  1.4000           0.9527       362.11
  1.5000           0.9546       362.03
  1.6000           0.9546       361.84
  1.7000           0.9540       361.63
  1.8000           0.9534       361.42
  1.9000           0.9527       361.23
  2.0000           0.9520       361.05
```









R.L. Curl 10-30-9

CDP8-N

a) Using only P as the solvent we come up with the following as the equations for the equilibrium conversion.

$$-r_A = k\left(C_A^2 - \frac{C_B^2}{K_e}\right)$$

$$-r_A = 0$$

$$C_A = \frac{C_B}{\sqrt{K_e}}$$

$$C_{A0}(1-X_e) = \frac{C_{A0}X_e}{\sqrt{K_e}}$$

$$X_e = \frac{\sqrt{K_e}}{1+\sqrt{K_e}}$$

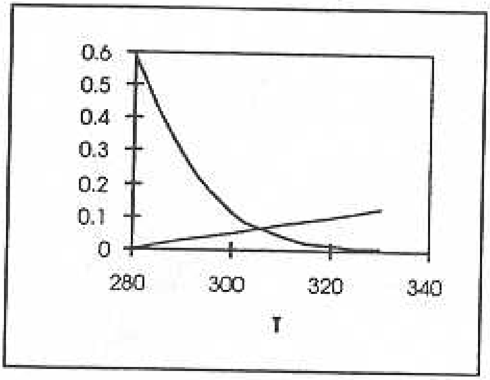
The equation for the energy balance part is this:

$$X_{eb} = \frac{C_{pA}(T-T_0) + 4 * C_{pB}(T-T_0)}{-\Delta H_{rx}}$$

We then need an equation for K_e. (Assuming that K = 2 when T = 280K)

$$K = 2 * \exp\left[\frac{\Delta H_{rx}}{R}\left(\frac{1}{280} - \frac{1}{T}\right)\right]$$

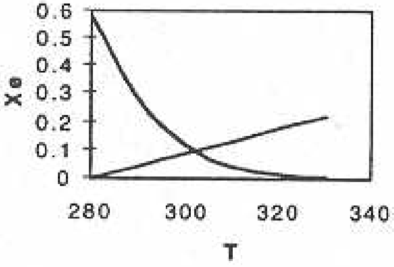
This graph is the result of these two equations:



We find the equilibrium temperature and conversion are 305.7K and 0.064.

CDP8-N cont'd

b) The same equations are used just the inert has been changed:



The equilibrium conversion and temperature are then 301.6K and 0.097

c) To find the place where the conversion is the maximum depending on the inert we must come up with the new energy equation where the inert amount can change.

$$X_{eb} = \frac{C_{pA}(T - T_0) + 4 * (y * C_{pP}(T - T_0) + (1 - y)C_{pQ}(T - T_0))}{-\Delta H_{rx}}$$

where y is the percentage of P in the inert. We find that the maximum occurs when only Q is fed in. X = 0.097

CDP8-O

Gas phase reactions:

$$A \longrightarrow 2B$$

$$2A + B \longrightarrow C$$

Write design equation in terms of flow rate since there are multiple reactions:

$$\frac{dF_A}{dV} = r_A \qquad \frac{dF_B}{dV} = r_B$$

$$r_A = -k_1 C_A - k_2 C_A C_B^2 \qquad r_B = -k_2 C_A C_B^2 + k_1 C_A$$

$$k_1 = 2 * \exp\left[-\frac{E_1}{R}\left(\frac{1}{T} - \frac{1}{310}\right)\right]$$

$$k_2 = .2 * \exp\left[-\frac{E_2}{R}\left(\frac{1}{T} - \frac{1}{596}\right)\right]$$

$$C_A = C_t \frac{F_A}{F_t} \frac{T_0}{T} \qquad C_B = C_t \frac{F_B}{F_t} \frac{T_0}{T}$$

Also write energy balance in terms other than conversion:

$$\frac{dT}{dV} = \frac{-\Delta H_R 1 * -r_{A1} - \Delta H_{R2} * -r_{A2}}{F_{A0} * C_{pA}}$$

The following is the POLYMATH program used:

CDP8-Q cont'd

```
8-o
Equations:                                                          Initial value
d(fa)/d(V)=ra                                                       100
d(T)/d(V)=(-DHr1*-ra1+-DHr2*-ra2)/(fao*cpa)                         596
d(fb)/d(V)=rb                                                       0
DHr1=-20000
DHr2=-40000
fao=100
cpa=50
E1=5000
R=1.987
E2=25000
cto=.5
ft=100
To=596
ct=cto
ca=cto*fa/ft*To/T
cb=ct*fb/ft*To/T
ra1=-2*exp(-E1/R*(1/T-1/310))*ca
ra2=-.2*exp(-E2/R*(1/T-1/596))*ca*cb^2
ra=ra1+ra2
rb=-ra1+ra2
V0 = 0,   Vf = 7.12
```

a) POLYMATH gives the following table for the maximum temperature:

```
8-o
Variable      Initial value   Maximum value   Minimum value   Final value
V             0               7.12            0               7.12
fa            100             100             8.21231e-05     8.21231e-05
T             596             1129.84         596             1129.84
fb            0               94.3924         0               94.3924
DHr1          -20000          -20000          -20000          -20000
DHr2          -40000          -40000          -40000          -40000
fao           100             100             100             100
cpa           50              50              50              50
E1            5000            5000            5000            5000
R             1.987           1.987           1.987           1.987
E2            25000           25000           25000           25000
cto           0.5             0.5             0.5             0.5
ft            100             100             100             100
To            596             596             596             596
ct            0.5             0.5             0.5             0.5
ca            0.5             0.5             2.16604e-07     2.16604e-07
cb            0               0.265046        0               0.248965
ra1           -49.1661        -0.000156578    -49.1661        -0.000156578
ra2           -0              -0              -1.96272        -5.76525e-05
ra            -49.1661        -0.000214231    -49.1661        -0.000214231
rb            49.1661         49.1661         9.89256e-05     9.89256e-05
```

8-120

CDP8-Q cont'd

$V = 7.12\ dm^3$

b) POLYMATH gives the following table for the maximum temperature:

$V = 6.82\ dm^3$

```
8-o
Variable          Initial value   Maximum value    Minimum value    Final value
V                 0               6.82             0                6.82
fa                100             100              0.00145911       0.00145911
T                 596             1005.52          596              1005.52
fb                0               95.2381          0                95.2381
DHr1              -20000          -20000           -20000           -20000
DHr2              -40000          -40000           -40000           -40000
fao               100             100              100              100
cpa               50              50               50               50
E1                5000            5000             5000             5000
R                 1.987           1.987            1.987            1.987
E2                25000           25000            25000            25000
cto               0.5             0.5              0.5              0.5
ft                100             100              100              100
To                596             596              596              596
ct                0.5             0.5              0.5              0.5
ca                0.5             0.5              4.32431e-06      4.32431e-06
cb                0               0.282253         0                0.282253
ra1               -49.1661        -0.0023735       -58.1183         -0.0023735
ra2               -0              -0               -1.4921          -0.000373347
ra                -49.1661        -0.00274685      -58.1526         -0.00274685
rb                49.1661         58.0922          0.00200016       0.00200016
```

CDP8-P

Gas phase

$$2A \rightleftarrows B$$

a)

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$-r_A = k\left[C_A^2 - \frac{C_B^2}{K_e}\right]$$

$$C_A = C_{A0}(1-X)\frac{T_0}{T}$$

$$C_B = C_{A0}X\frac{T_0}{T}$$

CDP8-P cont'd

$$K_e = \frac{X^2}{(1-X)^2}$$

$$k = 30 * \exp\left[\frac{E}{R}\left(\frac{1}{273} - \frac{1}{T}\right)\right]$$

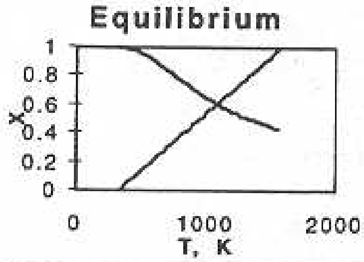
$$\frac{dX}{dW} = \frac{30 * \exp\left[\frac{4000}{1.987}\left(\frac{1}{273} - \frac{1}{T}\right)\right]\left[(.1)^2(1-X)^2 - \frac{(.1)^2 X^2}{100 * \exp\left[\frac{-10000}{1.987}\left(\frac{1}{600} - \frac{1}{T}\right)\right]}\right]}{100}$$

$$K_e = \frac{X^2}{(1-X)^2}$$

$$X_{EB} = \frac{C_{pA}(T - T_0)}{-DH_R} = 8 \times 10^{-4}(T - 323)$$

$$T = 323 + \frac{X(10000)}{8}$$

b)



At a temperature of 1081 K there is a equilibrium conversion of 0.61

c) (0.98)(0.61) = 0.598

The following POLYMATH program is used to determine how much catalyst weight is needed to achieve this conversion. We find that 42 kg of catalyst must be used.

CDP8-P cont'd

```
8-p
Equations:                                                    Initial value
d(w)/d(x)=fao/-ra                                             0
To=323
fao=100
Dhr1=-10000
cpa=8
E=4000
R=1.987
cao=.1
T=To+x*(-Dhr1)/cpa
ca=cao*(1-x)*To/T
cb=cao*x*To/T
Ke=100*exp(Dhr1/R*(1/600-1/T))
k=30*exp(E/R*(1/273-1/T))
ra=-k*(ca^2-cb^2/Ke)
x0 = 0,   xf = 0.598
```

```
8-p
Variable         Initial value    Maximum value    Minimum value    Final value
x                0                0.598            0                0.598
w                0                42.1613          0                42.1613
To               323              323              323              323
fao              100              100              100              100
Dhr1             -10000           -10000           -10000           -10000
cpa              8                8                8                8
E                4000             4000             4000             4000
R                1.987            1.987            1.987            1.987
cao              0.1              0.1              0.1              0.1
T                323              1070.5           323              1070.5
ca               0.1              0.1              0.0121295        0.0121295
cb               0                0.0180433        0                0.0180433
Ke               133049           133049           2.50575          2.50575
k                93.9416          7292.68          93.9416          7292.68
ra               -0.939416        -0.12542         -2.93041         -0.12542
```

Chapter 9

P9-1. An open-ended problem that requires students to create and original problem and solution.

P9-2. "What if. . ." problem. These problems build in the **Living Example Problems** in this chapter. By this point in the point the student is in a position to carry out in-depth and meaningful parameter sensitivity studies. If there is only time to assign one or two parts of this problem I would choose part **(a)** and then either **(d)** or **(e)**. However, one could rotate the assignments of **(a)** through **(e)** from year to year.

P9-3. Although this problem on an explosion is a continuation of **P8-3**, it is not necessary to have worked **P8-3** to work this problem. The students are asked to calculate the time before the reactor explodes.

P9-4. Alternative problem to **P9-3**.

P9-5. Straight forward problem on heat effects in a semibatch reactor.

P9-6. Another one that involves a lot of thinking and not a large number of calculations.

P9-7. A straight forward problem concerning an adiabatically operated batch reactor. Alternate to **P9-8** and **P9-9**.

P9-8. Straight forward adiabatic batch reactor calculation.

P9-9. Similar to **P8-19**, but with different specific reaction rates.

P9-10. Start up of a CSTR.

P9-11. Fairly, straight forward semibatch reactor problem. The volumetric feed rate must be varied, but within certain limits.

Problems **P9-12**, **P9-13**, and **P9-14**. involve the use of controllers during the operation of a CSTR. These problems provide excellent *What if. . .* problems because the student can vary the control parameters and observe the various outcomes.

P9-15. *<Prof. Fogler: Anything going here?>*

P9-16. The point of this problem is that what we learned in chapter 8 about the different multiple steady states being stable is not necessarily true. One will find in this problem that the extinction temperature is not exceeded, yet we still fall from the upper steady states to the lower steady states. This problem also allows the student to explore the parameter space.

P9-17. **Living Example Problem 8-12.** Can serve as a basis to study the adiabatic operation of a batch reactor.

P9-18. Straight forward problem on parallel reactions in a semibatch reactor.

Summary

		Assigned	Alternates	Difficulty	Time	Solution Given
	P9-1	AA				
●	P9-2	AA	(a),3,4,7	MD	75	Yes
	P9-3	AA	2(a),4	SF	60	Yes
	P9-4	AA	2(a),3	FSF	60	Yes
●	P9-5	AA	11,18,A	FSF	75	Yes
	P9-6	O		FSF	45	Yes
●	P9-7	AA	2(a),8,17	SF	60	Yes
	P9-8	AA	2(a),7,17	SF	60	Yes
	P9-9	I		MD	60	
	P9-10	G	10b/a	FSF	40/40	Yes
	P9-11	AA	5,18,A	FSF	60	Yes
●	P9-12	G/AA	13,14,15,B	SF	45	Yes
	P9-13	G/AA	12,14,15,B	SF	30	Yes
	P9-14	G/AA	12,13,15,B	SF	30	Yes
	P9-15	G/AA	12,13,14,B	MD	90	Yes
●	P9-16	G		MD	75	Yes
	P9-17	AA	(a),7,8	FSF	60	Yes
	P9-18	AA	5,11,A	FSF	90	Yes
	CDP9-A	AA	5,11,18	FSF	75	Yes
	CDP9-B	AA	12,13,14,15	FSF	75	Yes
	CDP9-C					
	CDP9-D					
	CDP9-E					
	CDP9-F					
	CDP9-G					
	CDP9-H					
	CDP9-I					

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-9

	Safety	Batch	Semi-Batch	Unsteady Start-up	Control
Review of Definitions and Assumptions					
Open-ended	2(a)	17(b,c)	18(b,c)	2(b,c),16(f)	2(d,e)
Straight forward	3	7,8			12,13,14
Fairly Straight Forward	4	17	5,6,11,18,A	2(b),2(c),10	B
More Difficult	2(a)			9,16	15
Critical Thinking					

Chapter 9

P9-1 No solution will be given

P9-2

a) 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:

$$Q_g < Q_r \quad \text{No explosion}$$

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.

$$Q_g = k\frac{N_{A0}(1-x)N_{Z0}(\theta_B - 2x)}{V}(-\Delta H_{Rx})$$
$$= 0.0001167\left[\frac{9.04^2(1-.38)(\theta_B - 2 * .38)}{5.119}\right]2.34 * 10^6$$
$$= 77844 \ \text{BTU/min.}$$

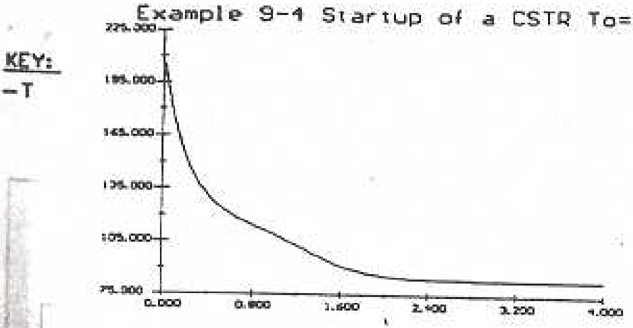
Adiabatic operation for 10 min. UA = 0

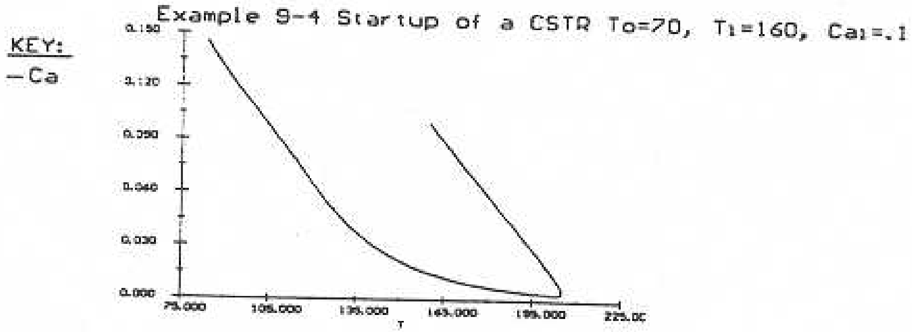
After 10 minutes

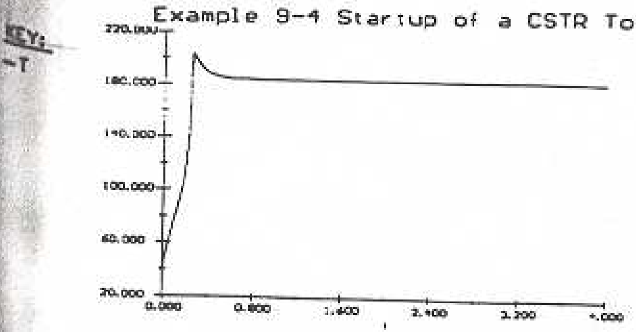
P9-2 cont'd

$x = 0.385$, $T = 184°C$
$Q_g = 10000$ BTU/min.
When we restart the cooling flow rate
$Q_r|_{max} = 21{,}300$ BTU/min.
Temperature will drop to 175°C
<u>No explosion</u>

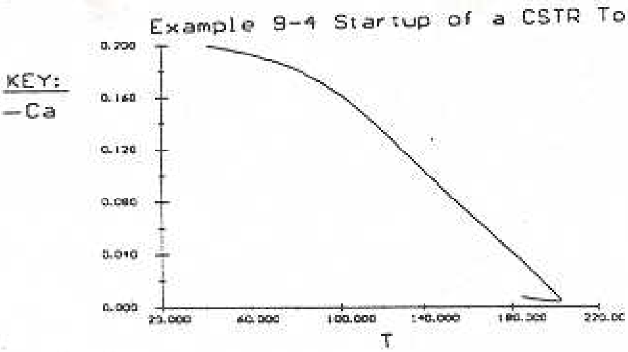
b) Using the same code as seen in Example 9-4, we were able to change the various parameters. The two graphs we have show $T_0 = 70$ and 120°C, $T_i = 160$ and 40°C, and $C_{ai} = .1$ and .2. Each set of parameters had a Temperature time trajectory and a temperature-concentration phase plane. These are the four graphs.



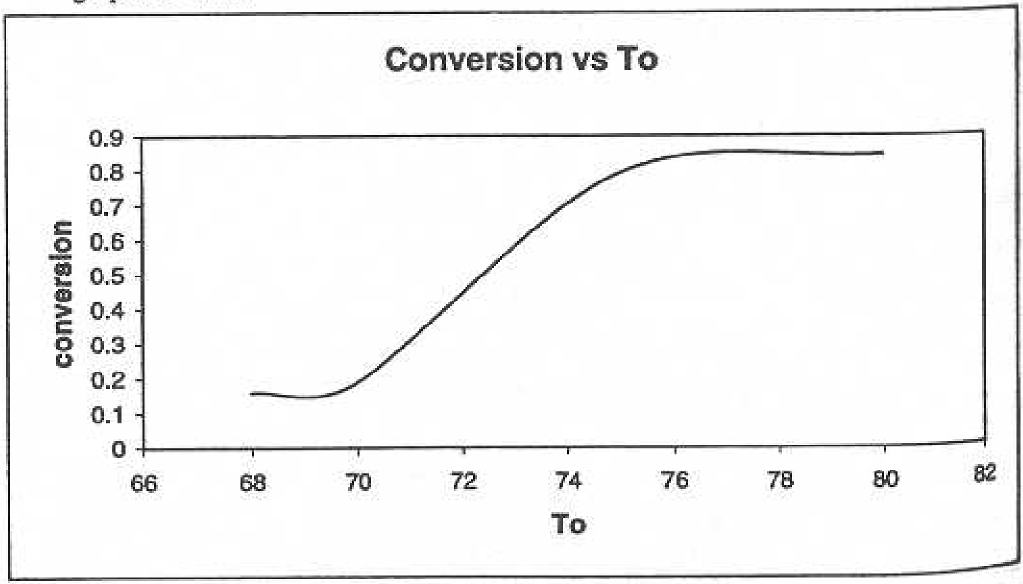




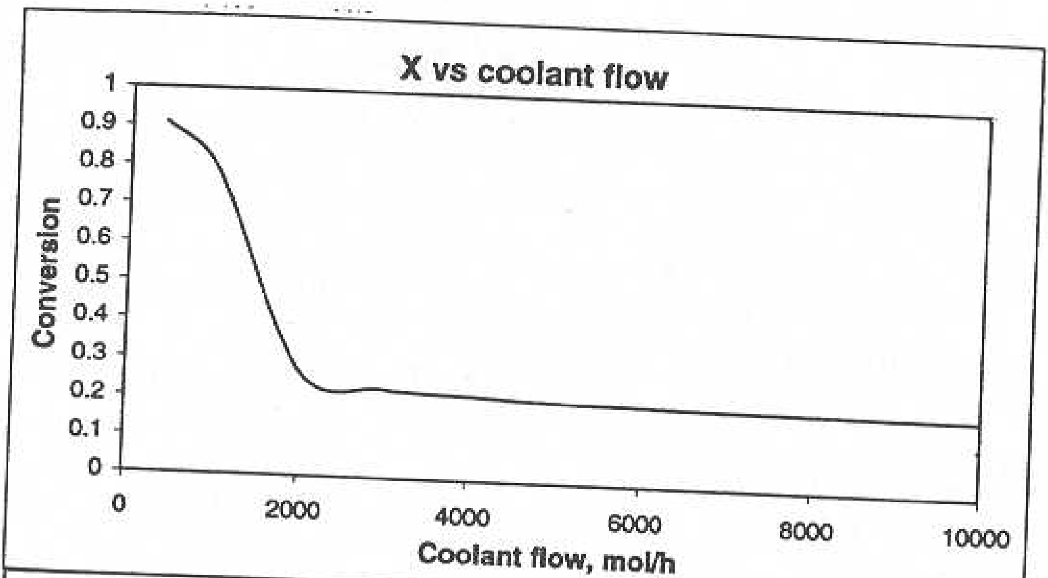
P9-2 cont'd

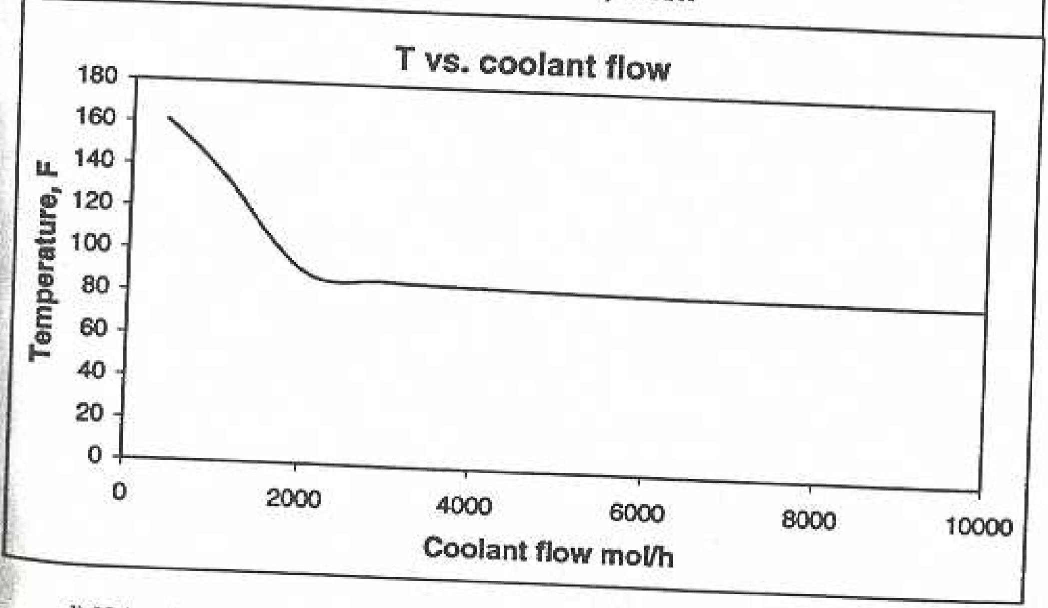


c) Using the code from Example 9-5, we could produce the following graphs either by changing T_0 and finding the steady-state conversion or changing the coolant flow rate and finding the steady-state conversion and temperature. These are the graphs of those.



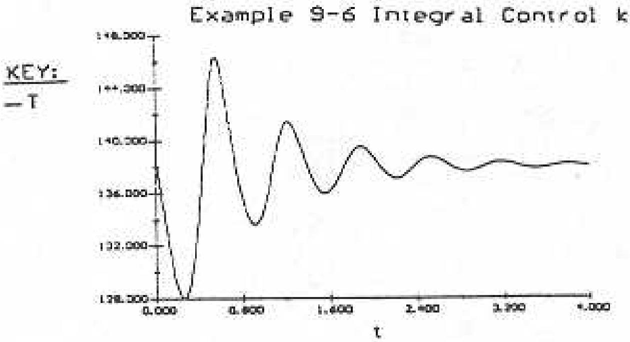
P9-2 **cont'd**

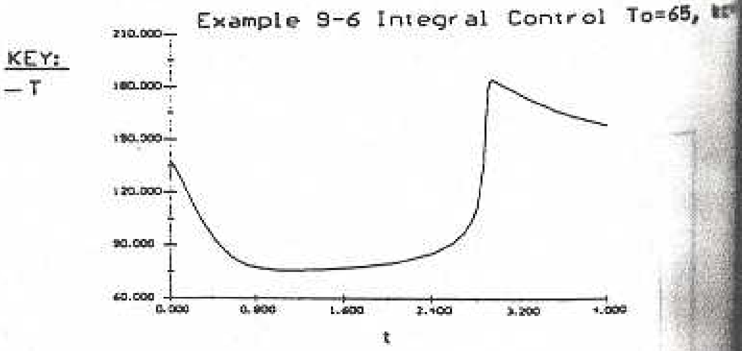




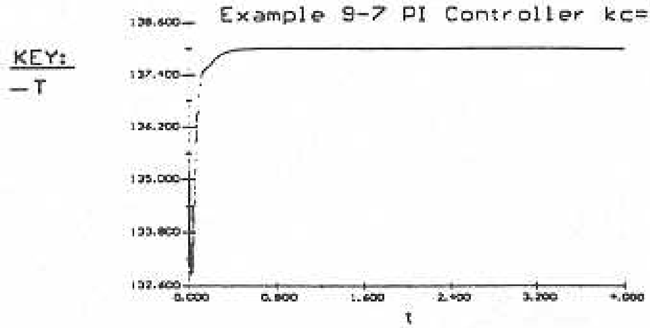
d) Using the code from Example 9-6, we can determine the value of k_c for which the reactor will fall to the lower steady-state and when it becomes unstable. The following two graphs show those points when $k_c = .2$ and 24 respectively. The third graph shows what happens when $T_0 = 65$. It becomes unstable at a much lower temperature.

P9-2 cont'd





e) Using the code from Example 9-7, 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.



P9-3

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:

$$\left(-\Delta H_R\right)\left(-r_A V\right) = N_A C_{p_A} \frac{dT}{dt}$$

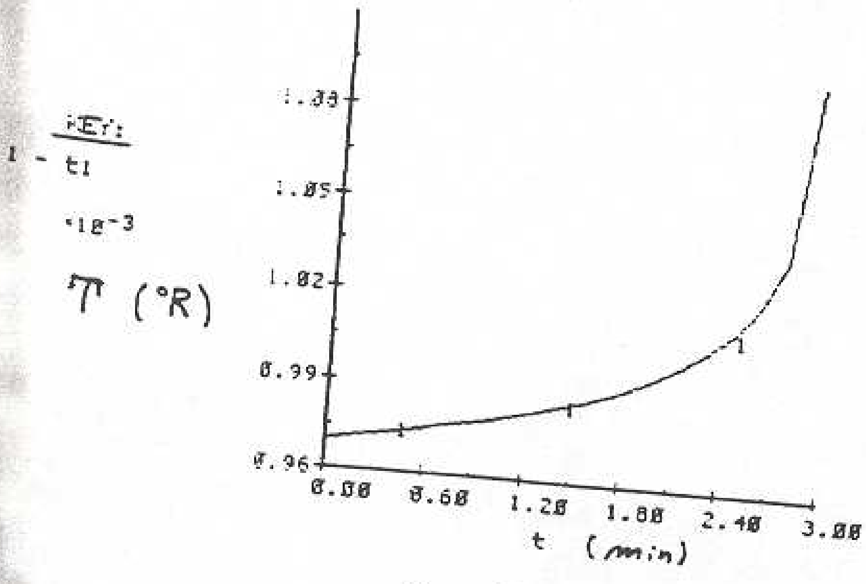
$$\left(-\Delta H_R\right)\left(k\dot{N}_A\right) = N_A C_{p_A} \frac{dT}{dt}$$

$$\frac{dT}{dt} = \frac{\Delta H_{Rxn}}{C_{p_A}} k(T)$$

$$k = .53 \exp\left(44499\left(\frac{1}{970} - \frac{1}{T}\right)\right) / 60 \text{ min.}$$

POLYMATH

```
The equations:
     d(t1)/d(t)=-dh*k/cpa
     dh=-336
     cpa=.38
     k=.53*exp(44499*(1/970-1/t1))/60
Initial values: t0= 0.0, t10= 970.00
Final value:    tf= 2.9000
```



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:

P9-4 **cont'd**

$$\ln\left(\frac{.19}{.32}\right)=\frac{E}{R}\left(\frac{1}{800}-\frac{1}{400}\right)$$

$$E=3467$$

$$k=.19\exp\left[\frac{3467}{8.314}\left(\frac{1}{400}-\frac{1}{T}\right)\right]$$

$$\Delta H(400)=-8kj/mol=\Delta H(800)=\Delta H(1200)=\Delta H(T)$$

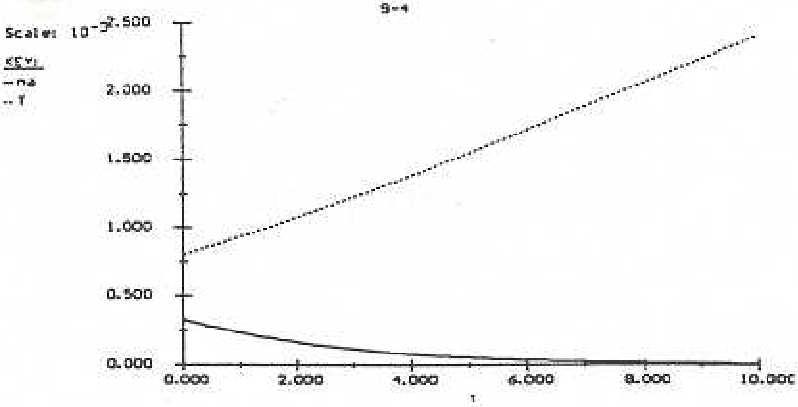
Assume a heat capacity for A of 20 J/molK and assume there is no A already in the reactor. We can plug these equations into POLYMATH and get this answer.

```
9-4
Equations:                                                          Initial value
d(na)/d(t)=fao+Vra                                                  1e-09
d(T)/d(t)=((Vra*Dhr1)-fao*cpa*(T-To))/(na*cpa)                      400
fao=100
Dhr1=-8000
cpa=20
To=400
k=.19*exp(3467/8.314*(1/400-1/T))
Vra=-k*na
t0 = 0,    tf = 100
9-4
Variable       Initial value   Maximum value   Minimum value   Final value
t              0               100             0               100
na             1e-09           326.125         1e-09           312.512
T              400             801.383         400             800
fao            100             100             100             100
Dhr1           -8000           -8000           -8000           -8000
cpa            20              20              20              20
To             400             400             400             400
k              0.19            0.320276        0.19            0.319988
Vra            -1.9e-10        -1.9e-10        -101.769        -100
```

N_A = 326.125

When the flow is turned off, F_{A0} = 0 and we get this graph of T and N_A.

P9-4 cont'd



P9-5$_B$

Semibatch problem

Part (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 :

$$Ca = \frac{Na}{V} \qquad Cb = \frac{Nb}{V} \qquad Cc = \frac{Nc}{V}$$

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 :

$$-ra = k(T).\frac{Na}{V}.\frac{Nb}{V}$$

P9-5 cont'd

$$k(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To}-\frac{1}{T}\right)\right]$$ where E = 10000 cal/mol ,

R = 1.987 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

ΔHrx(T) = ΔHrx(Tref) + ΔCp(T-Tref)

$$\Delta Cp = \frac{c}{a}.Cp - \frac{b}{a}.Cpb - Cpa = 30 - 15 - 15 = 0$$

ΔHrx(273) = [(-41)-(-20)-(-15)].10^3 = -6000 cal/mol

ΔHrx(T) = -6000 cal/mol

ΣFio.Cpi.(T-Tio) = Fbo.(15).(T-323)

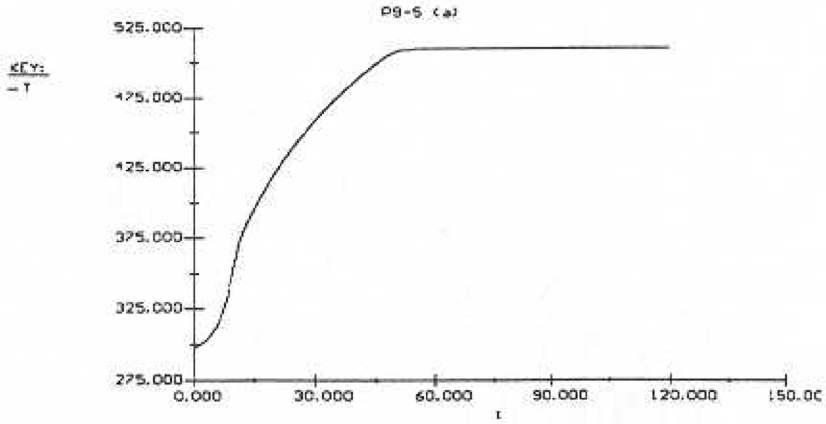
ΣNi.Cpi = NaCpa + Nb.Cpb + Nc.Cpc
= 15Na + 15Nb + 30Nc

POLYMATH solution P9-5B part(a)

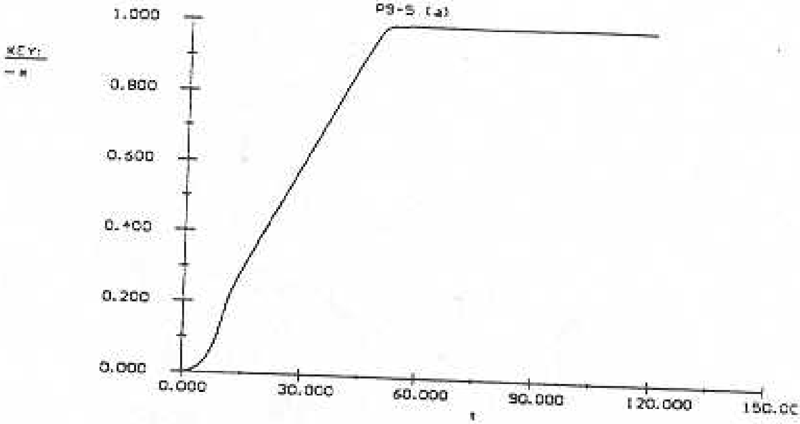
P9-5 cont'd

```
P9-5 (a)
Equations:                                                           Initial value
d(Na)/d(t)=ra*V                                                      500
d(Nb)/d(t)=(ra*V)+Fbo                                                0
d(Nc)/d(t)=-ra*V                                                     0
d(T)/d(t)=((6000*(-ra*V))-(Fbo*15*(T-323)))/((15*Na)+(15*            298
   Nb)+(30*Nc))
d(x)/d(t)=(-ra*V)/Nao                                                0
Fbo=if(t<50)then(10)else(0)
Nao=500
Cbo=10
k=0.01*exp((10000/1.987)*((1/300)-(1/T)))
vo=Fbo/Cbo
V=if(t<50)then(50+(vo*t))else(100)
ra=-k*Na*Nb/(V*V)
t0 = 0,    tf = 120
```

```
P9-5 (a)
Variable        Initial value   Maximum value   Minimum value   Final value
t               0               120             0               120
Na              500             500             0.139723        0.139723
Nb              0               42.6509         0               0.139723
Nc              0               499.86          0               499.86
T               298             510.444         298             510.444
x               0               0.999721        0               0.999721
Fbo             10              10              0               0
Nao             500             500             500             500
Cbo             10              10              10              10
k               0.00893518      10.0851         0.00893518      10.0851
vo              1               1               0               0
V               50              100             50              100
ra              -0              -0              -0.352221       -1.96886e-05
```



P9-5 **cont'd**



Part (b)

As for part(a) except

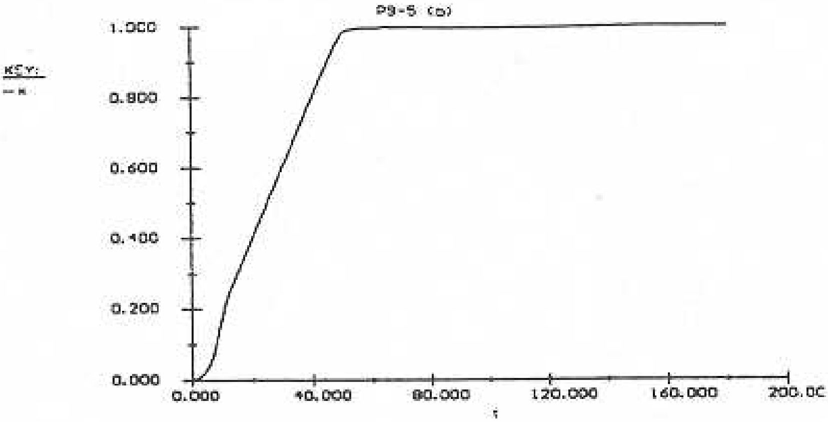
Energy balance :

$$\frac{dT}{dt}=\frac{Q-Ws-\sum Fio.Cpi.(T-Tio)+(-\Delta Hrx(T)).(-ra.V)}{\sum Ni.Cpi}$$

where Q = UA(Ta - T)   UA = 100 , Ta = 323

```
P9-5 (b)
Variable   Initial value   Maximum value   Minimum value   Final value
t          0               180             0               180
Na         500             500             0.397438        0.397438
Nb         0               40.9551         0               0.397438
Nc         0               499.603         0               499.603
T          298             476.955         298             389.364
x          0               0.999205        0               0.999205
Fbo        10              10              0               0
UA         100             100             100             100
Ta         323             323             323             323
Nao        500             500             500             500
Cbo        10              10              10              10
k          0.00893518      5.04699         0.00893518      0.470049
vo         1               1               0               0
V          50              100             50              100
ra         -0              -0              -0.341013       -7.42476e-06
```

P9-5 cont'd



Part (c)

As for part (b) except :

Rate law : -ra = k1(T).Ca.Cb - k2(T).Cc

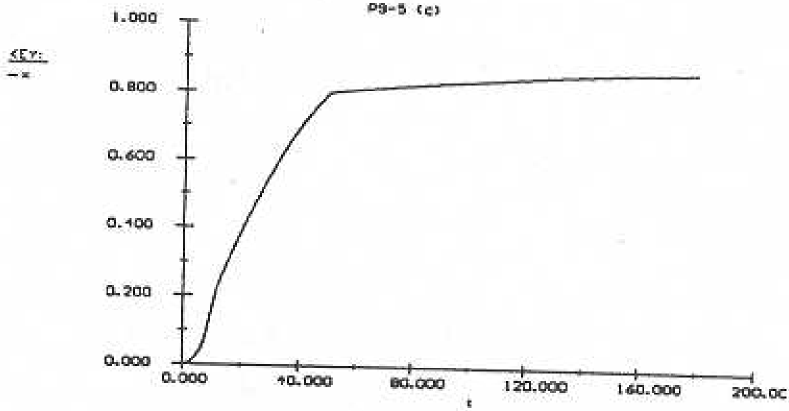
Combining :

$$-ra = k1(T).\left(\frac{Na}{V}.\frac{Nb}{V}\right) - k2(T).\left(\frac{Nc}{V}\right)$$

$$k2(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right]$$ where E = 16000 , R = 1.987 , ko = 10 , To = 300

```
P9-5 (c)
Variable   Initial value   Maximum value   Minimum value   Final value
t          0               180             0               180
Na         500             500             62.9262         62.9262
Nb         0               102.378         0               62.9262
Nc         0               437.074         0               437.074
T          298             444.058         298             383.479
x          0               0.874148        0               0.874148
Fbo        10              10              0               0
UA         100             100             100             100
Ta         323             323             323             323
Nao        500             500             500             500
Cbo        10              10              10              10
k1         0.00893518      2.30959         0.00893518      0.385471
k2         8.35152e-05     0.604861        8.35152e-05     0.0344816
vo         1               1               0               0
V          50              100             50              100
ra         -0              -0              -0.336444       -0.00192523
```

P9-5 cont'd



P9-6B

Part (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 :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi} = 0 \qquad \text{constant T}$$

$Q = Ws = 0$

$\sum Fi.Cpi(T - Tio) = (-\Delta Hrx)(-ra.V)$

$Fco.Cpc.(T - Tio) = (-\Delta Hrx)(k.Na)$

$= (-\Delta Hrx)(k.Nao.e^{-kt})$

<u>P9-6</u> cont'd

$$Fco = \frac{(-\Delta Hrx).(kNao.e^{-kt})}{Cpc.(T - Tio)}$$

$$= \frac{25000 \times 0.00012 \times 25 \times \exp(-0.00012 \times 2 \times 3600)}{0.5.(100 - 80)}$$

$= 3.16$ lb/s

Part (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 = = (-ΔHrx)(-ra.V)

$$Fs = \frac{(-\Delta Hrx).(kNao.e^{-kt})}{\lambda_v} = \frac{25000 \times 0.00012 \times 25 \times \exp(-0.00012 \times 2 \times 3600)}{1000}$$

$= 0.0316$ lb/s

<u>P9-7B</u>

Batch problem

Mol balance : $Nao\frac{dX}{dt} = -raV$ $Cao\frac{dX}{dt} = -ra$

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

P9-7 cont'd

$k1(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right]$ 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 $\sum Ni.Cpi = Nao(\sum \theta iCpi + \Delta CpX)$

$$\Delta Cp = \frac{c}{a}.Cpc - \frac{b}{a}.Cpb - Cpa = 40 - 25 - 25 = -10$$

$$\sum \theta i.Cpi = \frac{Cao}{Cao}.Cpa + \frac{Cbo}{Cao}.Cpb + \frac{Cco}{Cao}.Cpc$$

$$= 25 + {}^{0.125}/_{0.1}\,25 + 0 = 56.25$$

$\Delta Hrx(T) = \Delta Hrx(Tref) + \Delta Cp(T\text{-}Tref)$

$= -40000 - 10.(T\text{-}298)$

$$V = \frac{Nao}{Cao}$$

subs $$\frac{dT}{dt} = \frac{[40000 + 10.(T - 298)].\left(-ra.\frac{Nao}{Cao}\right)}{Nao(56.25 - 10X)}$$

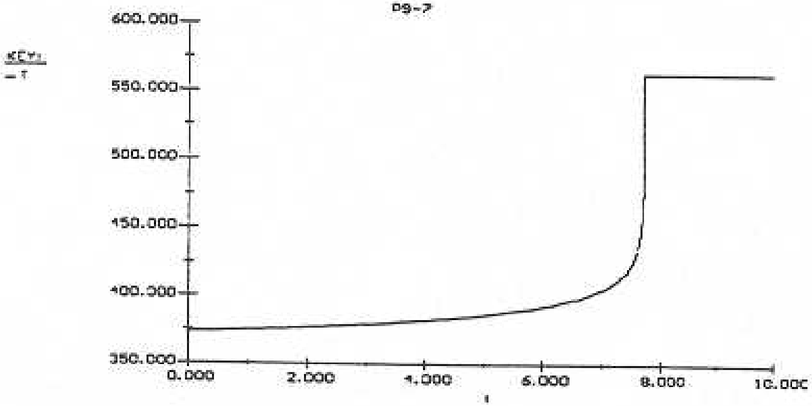
cancelling $$\frac{dT}{dt} = \frac{[40000 + 10.(T - 298)].\left(\frac{-ra}{0.1}\right)}{(56.25 - 10X)}$$

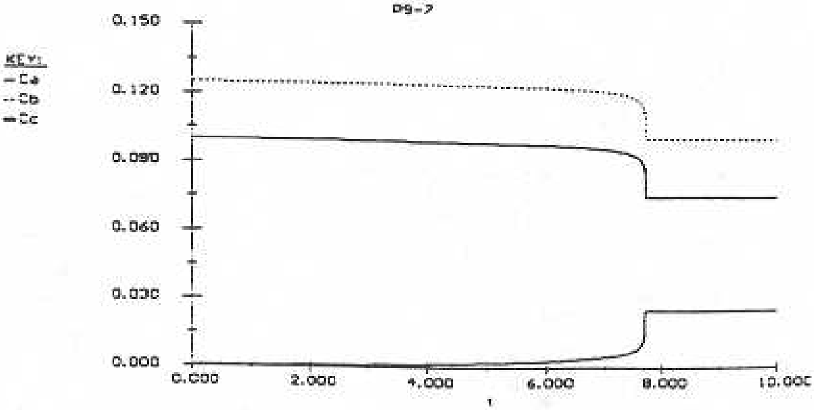
⇒ POLYMATH

P9-7 cont'd

```
Equations:                                                        Initial value
d(x)/d(t)=(-ra)/0.1                                               0
d(T)/d(t)=((40000+(10*(T-298)))*(-ra)*(1/0.1))/(56.25-(10          373
    *x))
k1=0.002*exp((100000/8.314)*((1/373)-(1/T)))
Ca=0.1*(1-x)
Cb=0.1*(1.25-x)
k2=0.00003*exp((150000/8.314)*((1/373)-(1/T)))
Cc=0.1*x
ra=-((k1*(Ca**0.5)*(Cb**0.5))-(k2*Cc))
t0 = 0,    tf = 10
```

```
P9-7
Variable        Initial value  Maximum value  Minimum value  Final value
t               0              10             0              10
x               0              0.250483       0              0.250483
T               373            562.918        373            562.918
k1              0.002          106.136        0.002          106.136
Ca              0.1            0.1            0.0749517      0.0749517
Cb              0.125          0.125          0.0999517      0.0999517
k2              3e-05          366.751        3e-05          366.751
Cc              0               0.0250483     0              0.0250483
ra              -0.000223607   3.90133e-09    -1.76905       3.89138e-09
```





P9-7 cont'd

Check answer : $\dfrac{Cc}{\sqrt{Ca}\sqrt{Cb}} = \dfrac{k1}{k2}$

$$\frac{0.02504}{\sqrt{0.07495} \times \sqrt{0.09995}} = \frac{1.06}{3.67} = 0.289$$

P9-8$_B$

Adiabatic, batch, reversible.

Design equation : $N_{AO}\dfrac{dX}{dt} = -r_A V$

Rate law : $-r_A = k_1\left[C_A - \dfrac{C_B{}^2}{Ke}\right]$

Stoichiometry : $C_A = C_{AO}\,(1 - X)$, $C_B = -\,2.C_{AO}.X$

Combining : $C_{AO}\dfrac{dX}{dt} = k_1\left[C_{AO}(1-X) - \dfrac{4C_{AO}{}^2(1-X)^2}{Ke}\right]$

$$\frac{dX}{dt} = k_1\left[(1-X) - \frac{4C_{AO}(1-X)^2}{Ke}\right]$$

Parameter evaluation : $E = \dfrac{Ln\dfrac{k_1}{k_2}}{\dfrac{1}{R.T_2} - \dfrac{1}{R.T_1}} = \dfrac{Ln\dfrac{0.217}{0.324}}{\dfrac{1}{8.314(340)} - \dfrac{1}{8.314(300)}} = 8498\,J/mol$

$$k_1 = 0.217\exp\left[\frac{8498}{8.314}\left(\frac{1}{340} - \frac{1}{T}\right)\right]$$

$$Ln\frac{Ke(T)}{Ke(300)} = \frac{\Delta Hrx}{R}\left(\frac{1}{300} - \frac{1}{T}\right)$$

$\Delta Cp = 2\ Cp_B - Cp_A = 20 - 12 = 8$ J/mol.K

$\Delta Hrx = \Delta Hrx\ (300) + \Delta Cp(T - 300) = -\ 75000 + 8\ (T - 300)$

P9-8 cont'd

$$N_{AO} = 0.6667 * 900 * 254 = 272\ 127 \text{ mol A}$$

$$N_{IO} = 0.3333 * 900 * 454 = 136\ 064 \text{ mol I}$$

$$C_{AO} = N_{AO} / V = 272127 / (50 * 28.12) = 192 \text{ mol / dm}^3$$

$$Cps = \sum \theta_i Cp_i = \theta_A Cp_A + \theta_B Cp_B + \theta_I Cp_I$$

$$= (1)(12) + 0 + (136064 / 272027)*(15) = 19.5 \text{ J/mol}$$

Energy balance : $$T = To + \frac{[-\Delta Hrx(300).X]}{Cp_A + \Delta Cp.X} = 300 + \frac{(-75000).X}{19.5 + 8.X}$$

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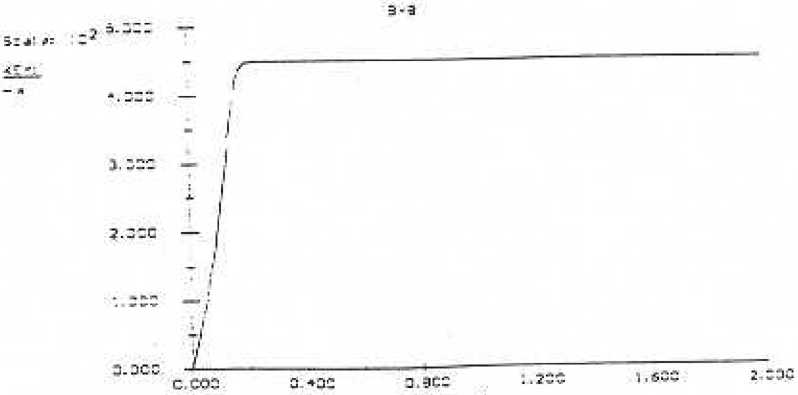
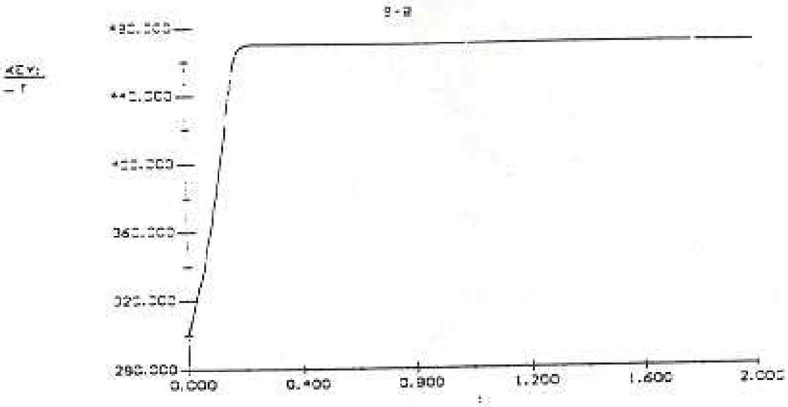
```
9-8
Equations:                                                   Initial value
d(x)/d(t)=k1*((1-x)-(4*cao*(x^2)/Ke))                        0
To=300
cao=192
T=To+(75000*x/(19.5+(8*x)))
k1=.217*exp(1022*(1/340-1/T))
Dhrx=-75000+(8*(T-300))
Ke=70000*exp(Dhrx/8.314*(1/300-1/T))
t0 = 0,   tf = 2
```

```
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
k1           0.145345        0.49785         0.145345        0.49785
Dhrx         -75000          -73641.8        -75000          -73641.8
Ke           70000           70000           1.62532         1.62532
```



P9-8 **cont'd**



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 :

$$C_{AO}(1-Xe)=\frac{4.C_{AO}^2X^2}{Ke}$$

$$(4.C_{AO}^2).Xe^2+(Ke.C_{AO}).Xe-Ke.C_{AO}=0$$

using the solution to a quadratic :

$$Xe=\frac{-Ke.C_{AO}\pm\sqrt{Ke^2.C_{AO}^2-16.Ke.C_{AO}^3}}{8.C_{AO}^2}$$

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

P9-9$_B$

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 : $$\frac{(C_{AO}-C_A)}{\tau}+r_A=\frac{dC_A}{dt}=0 \qquad -\frac{C_B}{\tau}-r_A.V=\frac{dC_B}{dt}=0$$

$$Ln\left(\frac{k1}{k2}\right)=\frac{E}{R.T2}-\frac{E}{R.T1}$$

$$E=\frac{Ln\left(\frac{k1}{k2}\right)}{\frac{1}{R.T2}-\frac{1}{R.T1}} \qquad =\frac{Ln\left(\frac{1.1}{3.4}\right)}{\frac{1}{8.314(323)}-\frac{1}{8.314(313)}}$$

$$94852 = \text{J/ mol K}$$

$$k=1.1\exp\left[\frac{94852}{8.314}\left(\frac{1}{313}-\frac{1}{T}\right)\right]=107.4\text{ /min} \quad \text{for } T = 358\text{ K}$$

Steady state solution :

$$\upsilon_o=\frac{F_{AO}}{C_{AO}}=\frac{90000}{90*2}=500dm^3/\min$$

$$\tau=\frac{V}{\upsilon}=\frac{200}{500}=0.4/\min$$

$C_{AO} = 2$ M $= 2*90 = 180$ g/dm^3

$C_A = C_{AO} + r_A.\tau = 180 + 0.4\ r_A$

$C_B = -\ r_A\ \tau = -\ 0.4\ r_A$

$-\ r_A = k.C_A$

$C_A = 180 - 107.4\ (0.4)\ C_A$

$$C_A=\frac{180}{1+(0.4*107.4)}=4.1g/dm^3$$

$r_A = -\ 107.4 * 4.1 = -\ 440$ g/min.dm^3

P9-9 cont'd

$$C_B = -(-440)\,0.4 = 175.9 \text{ g/dm}^3$$

Energy balance :
$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi} = 0$$

$$Q = UA(Ta - T) = (120*60)A(273 - T) \qquad \text{J/min}$$

$$F_{AO}.C_{pA}.(T - T_{AO}) = 90000*2*(T - 313) \qquad \text{J/min}$$

$$A = \frac{-180000.(358 - 313) + (250)(440x200)}{7200(273 - 358)} = 22.7m^2$$

Use the unsteady state equations to determine what heat exchange area A will give a runaway reaction.

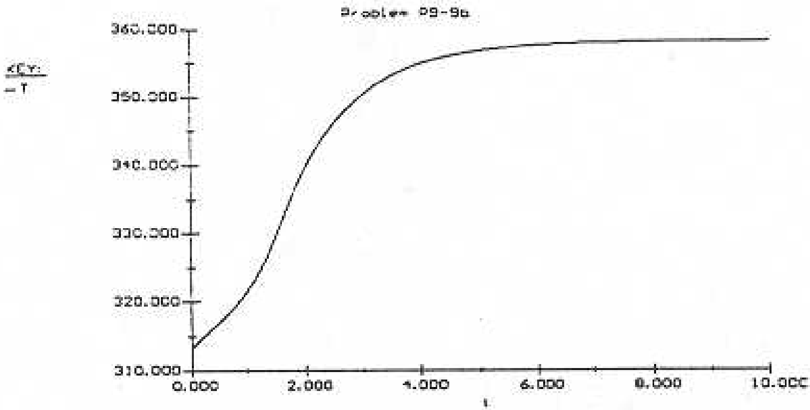
where $\sum Ni.Cpi = Cp_{sol}\,\rho_{sol}\,V = 2 \text{ x } 900 \text{ x } 200 = 360000$ J/K

The POLYMATH results for A = 22.6 m^2 are given

```
Problem P9-9b
Equations:
d(ca)/d(t)=((180-ca)/tau)+(ra)                                   Initial value
d(cb)/d(t)=-ra-(cb/tau)                                          180
d(T)/d(t)=((7200*A*(273-T))-(90000*2*(T-313))+((-250)*ra*       0
   V))/(2*900*200)                                               313
tau=.4
A=22.696
k=1.1*exp(11409*((1/313)-(1/T)))
V=200
ra=-k*ca
Na=ca/V
Nb=cb/V
t0 = 0,    tf = 10
```

```
Problem P9-9b
Variable        Initial value   Maximum value   Minimum value   Final value
t               0               10              0               10
ca              180             180             4.10076         4.10076
cb              0               175.899         0               175.899
T               313             357.977         313             357.977
tau             0.4             0.4             0.4             0.4
A               22.696          22.696          22.696          22.696
k               1.1             107.237         1.1             107.237
V               200             200             200             200
ra              -198            -197.967        -439.754        -439.754
Na              0.9             0.9             0.0205038       0.0205038
Nb              0               0.879496        0               0.879496
```

P9-9 cont'd



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$_B$

CSTR startup

Part (a) CSTR startup, gas phase, isobaric - no pressure drop

Mol balance :

$$\frac{dFa}{dt} = (Fao - Fa) + ra.V$$

$$\frac{dFb}{dt} = (0 - Fb) - 2.ra.V$$

$$Ca = \frac{Fa}{\upsilon_T} \qquad Cb = \frac{Fb}{\upsilon_T} \qquad \upsilon_T = \upsilon a + \upsilon b$$

$$F_T = C_T.\upsilon_T = \frac{P}{R.T}.\upsilon_T \qquad F_{TO} = C_{TO}.\upsilon_{TO} = \frac{P}{R.To}.\upsilon_{TO}$$

$$\upsilon_T = \upsilon_{TO}\frac{F_T}{F_{TO}}.\frac{T}{To}$$

$$F_T = Fa + Fb \qquad F_{TO} = Fao + Fbo$$

P9-10 **cont'd**

$$V = \upsilon_T.\tau \qquad \tau = 500\ \text{s}$$

Energy balance : $$\frac{dT}{dt} = \frac{Q - \sum Fio.Cpi.(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi}$$

$$\frac{UA}{\rho cat} = 5J / kgcat.s.K$$ but kg catalyst = 50 kg

UA = 5 x 50 = 250 J / s.K

$\Delta Cp = 0$

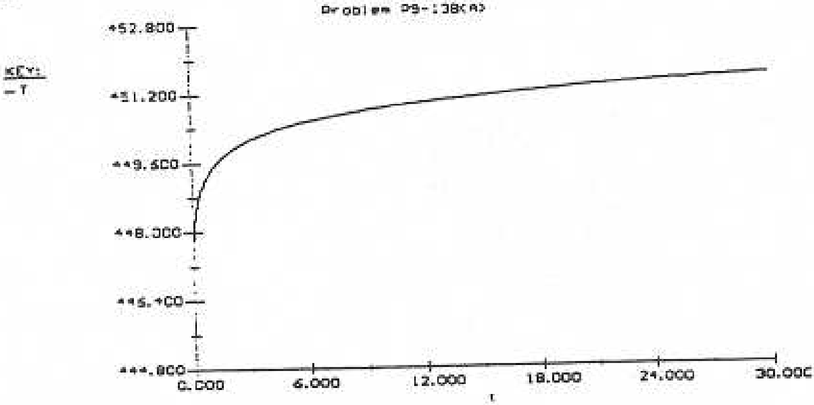
$$\frac{dT}{dt} = \frac{250.(Ta - T) - 40.Fao.(T - Tio) + 20000.(-ra.V)}{40.Ca.V + 20.Cb.V}$$

No control : Ta = 300 K, Tio = 450 K, Fao = 5 mol/s

```
Problem P9-13B(A)
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
t0 = 0,   tf = 30
```

P9-10 cont'd

```
Problem P9-13B(A)
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 : $$\frac{dCa}{dt} = \frac{(Cao - Ca)}{\tau} + ra$$

$Cao = 0.1\ \text{kmol/m}^3 = 0.1$ mol

P9-10 cont'd

$$\frac{dCb}{dt} = \frac{(Cbo - Cb)}{\tau} + ra \qquad Cbo = Cao$$

$$\frac{dCc}{dt} = \frac{(0 - Cc)}{\tau} - ra \qquad \tau = 50\ s$$

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 : $$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi}$$

$$V = \upsilon_o\ .\ \tau = 2 \times 50 = 100\ dm^3$$

$$Fao = Cao\ .\ \upsilon_o = 0.1 \times 2 = 0.2\ mol/s = Fbo\ \text{(equimolar feed)}$$

$$\Sigma Fio.Cpi.(T - Tio) = 2 \times 0.2 \times (15)(T - 300) = 6(T - 300)$$

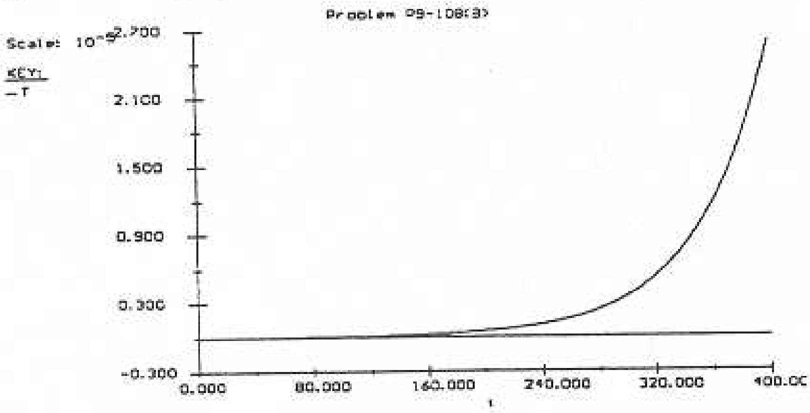
$$\begin{aligned}\Delta Hrx(T) &= \Delta Hrx(To) + \Delta Cp.(T - To) \qquad \text{but } \Delta Cp = 0\\ &= -41000 - (-20000) - (-15000)\\ &= -6000\ cal/mol\end{aligned}$$

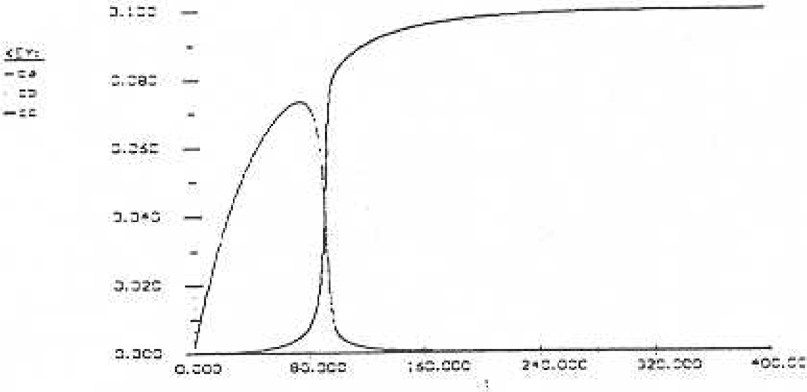
$$\frac{dT}{dt} = \frac{6(T - 300) + (6000).(-ra.V)}{15.Ca.v + 15.Cb.V + 30.Cc.V}$$

```
Problem P9-10B(B)
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*           300
   V)+(30*cc*V))
V=100
k=0.01*exp((10000/1.987)*((1/300)-(1/T)))
ra=-k*ca*cb
t0 = 0,   tf = 400
```

P9-10 cont'd

```
Problem P9-10B(B)
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
```





P9-11$_B$

Semibatch problem

Part (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 $Q = UA.(Ta - T) = 250.(390 - T)$

$Ws = 0$

$\Delta Hrx(T) = -55000$

$\Sigma Fio.Cpi = Fbo.Cpb = Cbo.\ \upsilon_o.Cpb = 4*\upsilon_o*20 = 80\upsilon_o$

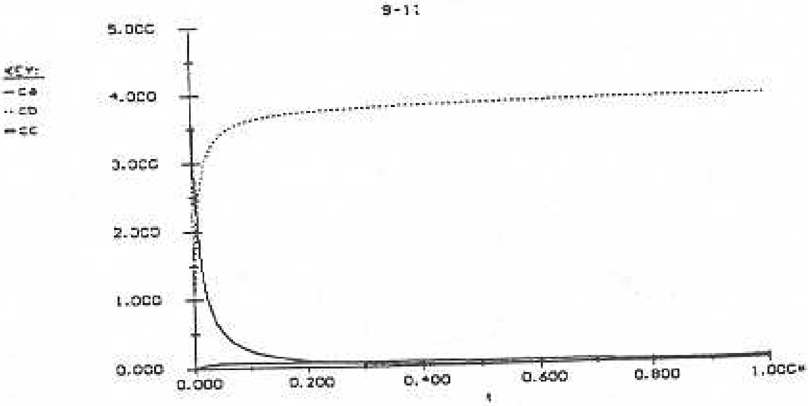
$\Sigma Ni.Cpi = NaCpa + Nb.Cpb + Nc.Cpc = 35Na + 20Nb + 75Nc$

$$\frac{dT}{dt} = \frac{250.(290 - T) - 80.\upsilon_o.(T - 325) + (-55000).(-ra.V)}{35.Na + 20.Nb + 75.Nc}$$

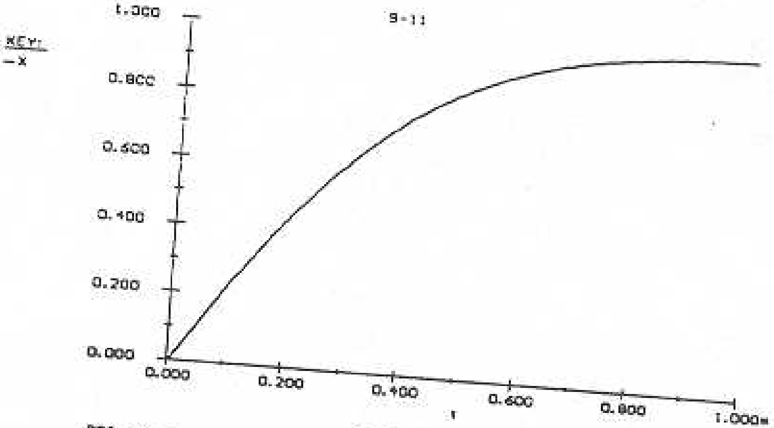
P9-11 cont'd

```
9-11
Equations:                                                          Initial value
d(na)/d(t)=ra*V                                                     50
d(X)/d(t)=(-ra*V/50)                                                0
d(nb)/d(t)=(2*ra*V)+fbo                                             0
d(nc)/d(t)=-ra*V                                                    0
d(T)/d(t)=((250*(290-T))-(80*vb*(T-325))+(-55000*(-ra*V))           300
    )/((35*na)+(20*nb)+(75*nc))
vb=1.5
k=0.0005*exp((8000/1.987)*((1/300)-(1/T)))
V=10+(vb*t)
fbo=4*vb
ca=na/V
cb=nb/V
cc=nc/V
ra=-k*ca*(cb^2)
t0 = 0,    tf = 1000
```

```
9-11
Variable      Initial value   Maximum value   Minimum value   Final value
t             0               1000            0               1000
na            50              50              0.332447        0.332447
X             0               0.993351        0               0.993351
nb            0               5900.66         0               5900.66
nc            0               49.6676         0               49.6676
T             300             300.182         283.593         298.764
vb            1.5             1.5             1.5             1.5
k             0.0005          0.000504079     0.000230027     0.000472992
V             10              1510            10              1510
fbo           6               6               6               6
ca            5               5               0.000220164     0.000220164
cb            0               3.90773         0               3.90773
cc            0               0.0718812       0               0.0328924
ra            -0              -0              -0.00411466     -1.59018e-06
```



P9-11 cont'd



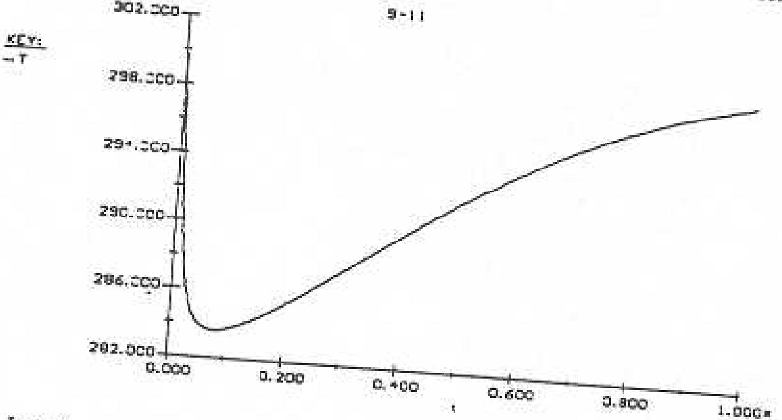


Table 1. Iterating wrt υ_0 for X=0.8 and T<403K and daily Nc ~ 120 molC

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 cont'd

Part (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 :

$$Q = m_c Cp_{cool}(Ta1 - Ta2) \qquad \text{where } Ta1 = \text{ambient T coolant entering}$$
$$Ta2 = \text{ambient T coolant leaving}$$

$$Ta2 = T - (T - Ta1).\exp\left(-\frac{UA}{m_c Cp_{cool}}\right)$$

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.

$\underline{P9\text{-}12_B}$

CSTR startup

Need steady-state values at To = 75°F

Mol balance : $\frac{dNa}{dt} = Fao - Fa + ra.V$

$$\frac{dCa}{dt} = \frac{(Cao - Ca).v_0}{V} + ra$$

$$\frac{dCb}{dt} = \frac{(Cbo - Cb)v_0}{V} + ra$$

$$\frac{dCc}{dt} = \frac{(Cco - Cc)v_0}{V} - ra$$

$$\frac{dC_M}{dt} = \frac{(C_{MO} - C_M)v_0}{V}$$

$$Cio = \frac{Fio}{\upsilon_o} \qquad Cao = \frac{Fao}{\upsilon_o} = 0.18157 \text{ lb mol/ ft}^3$$

$$Cbo = \frac{Fbo}{\upsilon_o} = 2.2696 \text{ lb mol/ ft}^3$$

$$Cco = 0$$

$$C_{MO} = \frac{F_{MO}}{\upsilon_o} = 0.22696 \text{ lb mol/ ft}^3$$

$$V = \frac{1}{7.484} \times 500$$

$$\upsilon_o = \frac{Fao}{\rho ao} + \frac{Fbo}{\rho bo} + \frac{F_{MO}}{\rho_{MO}} = \frac{80}{0.932} + \frac{1000}{3.45} + \frac{100}{1.54} = 440.6 \text{ ft}^3\text{/ hr}$$

Rate law : $-ra = k.Ca$ (Cb in excess)

$$k = 16.96e12.\exp\left(-\frac{32400}{1.987(T+460)}\right)$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi}$$

$Ws = 0$

$Q = m_c.Cp_{cool}.(Ta1 - Ta2) = 1000 \times 18 \times (60 - Ta2)$

$\Sigma Fio.Cpi.(T - Tio) = [Fao.Cpa + Fbo.Cpb + F_{MO}.Cp_M].(T - 75)$

$\Delta Hrx = -36000$ Btu/lb mol

$\Sigma Ni.Cpi = Na.Cpa + Nb.Cpb + Nc.Cpc + N_M.Cp_M$

$= 53Ca.V + 18Cb.V + 46Cc.V + 19.5C_M.V$

P9-12 cont'd

$$Ta2 = T - (T - Ta1).\exp\left(-\frac{UA}{m_c Cp_{cool}}\right)$$

$$= T - (T - 60).\exp\left(-\frac{16000}{1000x18}\right)$$

$$= \mathrm{T} - 0.41111(\mathrm{T} - 60)$$

$$\frac{dT}{dt} = \frac{18000(60 - (T - 0.41111(T - 60) - 22750(T - 75) + (36000)(-ra.V)}{35Ca.V + 18Cb.V + 46Cc.V + 19.5C_M.V}$$

⇒ POLYMATH

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

Part (a)

P-control only : manipulated variable = m_c

controlled variable = T

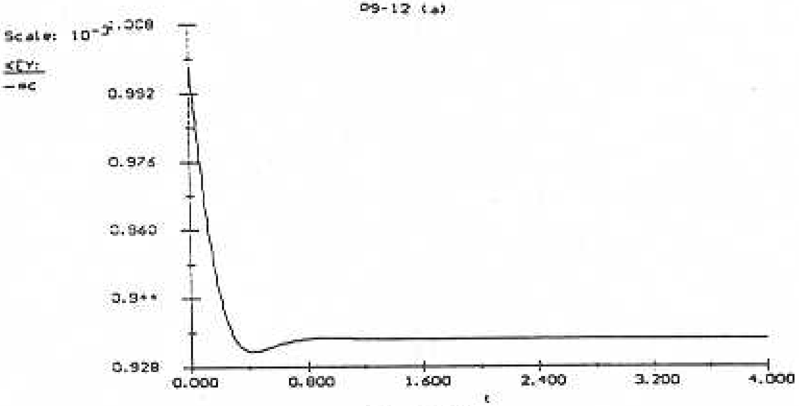
$m_c = m_{co} + kc.(T - Tsp)$ where m_{co} = 1000lb mol/h
Tsp = 138.5 °F
kc = 10

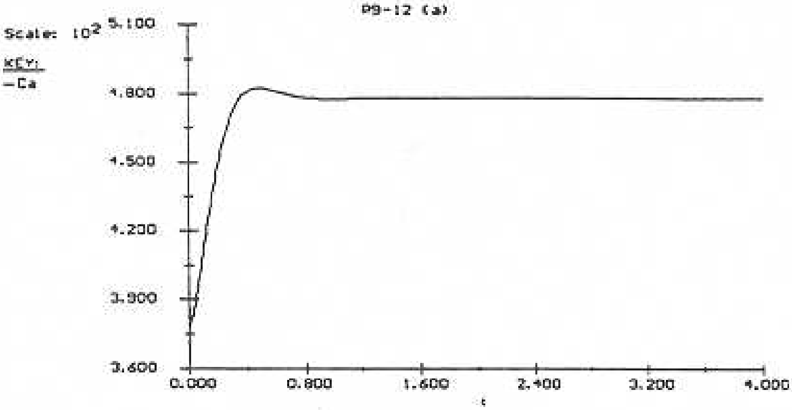
P9-12 cont'd

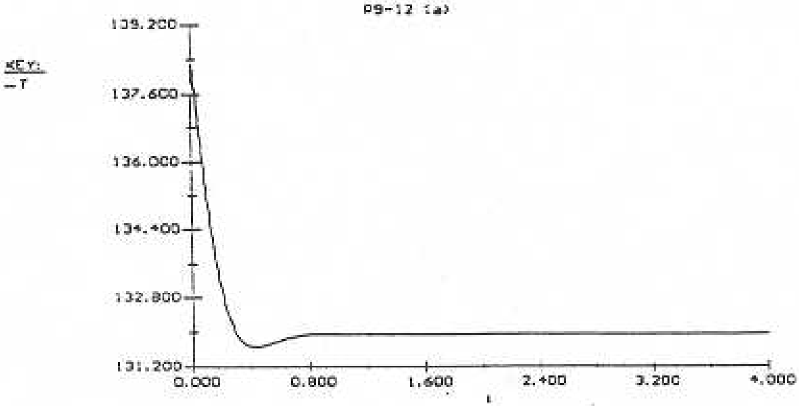
```
P9-12 (a)
Equations:                                                            Initial value
d(Ca)/d(t)=(((Cao-Ca)*vo)/V)+ra                                       0.0378
d(Cb)/d(t)=(((3.45-Cb)*vo)/V)+ra                                      3.3062
d(Cc)/d(t)=(((0-Cc)*vo)/V)-ra                                         0.0144
d(Cm)/d(t)=(((Cmo-Cm)*vo)/V)                                          0.2269
d(T)/d(t)=((mc*18*(60-(T-(0.41111*(T-60)))))-(22750*(T-To             138.5
    ))+(36000*(-ra*V)))/((35*Ca*V)+(46*Ca*V)+(19.5*Cm*V)+(
    18*Cb*V))
Cao=0.18157
vo=440.6
V=(1/7.484)*500
Cmo=0.22696
k=16.96e12*exp(-32400/(1.987*(T+460)))
Cbo=2.2696
To=70
mco=1000
kc=10
Tsp=138.5
ra=-k*Ca
mc=mco+(kc*(T-Tsp))
t0 = 0,    tf = 4
```

```
P9-12 (a)
Variable       Initial value   Maximum value   Minimum value   Final value
t              0               4               0               4
Ca             0.0378          0.0482444       0.0378          0.0478056
Cb             3.3062          3.31667         3.3062          3.31624
Cc             0.0144          0.133764        0.0144          0.133764
Cm             0.2269          0.22696         0.2269          0.22696
T              138.5           138.5           131.65          131.941
Cao            0.18157         0.18157         0.18157         0.18157
vo             440.6           440.6           440.6           440.6
V              66.8092         66.8092         66.8092         66.8092
Cmo            0.22696         0.22696         0.22696         0.22696
k              24.9561         24.9561         18.2047         18.4531
Cbo            2.2696          2.2696          2.2696          2.2696
To             70              70              70              70
mco            1000            1000            1000            1000
kc             10              10              10              10
Tsp            138.5           138.5           138.5           138.5
ra             -0.943341       -0.870142       -0.943341       -0.882163
mc             1000            1000            931.499         934.41
```

P9-12 cont'd


P9-12 (a)
Scale: 10^-3
KEY:
—Xc
1.008
0.992
0.976
0.960
0.944
0.928
0.000
0.800
1.600
2.400
3.200
4.000
t


P9-12 (a)
Scale: 10^2
KEY:
—Ca
5.100
4.800
4.500
4.200
3.900
3.600
0.000
0.800
1.600
2.400
3.200
4.000
t


P9-12 (a)
KEY:
—T
139.200
137.600
136.000
134.400
132.800
131.200
0.000
0.800
1.600
2.400
3.200
4.000
t

P9-12 cont'd

Part (b)

I-control only : manipulated variable = m_c

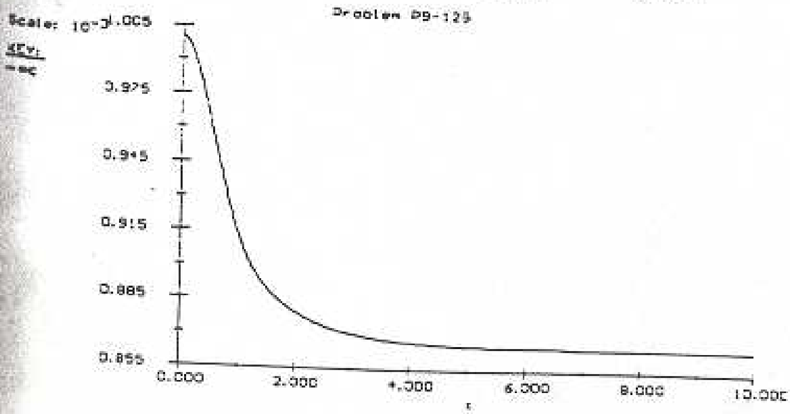
controlled variable = T

$$m_c = m_{co} + \frac{kc}{\tau_I} I$$ where m_{co} = 1000 lb mol/h

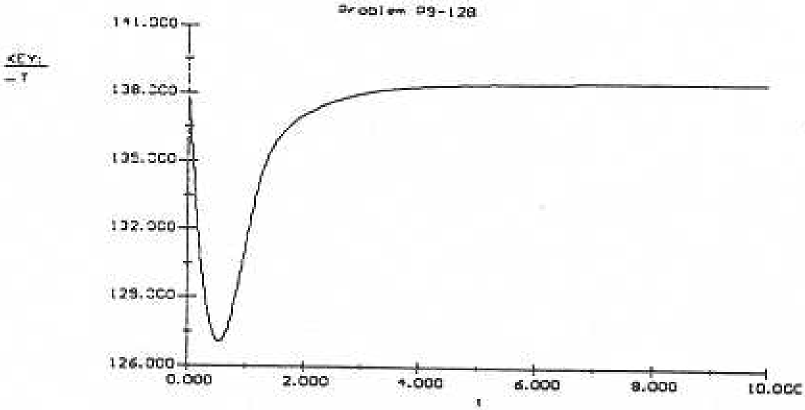
kc = 10, τ_I = 1

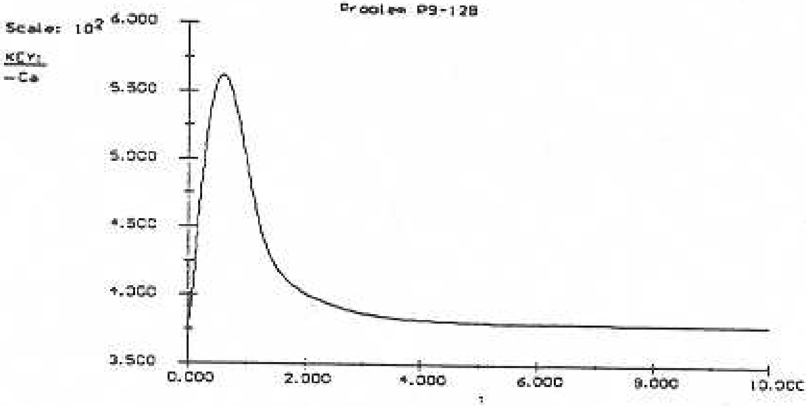
$$\frac{dI}{dt} = (T - Tsp)$$ Tsp = 138.5 °F

```
Problem P9-12B
Variable      Initial value   Maximum value   Minimum value   Final value
t             0               10              0               10
Ca            0.0378          0.0561803       0.0378          0.0379531
Cb            3.3062          3.32461         3.3062          3.30638
Cc            0.0144          0.143617        0.0144          0.143617
Cm            0.2269          0.22696         0.2269          0.22696
T             138.5           138.5           127.056         138.499
I             0               0               -13.516         -13.516
Cao           0.18157         0.18157         0.18157         0.18157
vo            440.6           440.6           440.6           440.6
V             66.8092         66.8092         66.8092         66.8092
Cmo           0.22696         0.22696         0.22696         0.22696
To            70              70              70              70
Tsp           138.5           138.5           138.5           138.5
k             24.9561         24.9561         14.6734         24.9555
Cbo           2.2696          2.2696          2.2696          2.2696
mco           1000            1000            1000            1000
kc            10              10              10              10
tauI          1               1               1               1
ra            -0.943341       -0.818007       -0.94714        -0.94714
mc            1000            1000            864.84          864.84
```



P9-12 cont'd





Part (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

$$\frac{dI}{dt} = (T - Tsp)$$

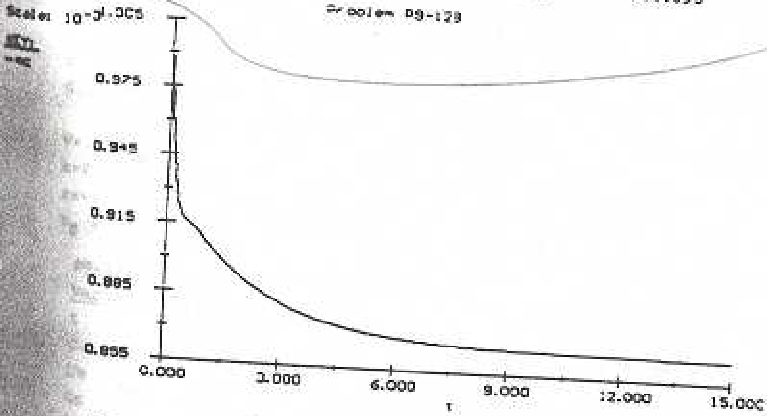
Tsp = 138.5 °F

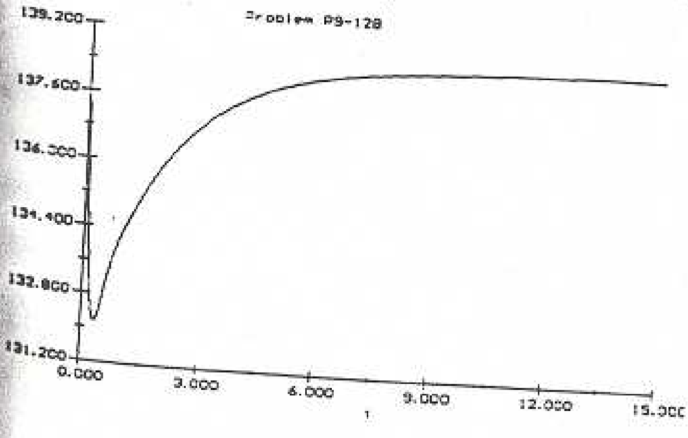
P9-12 cont'd

```
Problem P9-12B
Variable    Initial value   Maximum value   Minimum value   Final value
t           0               15              0               15
Ca          0.0378          0.0473519       0.0378          0.0379598
Cb          3.3062          3.31578         3.3062          3.30639
Cc          0.0144          0.14361         0.0144          0.14361
Cm          0.2269          0.22696         0.2269          0.22696
T           138.5           138.5           132.165         138.495
I           0               0               -13.5052        -13.5052
Cao         0.18157         0.18157         0.18157         0.18157
vo          440.6           440.6           440.6           440.6
V           66.8092         66.8092         66.8092         66.8092
Cmo         0.22696         0.22696         0.22696         0.22696
To          70              70              70              70
Tsp         138.5           138.5           138.5           138.5
k           24.9561         24.9561         18.6468         24.95
Cbo         2.2696          2.2696          2.2696          2.2696
mco         1000            1000            1000            1000
kc          10              10              10              10
tauI        1               1               1               1
ra          -0.943341       -0.872788       -0.947099       -0.947099
mc          1000            1000            864.895         864.895
```

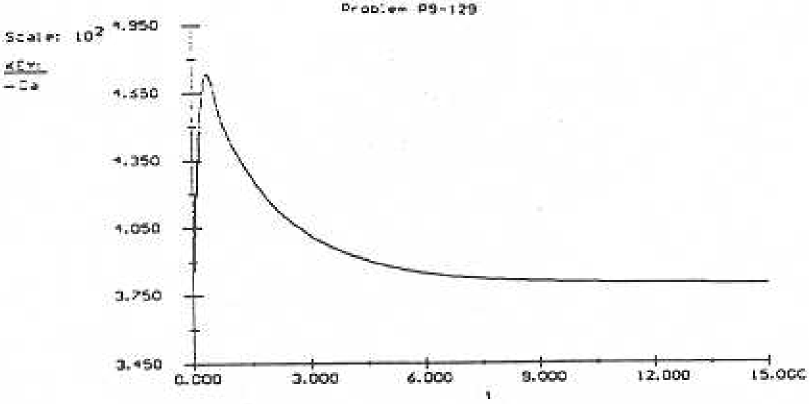
mc

mc





P9-12 cont'd



P9-13$_B$

CSTR startup

Part (b)

Mol balance : $$\frac{dCa}{dt} = \frac{(Cao - Ca)}{\tau} + ra$$ Cao = 0.1

kmol/m^3

mol/dm^3 = 0.1

$$\frac{dCb}{dt} = \frac{(Cbo - Cb)}{\tau} + ra$$ Cbo = Cao

$$\frac{dCc}{dt} = \frac{(0 - Cc)}{\tau} - ra$$ $\tau = 50$ 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 : $$\frac{dT}{dt} = \frac{Q - Ws - \sum Fio.Cpi(T - Tio) + (-\Delta Hrx)(-ra.V)}{\sum Ni.Cpi}$$

P9-13 cont'd

$$V = \upsilon_o \,.\, \tau = 2 \times 50 = 100 \text{ dm}^3$$

$$Fao = Cao \,.\, \upsilon_o = 0.1 \times 2 = 0.2 \text{ mol/s} = Fbo \text{ (equimolar feed)}$$

$$\Sigma Fio.Cpi.(T - Tio) = 2 \times 0.2 \times (15)(T - 300) = 6(T - 300)$$

$$\Delta Hrx(T) = \Delta Hrx(To) + \Delta Cp.(T - To) \qquad \text{but } \Delta Cp = 0$$
$$= -41000 - (-20000) - (-15000)$$
$$= -6000 \text{ cal/mol}$$

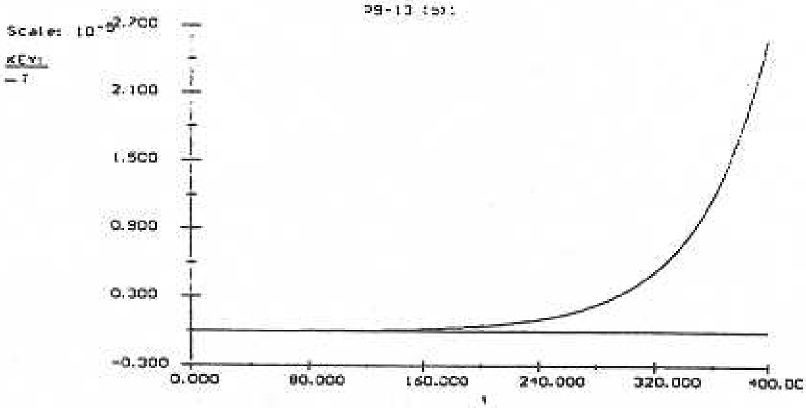
$$\frac{dT}{dt} = \frac{6(T-300)+(6000).(-ra.V)}{15.Ca.v+15.Cb.V+30.Cc.V}$$

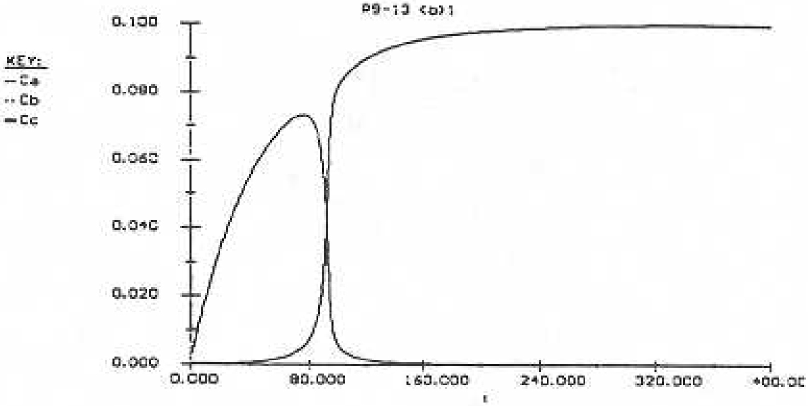
No control :

```
P9-13 (b)1
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*           300
   V)+(30*Cc*V))
V=100
k=0.01*exp((10000/1.987)*((1/300)-(1/T)))
ra=-k*Ca*Cb
t0 = 0,   tf = 400
```

```
P9-13 (b)1
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
```

P9-13 cont'd





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

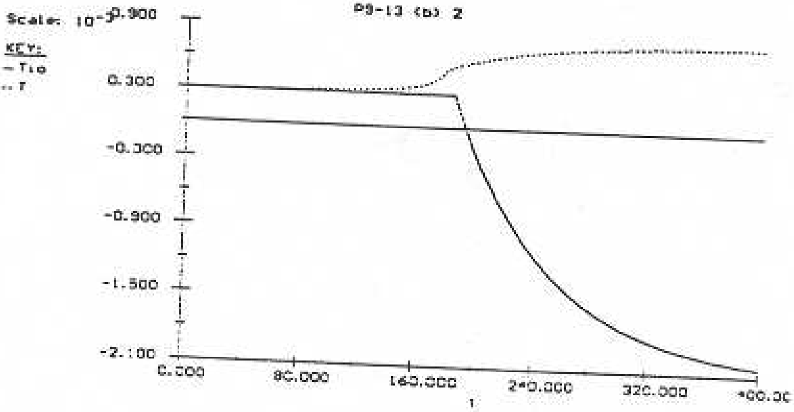
P-control : Tio = IF (T<550)THEN (300) ELSE (Tioo + kc.(T - Tsp))

where Tsp = 550 K, Tioo = 300 K, kc = -10

⇒ Tio manipulation not feasible for T control for any kc (requires Tio ~ - 2000 K)

P9-13 cont'd

```
P9-13 (b) 2
Equations:
d(Ca)/d(t)=((0.1-Ca)/tau)+ra                                        Initial value
d(Cb)/d(t)=((0.1-Cb)/tau)+ra                                        0.0001
d(Cc)/d(t)=((0-Cc)/tau)-ra                                          0.0001
d(T)/d(t)=((-2*Fao*(T-Tio))+(6000*(-ra*V)))/((15*Ca*V)+(1           0
   5*Cb*V)+(30*Cc*V))                                               300
tau=50
k=0.01*exp((10000/1.987)*((1/300)-(1/T)))
kc=-10
Tsp=550
vo=2
Tioo=300
ra=-k*Ca*Cb
Fao=0.1*vo
V=tau*vo
Tio=if(T<550)then(Tioo)else(Tioo+(kc*(T-Tsp)))
t0 = 0,    tf = 400
```



Try

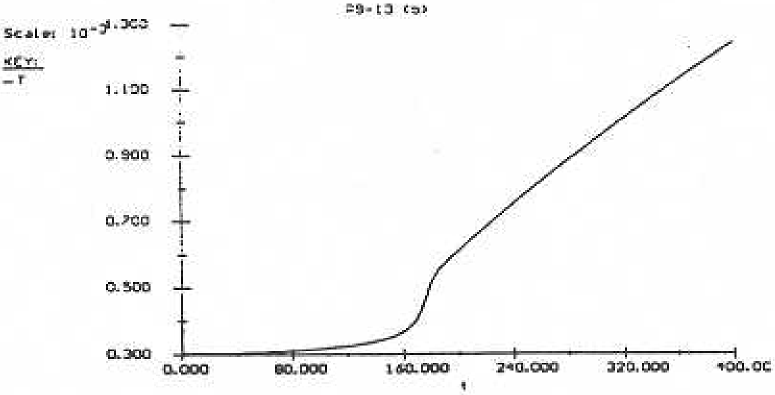
manipulated variable = υ_o (inlet volumetric flowrate)
controlled variable = T

P-control : υ_o = IF (T<550) THEN (2) ELSE (υ_{oo} + kc.(T - Tsp))

where Tsp = 550 K, $\upsilon_{oo} = 2\ dm^3$, kc = 10

⇒ T insensitive to υ_o for any kc

P9-13 cont'd



It is concluded that the addition of I-action will not improve control and that the only feasible control strategy is to add a heat exchange device , and to manipulate the coolant flowrate for T control.

P9-14$_B$

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

Part (a)

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

P9-14 cont'd

controlled variable = T

$$Fao = Faoo + \frac{kc}{\tau_I} I$$ where Faoo = 80 lb mol/h,

say kc = -0.2 , $\tau_I = 0.1$

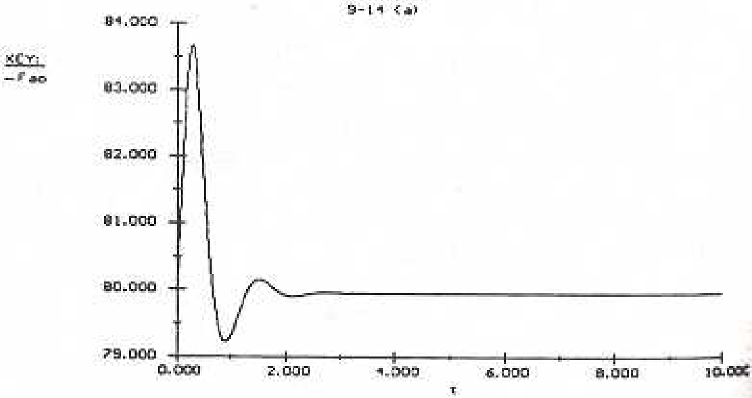
$$\frac{dI}{dt} = (T - Tsp)$$ Tsp = 138.5 °F

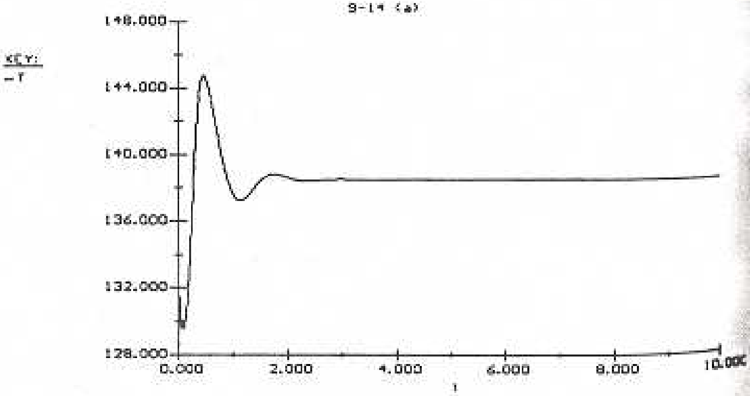
```
9-14 (a)
Equations:                                                           Initial value
d(Ca)/d(t)=((Fao-(Ca*vo))/V)+ra                                      0.0378
d(Cb)/d(t)=(((3.45-Cb)*vo)/V)+ra                                     2.12
d(Cc)/d(t)=(((0-Cc)*vo)/V)-ra                                        0.0144
d(Cm)/d(t)=(((Cmo-Cm)*vo)/V)                                         0.2269
d(T)/d(t)=((mc*18*(60-(T-(0.41111*(T-60)))))-(((Fao*35)+1           133.5
   9950)*(T-To))+(36000*(-ra*V)))/((35*Ca*V)+(18*Cb*V)+(4
   6*Ca*V)+(19.5*Cm*V))
d(I)/d(t)=T-Tsp                                                      0
V=(1/7.484)*500
Cmo=0.22696
mc=1000
To=75
Tsp=138.5
Cao=0.18157
k=16.96e12*exp(-32400/(1.987*(T+460)))
Cbo=2.2696
kc=-0.2
tauI=0.1
Faoo=80
ra=-k*Ca
Fao=Faoo+((kc/tauI)*I)
vo=(Fao/0.932)+354.8
t0 = 0,   tf = 10
```

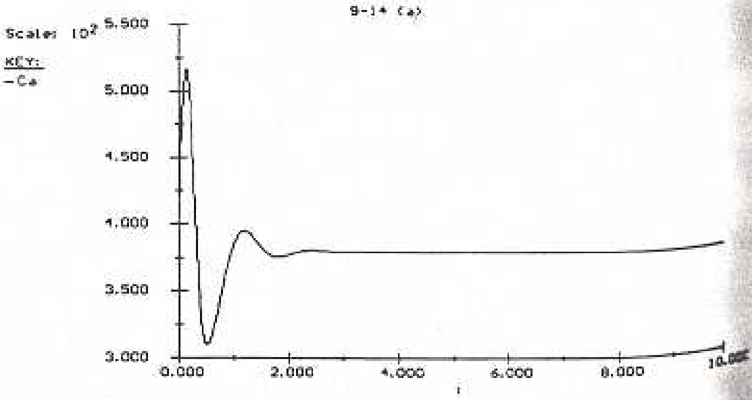
```
9-14 (a)
Variable      Initial value   Maximum value   Minimum value   Final value
t             0               10              0               10
Ca            0.0378          0.051674        0.0309845       0.0379292
Cb            2.12            3.30833         2.12            3.30646
Cc            0.0144          0.151372        0.0144          0.143535
Cm            0.2269          0.22696         0.2269          0.22696
T             133.5           144.771         129.556         138.5
I             0               0.391858        -1.83983        0.0248276
V             66.8092         66.8092         66.8092         66.8092
Cmo           0.22696         0.22696         0.22696         0.22696
mc            1000            1000            1000            1000
To            75              75              75              75
Tsp           138.5           138.5           138.5           138.5
Cao           0.18157         0.18157         0.18157         0.18157
k             19.8379         33.1033         16.5058         24.9561
Cbo           2.2696          2.2696          2.2696          2.2696
kc            -0.2            -0.2            -0.2            -0.2
```

P9-14 cont'd

```
tauI        0.1          0.1          0.1          0.1
Faoo        80           80           80           80
ra          -0.749871    -0.749871    -1.08581     -0.946566
Fao         80           83.6797      79.2163      79.9503
vo          440.637      444.585      439.796      440.584
```







P9-14 cont'd

Part (b)

I-control only : manipulated variable = T_o

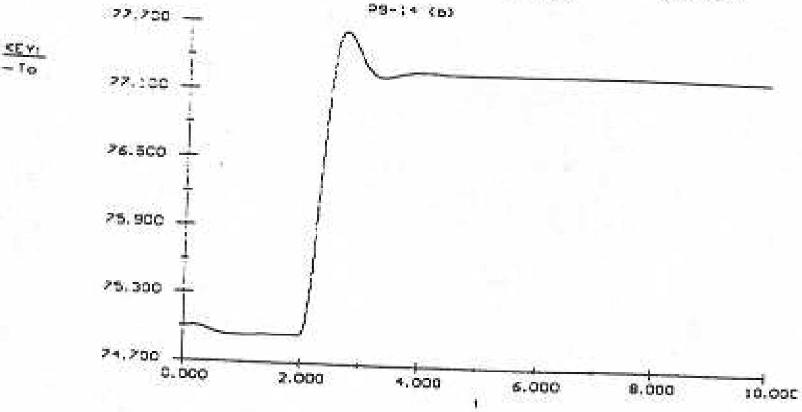
controlled variable = T

$$To = Too_o + \frac{kc}{\tau_I} I \qquad \text{where } Too = 75\ ^\circ F,$$

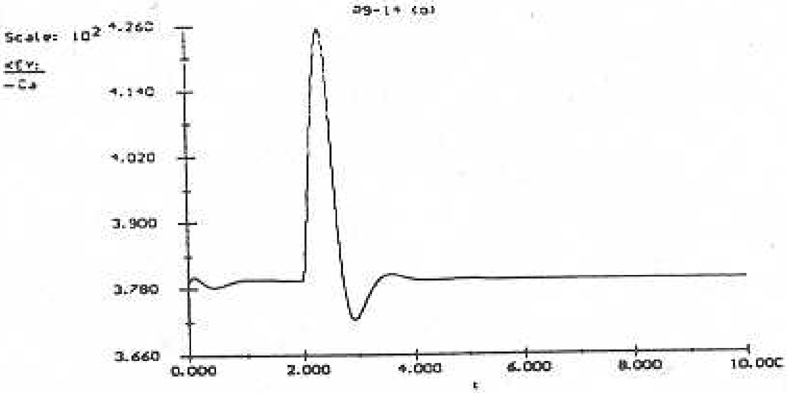
say kc = -0.2 , $\tau_I = 0.1$

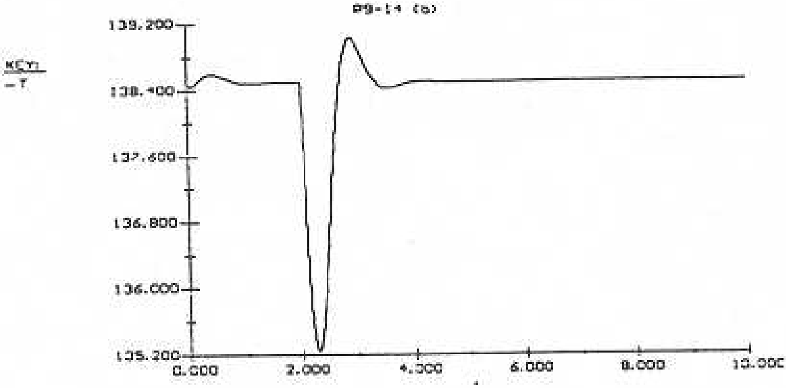
$$\frac{dI}{dt} = (T - Tsp) \qquad Tsp = 138.5\ ^\circ F$$

```
P9-14 (b)
Variable       Initial value  Maximum value  Minimum value  Final value
t              0              10             0              10
Ca             0.0378         0.0425433      0.0372412      0.0379524
Cb             3.3062         3.31097        3.30567        3.30638
Cc             0.0144         0.144329       0.0144         0.143618
Cm             0.2269         0.22696        0.2269         0.22696
T              138.5          139.035        135.24         138.5
I              0              0.032149       -1.31208       -1.13674
Cao            0.18157        0.18157        0.18157        0.18157
vo             440.6          440.6          440.6          440.6
V              66.8092        66.8092        66.8092        66.8092
Cmo            0.22696        0.22696        0.22696        0.22696
mc             1000           1000           1000           1000
Ta1            60             60             55             55
Tsp            138.5          138.5          138.5          138.5
k              24.9561        25.5704        21.4966        24.9561
Cbo            2.2696         2.2696         2.2696         2.2696
Too            75             75             75             75
kc             -0.2           -0.2           -0.2           -0.2
tauI           0.1            0.1            0.1            0.1
ra             -0.943341      -0.907591      -0.955192      -0.947144
To             75             77.6242        74.9357        77.2735
```



P9-14 cont'd


P9-14 (a)
Scale: 10²
KEY:
— Ca
4.260
4.140
4.020
3.900
3.780
3.660
0.000
2.000
4.000
6.000
8.000
10.000
t


P9-14 (b)
KEY:
— T
139.200
138.400
137.600
136.800
136.000
135.200
0.000
2.000
4.000
6.000
8.000
10.000

P9-15$_B$

CSTR

$$NH_4NO_3 \rightarrow N_2O + 2\,H_2O_g$$

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 :

P9-15 cont'd

$$\frac{dT}{dt}=\frac{Q-Ws-\sum mio.Cpi(T-Tio)-mco.(Hi-Hio)+(-\Delta Hrx)(-ra.V)}{\sum Mi.Cpi}$$

where $Ws = 0$

$Q = UA.(Ta - T)$

$\sum mio.Cpi.(T - Tio) = mao.Cpa.(T - Tio)$
$= 0.83 \times 310 \times 0.38 \times (T - 200)$

$mco.(Hi - Hio) = mco.[H_g(T) - H_l(Tio)]$
$= 0.17 \times 310 \times [(1202 + 0.47(T - 500)) - 168]$

assumes all liquid water in feed leaves as steam.

$H_g(T) = H_g(Tref) + Cpc.(T - Tref) = 1202 + 0.47.(T - 500)$
$H_l(200) = 168$ Btu /lb

$\sum Mi.Cpi = 0.38\ Ma + Cpb.Mb + 0.47\ Mc$

From ChemCAD III physical properties systems:

$$Cpb\ (N_2O, 516^{\circ}F) = 1065\ J/kg.K.\left(\frac{1}{1055}Btu\right).\left(0.454\frac{1}{kg}\right).\left(\frac{516F}{542K}\right)$$

$$= 0.44\ Btu/lb\ N_2O.\ K$$

$(-r_a V)$

Part (a)

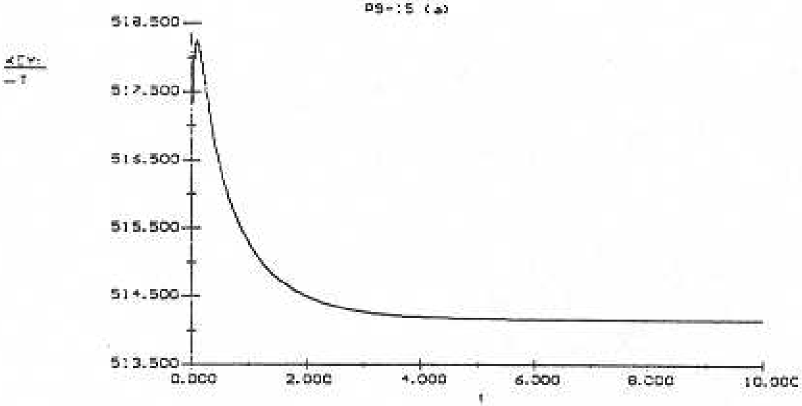
at $t = 0$ $Ca = 500$ lb, $T = 516\ ^{\circ}F$

$$\frac{dT}{dt}=\frac{10000.(515-T)-97.77(T-200)-52.7[(1202+0.47(T-500))-168]+336.(-ra.V)}{0.38Ma+0.44.Mb+0.47Mc}$$

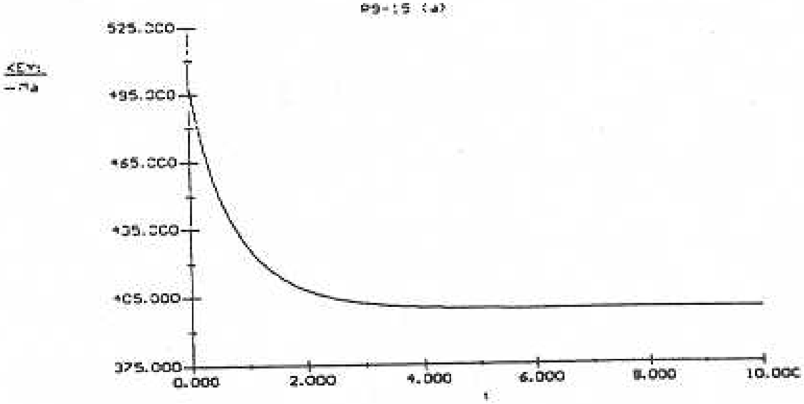
P9-15 cont'd

```
P9-15 (a)
Equations:                                                          Initial value
d(Ma)/d(t)=(310*0.83)+raV                                           500
d(Mb)/d(t)=-mb-raV                                                  0
d(Mc)/d(t)=mco-mc-(2*raV)                                           0
d(T)/d(t)=((10000*(515-T))-(99.77*(T-200))-(52.7*(1202+(0           516
    .47*(T-500)))-168)+(336*(-raV)))/((0.38*Ma)+(0.44*Mb)+
    (0.47*Mc))
mco=310*0.17
mao=310*0.83
k=0.53*exp(44540*((1/970)-(1/(T+460))))
raV=-k*Ma
mb=mao
mc=mco+(2*mao)
t0 = 0,    tf = 10
```

```
P9-15 (a)
Variable        Initial value   Maximum value   Minimum value   Final value
t               0               10              0               10
Ma              500             500             399.067         399.067
Mb              0               100.933         0               100.933
Mc              0               201.866         0               201.866
T               516             518.255         514.158         514.158
mco             52.7            52.7            52.7            52.7
mao             257.3           257.3           257.3           257.3
k               0.702859        0.78083         0.644758        0.644758
raV             -351.43         -257.301        -382.097        -257.301
mb              257.3           257.3           257.3           257.3
mc              567.3           567.3           567.3           567.3
```



P9-15 cont'd



Part (b)

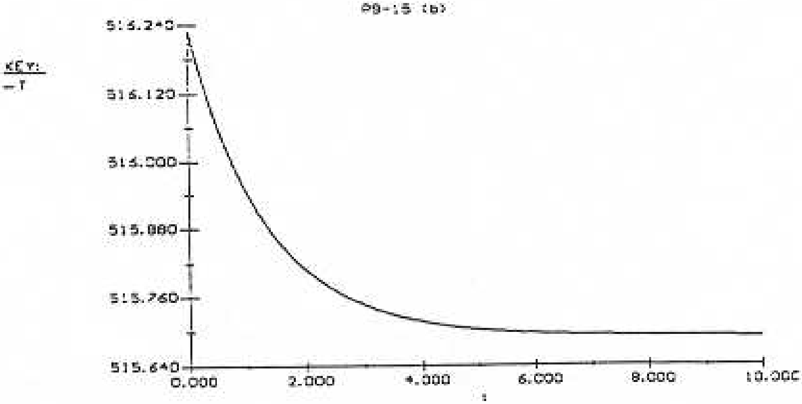
$UA = 10000\ Btu/h.ft^2$

P-control only :

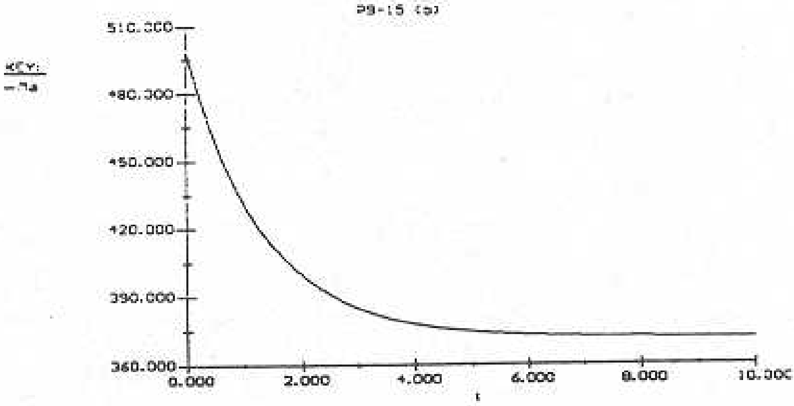
manipulated variable = Ta
controlled variable = T

$Ta = Tao + kc.(T - Tsp)$

where Tsp = 516 °F, kc = -5, Tao = 975 °R = 515 °F



P9-15 cont'd



Part (c)

UA = 10000 Btu /h.ft^2

PI-control : manipulated variable = Ta
controlled variable = T

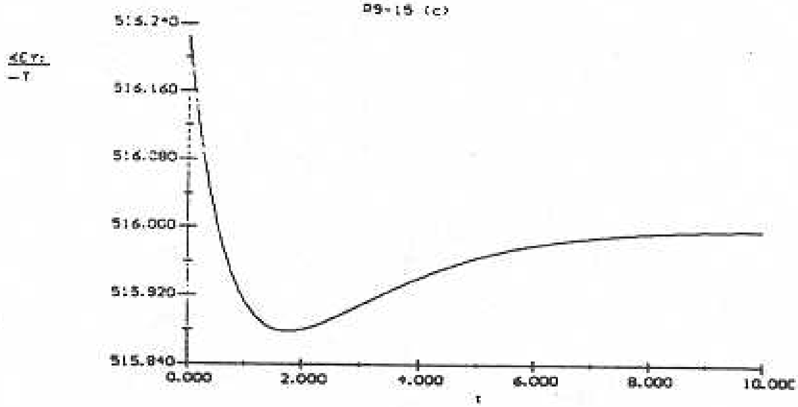
$$Ta = Tao + kc.(T - Tsp) + \frac{kc}{\tau_I}.I$$

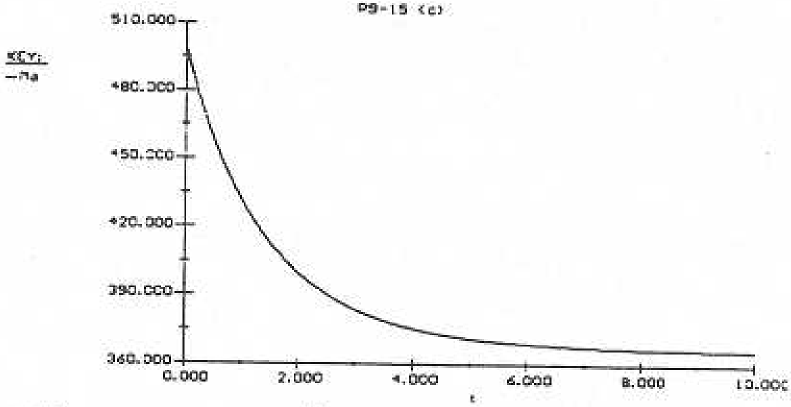
$$\frac{dI}{dt} = (T - Tsp)$$

where Tsp = 516 °F, kc = -5, τ_I = 1, Tao = 975 °R = 515 °F

```
P9-15 (c)
Variable          Initial value  Maximum value  Minimum value  Final value
t                 0              10             0              10
Ma                500            500            366.32         366.32
Mb                0              133.68         0              133.68
Mc                0              267.359        0              267.359
T                 516            516.228        515.878        515.998
I                 0              0.055709       -0.369513      -0.369513
M                 500            767.359        500            767.359
Tsp               516            516            516            516
k                 0.702859       0.710394       0.698867       0.702792
Tao               515            515            515            515
maoo              310            310            310            310
mao               257.3          257.3          257.3          257.3
kc                -5             -5             -5             -5
tauI              1              1              1              1
raV               -351.43        -257.447       -354.393       -257.447
mb                257.3          257.3          257.3          257.3
```

P9-15 cont'd





Part (d)

UA = 10000 Btu /h.ft^2

PI-control loop 1 : manipulated variable = Ta
controlled variable = T

$$Ta = Tao + kc1.(T - Tsp) + \frac{kc1}{\tau I1}.I1$$

$$\frac{dI1}{dt} = (T - Tsp)$$

where Tsp = 516 °F, kc1 = -5, $\tau_I 1$ = 1, Tao = 975 °R = 515 °F

PI-control loop 2 : manipulated variable = mao
controlled variable = M (= Ma + Mb + Mc)

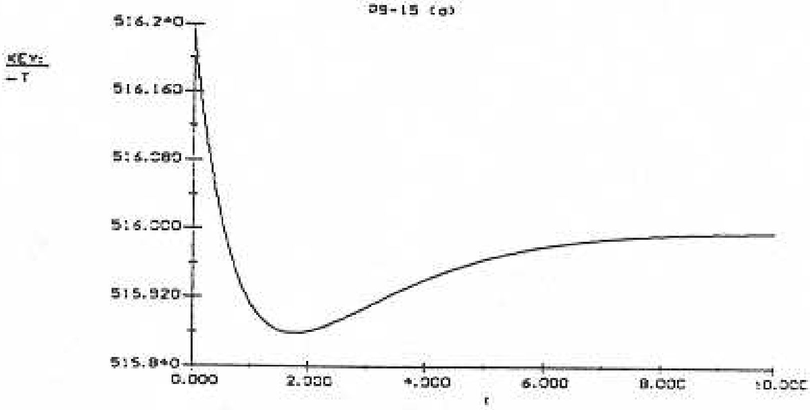
P9-15 cont'd

$$mao = maoo + kc2.(M - Msp) + \frac{kc2}{\tau I2}.I2$$

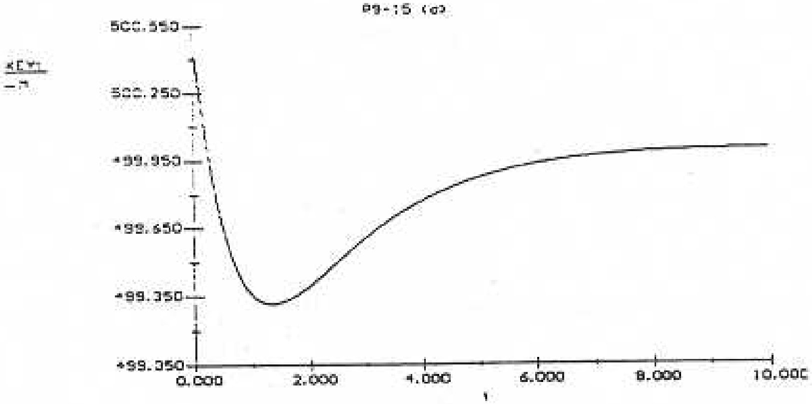
$$\frac{dI2}{dt} = (M - Msp)$$

where Msp = 500 lb, kc2 = 25, τ_I 2 = 1, maoo = 310 lb/h

```
P9-15 (d)
Variable          Initial value   Maximum value   Minimum value   Final value
t                 0               10              0               10
Ma                500             500             366.32          366.32
Mb                0               44.5579         0               44.5579
Mc                0               89.1157         0               89.1157
T                 516             516.228         515.878         515.998
I2                0               0.055698        -2.09812        -2.09812
I1                0               0.0556442       -0.369506       -0.369506
M                 500             500.416         499.317         499.994
Msp               500             500             500             500
Tsp               516             516             516             516
k                 0.702859        0.710395        0.69887         0.702792
Tao               515             515             515             515
maoo              310             310             310             310
kc2               25              25              25              25
kc1               -5              -5              -5              -5
tauI1             1               1               1               1
tauI2             1               1               1               1
raV               -351.43         -257.447        -354.394        -257.447
Ta                515             516.858         513.843         516.858
mao               310             320.708         257.397         257.397
mb                310             320.708         257.397         257.397
mco               63.494          65.6872         52.7198         52.7198
mc                683.494         707.104         567.513         567.513
```



P9-15 cont'd



P9-16

a) Plot R(T) vs G(T):

$$R(T) = UA(T - T_a) + \rho v_0 C_p (T - T_0)$$
$$G(T) = -\Delta H_{Rx} VkC_A$$

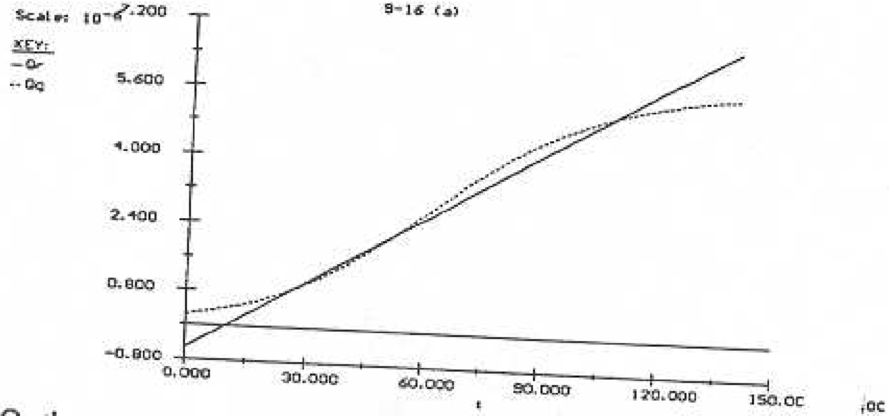
Evaluate the parameters in those equations:

$$k = 2 * 7.08 * 10^{11} \exp(-30000/1.987/T)$$
$$\Delta H_{RX} = -30000 BTU/lbmol$$
$$\rho = 50 lb/ft^3$$
$$UA = 150 * 250 = 37500$$

Use the following POLYMATH program to achieve the correct graph.

P9-16 cont'd

```
Equations:                                                    Initial value
d(T)/d(t)=1                                                   520
dhrxn=-30000
V=48
Cao=0.5
vo=400
UA=250*150
Ta=530
rho=50
Cp=.75
To=530
E=30000
k=2*7.08*10^11*exp(-E/1.987/T)
tau=V/vo
Ca=Cao/(1+tau*k)
Qr=UA*(T-Ta)+rho*vo*Cp*(T-To)
Qg=-dhrxn*V*k*Ca
delta=Qr-Qg
t0 = 0,     tf = 140
```



b) On the graph we can see that there are three steady states. We can use the following POLYMATH program to find the exact numbers of the steady-state with the design equation for a CSTR and the temperatures at which G(T) and R(T) intersect.

$$V = \frac{v_0 \left(C_{A0} - C_A \right)}{k C_A}$$

$$R(T) - G(T) = 0$$

P9-16 cont'd

```
Equations:
f(Ca)=vo*(cao-Ca)/V-k*Ca
f(T)=Qr-Qg
vo=400
cao=.5
V=48
E=30000
UA=150*250
Ta=530
rho=50
To=530
Cp=.75
dhrxn=-30000
k=2*7.08&10^11*exp(-E/1.987/T),
Qg=-dhrxn*V*k*Ca
Qr=UA*(T-Ta)+rho*vo*(T-To)*Cp
```

```
                        9-16 b
                       Solution
Variable               Value              f()
Ca                     0.446429           -2.22e-16
T                      542.245            -2.91e-09
vo                     400
cao                    0.5
V                      48
E                      30000
UA                     37500
Ta                     530
rho                    50
To                     530
Cp                     0.75
dhrxn                  -30000
k                      1
Qg                     642857
Qr                     642857
```

```
                       Solution
Variable               Value              f()
Ca                     0.319474           -7.117e-15
T                      571.263            -8.382e-09
vo                     400
cao                    0.5
V                      48
E                      30000
UA                     37500
Ta                     530
rho                    50
To                     530
Cp                     0.75
dhrxn                  -30000
k                      4.72895
Qg                     2.16632e+06
Qr                     2.16632e+06
```

```
                       Solution
Variable               Value              f()
Ca                     0.0684294          -5.292e-15
T                      628.645            -6.519e-09
vo                     400
cao                    0.5
V                      48
E                      30000
UA                     37500
Ta                     530
rho                    50
To                     530
Cp                     0.75
dhrxn                  -30000
k                      52.5567
Qg                     5.17885e+06
Qr                     5.17885e+06
```

The exact values are: $C_A = 0.425$ $T = 547.1°R$
$C_A = 0.319$ $T = 571.3°R$
$C_A = 0.068$ $T = 628.6°R$

The extinction temperature is around 555°R

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:

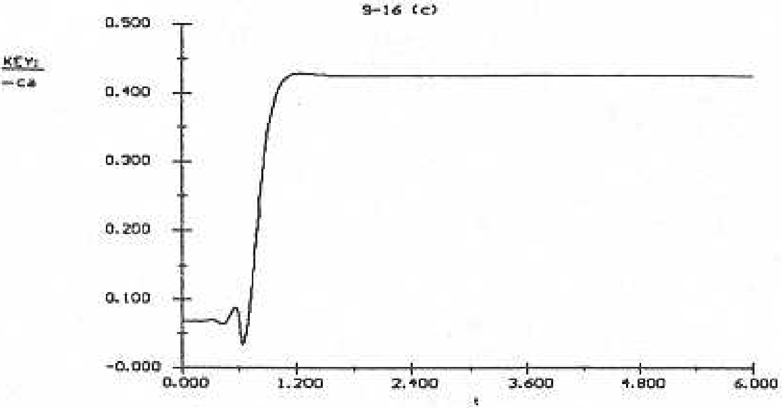
$$\frac{dT}{dt} = \frac{UA(T_a - T) - \rho v_0 C_p (T - T_0) - \Delta H_{Rx} k C_A V}{\rho V C_p}$$

From these we can plug into POLYMATH and come up with the following graphs.

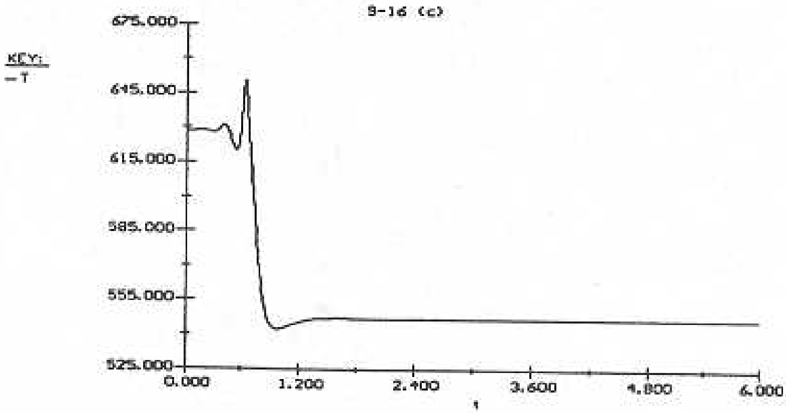
P9-16 cont'd

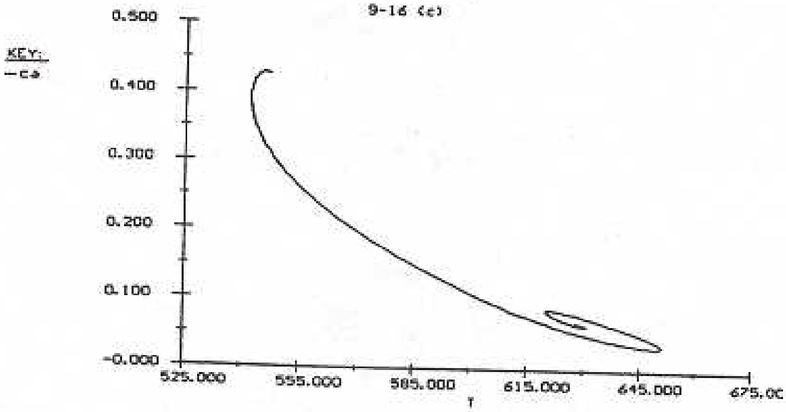
```
Equations:                                                   Initial value
d(ca)/d(t)=vo*(cao-ca)/V-k*ca                                0.0684
d(T)/d(t)=(UA*(Ta-T)-rho*vo*Cp*(T-To)-dhrxn*k*ca*V)/(rho*    628.645
   V*Cp)
d(T1)/d(t)=(J*tau*k*ca-(1+kappa)*(T-Tc))/tau                 628.645
vo=400
cao=.5
V=48
UA=250*150
Ta=530
rho=50
Cp=.75
To=530
dhrxn=-30000
E=30000
R=1.987
k=2*7.08*10^11*exp(-E/R/T)
 tau=V/vo
 J=-dhrxn/rho/Cp
 kappa=UA/rho/vo/Cp
 Tc=(Ta-kappa+To)/(1+kappa)
```

$t_0 = 0, \quad t_f = 6$

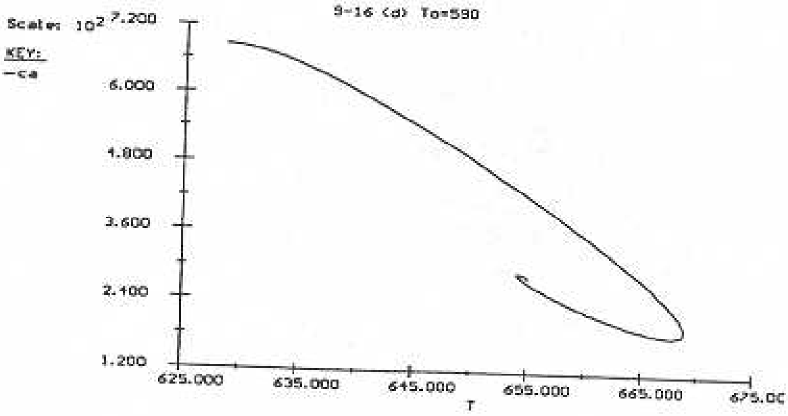


P9-16 cont'd

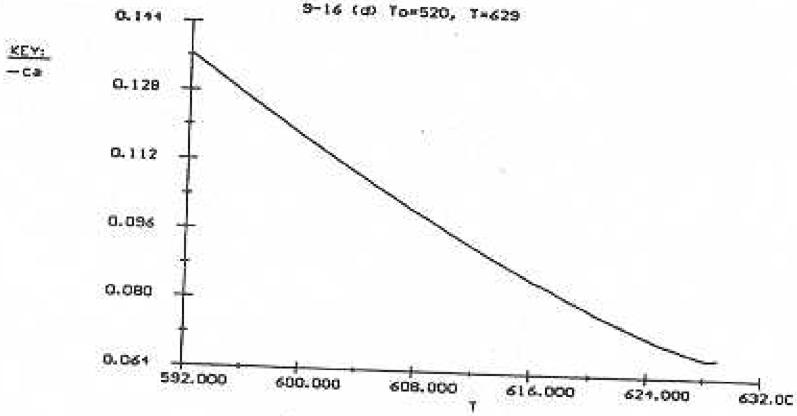


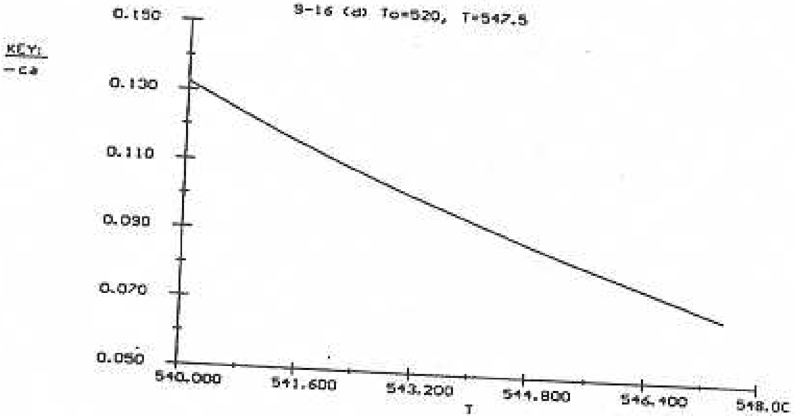


d) By varying to T = 547.5°R we get the following graphs which show a stable steady-state.



P9-16 cont'd





Varying $T_0 = 590$ shows that it is an unstable steady-state.

$T_0 = 520$, $T = 629$ it stabilizes towards the lower steady-state.

$T_0 = 520$, $T = 547.5$ is stable.

e) The graphs for C_A and T have already been created so we just need equations for x1 and y1.

$$\frac{dx}{dt} = \frac{-L*x + \frac{N}{J}y}{\tau}$$

$$\frac{dy}{dt} = \frac{J(1-L)x - (M-N)y}{\tau}$$

where

$L = 7.1$

$N = 14.21$

P9-16 cont'd

$$J = \frac{-\Delta H_{Rx}}{\rho C_p}$$

$$M = 3.5$$

$$\tau = \frac{V}{v_0}$$

then

$$x1 = \frac{x}{0.0684}$$

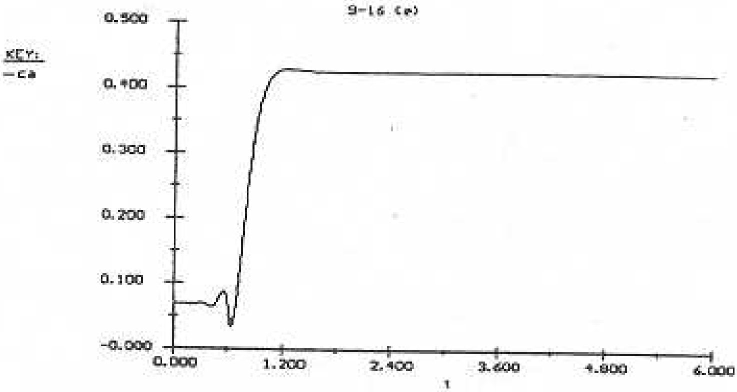
$$y1 = \frac{y}{628}$$

Plugging this into POLYMATH gives the following graphs.

```
9-16 (e)
Equations:                                                    Initial value
d(ca)/d(t)=vo*(cao-ca)/V-k*ca                                 0.0684
d(T)/d(t)=(UA*(Ta-T)-rho*vo*Cp*(T-To)-dhrxn*k*ca*V)/(rho*     628.645
   V*Cp)
d(x)/d(t)=(-L*x+N/J*y)/tau                                    -0.02
d(y)/d(t)=(J*(1-L)*x-(M*N)*y)/tau                             -2
vo=400
cao=.5
V=48
UA=150*250
Ta=530
rho=50
Cp=.75
To=530
dhrxn=-30000
L=7.1
N=14.21
M=3.5
E=30000
y1=y/628
x1=x/.0684
k=2*7.08*10^11*exp(-E/1.987/T)
tau=V/vo
J=-dhrxn/rho/Cp
```

$t_0 = 0, \quad t_f = 6$

P9-16 cont'd

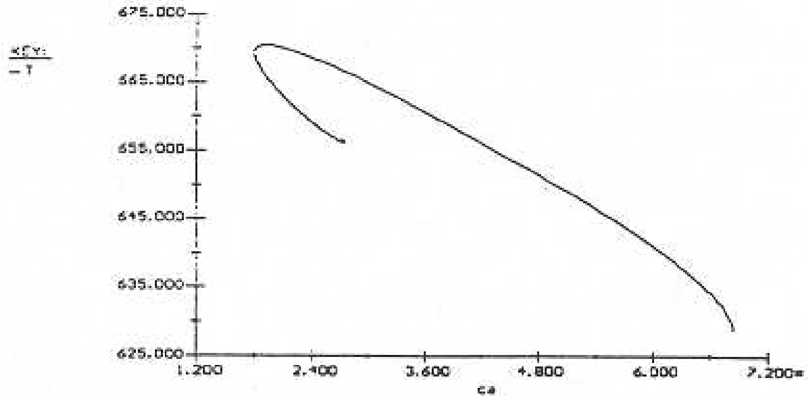


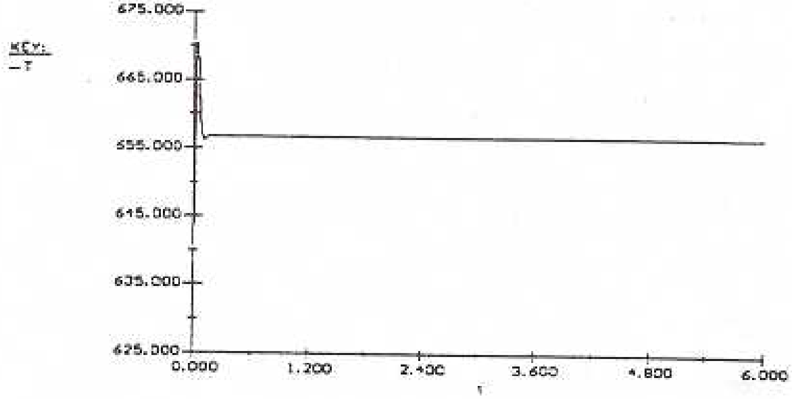
f) No solution will be given.

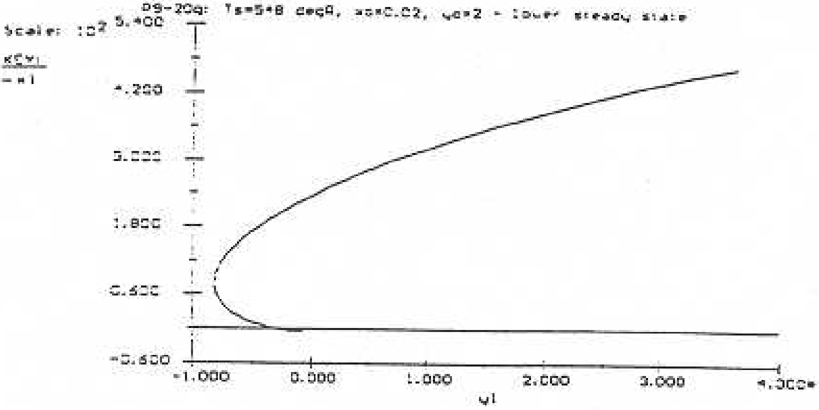
g) The following POLYMATH program gives the linear analysis of the problem.
L = 1.021, M = 2.51, N = 2.51, $\tau = .12$, J = 800

```
9-16 (g)
Equations:                                                            Initial value
d(ca)/d(t)=vo*(cao-ca)/V-k*ca                                         0.0684
d(T)/d(t)=(UA*(Ta-T)-rho*vo*Cp*(T-To)-dhrxn*k*ca*V)/(rho*             628.645
   V*Cp)
d(x)/d(t)=(-L*x+N/J*y)/tau                                            0.02
d(y)/d(t)=(J*(1-L)*x-(M*N)*y)/tau                                     2
vo=400
cao=.5
V=48
UA=150*250
Ta=530
rho=50
Cp=.75
To=595
dhrxn=-30000
L=1.021
N=2.51
M=3.5
E=30000
A=2*7.08*10^11
Cas=0.04253
Ts=547
k=2*7.08*10^11*exp(-E/1.987/T)
y1=y/Ts
x1=x/Cas
tau=V/vo
J=-dhrxn/rho/Cp
c=L*M-N
b=L+M-N
kappa=UA/rho/vo/Cp
Tc=(Ta*kappa-To)/(1+kappa)
Qg=J*tau*k*ca/tau
Qr=(1+kappa)*(T-Tc)/tau
t_0 = 0,   t_f = 6
```

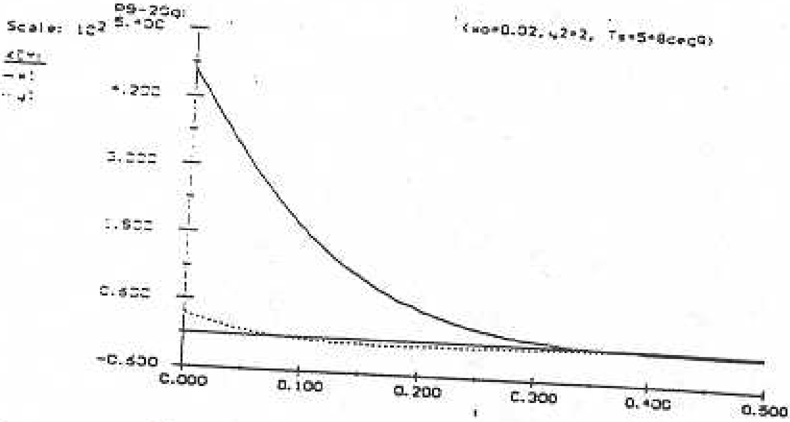
P9-16 cont'd

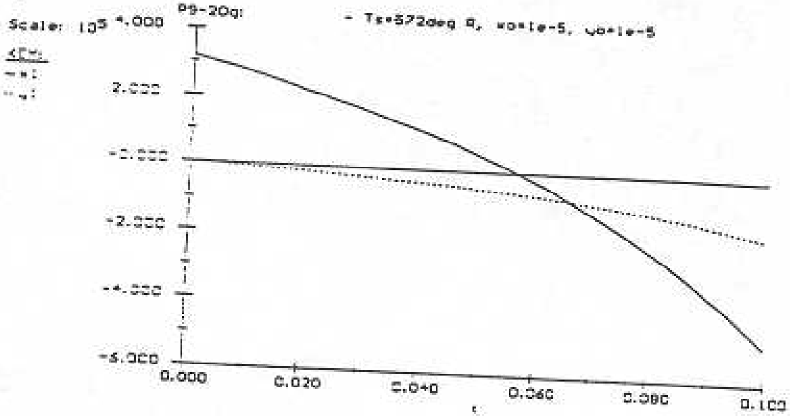

KEY:
— T
675.000
665.000
655.000
645.000
635.000
625.000
1.200
2.400
3.600
4.800
6.000
7.200*
ca

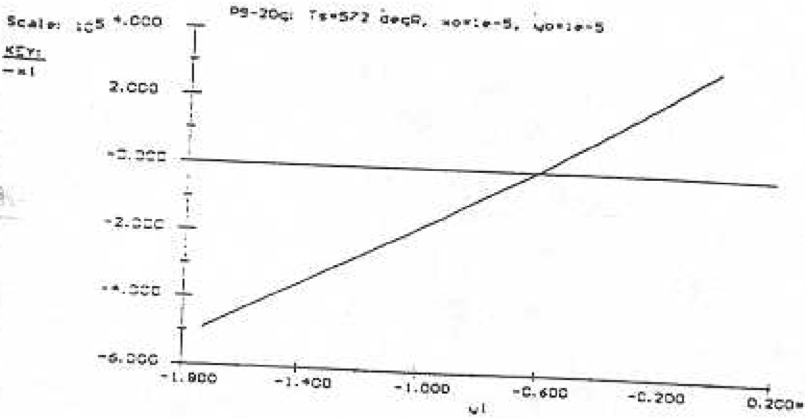

KEY:
— T
675.000
665.000
655.000
645.000
635.000
625.000
0.000
1.200
2.400
3.600
4.800
6.000
t


P9-20a: Ts=548 degR, xo=0.02, yo=2 - lower steady state
Scale: 10^2
KEY:
— x1
5.400
4.200
3.000
1.800
0.600
-0.600
-1.000
0.000
1.000
2.000
3.000
4.000*
y1

P9-16 cont'd


P9-20g:
(xo=0.02, y2=2, Ts=5*8degQ)
Scale: 10^2
KEY:
x:
y:
5.400
4.200
3.000
1.800
0.600
-0.600
0.000
0.100
0.200
0.300
0.400
0.500
t


P9-20g:
Ts=572deg R, xo=1e-5, yo=1e-5
Scale: 10^5
KEY:
x:
y:
4.000
2.000
0.000
-2.000
-4.000
-6.000
0.000
0.020
0.040
0.060
0.080
0.100
t


P9-20g: Ts=572 degR, xo=1e-5, yo=1e-5
Scale: 10^5
KEY:
x
4.000
2.000
0.000
-2.000
-4.000
-6.000
-1.800
-1.400
-1.000
-0.600
-0.200
0.200
y

P9-17$_B$

Batch reactor - series reaction

Mol balance on A :

$$\frac{dCa}{dt} = ra1$$

$-ra1 = k1.Ca$ Ca = Cao.exp(-k1.t)

Mol balance on B :

$$\frac{dCb}{dt} = rb1 + rb2$$

$rb1 = -ra1 = k1.Ca$ and $-rb2 = k2.Cb$

$$\frac{dCb}{dt} = k1.Cao.\exp(-k1.t) - k2Cb$$

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 :

$$\frac{dT}{dt} = \frac{Q + (-\Delta Hrxa1)(-ra1.V) + (-\Delta Hrxb2)(-rb2.V)}{\sum Ni.Cpi}$$

$Q = UA.(Ta - T)$

$\Sigma Ni.Cpi = Ca.V.Cpa + Cb.V.Cpb + Cc.V.Cpc$

$$\frac{dT}{dt} = \frac{UA.(330 - T) + 55000(-ra1.V) + 71500(-rb2.V)}{200.V.(Ca + Cb + Cc)}$$

P9-17 cont'd

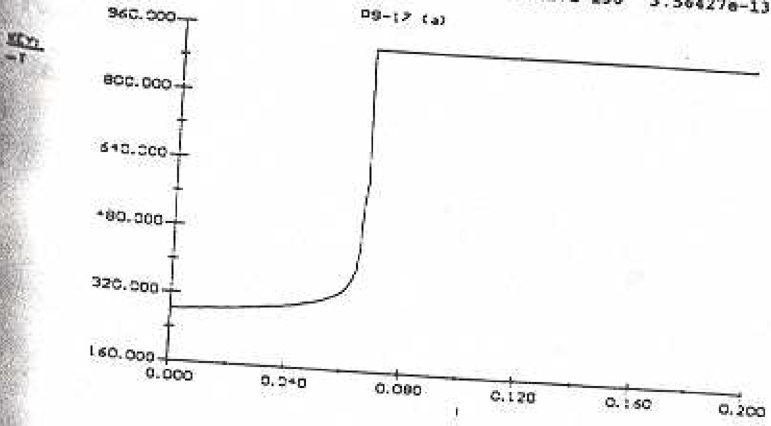
Part (a)

UA = 0

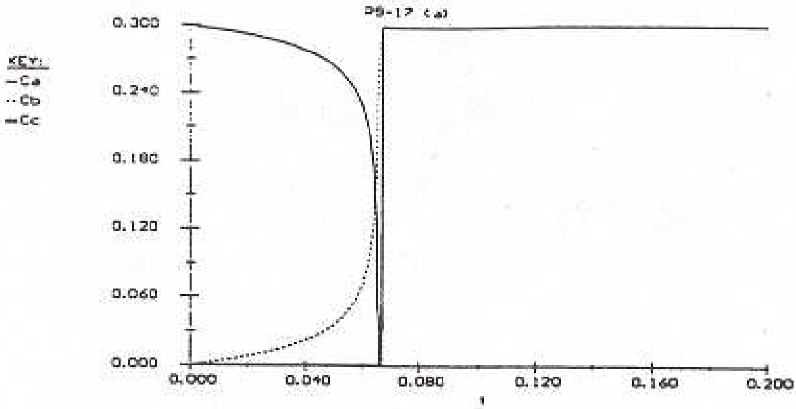
$$\frac{dT}{dt} = \frac{V[55000(-ra1.) + 71500(-rb2.)]}{200.V.(Ca + Cb + Cc)}$$

```
P9-17 (a)
Equations:                                                                     Initial value
d(Ca)/d(t)=ra1                                                                 0.3
d(Cc)/d(t)=-rb2                                                                0
d(Cb)/d(t)=rb1+rb2                                                             0
d(T)/d(t)=((UA*(330-T))+(55000*(-ra1*V))+(71500*(-rb2*V))
    )/(200*V*(Ca+Cb+Cc))                                                       283
UA=0
V=10
k1=3.03*exp((9900/1.987)*((1/300)-(1/T)))
k2=4.58*exp((27000/1.987)*((1/500)-(1/T)))
ra1=-k1*Ca
rb2=-k2*Cb
rb1=-ra1
t0 = 0,   tf = 0.2
```

```
P9-17 (a)
Variable      Initial value   Maximum value    Minimum value    Final value
t             0               0.2              0                0.2
Ca            0.3             0.3              1.66467e-141     1.66467e-141
Cc            0               0.3              0                0.3
Cb            0               0.286701         0                4.30972e-142
T             283             915.5            283              915.5
UA            0               0                0                0
V             10              10               10               10
k1            1.1173          214113           1.1173           214113
k2            4.08097e-09     1.04114e+06      4.08097e-09      1.04114e+06
ra1           -0.335189       -3.56427e-136    -144.724         -3.56427e-136
rb2           -0               -0               -18607.3         -4.48704e-136
rb1           0.335189        144.724          3.56427e-136     3.56427e-136
```

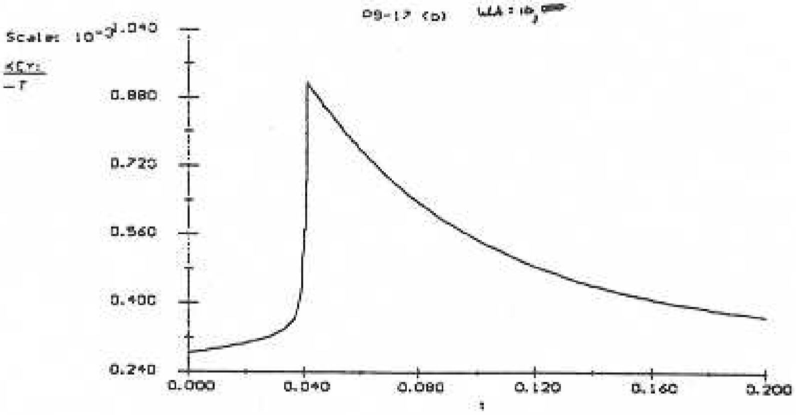


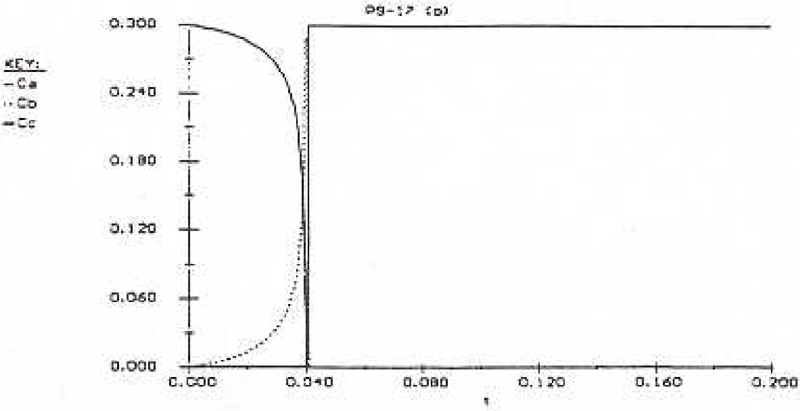
P9-17 cont'd



Part (b)

UA = 10000 J/min.K V = 10 dm^3

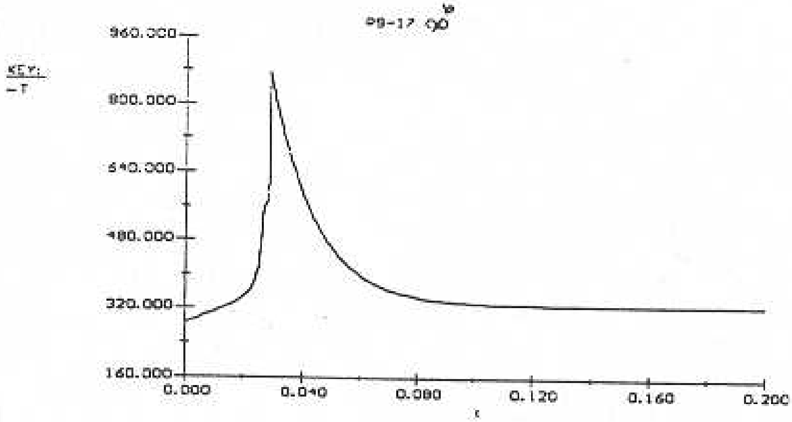


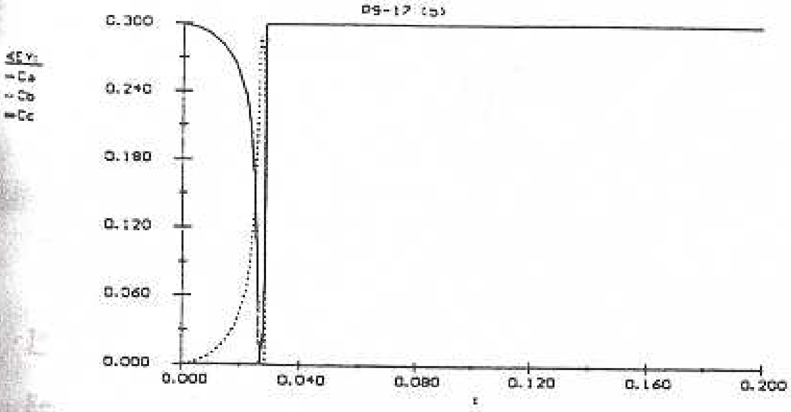


P9-17 cont'd

Part (b)

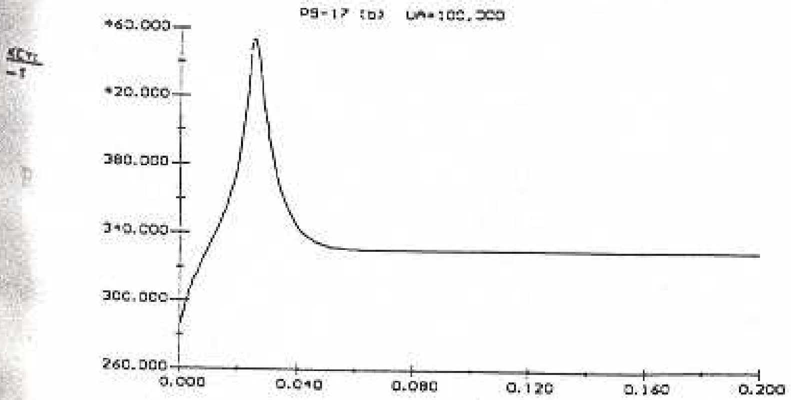
UA = 40000 J/min.K V = 10 dm^3



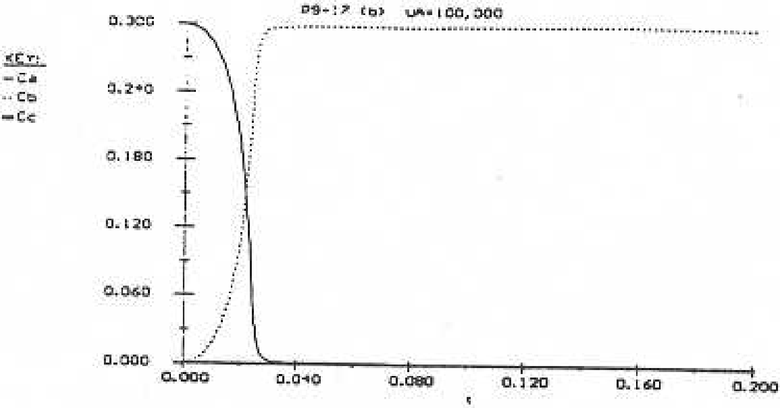


Part (b)

UA = 100000 J/min.K V = 10 dm^3



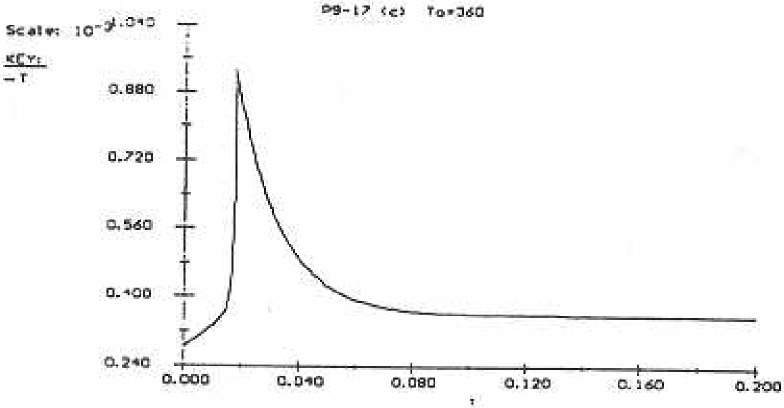
P9-17 cont'd

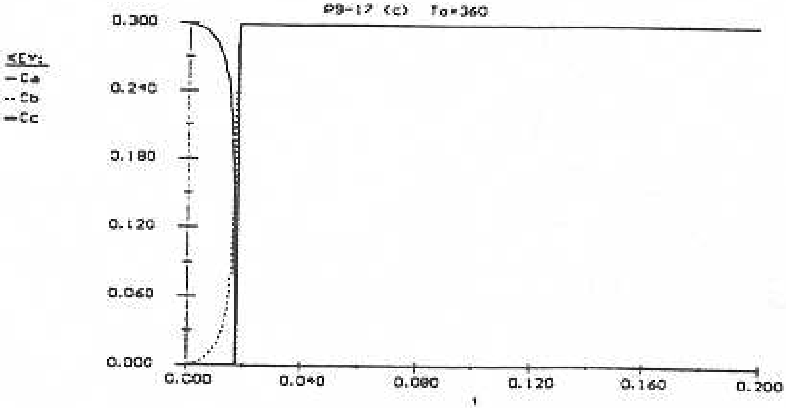


At UA = 10 0000 J/min.K the 2nd reaction for C is totally suppressed

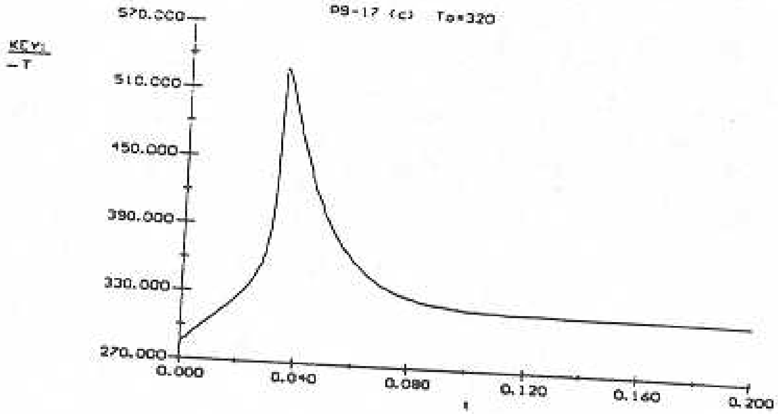
Part (c)

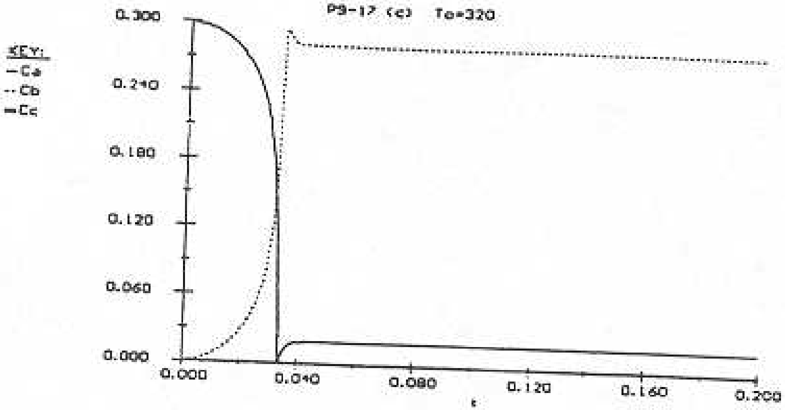
UA = 40000 J/min.K   To = 320 K





P9-17 cont'd





P9-18$_B$

Semibatch with parallel reactions

Mol balance :

$$\frac{dNa}{dt} = Fao + (r1 + r2).V \qquad \frac{dNb}{dt} = Fbo + (r1 + r2).V$$

$$\frac{dNd}{dt} = -r1.V \qquad \frac{dNu}{dt} = -r2.V$$

Rate laws :

$$-r1 = k1.Ca \qquad -r2 = k2.Cb$$

$$k1 = 1000.\exp\left(-\frac{2000}{T}\right) \qquad k1 = 2000.\exp\left(-\frac{3000}{T}\right)$$

P9-18 cont'd

Stoichiometry :

$$Ca = \frac{Na}{V} \qquad Cb = \frac{Nb}{V}$$

$$Cd = \frac{Nd}{V} \qquad Cu = \frac{Nu}{V}$$

$V = Vo + \upsilon a.t + \upsilon b.t$ assume Vo = 0

$$\upsilon a = \frac{Fao}{Cao} \qquad \upsilon b = \frac{Fbo}{Cbo}$$

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

P9-18 **cont'd**

$$\frac{dT}{dt}=\frac{20.Fao(T-Tao)+30.Fbo.(T-Tbo)+3000.(-r1.V)+[5000+10(T-300)](-r2.V)}{20.Na+30.Nb+50.Nd+40.Nu}$$

Selectivity $S=\frac{r1}{r2}$

Part (a)

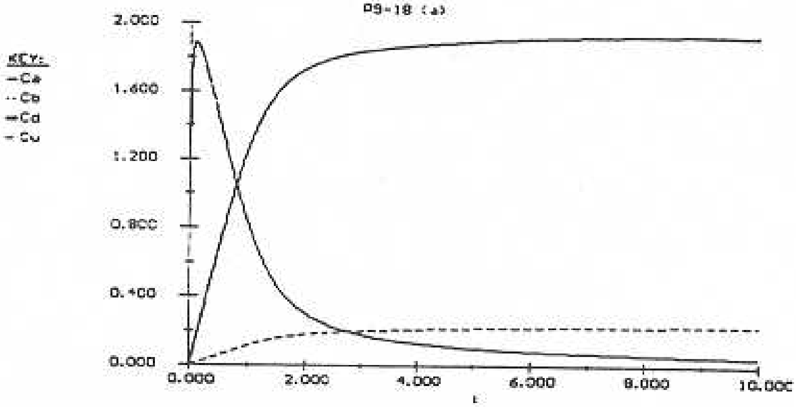
The selectivity is insensitive to υo and To (as the reactor is initially empty) but it is sensitive to Tio. The ratio of k1 to k2 dictates S, and from the given relationships between k1 and k2 with T, it is seen that a lower operating temperature is preferable for increased selectivity for D over U. Therefore ambient temperature feed is used (although cooling may increase the 1st reaction, extra costs would be incurred.)

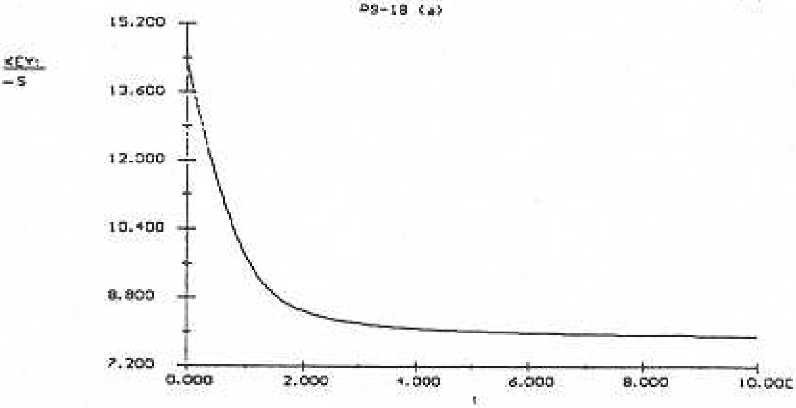
Choose Ti = 298 K Tao = 298 K Tbo = 298 K υo = 20 mol/min

```
P9-18 (a)
Equations:                                                          Initial value
d(Na)/d(t)=((r1+r2)*V)+Fao                                          0.001
d(Nb)/d(t)=((r1+r2)*V)+Fbo                                          0.001
d(Nd)/d(t)=-r1*V                                                    0
d(Nu)/d(t)=-r2*V                                                    0
d(T)/d(t)=((-20*Fao*(T-Tao))-(30*Fao*(T-Tbo))+(3000*(-r1*           298
   V))+((5000+(10*(T-300)))*(-r2*V)))/((20*Na)+(50*Nd)+(4
   0*Na))
Tao=298
Tbo=298
k1=1000*exp(-2000/T)
k2=2000*exp(-3000/T)
vo=20
Fao=vo/0.45
V=0.45*Fao*t
Fbo=Fao
Ca=Na/V
Cb=Nb/V
Cd=Nd/V
Cu=Nu/V
r1=-k1*Cb
r2=-k2*Cb
S=r1/r2
t0 = 0.01,   tf = 10
```

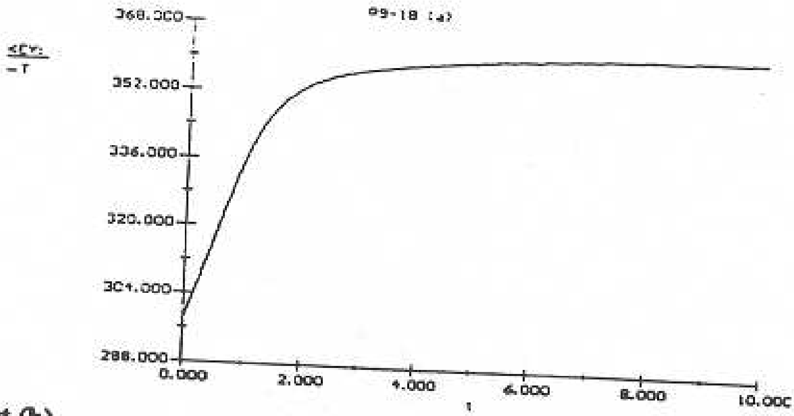
P9-18 cont'd

```
P9-18 (a)
Variable         Initial value   Maximum value   Minimum value   Final value
t                0.01            10              0.01            10
Na               0.001           17.0418         0.001           9.86331
Nb               0.001           17.0418         0.001           9.86331
Nd               0               387.317         0               387.317
Nu               0               46.8212         0               46.8212
T                298             362.267         298             362.267
Tao              298             298             298             298
Tbo              298             298             298             298
k1               1.21695         4.00271         1.21695         4.00271
k2               0.0849059       0.506478        0.0849059       0.506478
vo               20              20              20              20
Fao              44.4444         44.4444         44.4444         44.4444
V                0.2             200             0.2             200
Fbo              44.4444         44.4444         44.4444         44.4444
Ca               0.005           1.88957         0.005           0.0493165
Cb               0.005           1.88957         0.005           0.0493165
Cd               0               1.93658         0               1.93658
Cu               0               0.234106        0               0.234106
r1               -0.00608474     -0.00608474     -2.70229        -0.1974
r2               -0.00042453     -0.00042453     -0.235535       -0.0249777
S                14.3329         14.3329         7.90302         7.90302
```





P9-18 cont'd



Part (b)

Let the rate laws be :

$-r1 = k1.Cb$ $-r2 = k2.Ca$

$\Rightarrow$ No change in the system. ($S \sim 7.8$)

Let the rate laws be :

$-r1 = k1.Ca.Cb$ $-r2 = k2.Ca.Cb$
$-r1 = k1.Ca$ $-r2 = k2.Ca$
$-r1 = k1.Cb$ $-r2 = k2.Cb$

$\Rightarrow$ Small selectivity increase. ($S \sim 8$)

Let the rate laws be :

$-r1 = k1.Ca.Cb$ $-r2 = k2.Ca$
$-r1 = k1.Ca.Cb$ $-r2 = k2.Cb$

$\Rightarrow$ Large selectivity decrease. ($S \sim 1.3$)

Let the rate laws be :

$-r1 = k1.Ca$ $-r2 = k2.Ca.Cb$
$-r1 = k1.Cb$ $-r2 = k2.Ca.Cb$

$\Rightarrow$ Huge selectivity increase. ($S \sim 138$)

The decreasing concentrations of A and B (below 1.0) with time act to suppress the reaction rates to varying degrees depending on the order. A 2nd order reaction is suppressed much more than a 1st order reaction, hence the large selectivity in the latter two instances where the second reaction is second order.

P9-18 cont'd

Part (c)

ΔH_{rx1} cal/mol A	ΔH_{rx2}(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 ΔH_{rx2} is constant , then if ΔH_{rx1} increases, T increases and S decreases.
If ΔH_{rx1} is constant , then if ΔH_{rx2}(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.

Chapter 10

P10-1. An open-ended problem that requires students to create and original problem and solution.

P10-2. "What if. . ." problem. A number of parts to this problem require descriptive answers. Part **(h)** involves a parameter sensitivity of **Living Example Problem** 10-7.

P10-3. This problem is quite straight forward and is often used as an introduction problem on catalysis.

Problems **P10-4**, **P10-5**, **P10-6**, **P10-8**, **P10-9**, and **P10-10** all give data and ask the student to find the rate law, mechanism, and rate limiting step for a catalytic reaction. I would choose one problem from **P10-4** through **P10-6** and one problem from **P10-8** through **P10-10**. First choices might be **P10-6** and **P10-8** which are the most straight forward.

P10-7. This problem is similar to **P10-3**, but is more complicated.

P10-11. This problem is better adapted for a senior or graduate level course.

Problems **P10-12** through **P10-14** all concern chemical vapor deposition where the student is asked to find the rate law, mechanism and rate limiting step. In the past **P10-13** has been assigned as a homework problem and **P10-14** as a problem worked in class.

P10-15. California problem.

P10-16. This problem uses **Living Example Problem** E10-5 to apply to a moving bed reactor and to a PBR modeled as CSTRs in series. It is fairly advanced and may be best suited for a senior or graduate level course.

Problems **P10-17** through **P10-27** all involve catalyst decay.

P10-18. A very straight forward, but with a trap for those who go to quickly.

P10-19. is fairly straight forward using POLYMATH. If time is an issue, one can omit part (e).

P10-20. Uses real data from which the student is asked to determine the decay law parameters.

P10-21. This problem builds on **Living Example Problem** 10-7 and asks to recommend operating conditions.

P10-22. Part **(a)** is typically assigned from year to year. The remaining problems **(P10-17 through P10-27)** are more complicated and are more appropriate for a second undergraduate course or a graduate course.

P10-27. This problem encompasses the effects of catalyst decay with heat effects and is a typical digital age problem.

Summary

	Assigned	Alternates	Difficulty	Time	Solution Given
P10-1					
P10-2					
P10-3					
P10-4					
P10-5					
P10-6					
P10-7					
P10-8					
P10-9					
P10-10					
P10-11					
P10-12					
P10-13					
P10-14					
P10-15					
P10-16					
P10-17					
P10-18					
P10-19					
P10-20					
P10-21					
P10-22					
P10-23					
P10-24					
P10-25					
P10-26					
P10-27					
CDP10-A					
CDP10-B					
CDP10-C					
CDP10-D					
CDP10-E					
CDP10-F					
CDP10-G					

CDP10-H
CDP10-I
CD10-J

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.

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

Summary Table Ch-10

Cataly:

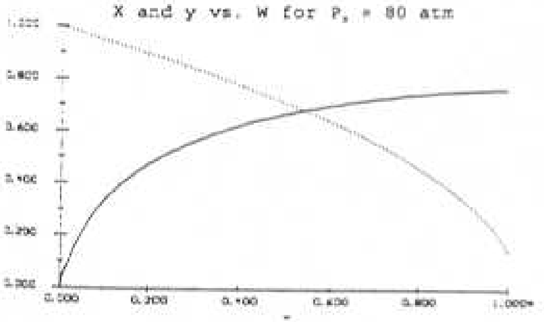
	Catalysis	CVD	Order	T vs. t Traj	Moving Bed	STTR
Basic Reinforcement Principles	3					
Straight forward	4,5,9,18	13,14			18	
Fairly Straight Forward	6,7,9,10, 15	12	17,12(a)	16(d)	16(a),14(b), 22(b),2_(b)	24(d)
More Difficult	7(c),11		23,24,25, 26	20,21(e)	16(c),27	
Open-ended				16(e)		
Critical Thinking					24(d)	

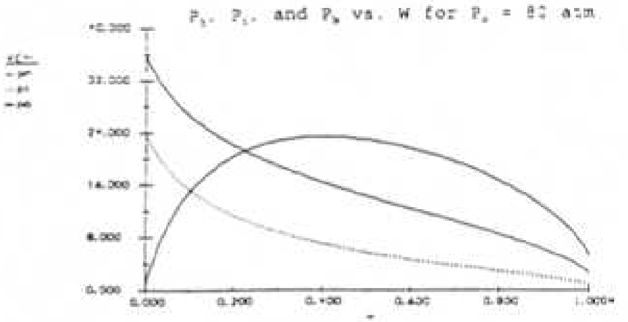
Chapter 10

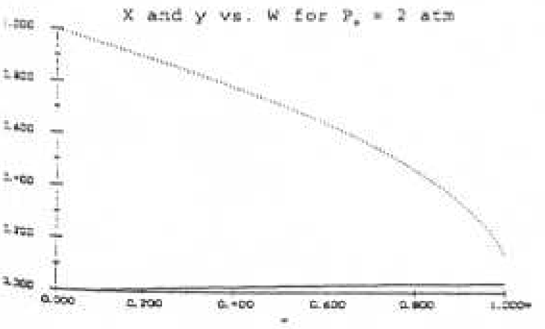
P10-1 No solution will be given.

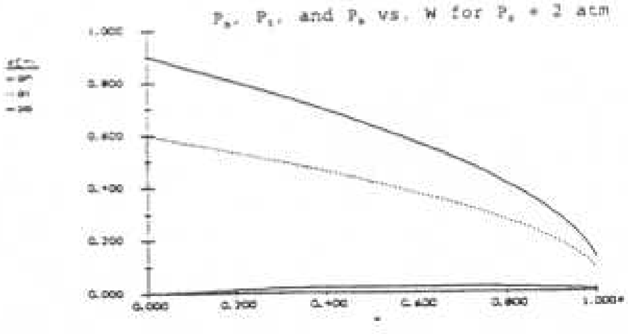
P10-2

(a) Use the equations from Example 10-3 in POLYMATH. Change P_o to 80 atm and then to 2 atm. The effects can be seen in the following four graphs:









(b) Temperature-time trajectories for 1st and 2nd order decay.

Case 1

$E_A = 35$ kcal/mol $E_d = 10$ kcal/mol $d_{do} = 0.01$ day-1 $T_o = 400$ K

1st order decay:

$$t = \frac{E_A}{k_{do}E_d}\left[1-\exp\left[\frac{E_d}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]\right] = \frac{35}{(0.01)(10)}\left[1-\exp\left[\frac{10}{0.001987}\left(\frac{1}{T}-\frac{1}{400}\right)\right]\right]$$

$$t = 350\left[1-\exp\left[5033\left(\frac{1}{T}-\frac{1}{400}\right)\right]\right]$$

P10-2 (cont'd)

2nd order decay:

$$t = \frac{1-\exp\left[\frac{E_d - E_A}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]}{k_{do}(E_d/E_A - 1)} = -140\left[1-\exp\left[-12{,}582\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]\right]$$

Case 2
E_A = 10 kcal/mol E_d = 35 kcal/mol d_{do} = 0.01 day-1 T_o = 400 K

1st order decay:

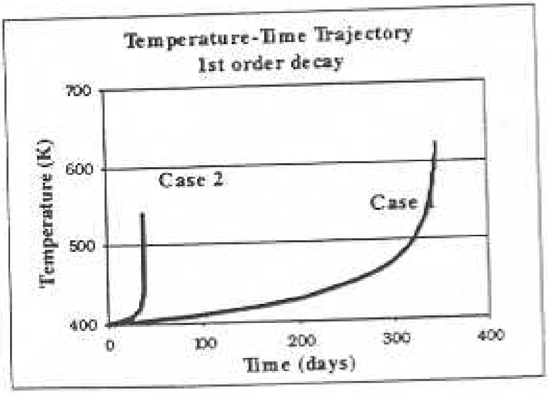
$$t = \frac{E_A}{k_{do}E_d}\left[1-\exp\left[\frac{E_d}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]\right] = \frac{10}{(0.01)(35)}\left[1-\exp\left[\frac{35}{0.001987}\left(\frac{1}{T}-\frac{1}{400}\right)\right]\right]$$

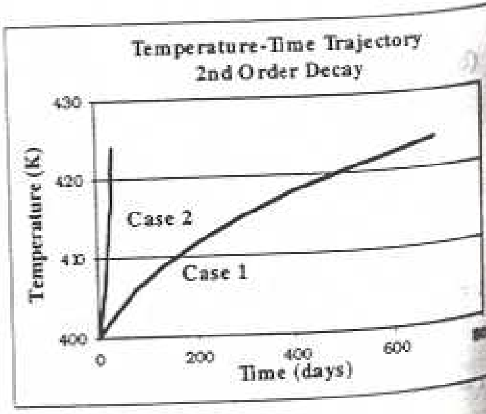
$$t = 38.57\left[1-\exp\left[17{,}614\left(\frac{1}{T}-\frac{1}{400}\right)\right]\right]$$

2nd order decay:

$$t = \frac{1-\exp\left[\frac{E_d - E_A}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]}{k_{do}(E_d/E_A - 1)} = 40\left[1-\exp\left[12{,}582\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]\right]$$

Use these equations in Excel to generate the following graphs:





P10-2 (cont'd)

(c) Use the POLYMATH program from Example 10-5.

By simply changing the value of τ we can see its effect on the minimum concentration. An increase in τ causes a decrease in the minimum concentration, while a decrease in τ causes an increase in concentration.

When the reactor is full of inerts, the catalyst lifetime is longer.

When we change the values of k and k_s to 120 and 12 respectively, we see a decrease in the catalyst lifetime.

(d) Again use the POLYMATH program from Example 10-5. When τ is changed to 0.005 h, $C_{Amin} = 0.607\ \text{mol/dm}^3$. When τ is changed to 0.01 h, $C_{Amax} = 0.509\ \text{mol/dm}^3$.

(e) For the solids and reactants entering from different ends of the reactor:

Decay Law : (for 1st order decay) $\frac{da}{dt} = -k_D a$

$$dt = \frac{dW}{U_s} \Rightarrow \frac{da}{dW} = \frac{k_D}{U_s}a \Rightarrow \frac{da}{a} = \frac{k_D}{U_s}dW$$

$$\ln(a) = \frac{k_D}{U_s}W + k_1$$

For $W = W_{max}$, $a = 1$: $\ln(1) = 0 = \frac{k_D}{U_s}W_{max} + k_1$

$$k_1 = -\frac{k_D}{U_s}W_{max} \Rightarrow \ln(a) = \frac{k_D}{U_s}(W - W_{max})$$

$$a = \exp\left[\frac{k_D}{U_s}(W - W_{max})\right]$$

Combine : $F_{Ao}\frac{dX}{dW} = \exp\left[\frac{k_D}{U_s}(W - W_{max})\right]kC_{Ao}^2(1-X)^2$

$$\int_0^X \frac{dX}{(1-X)^2} = \frac{kC_{Ao}^2}{F_{Ao}}\int_0^{W_{max}} \exp\left[\frac{k_D}{U_s}(W - W_{max})\right]dW$$

$$\frac{X}{1-X} = \frac{kC_{Ao}^2U_s}{F_{Ao}k_D}\left[1 - \exp\left(\frac{k_D}{U_s}(-W_{max})\right)\right]$$

$$\frac{X}{1-X} = \frac{(0.6)(0.075)^2(10{,}000)}{(30)(0.72)}\left[1 - \exp\left(\frac{0.72}{10{,}000}(-22{,}000)\right)\right] = 1.2419$$

$X = 0.55$

P10-2 (cont'd)

(f)

Design Equation : $F_{Ao}\dfrac{dX}{dW} = a(W)\left(-r_A'\right)$

Rate Law : $-r_A' = kC_A^2$

Decay Law : $-\dfrac{da}{dt} = k_d a^2 \quad \Rightarrow \quad -\dfrac{da}{dt} = \dfrac{k_d}{U_s}a^2 \quad \Rightarrow \quad a = \dfrac{1}{1+\left(\dfrac{k_d}{U_s}\right)W}$

$W = 0,\ a = 1$

Stoichiometry : $C_A = C_{Ao}(1-X)$

Combining : $F_{Ao}\dfrac{dX}{dW} = \dfrac{1}{1+\left(\dfrac{k_d}{U_s}\right)W}kC_{Ao}^2(1-X)^2$

$$\frac{F_{Ao}}{kC_{Ao}^2}\int_0^X \frac{dX}{(1-X)^2} = \int_0^W \frac{dW}{1+\dfrac{k_d}{U_s}W} \quad \Rightarrow \quad \frac{F_{Ao}}{kC_{Ao}^2}\left(\frac{X}{1-X}\right) = \frac{U_s}{k_d}\ln\left(1+\frac{k_d}{U_s}W\right)$$

$$\frac{(30)(1.24)}{(0.6)(0.075)^2} = y\left(\ln(1+22000/y)\right) \qquad \text{where } y = \frac{U_s}{k_d}$$

$$y = 8796.12 \text{ gcat} = \frac{U_s}{k_d} \qquad \Rightarrow \qquad U_s = 6333.2 \text{ gcat/min}$$

(g)

$$C_A = C_{A0}\frac{1-X}{1+\varepsilon X} = C_{A0}\frac{1-X}{1+2X}$$

Combining:

$$F_{Ao}\frac{dX}{dW} = e^{-(k_d/U_s)W}kC_{Ao}^2\left(\frac{1-X}{1+2X}\right)^2$$

$$\int_0^X\left(\frac{1-X}{1+2X}\right)^2 dX = \frac{kC_{Ao}^2}{F_{Ao}}\int_0^W e^{-(k_d/U_s)W}dW$$

$$4(1+2)\ln(1-X)+4X+\frac{9X}{1-X} = \frac{kC_{Ao}^2U_s}{F_{Ao}k_d}\left(1-e^{-k_dW/U_s}\right)$$

$$12\ln(1-X)+4X+\frac{9X}{1-X} = 1.24$$

Solve for X $\Rightarrow$ $X = 0.37$

37% Conversion

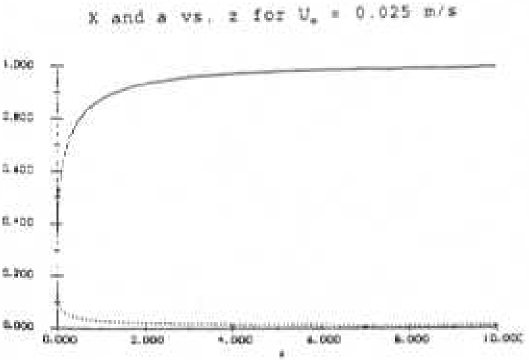
P10-2 (cont'd)

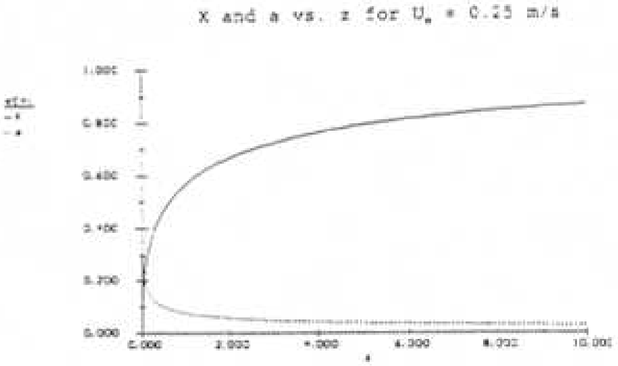
(h) Use the POLYMATH program given in the example problem and vary all of the stated parameters.

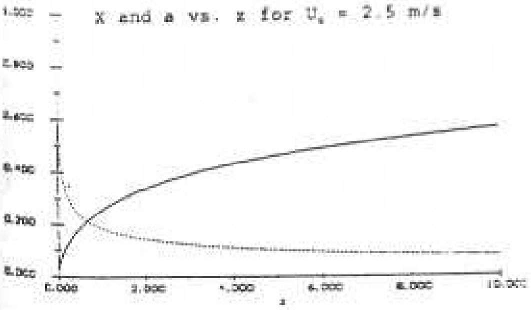
k' has the largest effect on the conversion, followed by A, U_s, and P_{A0}.

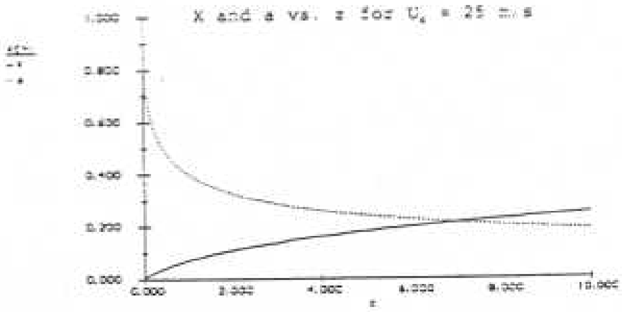
When the ratio of k to U_s and k to A is increased, the conversion is increased. When these are decreased the conversion decreases.

Use the following POLYMATH program to generate graphs of the conversion and activity profiles for U_s = 0.025 m/s, 0.25 m/s, 2.5 m/s, and 25 m/s:





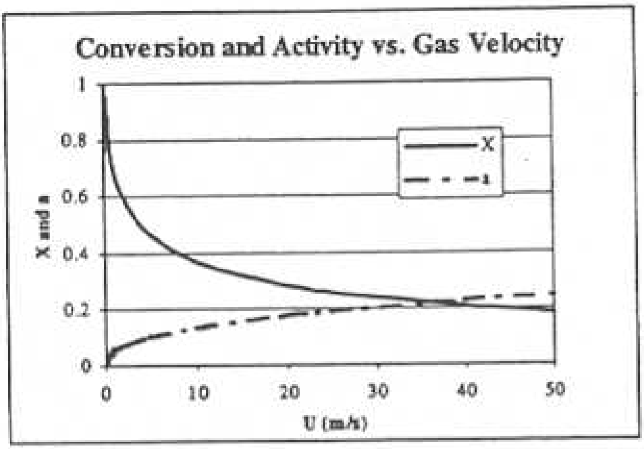




It is apparent that as U_s increases, activity increases and conversion decreases.

Use the same program to vary U_s and generate values for the exit conversion and activity. Use these values in Excel to generate the following graph:

P10-2 (cont'd)



P10-3

I + S ↔ I • S $\qquad r_{ADI} = k_{AI}\left[C_I C_V - \frac{C_{I\bullet S}}{K_I}\right]$

W + S ↔ W • S $\qquad r_{ADW} = k_{AW}\left[C_W C_V - \frac{C_{W\bullet S}}{K_W}\right]$

W • S + I • S ↔ TBA • 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•S ↔ TBA + S $\qquad r_D = K_D\left[C_{TBA\bullet S} - \frac{C_{TBA}C_V}{K_D}\right]$

(a) Surface Rxn Limited

$\frac{r_{ADI}}{k_A} = 0 \qquad C_{I\bullet S} = K_I C_I C_V \qquad C_{W\bullet S} = K_W P_W C_V \qquad \frac{r_{ADW}}{k_W} = 0$

$\frac{r_D}{k_D} = 0 \qquad C_{TBA\bullet S} = \frac{C_{TBA}C_V}{K_D} = K_{TBA}C_{TBA}C_V$, since $\frac{1}{K_D} = K_{TBA}$

$$r_S = \overbrace{k_S K_I K_W}^{k} C_V^2\left[C_I C_W - \frac{C_{TBA}}{K_P}\right] \qquad K_P = \frac{K_S K_I K_W}{K_{TBA}}$$

P10-3 (cont'd)

$$C_T = C_V + C_{I\bullet S} + C_{W\bullet S} + C_{TBA\bullet S} = C_V(1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA})$$

$$-r'_I = -r'_W = r_S = \frac{\overbrace{k_S K_I K_W}^{k} C_T^2 \left[C_I C_W - \frac{C_{TBA}}{K_P} \right]}{\left(1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA}\right)^2}$$

(b) Adsorption Isobutene Limited

$$r_{ADI} = k_{AI} \left[C_I - \frac{C_{TBA}}{C_W K_P} \right] C_V \quad , \quad \left(\frac{r_{ADW}}{k_{AW}} \right) = 0 \quad , \quad \left(\frac{r_D}{k_D} \right) = 0$$

$$C_{W\bullet S} = C_W C_V K_W \quad , \quad C_{TBA\bullet S} = C_{TBA} C_V K_{TBA}$$

$$\left(\frac{r_S}{k_S} \right) = 0 \quad C_{I\bullet S} = \frac{C_V C_{TBA\bullet S}}{C_{W\bullet S} K_S} \qquad C_{I\bullet S} = \frac{C_{TBA} K_{TBA} C_V}{C_W K_W K_S}$$

$$r_{ADI} = k_{AI} \left[C_I - \frac{C_{TBA}}{C_W K_P} \right] C_V \qquad K_P = \frac{K_W K_S}{K_{TBA}}$$

$$-r'_I = \frac{k_{AI} C_T \left[C_I - \frac{C_{TBA}}{C_W K_P} \right]}{\left[1 + C_W K_W + K_{TBA} C_{TBA} + \frac{C_{TBA}}{C_W K_P} \right]}$$

(c) Eley Rideal Kinetics

$$r_S = k_S \left[C_W C_{I\bullet S} - \frac{C_{TBA\bullet S}}{K_S} \right]$$

$$C_{I\bullet S} = K_I C_I C_V$$

$$C_{TBA\bullet S} = K_{TBA} C_{TBA} C_V$$

$$-r'_I = \frac{k \left[C_W C_I - \frac{C_{TBA}}{K_H} \right]}{1 + K_I C_I + K_{TBA} C_{TBA}} \text{, where } k = k_S K_I C_T \text{ and } K_H = \frac{K_I K_S}{K_{TBA}}$$

P10-3 (cont'd)

(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

$$H_2 + C_2H_4 \underset{Cat}{\rightarrow} C_2H_6$$

$$H + E \rightarrow A$$

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 A (butanol) $\rightleftarrows$ B (butene) + C (water)

(a) Possible mechanism:

$$A + S \rightleftarrows A \cdot S \qquad r_{AA} = K_{AA}\left(P_A C_S - \frac{C_{AS}}{K_{AA}}\right)$$

$$A \cdot S + S \rightleftarrows B \cdot S + C \cdot S \qquad r_S = k_S\,(C_{A \cdot S}\, C_S - C_{B \cdot S}\, C_{C \cdot S} / K_S)$$

$$B \cdot S \rightleftarrows B + S \qquad r_{DB} = k_{DB}\,(C_{B \cdot S} - P_B\, C_S/K_{DB})$$

$$C \cdot S \rightleftarrows C + S \qquad r_{DC} = k_{DC}\,(C_{CS} - P_C\, C_S/K_{DC})$$

Assume surface reaction controlling:

$$\frac{-r_{AA}}{k_{AA}} \equiv 0 \qquad C_{A \cdot S} = P_A\, K_{AA}\, C_S$$

$$\frac{-r_{DB}}{k_{DB}} \equiv 0 \qquad C_{B \cdot S} = \frac{P_B\, C_S}{K_{DB}} = P_B\, K_{AB}\, C_S$$

$$\frac{-r_{DC}}{k_{DC}} \equiv 0 \qquad C_{C \cdot S} = \frac{P_C\, C_S}{K_{DC}} = P_C\, K_{AC}\, C_S$$

$$-r'_A = r_S = k_S\left(P_A K_{AA} C_S^2 - \frac{P_B P_C C_S^2}{K_S K_{DB} K_{DC}}\right) = k_S K_{AA} C_S^2\left(P_A - \frac{P_B P_C}{K_{eq}}\right) \text{ where } K_{eq} = K_S K_{AA} K_{DC} K_{DB}$$

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

$$-r'_{A0} = \frac{k_S\, K_{AA}\, C_T^2\, P_{A0}}{(1 + P_{A0}\, K_{AA})^2} = \frac{k_1\, P_{A0}}{1 + k_2\, P_{A0}^2 + k_3\, P_{A0}} \qquad \text{where} \left\{\begin{array}{l} k_1 = k_3\, K_{AA}\, C_T^2 \\ k_2 = K_{AA}^2 \\ k_3 = 2\, K_{AA} \end{array}\right)$$

This is consistent with the observation.

(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

P10-5 (cont'd)

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 : $k_1 = 0.061 \Rightarrow k_2 = 5.34\times10^{-4}$

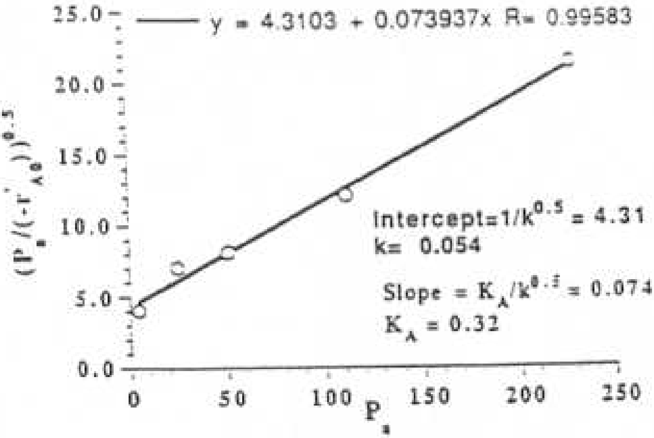
$$-r'_{A0} = \frac{0.061\ P_{A0}}{1 + 5.34\times10^{-4}\ P_{A0}^2 + k_3 P_{A0}} \ ; \text{ so } \quad k_3 = \frac{0.061}{-r'_{A0}} - \frac{1}{P_{A0}} - 5.34\times10^{-4}\ P_A$$

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)



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:

$$\%\text{vacant} = \frac{1}{1 + K_{AA}P_{A0}} = \frac{1}{1 + 0.01596 * 90} = 0.41$$

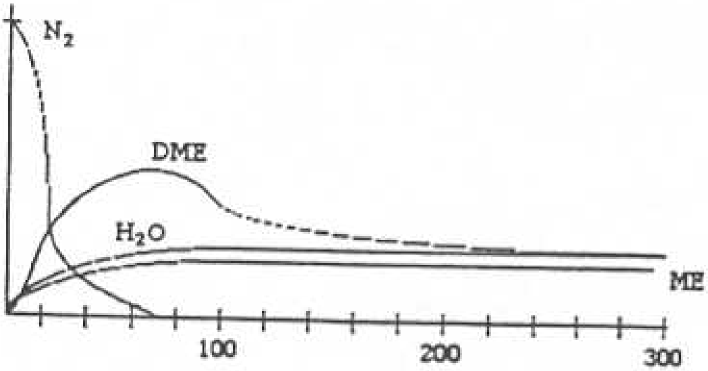
Find the percent of sites occupied by A and B. No B will have occupied any sites at X = 0. So:

$$\%A = \frac{K_{AA}P_A}{1 + K_{AA}P_A} = \frac{0.01595 * 90}{1 + 0.01595 * 90} = 0.59$$

d) No solution will be given.

P10-6

$ME \rightarrow DME + H_2O$



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

$$r_S = k_S C_{ME \cdot S}^2$$

$$C_{ME \cdot S} = K_{ME} P_{ME} C_V$$

$$C_{W \cdot S} = K_W P_W C_V$$

$$r'_{ME} = r_S = \frac{kP_{ME}^2}{\left(1 + K_W P_W + K_{ME} P_{ME}\right)^2} \quad \text{where } k = k_S K_{ME}^2 C_t^2$$

P10-7

Given: Kinetic rate expression for the reduction of NO over a solid catalyst:

$$r = \frac{k\,P_N\,P_C}{(1 + K_1\,P_N + K_2\,P_C)^2} \qquad \begin{array}{l} P_N = \text{partial pressue NO} \\ P_C = \text{partial pressure CO} \end{array}$$

Assume that overall reaction is of the form

$$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$$

(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.

$$NO(g) + S \overset{k_{AN}}{\rightleftarrows} NO \cdot S \qquad \begin{array}{l} P_N = P_{NO} \\ P_C = P_{CO} \end{array} \qquad -r_{AN} = k_{AN}\left[P_N C_S - C_{NO \cdot S}/K_{AN}\right]$$

$$CO(g) + S \overset{k_{CN}}{\rightleftarrows} CO \cdot S \qquad -r_{CN} = k_{CN}\left[P_C C_S - C_{CO \cdot S}/K_{CN}\right]$$

$$NO \cdot S + CO \cdot S \xrightarrow{k_S} \frac{1}{2}N_2 + CO_2 + 2S \qquad -r_S = k_S C_{NO \cdot S} C_{CO \cdot S}$$

With the surface reaction controlling

$$\frac{-r_{AN}}{k_{AN}} \cong 0 \qquad C_{NO \cdot S} = K_{AN}\,P_N\,C_S$$

$$\frac{-r_{CN}}{k_{CN}} \cong 0 \qquad C_{CO \cdot S} = k_{CN}\,P_C\,C_S$$

Then $C_T = C_S + C_{NO \cdot S} + C_{CO \cdot S} = C_S\left[1 + K_{AN}\,P_N + K_{CN}\,P_C\right]$

and therefore reaction is $-r_S = k_S\,C_{NO \cdot S}\,C_{CO \cdot S} = k_S\,C_S^2\,P_N\,P_C\,K_{AN}\,K_{CN}$

$$\text{or} \quad -r_S = \frac{k_S\,K_{AN}\,K_{CN}\,P_N\,P_C\,C_T^2}{\left[1 + K_{AN}\,P_N + K_{CN}\,P_C\right]^2} \qquad \text{with} \qquad \begin{array}{l} k_1 = k_S\,C_T^2\,K_{AN}\,K_{CN} \\ K_1 = K_{AN} \\ K_2 = K_{CN} \end{array}$$

$$-r_S = \frac{k_1\,P_C\,P_N}{\left[1 + K_1\,P_N + K_2\,P_C\right]^2}$$

(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:

P10-7 (cont'd)

$$\frac{\partial(-r_S)}{\partial P_C} = \frac{k_1 P_N}{[1 + K_1 P_N + K_2 P_C]^2} - \frac{2 k_1 P_C P_N K_2}{[1 + K_1 P_N + K_2 P_C]^3} = 0$$

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.

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).

P10-8

(a) From the data we see that H_2 and MEK are weakly adsorbed and the rate goes through a maximum wrt butanol. This maximum suggests a dual site mechanism

$$Bu + S \rightleftarrows Bu \cdot S$$

$$Bu \cdot S + S \rightleftarrows MEK \cdot S + H \cdot S$$

$$MEK \cdot S \rightleftarrows MEK + S$$

$$2H \cdot S \rightleftarrows H_2 + 2S$$

$$r'_{Bu} = r'_{MEK} = \frac{k\ P_{Bu}}{(1 + K_{Bu}\,P_{Bu})^2}$$

The partial pressures of MEK and H_2 do not appear in the denominator because they are assumed to be weakly adsorbed.

P10-8 (cont'd)

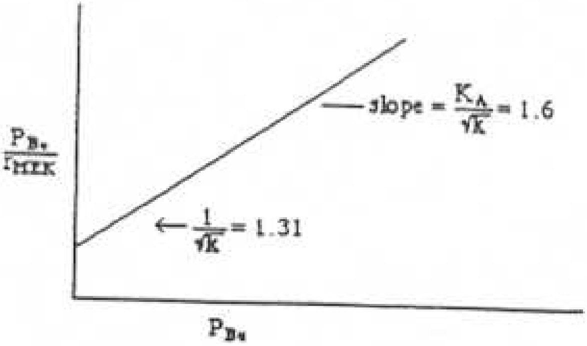
(b)

$$\sqrt{\frac{P_{Bu}}{r'_{MEK}}} = \frac{1}{\sqrt{k}} + \frac{K_{Bu}}{\sqrt{k}} P_{Bu}$$

Mole Balance on differential reactor

$$W = \frac{F_{MEK}}{r'_{MEK}}$$

P_{Bu}	$\sqrt{\frac{P_{Bu}}{r_{MEK}}}$
2	6.74
0.1	1.59
.5	2.69
1	4.08
2	6.82
1	4.12



$$k = 0.58 \ \frac{\text{mol}}{\text{hr g} \cdot \text{cal}}, \ K_A = 2.1 \text{ atm}^{-1}$$

$$\boxed{-r'_A \equiv -r'_{BW} = \frac{0.58 \ P_A}{(1 + 2.1 \ P_A)^2} \frac{\text{mol}}{\text{hr g} \cdot \text{cal}}}$$

(c)

Design Equation : $\frac{dX}{dW} = \frac{-r'_A}{F_{Ao}}$

Rate Law : $-r'_A = \frac{kP_A}{(1 + K_A P_A)^2}$ $\varepsilon = 1$

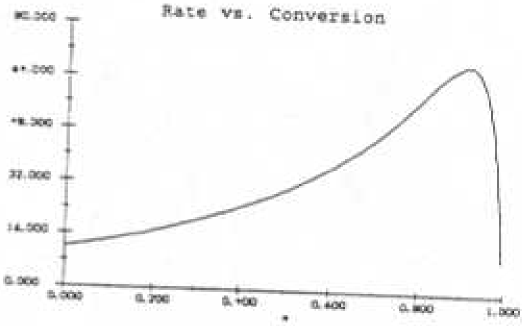
Stoichiometry : $P_A = C_A RT = C_{Ao}\left(\frac{1-X}{1+\varepsilon X}\right)\frac{P}{P_o}RT \Rightarrow P_A = P_{Ao}\left(\frac{1-X}{1+X}\right)$

Use these equations in POLYMATH to find the catalyst weight necessary to achieve 90% conversion.

W = 21.8 kg

(d) Use this same POLYMATH program to generate the desired graph:

```
No pressure change
Equations:                                    Initial value
d(x)/d(w)=-ra/fao                             0
pao=10
fao=600
ka=2.1
pa=pao*((1-x)/(1+x))
ra=-580*pa/(1+ka*pa)**2
rate=-ra
w0 = 0,    wf = 23
```



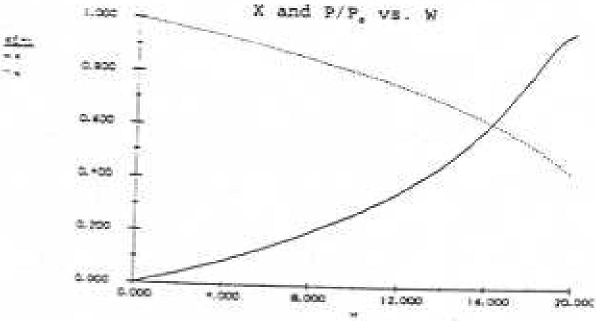
(e) Now consider the change in pressure:

Stoichiometry: $P_A = C_A RT = C_{A0}\left(\frac{1-X}{1+\varepsilon X}\right)\frac{P}{P_o}RT \Rightarrow P_A = P_{A0}\left(\frac{1-X}{1+X}\right)y$

Pressure: $\frac{dy}{dW} = \frac{-\alpha}{2y}(1+X)$

Use these new equations in POLYMATH to find that the same amount of catalyst would be required. W = 21.8 kg

```
Pressure Change
Equations:                                    Initial value
d(x)/d(w)=-ra/fao                             0
d(y)/d(w)=-alpha*(1+x)/2/y                    1
pao=10
fao=600
ka=2.1
alpha=0.03
pa=pao*((1-x)/(1+x))
ra=-580*pa/(1+ka*pa)**2
rate=-ra
w0 = 0,    wf = 23
```



P10-9 Iso-octene + Hydrogen → iso-octane

$$A \quad + \quad B \quad \rightarrow \quad C$$

(a) 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:

$$y = 3.0 + 1.42\, P_A + 0.97\, P_B + 1.42\, P_C$$

P10-9 (cont'd)

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

|sum| = 59.2

avg. = 4.9

(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.

(c)
$$-r'_A = \frac{0.2223\, C_{A0}^2 (RT)^2 (1-X)^2/(1-0.5X)^2}{\left[1 + \frac{C_{A0} RT}{1-0.5X}\{(0.475 + 0.322\,(1-X)) + 0.414X\}\right]^2}$$

$$-r_A = \frac{0.1113\,(RT\, C_{A0})^2 (1-X)^2/(1-0.5X)^2}{\left[1 + \frac{C_{A0} RT}{1-0.5X}(0.797 - 0.383\, X)\right]^2}$$

$P_{A0} = C_{A0} RT = 1.5$ atm

$F_{A0} = 2.5 \frac{mol}{min} = 150 \frac{mol}{hr}$

P10-9 (cont'd)

CSTR :
$$W = \frac{150 \times 0.8}{\dfrac{0.1113\,(1.5)^2\,(1-0.8)^2/(1-0.5\times 0.8)^2}{\left[1 + \dfrac{1.5}{1-0.5\times 0.8}(0.797 - 0.383\times 0.8)\right]^2}}$$

$$W = 21{,}380 \text{ g} = 21.4 \text{ kg}$$

PFR :
$$W = F_{A0}\int_0^x \frac{dX}{-r_A}$$

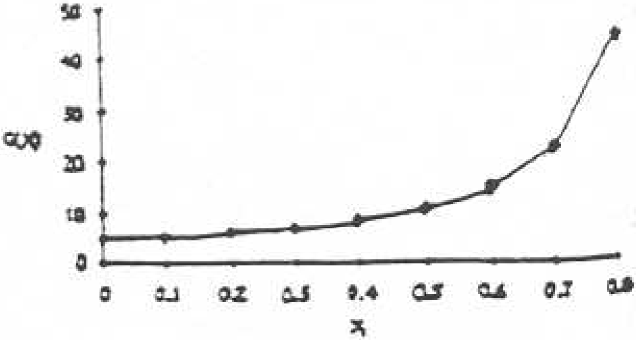
$$W = 150\int_0^x \frac{dX}{\dfrac{0.1113\,(1.5)^2\,(1-X)^2/(1-0.5\,X)^2}{\left[1+\dfrac{1.5}{1-0.5\,X}(0.797-0.383\,X)\right]^2}}$$

$$W = \frac{150}{0.1113\times 2.25}\int_0^x G(X)\,dX$$

where
$$G(X) = \frac{\left[1+\dfrac{1.5\,(0.797-0.383\,X)}{1-0.5\,X}\right]^2 (1-0.5\,X)^2}{(1-X)^2}$$

$$G(X) = \left(\frac{2.1955 - 1.0745\,X}{1-X}\right)^2$$

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

$$W = \frac{150}{0.1113\times 2.25}\times 10 = 6000 \text{ g} = 6 \text{ kg}$$

P10-9 (cont'd)

(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 :

$F_A = F_{A0}(1-X) = \frac{1}{2}F_o(1-X)$

$F_B = F_{B0}(1-X) = \frac{1}{2}F_o(1-X)$ $\qquad F_T = \frac{1}{2}(2-X)$

$F_C = F_{A0}X = \frac{1}{2}F_o X$ $\qquad P_A = \frac{F_A}{F_T} = \frac{1-X}{2-X}$

$P_A = P_A = \frac{1-X}{2-X}P_T$; $P_C = \frac{X}{2-X}P_T$

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

$$\rho = \rho_0\left(\frac{P}{P_0}\right)\left(\frac{2}{2-X}\right)$$

$$\frac{dP}{dL} = \frac{2-X}{2}\left(\frac{P_o}{\rho_o}\right)\left(\frac{1}{P}\right)\frac{G}{g_C D_P}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150\,(1-\phi)\,\mu}{D_P} + 1.75\,G\right]$$

$$\frac{dP}{dL} = \frac{2-X}{2P}\,\beta_o \text{ where } \beta_o = \frac{P_o G}{\rho_o g_C D_P}\frac{(1-\phi)}{\phi^3}\left[\frac{150\,(1-\phi)\,\mu}{D_P} + 1.75\,G\right]$$

Let $L^* = \frac{L}{L_{des}}$: $P^* = \frac{P}{P_o}$. then : $\frac{dP}{dL} = \frac{2-X}{2P^*}\beta_o^*$

where $\beta_o^* = \frac{L_{des}}{P_o^2}\beta_o$

P10-9 (cont'd)

$$\beta_o^* = \frac{LG\,(1-\phi)}{P_o\,\rho_o\,g_c\,D_P\,\phi^3}\left[\frac{150\,(1-\phi)\,\mu}{D_P} + 1.75\,G\right]$$

$$\phi = 0.4$$

$$D_P = \left(\frac{1}{16}\text{ in}\right)\left(\frac{1\text{ ft}}{12\text{ in}}\right) = \frac{1}{192}\text{ ft}$$

$$g_c = 32.174\,\frac{\text{lbm}}{\text{lb}_f}\,\frac{\text{ft}}{\text{sec}^2}$$

$$G = \frac{(F_{A0}\,m_A + F_{B0}\,m_B)}{AT} = \frac{\left(150\,\frac{\text{gmol}}{\text{hr}}\right)(2+112)\,\frac{\text{g}}{\text{gmol}}\left(\frac{\text{lb}}{453.6\text{ g}}\right)}{T\,\frac{\pi}{4}\left(\frac{0.957}{12}\right)^2\text{ ft}^2}$$

$$G = \frac{7546.9}{T}\;\frac{\text{lbm}}{\text{ft}^2\text{ hr}}$$

$$P_o = (3\text{ atm})\left(\frac{14.7\text{ psi}}{1\text{ atm}}\right)\left(\frac{144\text{ in}^2}{1\text{ ft}^2}\right) = 6348.7\,\frac{\text{lb}}{\text{ft}^2}$$

$$\rho_o = C_T\,\overline{m} = \left(\frac{57\text{ lb}}{\text{lbmol}}\right)\frac{P}{RT} = \frac{\left(57\,\frac{\text{lb}}{\text{lbmol}}\right)(3\text{ atm})}{\left(0.7301\,\frac{\text{ft}^3\text{ atm}}{\text{lbmol}\,°\text{R}}\right)[(200+273.15)(1.8)]\,°\text{R}}$$

$$\rho_o = 0.2750\,\frac{\text{lbm}}{\text{ft}^3}$$

$$\left.\begin{aligned}\mu\left(3\text{ atm}, 200°\text{C}\right) &= 9.4719\times10^{-3}\text{ cp}\quad\left(\tfrac{1}{2}\,C_8,\ \tfrac{1}{2}\,H_C\right)\\ &= 8.6211\times10^{-3}\text{ cp}\quad(\text{all } C_8)\end{aligned}\right\}\ \text{PPROP}$$

$$\Rightarrow \mu = \frac{\left(9.4719\times10^{-3} + 8.6211\times10^{-3}\right)}{2}\text{ cp}\;6.7197\times10^{-4}\,\frac{\text{lbm}}{\text{ft sec cp}}\times\frac{3600\text{ sec}}{\text{hr}}$$

$$\mu = 0.02188\,\frac{\text{lbm}}{\text{ft hr}}$$

$$\beta_o^* = \frac{(35\text{ ft})\left(\frac{7546.9}{T}\,\frac{\text{lbm}}{\text{ft}^2\text{ hr}}\right)(1-0.4)\left(\frac{1\text{ hr}}{3600\text{ sec}}\right)^2}{\left(6348.7\,\frac{\text{lb}_f}{\text{ft}^2}\right)\left(0.2750\,\frac{\text{lbm}}{\text{ft}^2}\right)\left(82.174\,\frac{\text{lbm ft}}{\text{lb}_f\text{ sec}^2}\right)\left(\frac{1\text{ ft}}{192}\right)(0.4)^3}$$

$$\times\left[\frac{150\,(1-0.4)\left(0.02188\,\frac{\text{lbm}}{\text{ft hr}}\right)}{\left(\frac{1}{192}\text{ ft}\right)} + 1.75\left(\frac{7546.9}{T}\right)\frac{\text{lbm}}{\text{ft}^2\text{ hr}}\right]$$

P10-9 (cont'd)

$$\frac{dX}{dL^*} = \left[\frac{L d A T \rho_C (1-\phi)}{F_{A0}}\right] R_A(X_1 P^*)$$

where $R_A = \dfrac{k P_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2}$

$$R_A = \frac{K P_o^2 \left(\frac{1-X}{2-X}\right)^2 P^{*2}}{\left[1 + (K_A P_o + K_B P_o)\left(\frac{1-X}{2-X}\right) P^* + K_C P_o \left(\frac{X}{2-X}\right) P^*\right]^2}$$

$$R_A = \frac{K P_0^2 (1-X)^2}{P_0^2 \left[\frac{1}{P_0^2 P^{*2}} + (K_A + K_B)\left(\frac{1-X}{2-X}\right) + K_C \left(\frac{X}{2-X}\right)\right]^2}$$

$$R_A = \frac{K P_0^2 (1-X^2)}{\left[\frac{2-X}{P^{*2}} + (K_A + K_B) P_0 (1-X) + K_C P_0 X\right]^2}$$

Let: $\alpha^* = \dfrac{LAT \rho_B (1-\phi) K P_o^2}{F_{A0}}$; $K_1^* = (K_A + K_S) P_o$; $K_2^* = (K_C - K_A - K_B) P_o$

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)

$K = 0.1118 \dfrac{\text{gmol}}{\text{gcat} \cdot \text{hr} \cdot \text{atm}^2}$; $K_A = 0.475\ \text{atm}^{-1}$; $K_B = 0.322\ \text{atm}^{-1}$

$K_C = 0.414\ \text{atm}^{-1}$

$\therefore\ K_1^* \cdot (0.475 + 0.322)\, 3 = 2.391$

$K_2 = (0.414 - 0.475 - 0.332)\, 3 = -1.149$

$\rightarrow \alpha'$

$$= \frac{LAT \rho_B (1-\phi) K P_o^2}{F_{A0}} = \frac{T (35\ \text{ft})(3.14/4)\left(\frac{0.957}{12}\right)^2 \text{ft}^2 \left(2.6 \frac{\text{g}}{\text{cm}^3}\right)}{\left(2.5 \frac{\text{gmol}}{\text{min}}\right)\left(\frac{60\ \text{min}}{1\ \text{hr}}\right)}$$

$$\times \left(0.113 \frac{\text{gmol}}{\text{gcat hr atm}^2}\right)(3\ \text{atm})^2 \left(\frac{30.41\ \text{cm}}{\text{ft}}\right)$$

= 85.958 T

$\rightarrow \alpha'$

P10-9 (cont'd)

$$\beta_o^* = \left(\frac{6.531}{T} \times 10^{-4}\,\frac{\text{ft}^2\,\text{hr}}{\text{lbm}}\right)\left(378.09 + \frac{13207}{T}\right)\frac{\text{lbm}}{\text{ft}^2\,\text{hr}}$$

$$\beta_o^* = -\frac{0.24693}{T} - \frac{8.6255}{T^2}$$

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 $P = 0.6903$

P10-10

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-litmiting step; start with surface reaction

$$-r_A = r_s = k_s C_v P_{A \cdot S}$$

Come up with ways to find $P_{A \bullet S}$, $P_{B \bullet S}$, and $P_{H \bullet S}$.

$$\frac{r_{AD}}{k_{AD}} = 0 \qquad C_{A \bullet S} = K_{AA} P_A C_V$$

$$\frac{r_{BD}}{k_{BD}} = 0 \qquad C_{B \bullet S} = \frac{P_B C_V}{K_{DB}} = K_{AB} P_B C_V$$

$$\frac{r_{HD}}{k_{HD}} = 0 \qquad C_{H \bullet S} = \frac{P_H C_H}{K_{DH}} = K_{DH} P_B C_V$$

Find the expression for C_v

$$C_t = C_v + C_{A \bullet S} + C_{B \bullet S} + C_{H \bullet S}$$

Combine all of those to get the following rate law suggestion.

$$r_s = \frac{k_s K_A P_A C_t^2}{(1 + K_A P_A + K_B P_B + K_H P_H)^2} = \frac{k P_A}{(1 + K_A P_A + K_B P_B + K_H P_H)^2}$$

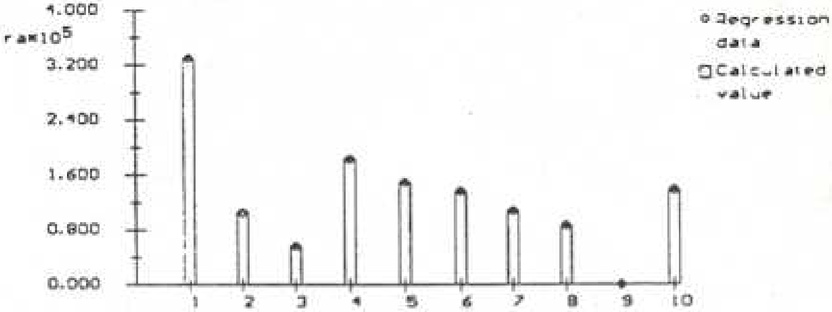
Checking to see if it fits, we see that for high P_A, increases in P_A cause decreases in the rate. We see that if P_B or P_H increase the rate will go down, which is consistent with the rate law.

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.

P10-10 (cont'd)



```
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
```

c) No solution will be given.

P10-11

Rate law:

$$-r_{AC} = \frac{kC_{CO}C_{AC}C_{NaOH}}{(1+K_{AC}C_{AC})^2}$$

Proposed Mechanism:

$$Pd + CO \rightleftarrows Pd \cdot CO$$

$$Pd \cdot CO + NaOH \rightleftarrows Pd \cdot CO \cdot NaOH$$

$$AC + Pd \rightarrow AC \cdot Pd$$

$$AC \cdot Pd + Pd \cdot CO \cdot NaOH \longrightarrow C_3H_5COOH + NaCl + 2Pd$$

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.

P10-11 (cont'd)

We will first try the third equation as the rate-limiting step:

$$r_A = kC_vP_{AC}$$

Then

$$C_t = C_v + C_{Pd\bullet CO} + C_{Pd\bullet CO\bullet NaOH} + C_{Pd\bullet AC}$$

Find equations for $C_{Pd\bullet CO}$, $C_{Pd\bullet CO\bullet NaOH}$, and $C_{Pd\bullet AC}$.

$$\frac{r_{ACO}}{k_{ACO}} = 0 \qquad C_{Pd\cdot CO} = C_vC_{CO}K_{CO}$$

$$\frac{r_{ACO\cdot NaOH}}{k_{NaOH}} = 0 \qquad C_{Pd\cdot CO\cdot NaOH} = K_{CO}K_{NaOH}C_vC_{NaOH}C_{CO}$$

$$\frac{r_{AC}}{k_{AC}} = 0 \qquad C_{Pd\cdot AC} = 0$$

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:

$$r_4 = k_4C_{Pd\bullet AC}C_{Pd\bullet CO\bullet NaOH}$$

$C_{Pd\bullet AC}$ cannot be found so therefore this rate law is also not rate-limiting so none of the mechanisms reactions agree with the rate law.

P10-12

a) Assume that the second reaction is the rate-limiting step.

$$r_S = k_2C_{SiH_4\cdot S}$$

Using PSSH, we know that

$$\dot{r}_{SiH_4\cdot S} = 0 = k_1C_{SiH_4\cdot S}C_v$$

$$C_{SiH_4\bullet S} = \frac{k_1C_{SiH_4}C_V}{k_2} = KC_{SiH_4}C_V$$

$$K = \frac{k_1}{k_2}$$

P10-12 (cont'd)

Perform a site balance:

$$C_t = C_V + C_{SiH_4 \cdot S}$$

$$C_v = \frac{C_t}{1 + KC_{SiH_4}}$$

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.

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

At low temperature (120°C) the reaction goes from 2nd order to zero order. At high temperatures only second order.

$VTTPO \rightarrow VO_2 + P$ Let $VI \equiv VTTPO$

$$VI + S \rightarrow VI \cdot S$$

$$2\,VI \cdot S \rightarrow 2VO_2 + P_1 + S$$

$$r'_{VO_2} = -r'_{VI} = r_S = k_S\, f_{VI}^2$$

$$f_{VI} = K_{VI}\, P_{VI}\, f_V$$

$$1 = f_V + f_{VI}$$

$$-r'_{VI} = \frac{\overbrace{k_S\, K_{VI}^2}^{k}\, P_{VI}^2}{(1 + K_{VI}\, P_{VI})^2} = k\,\frac{P_{VI}^2}{(1 + K_{VI}\, P_{VI})^2} = r'_{VO_2}$$

at high temperature $K_{VI}\, P_{VI} << 1$ and $-r'_{VI} = k\, P_{VI}^2$

P10-13 (cont'd)

Lineage

$$\frac{P_{VT}}{\sqrt{-r'_{VT}}} = \frac{1}{\sqrt{k}} + \frac{K_{VT}}{\sqrt{k}} P_{VT}$$

$-r'_{VT}$	0.004	0.015	0.03	0.06	0.085	0.16
P_{VT}	0.1	0.2	0.3	0.5	0.7	1.1
$(P_{VT}/\sqrt{-r_{VT}})$	1.58	1.63	1.73	2.04	2.40	2.84

$$\text{Intercept} = \frac{1}{\sqrt{k}} = 1.43 \text{ Torr/(μm/hr)}^{1/2}$$

$$k = 0.49 \text{ μm/hr} \cdot \text{Torr}^2$$

$$\text{Slope} = \frac{K_{VT}}{\sqrt{k}} = \frac{2.50 - 1.43}{1} = 1.13/(\text{μm/hr})^{1/2}$$

$$K_{VT} = 1.13\sqrt{k} = \frac{1.13}{1.43}$$

$$K_{VT} = 0.79/\text{Torr}$$

P10-14

$$r_{TiO_2} = k_S f_{I\cdot S}$$

$$f_{I\cdot S} = P_I K_I f_V$$

$$1 = f_V + f_{I\cdot S} = f_V\left(1 + K_I P_I\right)$$

$$f_{I\cdot S} = \frac{K_I P_I}{1 + K_I P_I}$$

$$\frac{P_I P_{P1}}{P^2_{TTIP}} = K_P \quad , \quad P_I = K_P P^2_{TTIP}/P_{P1}$$

$$r_{TiO_2} = \frac{k_S P_I K_I}{1 + P_I K_I}$$

$$r_{TiO_2} = \frac{kP^2_{TTIP}/P_{PI}}{1 + \left(P^2_{TTIP}/P_{PI}\right)K} = \frac{kP^2_{TTIP}}{P_{PI} + P^2_{TTIP}K}$$

Low P_{TTIP}: Rxn is second order

Since $1 \gg K P^2_{TTIP}/P_{P1}$

High P_{TTIP}: $1 \ll K P^2_{TTIP}/P_{P1}$

Reaction is zero order

High Temperature K_I very small such that

$$P^2_{TTIP} K_P K_I \ll P_{P1}$$

P10-15

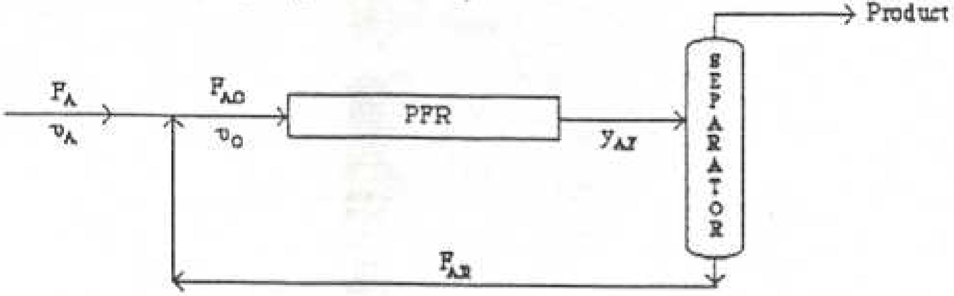
Given: Isomerization reaction $A \rightleftarrows B$ over a supported catalyst

$K_{eq} = 8.5$ at 350°F = 810°R

$K_{eq} = 6.0$ at 400°F = 860°R

E = 26,900 Btu/lbmol

$-r_A = k\,[C_A - C_B/K_{eq}]$ for fresh catalyst



$\theta_B = 0$

$\varepsilon = 0$

Let ρ_o = solution density (constant)

$(MW)_A$ = mol. wt.

$$y_{AF} = \frac{\text{mole recycled}}{\text{mole fed}}$$

Then $$F_{AF} = \frac{y_{AF}\,\rho_o\,v_o}{(MW)_A} \quad ; \quad F_{AO} = \frac{\rho_o\,v_o}{(MW)_A}$$

Assume total recycle of unreacted A. Then $F_{AR} = F_{AO} = \dfrac{y_{A0}\,\rho_o\,v_o}{(MW)_A}$

By material balance on the T upstream to the reactor:

$$F_A = F_{A0} - F_{AR} = \frac{\rho_0 v_0}{(MW)_A}\left(1 - y_{AR}\right) = \frac{\rho_0 v_A}{(MW)_A} \Rightarrow v_0 = \frac{v_A}{1 - y_{AR}}$$

$$X_{AR} = \frac{F_{A0} - F_{AR}}{F_{A0}} = \frac{\frac{\rho_0 v_0}{(MW)_A}\left(1 - y_{AR}\right)}{\frac{\rho_0 v_0}{(MW)_A}} = 1 - y_{AR}$$

Then $-r_A = \alpha\, k\,[C_A - C_B / K_C]$ where α = activity

$$C_A = C_{A0}(1-X) \;;\; C_B = C_{A0}X \;;\; V = F_{A0}\int \frac{dX}{-r_A}$$

P10-15 (cont'd)

$$V = F_{A0}\int_0^{X_{AF}} \frac{dX}{\alpha k\left[C_A - C_B/K_C\right]} = \frac{F_{A0}}{\alpha k C_{A0}} \int_0^{X_{AF}} \frac{dX}{\left[1-\left(1+\frac{1}{K_C}\right)X\right]}$$

$$\alpha k V = \frac{\upsilon_0}{1+\frac{1}{K_C}} \ln \frac{1}{\left[1-\left(1+\frac{1}{K_C}\right)X_{AF}\right]} = \frac{\upsilon_A}{(1-y_{AF})\left(1+\frac{1}{K_C}\right)} \ln \frac{1}{\left[1-\left(1+\frac{1}{K_C}\right)X_{AF}\right]} \quad \text{(a)}$$

Case I: Fresh catalyst: $\alpha = 1$; $T = 350°F$; $\upsilon_A = 310 \frac{gal}{hr}$; $y_{AF} = 0.25$

$\therefore X_{AF} = 1 - y_{AF} = 0.75$

$$\alpha k_1 V = \frac{310\ gal/hr}{(0.75)\left(1+\frac{1}{8.5}\right)} \ln \frac{1}{\left[1-\left(1+\frac{1}{8.5}\right)(0.75)\right]} = 674 \frac{gal}{hr}$$

Case II: Spent catalyst , $T = 400°F$, $\upsilon_A = 300 \frac{gal}{hr}$, $y_{AF} = 0.32$

$\therefore X_{AF} = 1 - y_{AF} = 0.68$ By Arrhenius relationship, with:

k_1 = velocity constant at $T_1 = 810°R$

k_2 = velocity constant at $T_2 = 860°R$

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

$$\therefore k_2 = k_1 \exp\left\{-\frac{26900\ Btu/lbmol}{1.987\ Btu/lbmol°R}\left(\frac{1}{860°R} - \frac{1}{810°R}\right)\right\} = 2.6\ k_1$$

From equaiton (a)

$$\alpha k_2 V = \frac{300\ gal/hr}{(0.68))\left(1+\frac{1}{6}\right)} \ln \frac{1}{1-\left(1+\frac{1}{6}\right)(0.68)} = 596 \frac{gal}{hr}$$

$$\alpha = \frac{596}{k_2 V} = \frac{596}{2.6\ k_1\ V} = \frac{596}{(2.6)(674)} = 0.340$$

Case III: After ACC regenerative treatment $T = 350°F$; $\upsilon_A = 220 \frac{gal}{hr}$; $y_{AF} = 0.19$

$X_{AF} = 1 - y_{AF} = 0.81$

From equation (a):

$$\alpha k_1 V = \frac{220\ gal/hr}{(0.81))\left(1+\frac{1}{8.5}\right)} \ln \frac{1}{\left[1-\left(1+\frac{1}{8.5}\right)(0.81)\right]} = 573 \frac{gal}{hr}$$

$$\alpha = \frac{573}{k_1 V} = \frac{573}{674} = 0.850 < 0.9$$

$\therefore$ Part (a) of ACC guarantee is not satisfied comparing Case III to Case II

$\frac{\alpha_{III}}{\alpha_{II}} = \frac{0.850}{0.340} = 2.50 > 2.25$. However regenerative technique more than satisfies part (b) of the ACC guarantee. Therefore the ACC guarantee was met.

P10-16

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:

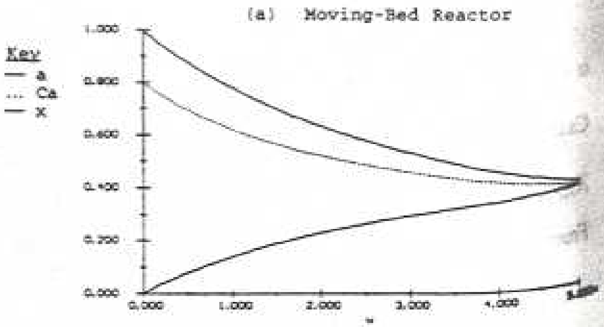
$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

Evaluate the parameters:

$$\varepsilon = .8$$

POLYMATH

```
Equations:                                                      Initial value
d(x)/d(w)=a*(-ra)/fao                                           0
d(a)/d(w)=-kd*a*ca/Us                                           1
kd=9
fao=4000000
Us=250000
k=90
cao=.8
eps=.8
ca=cao*(1-x)/(1+eps*x)
ra=-k*ca
w0 = 0,    wf = 50000
```



b) Mole balance:

$$\frac{dC_{A1}}{dt} = \frac{C_{A0}}{\tau} - \left(\frac{1 + y_{A0}}{1 + \dfrac{C_{A1}}{C_{T0}}} + \tau a k \right) \frac{C_{A1}}{\tau}$$

$$\frac{dC_{A2}}{dt} = \frac{C_{A1}}{\tau} - \left(\frac{1 + y_{A1}}{1 + \dfrac{C_{A2}}{C_{T0}}} + \tau a k \right) \frac{C_{A2}}{\tau}$$

$$\frac{dC_{A3}}{dt} = \frac{C_{A2}}{\tau} - \left(\frac{1 + y_{A2}}{1 + \dfrac{C_{A3}}{C_{T0}}} + \tau a k \right) \frac{C_{A3}}{\tau}$$

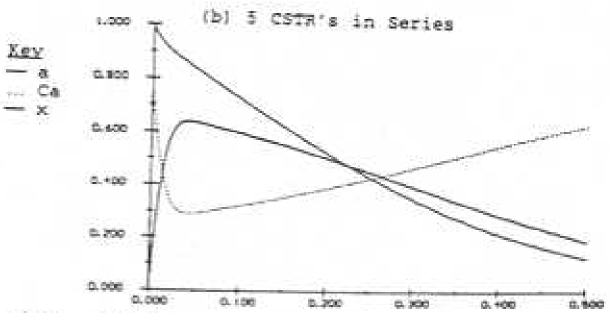
$$\frac{dC_{A4}}{dt} = \frac{C_{A3}}{\tau} - \left(\frac{1 + y_{A3}}{1 + \dfrac{C_{A4}}{C_{T0}}} + \tau a k \right) \frac{C_{A4}}{\tau}$$

$$\frac{dC_{A}}{dt} = \frac{C_{A4}}{\tau} - \left(\frac{1 + y_{A4}}{1 + \dfrac{C_{A}}{C_{T0}}} + \tau a k \right) \frac{C_{A}}{\tau}$$

Everything else is the same and we need to know τ.

$$\tau = \frac{V}{v_0} = 0.004$$

```
P10-16 (b) 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
t0 = 0,    tf = 0.5
```



P10-16 (cont'd)

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:

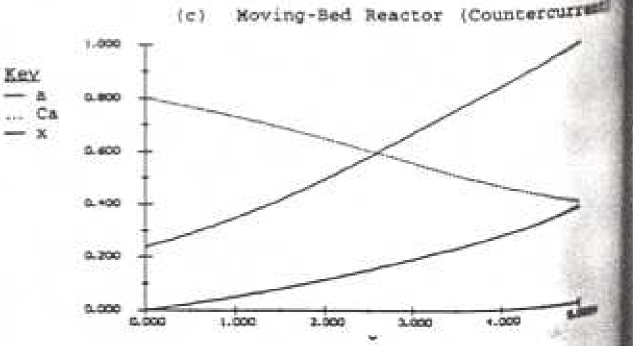
$$\ln a = \frac{k_d C_A W}{U_S} + k$$

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:                                              Initial value
d(x)/d(w)=a*(-ra)/fao                                   0
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))
w0 = 0,    wf = 50000
```

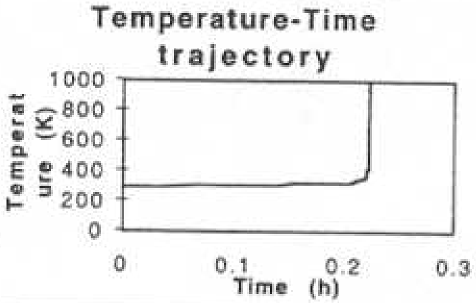

(c) Moving-Bed Reactor (Countercurr

d) To find the Time-Temperature Trajectory we need to use the following equation for first-order decay.

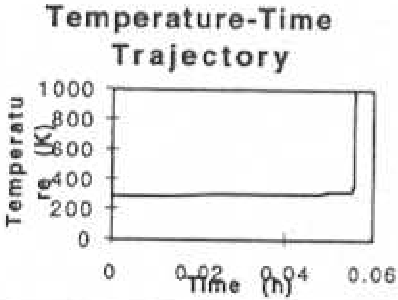
$$t = \frac{E_A}{k_{d0} C_A E_d}\left[1 - \exp\left[\frac{E_d}{R}\left(\frac{1}{T} - \frac{1}{300}\right)\right]\right]$$

P10-16 (cont'd)

Since no initial temperature was given, we assumed one of 300K. This is the graph of that equation.



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.

P10-17

For all of the parts, the mole balances and rate laws are the same. They are:

$$\frac{dC_A}{dW} = r_A v_0 \qquad \frac{dC_B}{dW} = r_B v_0$$

$$r_A = -kaC_A \qquad r_B = kaC_A$$

a) Find the equation needed for a.

$$-\frac{da}{dt} = k_d a C_A$$

$$a = \exp(-k_d C_A t)$$

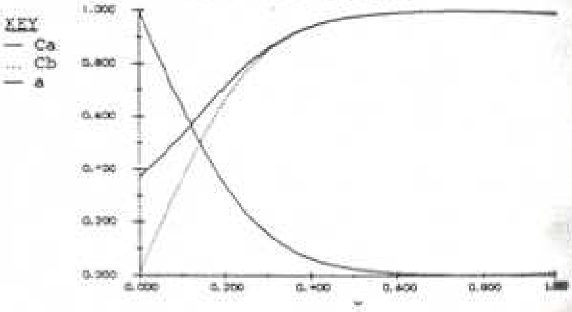
a=1 when t=0

Assuming values for v_0, k, and k_d come up with the following graphs according to the cases described.

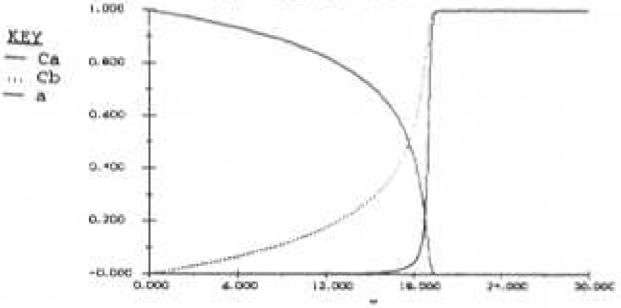
P10-17 (cont'd)

```
Equations:                                  Initial value
d(cb)/d(w)=rb*vo                            0
d(ca)/d(w)=ra*vo                            1
vo=10
a=1
kd=1
t=20
k=1
ra=-k*a*ca
rb=k*a*ca
w0 = 0,    wf = 50
```

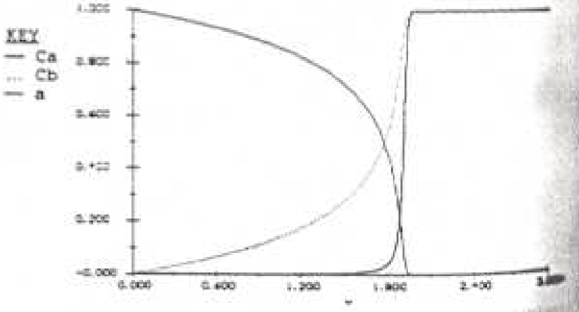
(a) Case I @ t=1000



(a) Case II @ t=7



(a) Case III @ t=7



b) Find the new equation for a:

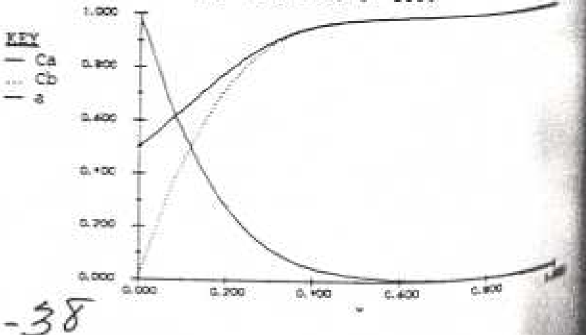
$$-\frac{da}{dt} = k_d a^2 C_A$$

$$a = \frac{1}{1+k_d C_A t}$$

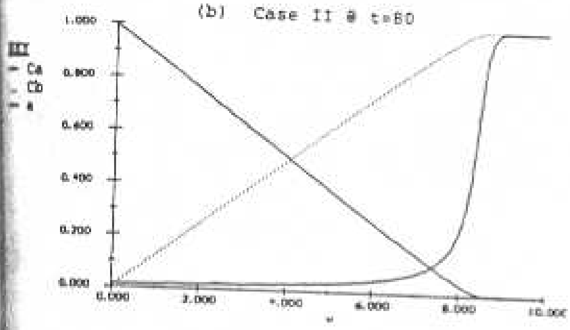
Using same values come up with these graphs:

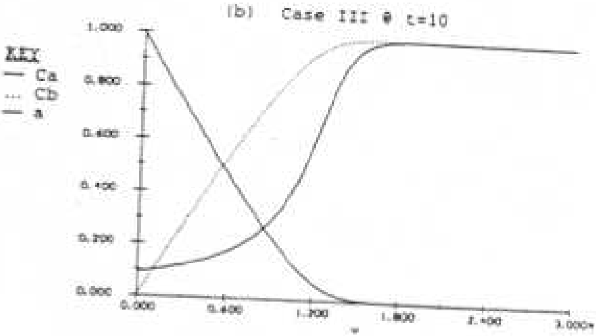
```
Equations:                                  Initial value
d(cb)/d(w)=rb*vo                            0
d(ca)/d(w)=ra*vo                            1
vo=10
kd=.001
t=1000
k=1
a=1/(1+kd*ca*t)
ra=-k*a*ca
rb=k*a*ca
w0 = 0,    wf = 1
```

(b) Case I @ t= 1000



P10-17 (cont'd)





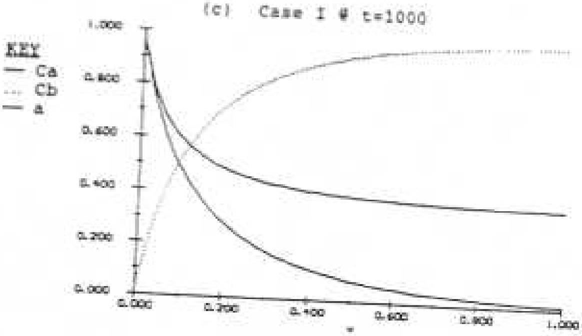
c) Find the new equation for a:

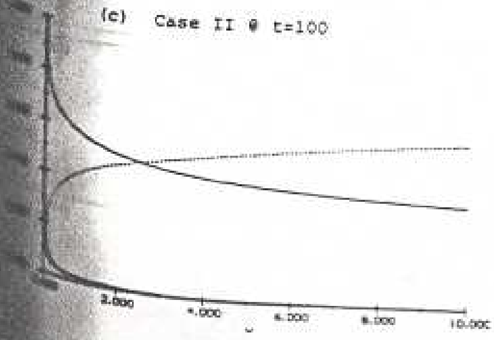
$$-\frac{da}{dt} = k_d a C_B$$

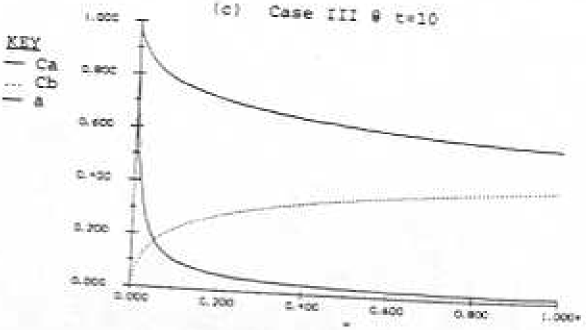
$$a = \exp(-k_d C_B t)$$

The following graphs are made:

```
Equations:                                    Initial value
d(ca)/d(w)=ra*vo                              1
d(cb)/d(w)=rb*vo                              0
vo=10
kd=.001
t=1000
k=1
a=exp(-kd*cb*t)
rb=k*a*ca
ra=-k*a*ca
w0 = 0,   wf = 1
```







P10-17 (cont'd)

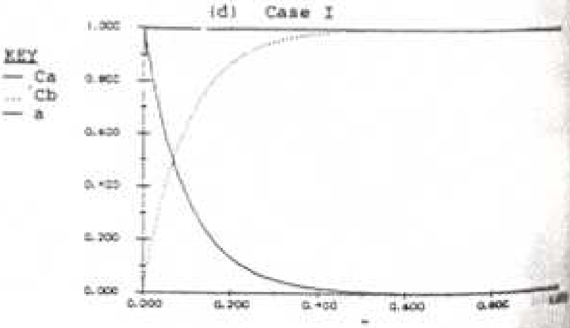
d) Making a into a differential equation we come up with this:

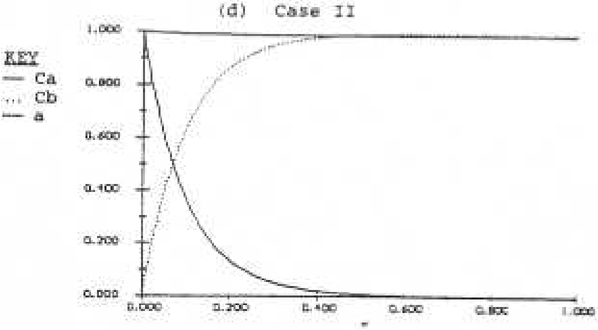
$$-\frac{da}{dt} = k_d C_A a$$

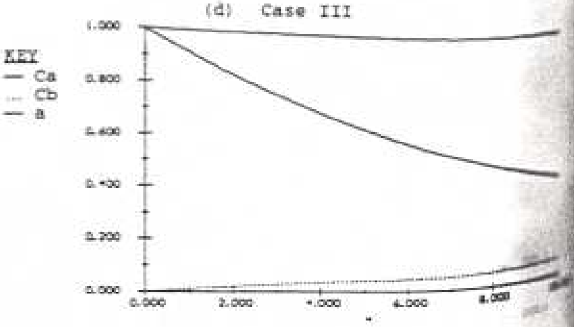
$$t = \frac{W}{U_s}$$

$$-\frac{da}{dW} = \frac{k_d C_A a}{U_s}$$

```
Equations:                                   Initial value
d(ca)/d(w)=ra*vo                             1
d(cb)/d(w)=rb*vo                             0
d(a)/d(w)=-kd*a*ca/Us                        1
vo=10
kd=.001
Us=10
k=1
rb=k*a*ca
ra=-k*a*ca
w0 = 0,    wf = 1
```







e) Everything from part (d) is the same except for the decay law.

$$\frac{da}{dt} = -k_d a C_A$$

$$t = \frac{W_{MAX} - W}{U_S}$$

$$dt = -\frac{dW}{U_S}$$

P10-17 (cont'd)

$$\frac{da}{dW} = \frac{k_d C_A a}{U_S}$$

Integrating:

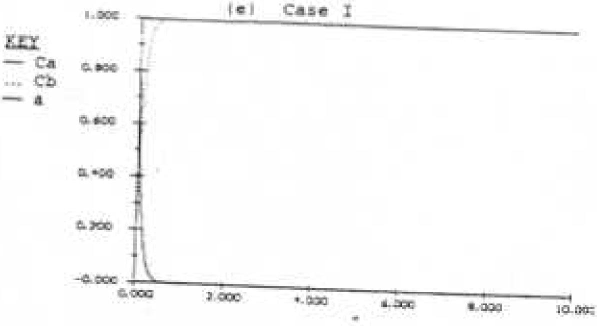
$$\ln a = \frac{k_d C_A W}{U_S} + k$$

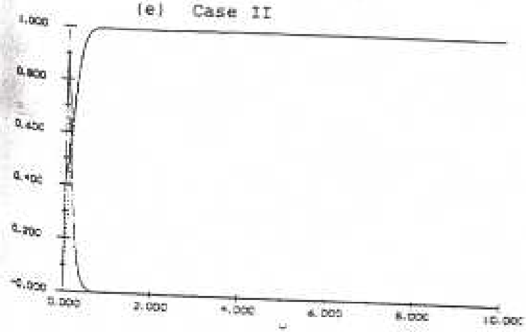
$W = W_{MAX}$ @ $a = 1$

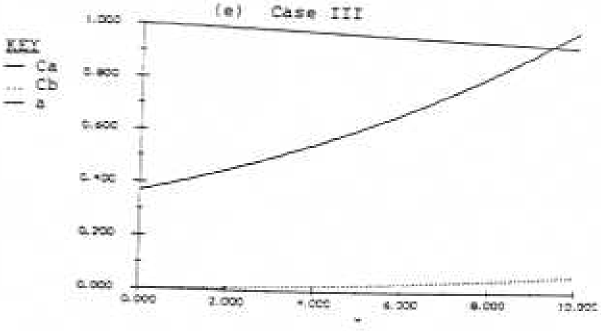
$$k = -\frac{k_d C_A W_{MAX}}{U_S}$$

$$a = \exp\left[\frac{k_d C_A (W - W_{MAX})}{U_S}\right]$$

```
Equations:                                      Initial value
d(ca)/d(w)=ra*vo                                1
d(cb)/d(w)=rb*vo                                0
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
w0 = 0,    wf = 10
```







P10-18

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.

```
10-18a
Equations:                                              Initial value
d(a)/d(w)=-kd/Us                                        1
d(x)/d(w)=-ra/fao                                       0
fao=1
kd=2
Us=4
kr=1
ra=-kr*a
fb=fao*x
P=160*fb-10*Us
w0 = 0,    wf = 1
```

```
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
```

P10-18 (cont'd)

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:                                                        Initial value
d(x)/d(w)=-ra/fao                                                 0
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
w0 = 0,    wf = 1
                                  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              -5.245e-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.

P10-19

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:

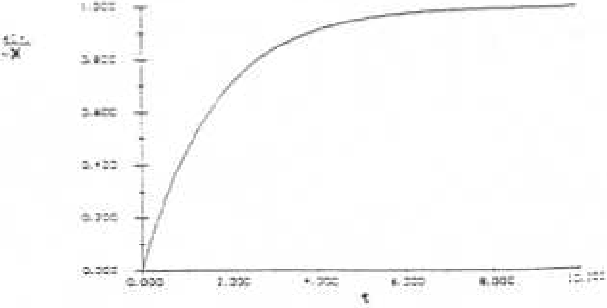
$$-\frac{da}{dt} = k_d a^2$$

Stoichiometry:

$$P_T = P_{T0}(1 - X)$$

Plugging those into POLYMATH gets the following program and the following graph

```
Equations:                                      Initial value
d(x)/d(t)=-rt*w/nto                             0
d(a)/d(t)=-kd*a^2                               1
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)
t0 = 0,    tf = 0.001
```



b) For the moving-bed reactor the mole balance now becomes:

$$\frac{dX}{dW} = \frac{-r_T'}{F_{A0}}$$

The decay law now becomes:

$$-\frac{da}{dW} = \frac{k_d a^2}{U_S}$$

P10-19 (cont'd)

Everything stays the same. Plug into POLYMATH.
The conversion achieved is X = 0.266

```
10-19b
Equations:                                            Initial value
d(x)/d(w)=-rt/fao                                     0
d(a)/d(w)=-kd*a^2/Us                                  1
kt=20
fao=600
kd=1.6
Us=2
pto=2
pt=pto*(1-x)
rt=-kt*pt*a
w0 = 0,    wf = 50
```

```
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
```

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
```

(d) For second-order decay:

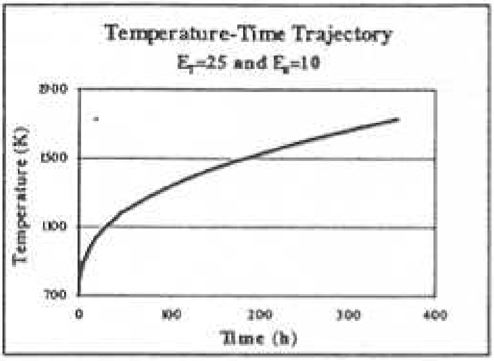
$$t = \frac{1-\exp\left[\frac{E_T - 2E_T + E_d}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]}{k_{do}\left(1-2+E_d/E_T\right)} = \frac{1-\exp\left[\frac{E_d - E_T}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]}{k_{do}\left(E_d/E_T - 1\right)}$$

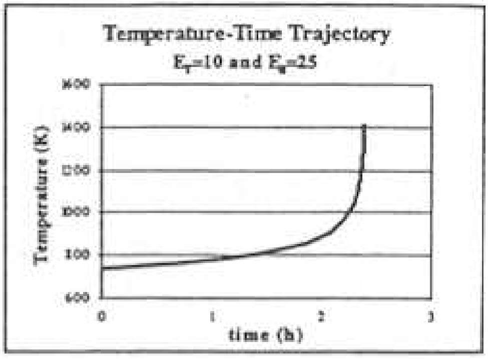
For E_T = 25 kcal/mol and E_d = 10 kcal/mol:

$$t = \frac{1-\exp\left[\frac{10-25}{0.001987}\left(\frac{1}{T}-\frac{1}{735}\right)\right]}{(1.6)(10/25-1)} = -0.96\left[1-\exp\left[-7{,}549\left(\frac{1}{T}-\frac{1}{735}\right)\right]\right]$$

Use this equation in Excel to generate the following graph:

P10-19 (cont'd)





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.

(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:                                        Initial value
d(x)/d(w)=-ra/fao                                 0
d(a)/d(w)=-kd*pt^2*a^2/Us                         1
kd=.2
Us=2
fao=600
kt=20
pto=2
pt=pto*(1-x)
ra=-kt*pt*a
w0 = 0,   wf = 50
```

```
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
```

P10-19 (cont'd)

```
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
```

P10-20

(a)

Design Equation : $W = \dfrac{F_{Ao}X}{(-r_A)a(t)} \Rightarrow a(t) = \dfrac{\upsilon_o}{W}\left(\dfrac{C_{Ao}-C_A}{kC_A^n}\right)$ For n^th order kinetics.

Assume at $t = 0$, $a(0) = 1$ and $X = 1$.

$$\Rightarrow F_B(0) = F_{Ao}X = F_{Ao} = 106 \quad \Rightarrow \quad F_{Ao} = 106$$

Now

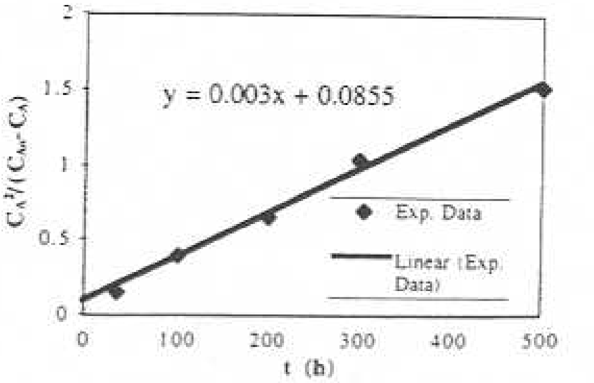
$$F_B(t) = F_{Ao}X(t) = RON(t)$$

$$X(t) = \frac{RON(t)}{106} = \frac{RON(t)}{RON(0)}$$

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:



P10-20 (cont'd)

From the graph: intercept $= 1/k = 0.0835 \Rightarrow k = 11.98$

slope $= k_d/k = 0.003 \Rightarrow k_d = 0.00025$

(b) Activation Energies both for rate constant and decay constant can be estimated from the temperature-time trajectory.

P10-21

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.

b) The problem with such a low flow rate is that the activity will remain low.

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:

$$-r_a' = kP_A^2$$

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.

P10-21 (cont'd)

```
Equations:                                              Initial value
d(a)/d(z)=-kd*a*ccoke/U                                 1
d(x)/d(z)=-ra/U/cao                                     0
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
z0 = 0,   zf = 15
```

```
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
```

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
z0 = 0,   zf = 15
```

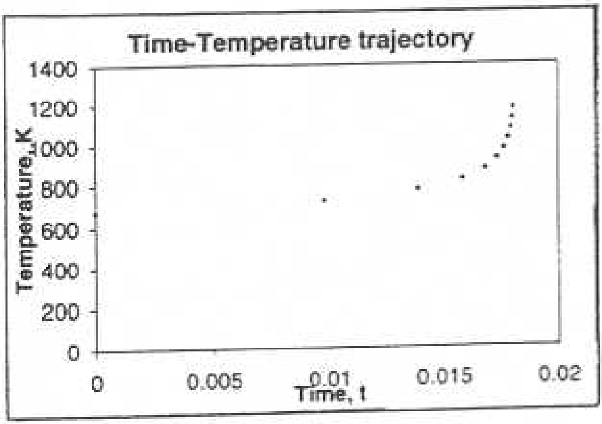
P10-21 (cont'd)

```
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
```

e) To find the temperature-time trajectory, use equation (10-119) and add C_{coke} where necessary:

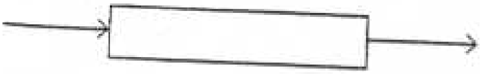
$$t = \frac{1 - \exp\left[\frac{E_A - nE_A + E_d}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{k_{d0}\left(1 - n + E_d/E_A\right)C_{coke}}$$

The following curve is generated from that equation.



P10-22

(a)



Design equation: $r = \frac{F_{A0}X}{W}$

Assume W = 1g $\therefore$ $r = F_{A0}X$

$$\underset{F_{A0}(1-X)}{\underset{(A)}{\text{Cumene}}} \rightarrow \underset{F_{A0}X}{\underset{(R)}{\text{Propene}}} + \underset{F_{A0}X}{\underset{(S)}{\text{Benzene}}}$$

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})

(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 : $F_{A0}\,dX = r\,dW$

$r = e^{-\alpha t}\,k\,P_A$

$t = \frac{W}{U_S}$

P10-22 (cont'd)

$$\therefore\ F_{A0}\,dX = e^{-\left(\frac{\alpha W}{U_s}\right)} k\,P_A\,dW$$

$$\text{or}\ \frac{F_{A0}}{C_{A0}RT}\int_0^X \frac{1+X}{1-X}\,dX = k\int_0^W e^{-\left(\frac{\alpha W}{U_s}\right)}dW \qquad (1)$$

F_{A0} = 20 mol/min = 1/3 mol/sec

C_{A0} = 0.06 kmol/m^3 = 0.06 mol/l

$R = 0.082\ \frac{\text{atm}\cdot\text{l}}{\text{K}\cdot\text{mol}}$

T = 273 + 420 = 693 K

$k = 3.8\times10^{-3}$ mol/g sec atm

$\alpha = 4.27\times10^{-3}\ \text{sec}^{-1}$

W = 100 kg

U_S = 10 kg/min = 1/6 kg/sec

Equation (1) becomes:

$$2\ln(1-X) + X = \frac{C_{A0}RT\,k\,U_S}{F_{A0}\alpha}\left[e^{-\left(\frac{\alpha W}{U_s}\right)} - 1\right]$$

$$2\ln(1-X) + X = \frac{(0.06)(0.082)(693)(3.8\times10^{-3})\left(\frac{1000}{6}\right)}{\left(\frac{1}{3}\right)(4.27)\times10^{-3}}\left[\exp\left\{-\frac{4.27\times10^{-3}\times1000}{\frac{1}{6}}\right\} - 1\right]$$

$$= -1.4\times10^3$$

$$\therefore\quad X \equiv 1.00$$

P10-23

Given $A \rightarrow R + S$

Batch constant volume reactor, P increases with time

$$N_{A0}\,dX = a\,r_o\,W dt$$

Assume $a = e^{-\alpha t}$

$r_o = kP_A$

$\therefore\ P_A = C_A RT$

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

$\therefore\ N_{A0}\,dX = We^{-\alpha t}k\,C_{A0}(1-X)RT\,dt$

P10-23 (cont'd)

$$\int_0^X \frac{dX}{1-X} = \frac{W\,k\,C_{A0}\,RT}{N_{A0}} \int_0^t e^{-\alpha t}\,dt = \left(\frac{W}{V_o}\right) k\,RT \int_0^t e^{-\alpha t}\,dt$$

$$= \beta \int_0^t e^{-\alpha t}\,dt \quad \text{where} \quad \beta = \left(\frac{W}{V_o}\right) k\,RT$$

$$-\ln(1-X) = \frac{\beta}{\alpha}\left(1-e^{-\alpha t}\right)$$

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, $e^{-\alpha t} = 0$

$$\frac{\beta}{\alpha} = -\ln(1-X)$$

$$\alpha = \frac{\beta}{\ln\left(\frac{1}{1-X}\right)} = \frac{3.37 \times 10^{-3}}{\ln\left(\frac{1}{1-0.517}\right)} = 5.18 \times 10^{-3}\ \text{sec}^{-1}$$

$$\therefore\ -\ln(1-X) = 0.728\left(1-e^{-5.18\times10^{-3}t}\right)$$

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

∴ The assumption of a first order reaction kinetics and a first order decay kinetics is justified.

P10-24

$$\text{cyclopentane} \left\langle \begin{array}{l} \text{n - pentane} \\ \text{coke} \end{array} \right.$$

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 : $a = \frac{1}{1 + k_d' t}$

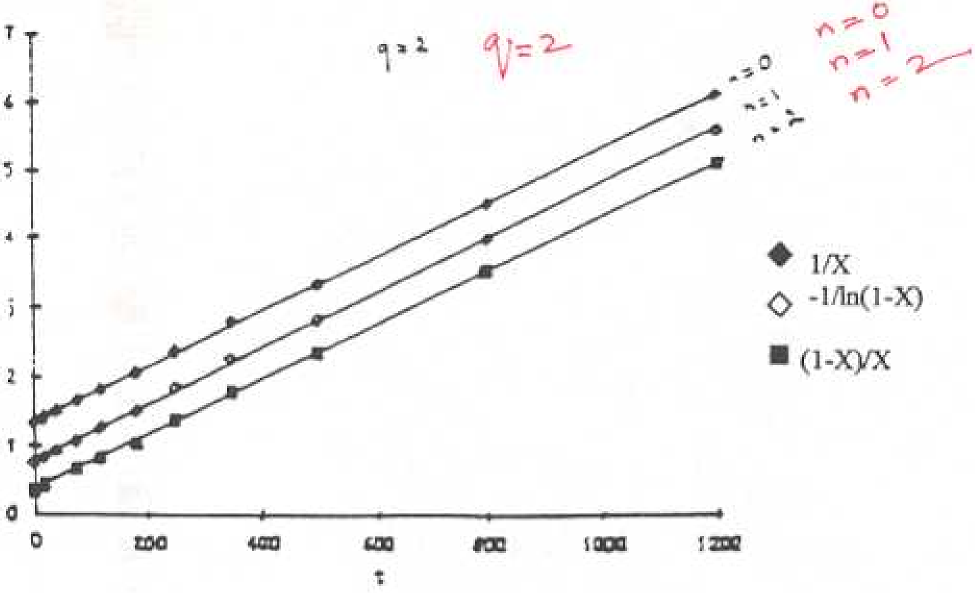
If n = 0 : $\frac{1}{X} = \frac{1}{k\tau} + \frac{k_d'}{k\tau} t$

If n = 1 : $\frac{1}{-\ln(1-X)} = \frac{1}{k\tau'} + \frac{k_d'}{k\tau'} t$

If n = 2 : $\frac{(1-X)}{X} = \frac{1}{k\tau''} + \frac{k_d'}{k\tau^n} t$

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

P10-24 (cont'd)



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 Δt = 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 : $-\frac{dC_A}{dt} = K_R\left(\frac{1}{1 + k_d^{'} t}\right)$

$$\frac{dX}{dt} = \frac{K_R}{C_{A0}}\left(\frac{1}{1 + k_d^{'} t}\right)$$

$$\frac{dt}{dX} = \frac{C_{A0}}{K_R} + \frac{C_{A0}\, k_d^{'}}{K_R}\, t$$

P10-24 (cont'd)

If n=2 : $-\frac{dC_A}{dt} = K_R\left(\frac{1}{1+k_d^{'}t}\right)C_A^2$

$$\frac{1}{(1-X)^2}\frac{dX}{dt} = \frac{K_R C_{A0}}{1+k_d^{'}t}$$

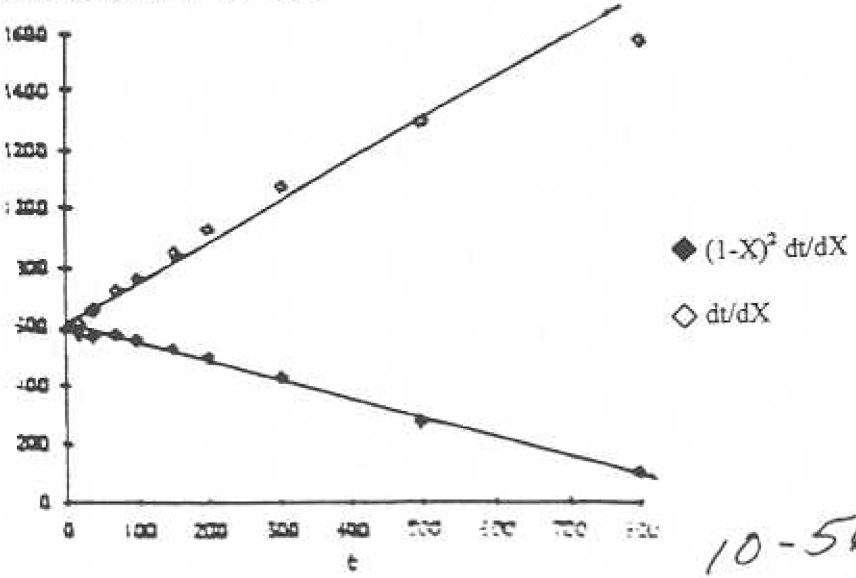
$$(1-X)^2\frac{dt}{dX} = \frac{1}{K_R C_{A0}} + \frac{k_d^{'}}{K_R C_{A0}}t$$

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				

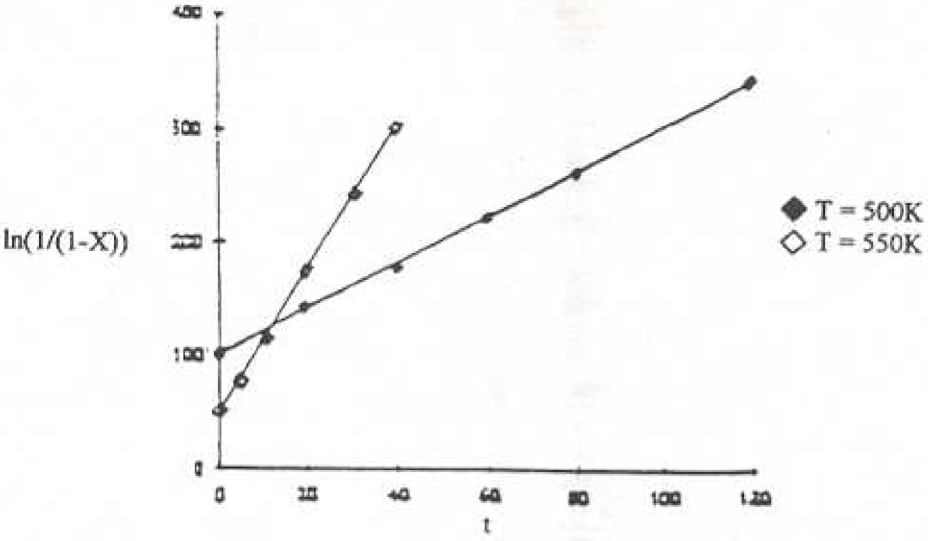
n=2 : Slope is negarive. It is unreasonable

n=0 : $\frac{dt}{dX}$ vs. t is a straight line.

The reaction is zero-order : $-r_A = k_A a$



P10-25 (cont'd)



They are straight lines ∴ n=2

For $T_1 = 500$ K :
$$\left.\begin{array}{l} \text{slope} = 2.04 \dfrac{K_{d_1}}{(\tau K)_1} \\ [1/\text{intercept}] = 0.01 = (\tau K)_1 \end{array}\right\} \Rightarrow K_{d_1} = 0.02$$

For $T_2 = 550$ K :
$$\left.\begin{array}{l} \text{slope} = 6.325 \\ (\tau K)_2 = 0.02 \end{array}\right\} \Rightarrow K_{d_2} = 0.1265$$

$$\frac{K_{d_1}}{K_{d_2}} = \frac{0.02}{0.1265} = \exp\left\{\frac{E_d}{8.314}\left(\frac{1}{550} - \frac{1}{500}\right)\right\}$$

$$E_d = 84.344 \ \frac{J}{mol}$$

$$K_{d_1} = K_{d_2} \exp\left\{-\frac{E_d}{R}\left(\frac{1}{T_1}\right)\right\} = K_{d_2} \exp\left\{-\frac{84,344}{8.314}\left(\frac{1}{500}\right)\right\} = 0.02$$

$$K_{d_2} = 1.296 \times 10^{-3}$$

We want to maintain Ka = constant

$$K\left(\frac{1}{1 + K_d t}\right) = K_o$$

$$K_o \exp\left\{\frac{E}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right\} = K_o (1 + K_d t)$$

$$\exp\left\{\frac{E}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right\} - 1 = K_d t$$

$$t = \frac{\exp\left\{\dfrac{E}{R}\left(\dfrac{1}{T_o} - \dfrac{1}{T}\right)\right\} - 1}{K_d}$$

$C_{A0} = 0.03 \ \frac{\text{kmol}}{\text{m}^3}$

$W = 0.01 \ \text{kg/m}^3$

$$\tau = \frac{C_{A0}W}{F_{A0}} = \frac{\left(0.03 \ \frac{\text{kmol}}{\text{m}^3}\right)\left(0.01 \ \frac{\text{kg}}{\text{m}^3}\right)}{1.5 \times 10^{-5} \ \text{kmol/min}} = 20 \ \frac{\text{kg}}{(\text{m}^3)^2} \ \text{min}$$

(b) The order of decay is q=2

$$\frac{k_d'}{k_A} = 4 \times 10^{-3} \Rightarrow k_d' \ 3 \times 10^{-3} \ \text{min}^{-1}$$

(c) Moving bed reactor: $F_{A0} = \frac{2 \ \text{kmol}}{\text{min}}$; $X = 0.80$

$$-\frac{da}{dt} = k_d' a^2 \qquad (1)$$

$$F_{A0}\frac{dX}{dW} = -r_A = k_A a \qquad (2)$$

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:

$$F_{A0}\int_0^X \frac{dX}{k_A a} = F_{A0}\int_0^X \frac{dX}{k_A\left(\frac{1}{1 + \frac{k_d W}{u}}\right)} = \int_0^W dW$$

$$\frac{F_{A0}}{k_A}\int_0^X dX = \int_0^W \frac{dW}{1 - \frac{k_d W}{u}}$$

$$\frac{u}{k_d} \ln\left[1 - \frac{k_d W}{u}\right]$$

$$\frac{F_{A0}}{k_A} X = \frac{u}{k_d} \ln\left(1 - \frac{k_d W}{u}\right)$$

$$W = \frac{u}{k_d}\left\{\exp\left(X \frac{F_{A0} k_d}{u k_A}\right) - 1\right\}$$

P10-24 (cont'd)

$$W = \frac{u}{3 \times 10^{-3}}\left\{\exp\left(\frac{0.8 \times 2 \times 3 \times 10^{-3}}{0.0375\times}\right) - 1\right\}$$

If $u = 1\,\frac{kg}{min}$ $W = 45.5$ kg

(d) If $u = 0.5\,\frac{kg}{min}$ $W = 48.6$ kg

P10-25

a) $S \rightarrow W + CO_2$: 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

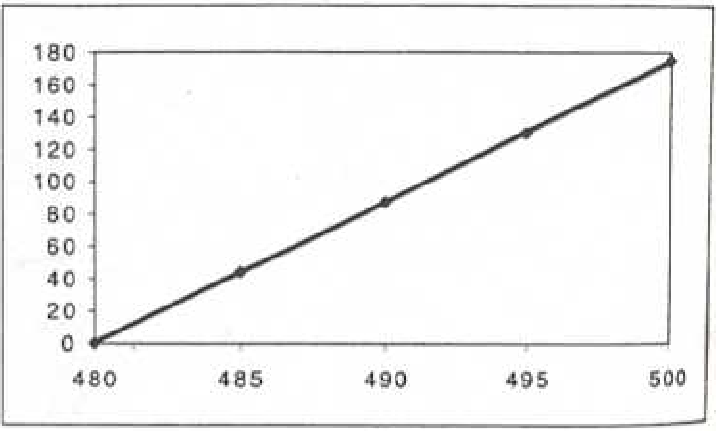
For T = 550 K

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

P10-25 (cont'd)

$$t = \frac{\exp\left\{\frac{150{,}000}{8.314}\left(\frac{1}{480} - \frac{1}{T}\right)\right\} - 1}{1.296 \times 10^{7} \exp\left\{-\frac{84{,}344}{8.314\ T}\right\}}$$

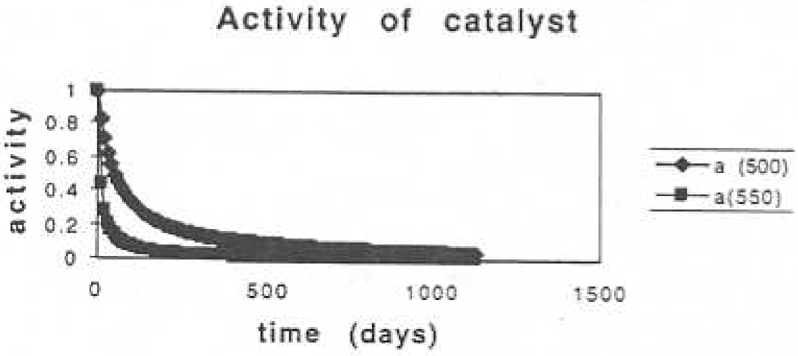
T(°K)	t(min)
480	0
485	44.3
490	87.3
495	130.4
500	174.9



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.

P10-26

First we need to find C_{A0}.

$$\frac{H_2}{ETB} = 10$$

$$y_{ETB} = 0.1$$

$$C_{A0} = \frac{P y_{ETB}}{RT} = \frac{3*10^3(0.1)}{(8.309)553} = 0.065$$

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.

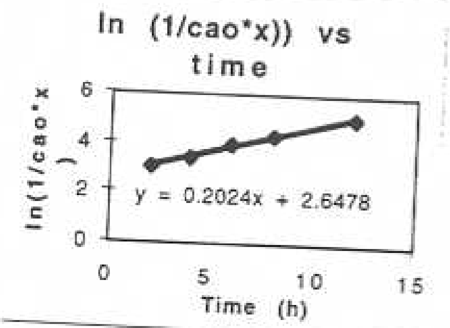
$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

$$C_{A0} - C_A = C_{A0}X$$

So we graph this:

$$\ln\frac{1}{C_{A0}X} \quad \text{vs. } t$$

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 $k_d = 0.2024$.

P10-27

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_s to get maximum conversion will be 17 kg/s.

P10-27 (cont'd)

```
10-27
Equations:                                                           Initial value
d(a)/d(w)=-kd*a/U                                                    1
d(x)/d(w)=-ra/fao                                                    0
d(T)/d(w)=(Ua*(Ta-T)+(-ra)*(-Dhr1))/(U*cps+fao*cpa)                  450
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
w0 = 0,    wf = 50
```

```
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         -0.0193928      -0.14641        -0.0193928
```

b) Using the same program we can see that the maximum conversion is 0.887.

c) Everything is the same except the energy balance:

$$\frac{dT}{dW} = \frac{U\bar{a}_W(T_a - T) + h\bar{a}_p(T_s - T) + (r_A')(\Delta H_{Rx})}{F_{A0}C_{pA}}$$

We also need an energy balance on the catalyst particles.

$$\frac{dT_s}{dW} = -\frac{h\bar{a}_p(T_s - T)}{U_sC_{ps}}$$

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: $A\,[=]\,CH_3\,CH_2\,OH$, $B\,[=]\,CH_3\,CHO$, $W\,[=]\,H_2O$, $A{\cdot}S\,[=]\,CH_3\,CH_2\,O{\cdot}S$

Mechanism is belived to be the following:

$$A + 2S \rightleftarrows A{\cdot}S + H{\cdot}S \qquad -r_A = k_A\left[P_A C_S^2 - C_{A\cdot S}\,C_{H\cdot S}/K_A\right]$$

$$O_2 + 2S' \rightleftarrows 2O{\cdot}S' \qquad -r_O = k_O\left[P_{O_2} C_{S'}^2 - C_{O\cdot S'}^2/K_O\right]$$

$$A{\cdot}S + O{\cdot}S' \rightleftarrows B + OH{\cdot}S' + S \qquad -r_{AO} = k_{AO}\left[C_{A\cdot S}\,C_{O\cdot S'} - P_B\,C_{OH\cdot S'}\,C_S/K_{AO}\right]$$

$$OH{\cdot}S' + H{\cdot}S \rightleftarrows W + S + S' \qquad -r_W = k_W\left[C_{OH\cdot S'}\,C_{H\cdot S} - P_W\,C_S\,C_{S'}/K_W\right]$$

It is given also that $C_{H\cdot S} = C_{A\cdot S}$

With reaction ($-r_{AO}$) controlling

$$\frac{-r_A}{k_A} \equiv 0 \quad C_{A\cdot S}\,C_{H\cdot S} = K_A\,P_A\,C_S^2 \text{ or } C_{H\cdot S} = C_{A\cdot S} = \sqrt{K_A\,P_A}\,C_S$$

$$\frac{-r_O}{k_O} \equiv 0 \quad C_{OS'}^2 = K_O\,P_{O_2}\,C_{S'}^2 \text{ or } C_{OS'} = \sqrt{K_O\,P_{O_2}}\,C_{S'}^2$$

$$\frac{-r_W}{k_W} \equiv 0 \quad C_{OH\cdot S'}\,C_{H\cdot S} = \frac{P_W\,C_S\,C_{S'}}{K_W} \text{ with } C_{H\cdot S} = \sqrt{K_A\,P_A}\,C_S$$

$$C_{OH\cdot S'} = \frac{P_W\,C_{S'}}{K_W\sqrt{K_A\,P_A}}$$

$$C_T = C_S + C_{H\cdot S} + C_{A\cdot S} = C_S\left[1 + 2\sqrt{K_A\,P_A}\right]$$

$$C_T = C_{S'} + C_{O\cdot S'} + C_{OH\cdot S'} = C_{S'}\left[1 + \sqrt{K_O\,P_{O_2}} + \frac{P_W}{K_W\sqrt{K_A\,P_A}}\right]$$

$$-r_{AO} = k_{AO}\left[C_{AS}\,C_{OS'} - \frac{P_B\,C_{OH\cdot S'}\,C_S}{K_{AO}}\right] = k_{AO}\left[\sqrt{K_A\,P_A\,K_O\,P_{O_2}}\,C_S\,C_{S'} - \frac{P_B\,P_W\,C_S\,C_{S'}}{K_W\,K_{AO}\sqrt{K_A\,P_A}}\right]$$

$$-r_{AO} = \frac{k_{AO}\sqrt{K_A\,K_O}\,C_S\,C_{S'}}{\sqrt{P_A}}\left[P_A\sqrt{P_{O_2}} - \frac{P_B\,P_W}{K_A\,K_W\,K_{AO}\sqrt{K_O}}\right]$$

$$K_{eq} = K_A\,K_W\,K_{AO}\sqrt{K_O}$$

$$-r_{AO} = \frac{k_{AO}\sqrt{K_A\,K_O}\,C_T\,C_T\left[P_A\sqrt{P_{O_2}} - \dfrac{P_B\,P_W}{K_{eq}}\right]}{\sqrt{P_A}\left[1 + 2\sqrt{K_A\,P_A}\right]\left[1 + \sqrt{K_O\,P_{O_2}} + \dfrac{P_W}{K_W\sqrt{K_A\,P_A}}\right]}$$

CDP10-A (cont'd)

Initially $P_B = P_W = 0$

$$-r_{AO} = \frac{k_{AO}\sqrt{K_A P_A K_O P_{O_2}}\, C_T C_{T'}}{(1 + 2\sqrt{K_A P_A})(1 + 2\sqrt{K_O P_{O_2}})}$$

(b) With reaction 3 irreversible, $-r_{A0} = k_{A0} C_{A\cdot S} C_{OS'}$. Since A·S, H·S, OH·S′ are created (and destroyed) only at the reaction surface. A stoichiometric relationship exists between them:

$$C_{H\cdot S'} = C_{A\cdot S'} + C_{OH\cdot S'} \qquad \text{(a)}$$

The same equilibrium expressions for reactions (1), (2) and (4) exist as before:

$$C_{A\cdot S}\, C_{H\cdot S} = K_A P_A C_S^2 \qquad \text{(b)}$$

$$C_{OH\cdot S'}\, C_{H\cdot S} = \frac{P_W C_S C_{S'}}{K_W} \qquad \text{(c)}$$

$$\therefore (C_{H\cdot S} - C_{A\cdot S})\, C_{H\cdot S} = \frac{P_W C_S C_{S'}}{K_W} \Rightarrow C_{H\cdot S}^2 = K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}$$

$$\text{or } C_{H\cdot S} = \sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}$$

$$C_{A\cdot S} = \frac{K_A P_A C_S^2}{\sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}}$$

$$C_{OH\cdot S'} = \frac{\frac{P_W C_S C_{S'}}{K_W}}{\sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}}$$

Expressions for C_T and C_T' become

$$C_T = C_S + C_{H\cdot S} + C_{A\cdot S} = C_S + \sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}} + \frac{K_A P_A C_S^2}{\sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}}$$

$$C_T' = C_{S'} + \sqrt{K_O P_{O_2}}\, C_{S'} + \frac{P_W C_S C_{S'}}{\sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}}$$

CDP10-A (cont'd)

with $K_A P_A C_S^2 >> \frac{P_W C_{S'} C_S}{K_W}$

$$C_T = C_S[1 + 2\sqrt{K_A P_A}]$$

$$C_T' = C_{S'}\left[1 + \sqrt{K_O P_{O_2}} + \frac{P_W}{\sqrt{K_A P_A}}\right]$$

Rate expression becomes:

$$-r_A = k_{AO}\, C_{A\text{-}S}\, C_{O\text{-}S'} = k_{AO}\, K_O \sqrt{P_{O_2}}\, C_{S'} \sqrt{K_A P_A}\, C_S \left[\frac{1}{\left(1 + \frac{P_W C_S'}{K_W K_A P_A C_S}\right)^{1/2}}\right]$$

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:

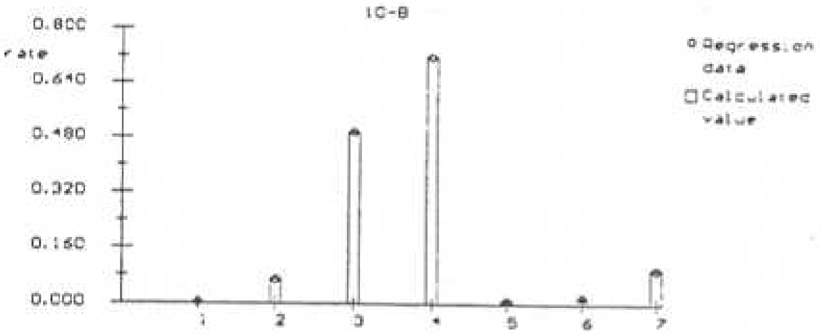
$$-r_A' \sim \frac{P_H}{1 + K_H P_H}$$

Since both reactants are adsorbed the mechanism must be a dual site. This makes the rate law:

$$-r_A' = \frac{k P_E P_H}{1 + K_E P_E + K_H P_H}$$

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 = 1.75787
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) $$\frac{dF_A}{dV} = r'_A a$$ (Plug Flow Reactor)

$$F_{A0} \frac{dX}{dV} = -r'_A a$$

CDP10-C (cont'd)

$$V = F_{A0}\int_0^X \frac{dX}{-r_A' a}$$

$$\frac{Va}{F_{A0}} = \int_0^X \frac{dX}{-r_A'}$$

$$-r_A' = \frac{k P_{N_2O} P_{DCS}}{1 + K_{N_2O} P_{N_2O}}$$

$$P_{DCS} \equiv P_A = P_{A0}\frac{(1-X)}{(1+\varepsilon X)}$$

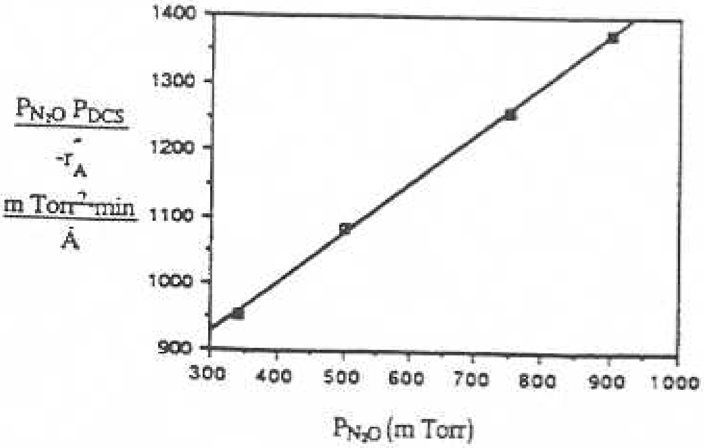
$$P_{N_2O} \equiv P_B = P_{A0}\frac{(\theta_B - 2X)}{(1+\varepsilon X)}$$

$$-r_A' = \frac{k P_{A0}^2 (1-X)(\theta_B - 2X)/(1+\varepsilon X)^2}{1 + K_B P_{A0}\dfrac{(\theta_B - 2X)}{(1+\varepsilon X)}}$$

$$= \frac{k P_{A0}^2 (1-X)(\theta_B - 2X)}{(1+\varepsilon X)^2 + K_B P_{A0}(\theta_B - 2X)(1+\varepsilon X)}$$

$$\theta_B = \frac{11.3}{3.68} = 3.07$$

$$\varepsilon = \left(\frac{3.68}{11.3 + 3.68}\right)(2 + 2 - 1 - 2) = 0.25$$



$$\text{Slope} = \frac{K}{k'} = 0.7465$$

$$\text{Intercept} = \frac{1}{k} = 703$$

$k = 1.49\times10^{-3}$ Å/mTorr^2-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

CDP10-C (cont'd)

$$-r_A^{\cdot} = 36.7\ \text{Å/min}\ \frac{(3.07 - 2X)(1-X)}{(1 + .25X)^2 + .173\,(3.07 - 2X)(1 + .25X)}$$

$F_{A0} = 3.68 \times 10^{-3}$ gmole/min

$$-r_A^{\cdot} = (\text{Å/min}) = 4.4 \times 10^{-6}\, r_A^{\cdot}\, \frac{(\text{gmole})}{(\text{m}^2\ \text{min})}$$

$a = 250$ m²/min

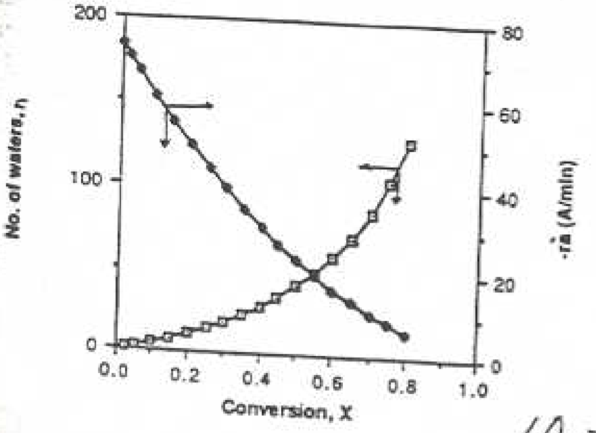
$$\frac{Va}{F_{A0}} = \int_0^X \frac{dX}{r_A^{\cdot}} \Rightarrow \text{Area under curve of } X \text{ vs. } \frac{1}{r_A^{\cdot}}$$

X	$-r_A^{\cdot}$ (Å/min)	$-1/-r_A^{\cdot}\left(\frac{\text{min}}{\text{Å}}\right)$	$1/-r_A^{\cdot}$ (m²/gmole)	$\frac{Va}{F_{A0}}$	V(m³)
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} m³/wafer

∴ Number of wafers, $n = V/9.8 \times 10^{-4}$

A plot of conversion X, vs. number, of wafers can be obtained



CDP10-C (cont'd)

The thickness on these wafers can be obtained from the same plot.

Wafer #1 : $X = 0$

$-r'_A = 73.6$ Å/min

$\therefore$ After 30 min: <u>2208 Å</u>

Wafer #50 : $X = 0.52$

$-r'_A = 20$ Å/min

$\therefore$ After 30 min: <u>600 Å</u>

Wafer #110 : $X = 0.78$

$-r'_A = 6$ Å/min

$\therefore$ After 30 min: <u>180 Å</u>

CDP10-D

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:

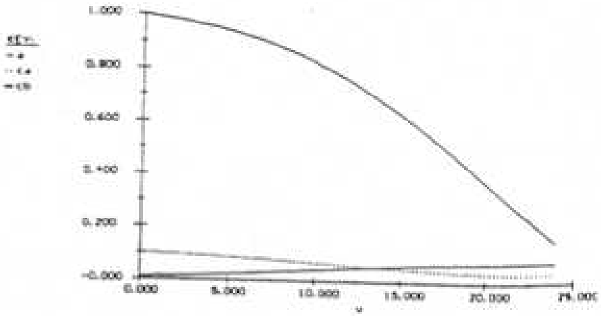
$$C_A = C_{A0}(1-X)$$
$$C_B = C_{A0}(\theta_B + X)$$

Evaluate the parameters:

$$\theta_B = \frac{C_{B0}}{C_{A0}} = \frac{0.01}{0.1} = 0.1$$

CDP10-D (cont'd)

```
Equations:                                   Initial value
d(x)/d(w)=a*(-ra)/fao                        0
d(a)/d(w)=-kd*cb/U                           1
kd=6
fao=20
U=8
k=350
cao=.1
theta=.1
ca=cao*(1-x)
cb=cao*(theta+x)
ra=-k*ca*cb
w0 = 0,    wf = 24
```



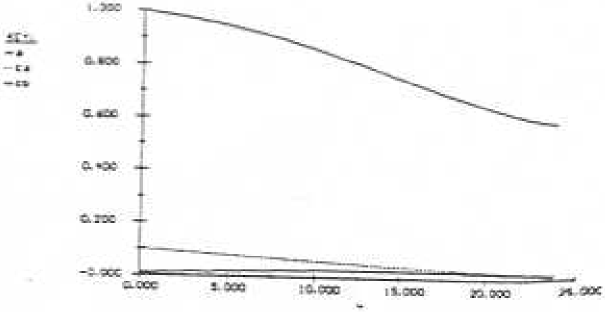
b) The only change is in the stoichiometry:

$$C_A = C_{A0}(1-X)(1-\alpha W)^{0.5}$$

$$C_B = C_{A0}(\theta_B + X)(1-\alpha W)^{0.5}$$

POLYMATH

```
Equations:                                   Initial value
d(x)/d(w)=a*(-ra)/fao                        0
d(a)/d(w)=-kd*cb/U                           1
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
```



CDP10-F

(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.

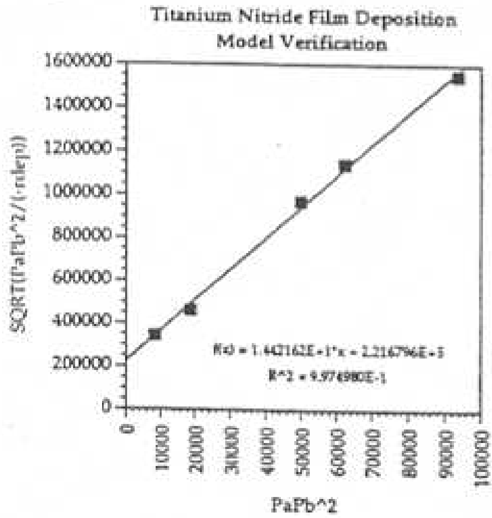
- The rate of deposition is independent of Ar and H_2.--YES
- At low partial pressures of $TiCl_4$ and NH_3, the deposition appears to be first order in $TiCl_4$ and second order in NH_3.--YES

- 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.



$$\frac{1}{\sqrt{k_1}} = \text{y} - \text{intercept} = 2.2168 \times 10^5$$

$$k_1 = 2.035 \times 10^{-11} \frac{\text{mol}}{\text{cm}^2 \cdot \text{min} \cdot \text{mT}^3}$$

$$\frac{k_2}{\sqrt{k_1}} = \text{slope} = 14.42$$

$$k_2 = 6.505 \times 10^{-5} \frac{1}{\text{mT}^3}$$

(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.

(Solution by J.T. Santini, Jr.)

CDP10-G Cumene (A) → Propylene (k) + Benzene (S)

$a \equiv \frac{r}{r_o}$

(a) We find a relationship between a and C_A

$$r = \frac{F_{A0}X}{W} = \frac{F_R}{W} = F_R \qquad (W = 1g)$$

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

$$a = e^{-\alpha C_A} \quad , \quad \alpha = 28.9$$

$$\therefore \quad r_o = \frac{k_1^* K_A [P_A - P_R P_S / K_{eq}]}{1 + K_A P_A + K_R P_R}$$ (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 $r_O = k_1^* K_A P_A$.

Using data at time zero from runs 1 and 2 : $k_1^* K_A = 3.2 \times 10^{-3}$

Hence, overall apparent rate law is

$r = k_1^* K_A e^{-\alpha C_A} P_A \quad ; \quad k_1^* K_A = 3.2 \times 10^{-3}$

$\alpha = 28.9$

(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 : $k_d P_A^n = 5.767 \times 10^{-3}$

CDP10-G (cont'd)

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 $\Rightarrow$ $n = 1.29$

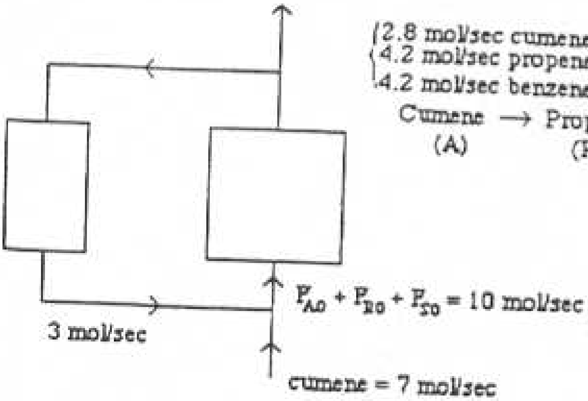
$$r = ar_o = \frac{k_1^* K_A P_A}{1 + k_d P_A^n t} \quad ; \quad k_1^* K_A = 3.2\times10^{-3}$$

$$k_d = 5.767\times10^{-3}$$

$$n = 1.29$$

t in minutes

(c) Overall conversion = 0.60



$\left.\begin{array}{l}\text{2.8 mol/sec cumene}\\ \text{4.2 mol/sec propene}\\ \text{4.2 mol/sec benzene}\end{array}\right\}\Sigma = 11.2$ mol sec

$$\underset{(A)}{\text{Cumene}} \longrightarrow \underset{(R)}{\text{Propene}} + \underset{(S)}{\text{Benzene}}$$

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

$$\begin{array}{lcl} F_{A0} = 7 + 3(0.25) = 7.75 & & y_A = 0.775 \\ F_{R0} = 3(0.375) = 1.125 & \Rightarrow & y_R = 0.1125 \\ F_{S0} = 3(0.375) = 1.125 & & y_S = 0.1125 \end{array}$$

Let $X_f \equiv$ conversion per pass

Total flow at reactor outlet before the recycle stream is:

$$F_{A0}(1-X_f) + 2\,F_{A0}X_f + F_{R0} + F_{S0} = F_{A0}(1+X_f) + F_{R0} + F_{S0}$$

$$\therefore\ y_A = \frac{F_{A0}(1-X_f)}{F_{A0}(1+X_f) + F_{R0} + F_{S0}} = 0.25 \ \Rightarrow\ X_f = 0.542$$

At any point along the reactor:

$$P_A = y_A P_1 = y_A \frac{F_{A0}(1-X)}{F_{A0}(1+X) + F_{R0} + F_{S0}} = \frac{1-X}{\beta+X}$$

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)

$$\therefore r = a\,\dot{k}_1\,K_A\,P_A = \frac{\dot{k}_1\,K_A\,P_A}{1 + k_d P_A^n t}$$

Moving bed reactor: $t = \frac{W}{U_S}$

$$F_{A0}\,dX = -r\,dW$$

$$\frac{dW}{dX} = \frac{F_{A0}}{-r} = F_{A0}\left[\frac{1 + k_d P_A^n \frac{W}{U_S}}{\dot{k}_1\,K_A\,P_A}\right] = \frac{F_{A0}\,k_d}{\dot{k}_1\,K_A\,U_S}\left(\frac{\beta+X}{1-X}\right)^{n-1} W + \frac{F_{A0}}{\dot{k}_1\,K_A}\left(\frac{\beta+X}{1-X}\right)$$

$$= \frac{7.75\times5.767\times10^{-3}}{3.2\times10^{-3}\times2000}\left(\frac{1.29+X}{1-X}\right)^{0.29} W + \frac{7.75}{3.2\times10^{-3}}\left(\frac{1.29+X}{1-X}\right)$$

$$= 6.98\times10^{-3}\left(\frac{1.29+X}{1-X}\right)^{0.29} W + 2421\left(\frac{1.29+X}{1-X}\right)$$

With $X = 0$, $W = 0$

If $X = 0.542$, using digital computer $W \cong 3.1$ kg

CDP10-H 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.

CDP10-H (cont'd)

$$E + S \leftrightarrow E \bullet S \qquad -r_A = k_A[P_E C_S - C_{E\cdot S}/K_A]$$

$$E \bullet S \leftrightarrow St \bullet S + H_2 \qquad -r_S = k_S[C_{E\cdot S} - C_{St\cdot S}\,P_{H_2}/K_S]$$

$$St \bullet S \leftrightarrow St + S \qquad -r_D = k_D[C_{St\cdot S} - P_{St}C_S/K_D]$$

To insure that P_{H_2} does not appear in the rate expression assume that the surface reaction controls:

$$\frac{-r_A}{k_A} \cong 0 \quad C_{E\cdot S} = K_A\, C_S\, P_E$$

$$\frac{-r_D}{k_D} \cong 0 \quad C_{St\cdot S} = \frac{C_S\, P_{St}}{K_D}$$

Then: $C_T\, C_S + C_{E\cdot S} + C_{St\cdot S} = C_S\left[1 + K_A\, P_E + \frac{P_{St}}{K_D}\right]$

And $-r_S = k_S\left[C_{E\cdot S} - \frac{C_{St\cdot S}\, P_{H_2}}{K_S}\right] = k_S\, K_A\, C_S\left[P_E - \frac{P_{St}\, P_{H_2}}{K_A\, K_S\, K_D}\right]$

or $-r_S = \dfrac{k_S\, C_T\, K_A\left[P_E - \dfrac{P_{St}\, P_{H_2}}{Keq}\right]}{1 + K_A\, P_E + \dfrac{P_{St}}{K_D}}$, 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 : $\frac{1}{k} = \dfrac{\left(\frac{P_E}{r_S}\right)_2 - \left(\frac{P_E}{r_S}\right)_1}{(P_E)_2 - (P_E)_1} = \dfrac{46.73 - 706.7}{0.01 - 1.0} = 666.7\ \dfrac{\text{gmcat-min}}{\text{gmole}}$

$$k = 1.50 \times 10^{-3}\ \frac{\text{gmol}}{\text{gmcat}\cdot\text{min}}$$

CDP10-H (cont'd)

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) $(MW)_E = 106.1\,\frac{\text{g}}{\text{gmole}}$, $(MW)_S = 18\,\frac{\text{g}}{\text{gmole}}$, $(MS)_{St} = 104.1\,\frac{\text{g}}{\text{gmole}}$

Then $\theta_1 = \frac{1\text{ gmole }H_2O}{5\text{ gmole E}} = 0.2$

$y_{E,0} = \frac{1}{1+\theta_1} = 0.833$; $P = P_o = 0.415$; $X_F = 0.60$; $\delta = 2-1 = 1$; $T = 903°K$

∴ $\varepsilon = y_{E,0}\,\delta = 0.833$; $F_{St} = \frac{2000\text{ Kg}}{\text{day}}\left(\frac{1\text{ kg mol}}{104.1\text{ kg}}\right) = 19.2\,\frac{\text{kg mol}}{\text{day}} = F_{E,0}X_F$

$$P_E = C_E RT = \frac{F_E RT}{\upsilon} = \frac{F_{E,0}(1-X)RT}{\upsilon_0(1+\varepsilon X)} = \frac{C_{E,0}RT(1-X)}{1+\varepsilon X} = \frac{y_{E,0}P_0(1-X)}{1+\varepsilon X}$$

$$P_{St} = C_{St}RT = \frac{F_{St}RT}{\upsilon} = \frac{F_{E,0}\,X\,RT}{\upsilon_0(1+\varepsilon X)} = \frac{y_{E,0}P_o\,X}{1+\varepsilon X}$$

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:

$$W = F_{E,0}\int_0^{X_F}\frac{dX}{-r_E} = \frac{F_{St}}{.025\ X_F}\int_0^{X_F}\left[\frac{1+\varepsilon X}{y_{E,0}\ P_o\ (1-X)}+16.64+\frac{132.7X}{1-X}\right]dX$$

$$W = \frac{F_{St}}{0.025\ X_F}\left\{\frac{1}{y_{E,0}\ P_o}(-\varepsilon X-[1+\varepsilon]\ln[1-X])+16.64X+132.7[-X-\ln(1-X)]\right\}\Bigg|_0^{X_F}$$

$$W = \frac{F_{St}}{0.025\ X_F}\left\{\frac{1}{y_{E,0}\ P_o}(-\varepsilon X_F-[1+\varepsilon]\ln[1-X_F])+16.64X_F+132.7[X_F+\ln(1-X_F)]\right\}$$

$$W = \frac{19.2\times10^3\ \text{gmol}}{\text{day}}\times\frac{1}{0.025\times0.45}\ \frac{\text{gm cat-min}}{\text{gmol}}$$

$$\left\{\frac{-.833(.45)+1.833\ln(1-.45)}{(0.833)(0.415)}+16.64\,(0.45)-132.7\,[0.45+\ln(1-0.45)]\right\}\times\frac{1\text{day}}{24*60\ \text{min}}$$

$$W = 2.71\times10^4$$

$$\text{Cost} = 27.1\times\frac{\$11}{\text{kg}} = \$298$$

CDP10-I

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

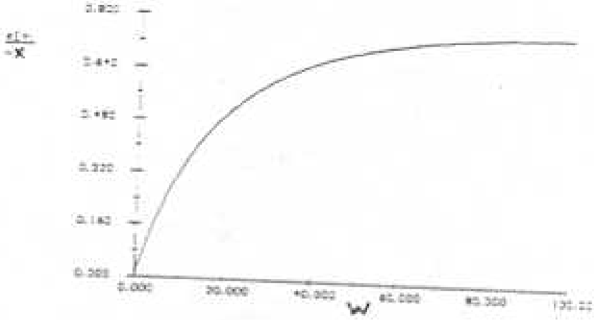
```
Equations:                                           Initial value
d(x)/d(w)=-ra*a/fao                                  0
d(a)/d(w)=-kd*a                                      1
kd=.023
fao=4
k=.09
cao=2
alp=.0099
ca=cao*(1-x)*(1-alp*w)^.5
ra=-k*ca
w0 = 0,    wf = 100
```

```
Variable      Initial value  Maximum value  Minimum value  Final
w             0              100            0              100
x             0              0.757161       0              0.7571
a             1              1              0.100259       0.1002
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      0.048
ra            -0.18          -0.0043711     -0.18          -0.00
```

X = 0.75

CDP10-I (cont'd)

b) POLYMATH



CDP10-J

Design Equation : $F_{A0}\dfrac{dX}{dW} = a(W)(-r_A')$

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 : $T = T_o \Rightarrow C_A = C_{A0}(1-X)$

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 $\dfrac{k_d}{U_s}$.

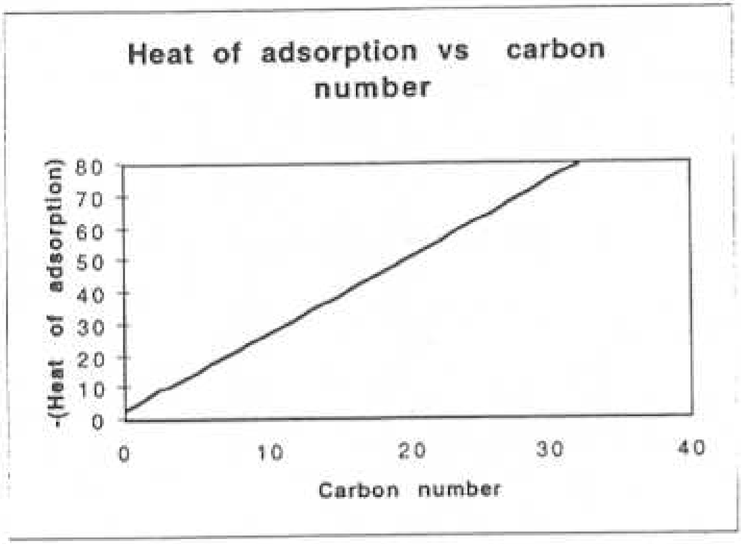
$\dfrac{k_d}{U_s} = 0.03$

$\ln\left(\dfrac{1}{1-X}\right) = \dfrac{(0.10)}{(3.75)(0.03)}\ln(1+(0.03)(100)) = 1.232 \Rightarrow \dfrac{1}{1-X} = 3.43$

$X = 0.708$

CDP10-K

The heat of activation is given in the problem as a function of the carbon number so we can just graph that:



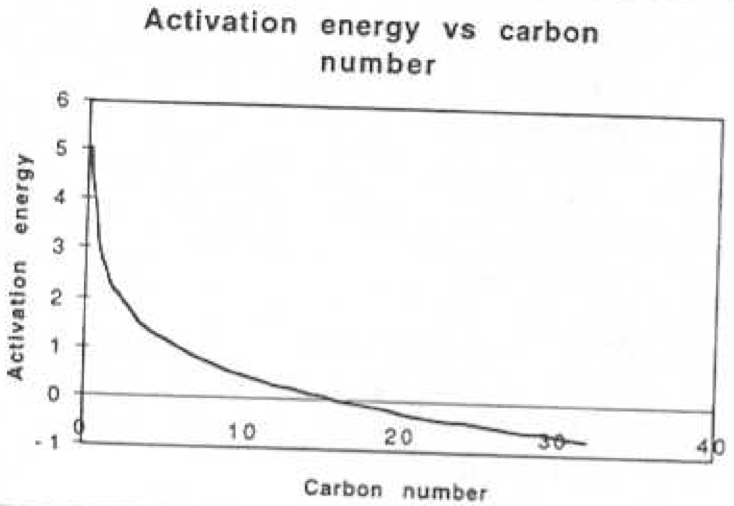
To graph the activation energy we need to find its equation. It is the Arrhenius equation.

$$k = Ae^{-E/RT}$$

Solving for E we get:

$$E = -RT\ln\left(\frac{k}{A}\right)$$

We know that as the temperature increases when $n \le 15$, 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-L 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:

$$H_2 + S \overset{k_1}{\rightleftarrows} H_2\cdot S \qquad -r_1 = k_1\left[P_{H_2}C_S - C_{H_2\cdot S}/K_1\right]$$

$$H_2\cdot S + S \overset{k_2}{\rightleftarrows} 2H\cdot S \qquad -r_2 = k_2\left[C_{H_2\cdot S}C_S - C_{H\cdot S}^2 / K_2\right]$$

CDP10-L (cont'd)

$$H\cdot S + CO \overset{k_3}{\rightleftarrows} CHO\cdot S \qquad -r_3 = k_3\left[C_{H\cdot S}P_{CO} - C_{HO\cdot S}/K_3\right]$$

$$CHO\cdot S + H\cdot S \overset{k_4}{\rightleftarrows} C\cdot S + H_2O + S \qquad -r_4 = k_4\left[C_{CHO\cdot S}\,C_{H\cdot S} - C_{C\cdot S}\,P_{H_2O}\,C_S/K_4\right]$$

$$C\cdot S + 2H_2 \overset{k_5}{\rightleftarrows} CH_4 + S \qquad -r_5 = k_5\left[C_{C\cdot S}\,P^2_{H_2} - P_{CH_4}\,C_S/K_5\right]$$

Remarks made in Chapter 5 of the text suggest that reaction 3 is rate controlling:

$$\frac{-r_1}{k_1} \cong 0 \qquad C_{H_2\cdot S} = K_1\,P_{H_2}\,C_S$$

$$\frac{-r_2}{k_2} \cong 0 \qquad C_{H\cdot S} = \sqrt{K_2\,C_{H_2\cdot S}\,C_S} = \sqrt{K_1\,K_2\,P_{H_2}}\;C_S$$

$$\frac{-r_5}{k_5} \cong 0 \qquad C_{C\cdot S} = \frac{P_{CH_4}}{K_5\,P^2_{H_2}}\cdot C_S$$

$$\frac{-r_4}{k_4} \cong 0 \qquad C_{CHO\cdot S} = \frac{C_{C\cdot S}\,P_{H_2O}\,C_S}{K_4\,C_{H\cdot S}} = \frac{P_{CH_4}\,P_{H_2O}\,C_S^2}{K_4\,K_5\,P^2_{H_2}\,C_{H\cdot S}} = \frac{P_{CH_4}\,P_{H_2O}\,C_S}{K_4\,K_5\,\sqrt{K_1\,K_2}\,P^{5/2}_{H_2}}$$

$$-r_3 = k_3\left[C_{H\cdot S}\,P_{CO} - \frac{C_{CHO\cdot S}}{K_3}\right] = k_3\left[\sqrt{K_1\,K_2\,P_{H_2}}\;P_{CO}\,C_S - \frac{P_{CH_4}\,P_{H_2O}\,C_S}{K_3\,K_4\,K_5\sqrt{K_1\,K_2}\,P^{5/2}_{H_2}}\right]$$

$$\text{or } (-r_3) = \frac{k_3\sqrt{K_1\,K_2}}{P^{5/2}_{H_2}}\,C_S\left[P^3_{H_2}\,P_{CO} - \frac{P_{CH_4}\,P_{H_2O}}{K_1\,K_2\,K_3\,K_4\,K_5}\right]$$

$$C_T = C_S + C_{H_2S} + C_{C\cdot S} + C_{CHO\cdot S}$$

$$C_T = C_S\left[1 + K_1\,P_{H_2} + \sqrt{K_1\,K_2\,P_{H_2}} + \frac{P_{CH_4}}{K_5\,P^2_{H_2}} + \frac{P_{CH_4}\,P_{H_2O}}{P^{5/2}_{H_2}\,K_4\,K_5\,\sqrt{K_1\,K_2}}\right]$$

Kinetic expression becomes

$$-r_3 = \frac{k_3\sqrt{K_1\,K_2}\,C_T\left[P^3_{H_2}\,P_{CO} - \dfrac{P_{CH_4}\,P_{H_2O}}{K_1\,K_2\,K_3\,K_4\,K_5}\right]}{\left[P^{5/2}_{H_2} + K_1\,P^{7/2}_{H_2} + \sqrt{K_1\,K_2}\,P^3_{H_2} + \dfrac{P_{CH_4}\sqrt{P_{H_2}}}{K_5} + \dfrac{P_{CH_4}\,P_{H_2O}}{K_4\,K_5}\right]}$$

Reaction is irreversible $\therefore$ let $K_5 \to \infty$ Then

$$-r_3 = \frac{k_3\sqrt{K_1\,K_2}\,C_T\,P^3_{H_2}\,P_{CO}}{P^{5/2}_{H_2}\left[1 + K_1\,P_{H_2} + \sqrt{K_1\,K_2\,P_{H_2}}\right]} = \frac{k_3\sqrt{K_1\,K_2}\;C_T\,P^{1/2}_{H_2}\,P_{CO}}{1 + K_1\,P_{H_2} + \sqrt{K_1\,K_2}\,P^{1/2}_{H_2}}$$

with $K_1\,P_{H_2} >> \sqrt{K_1\,K_2}\,P^{1/2}_{H_2}$, we get

$-r_3 = \dfrac{k_3\sqrt{K_1\,K_2}\,C_T\,P^{1/2}_{H_2}\,P_{CO}}{1 + K_1\,P_{H_2}}$. This expression implies that at moderate pressures, most of the active sites are occupied by the H_2 molecules.

CDP10-L (cont'd)

(a) Design for a plug flow reactor. Denote A[=] CO, B[=] H_2; then $y_{A0} = 0.25$, $y_{B0} =$ 0.75, $\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{y_{B0}}{y_{A0}} = 3$, $X_F = 0.80$

$\delta = 1 + 1 - 2 - 1 = -1 \quad : \quad \varepsilon = y_{A0}\,\delta = -0.75$

$$F_{A0}\,X_F = F_{CH_4} = 2000\,\frac{\text{lb}}{\text{day}} \times \frac{\text{lbmole}}{16\text{ lb}} = 125\,\frac{\text{lbmol}}{\text{day}}$$

$$F_{A0} = \frac{125}{0.8}\,\frac{\text{lbmol}}{\text{day}} = 156.25\,\frac{\text{lbmol}}{\text{day}}$$

Design equation $F_{A0}\,dX = -r_A\,dW$ or $\frac{W}{F_{A0}} = \int_0^{0.80} \frac{dX}{-r_A}$

$$-r_A = \frac{0.0183\,P_A\,P_B^{1/2}}{1 + 1.5\,P_B}$$

$$P_A = C_A\,RT = \frac{C_{A0}\,RT\,(1-X)}{1+\varepsilon X} = \frac{y_{A0}\,P_B\,(1-X)}{1+\varepsilon X}$$

$$P_B = C_B\,RT = \frac{C_{A0}\,RT\,(\Theta_B - 3X)}{1+\varepsilon X} = \frac{C_{A0}\,RT\,(3 - 3X)}{1+\varepsilon X} = \frac{3\,y_{A0}\,P_o\,(1-X)}{1+\varepsilon X}$$

$$\therefore -r_A = \frac{0.0183\left[\frac{y_{A0}\,P_o\,(1-X)}{1+\varepsilon X}\right]\left[\frac{3\,y_{A0}\,P_o\,(1-X)}{1+\varepsilon X}\right]^{1/2}}{1 + 1.5\left[\frac{y_{A0}\,P_o\,(1-X)}{1+\varepsilon X}\right]} = \frac{0.0183\,\sqrt{3}\left[\frac{y_{A0}\,P_o\,(1-X)}{1+\varepsilon X}\right]^{3/2}}{1 + 1.5\left[\frac{y_{A0}\,P_o\,(1-X)}{1+\varepsilon X}\right]}$$

$$\therefore \frac{W}{F_{A0}} = \int_0^{X_F} \left\{\frac{1 + 1.5\left[\frac{y_{A0}\,P_o\,(1-X)}{1+\varepsilon X}\right]}{0.0183\,\sqrt{3}\left[\frac{y_{A0}\,P_o\,(1-X)}{1+\varepsilon X}\right]^{3/2}}\right\} dX$$

$$\frac{W}{F_{A0}} = \frac{1}{0.0183\,\sqrt{3}\,(y_{A0}\,P_o)^{3/2}} \int_0^{X_F} \left\{\left[\frac{1+\varepsilon X}{1-X}\right]^{3/2} + 1.5\,y_{A0}\,P_o\left[\frac{1+\varepsilon X}{1-X}\right]^{1/2}\right\} dX$$

$$\frac{W}{F_{A0}} = \frac{1}{0.0183\,\sqrt{3}\,(y_{A0}\,P_o)^{3/2}} \int_0^{0.8} \left\{\left[\frac{1+(-0.25)X}{1-X}\right]^{3/2} + 3.75\left[\frac{1-0.25X}{1-X}\right]^{1/2}\right\} dX$$

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 $\int_0^{X_F} f(X)\,dX \cong \frac{\Delta X}{3}\left[f(0) + \Delta f(0.2) + 2f(0.4) + 4f(0.6) + f(0.8)\right]$

CDP10-L (cont'd)

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-M

(a) a = 0 at the end of the reactor.

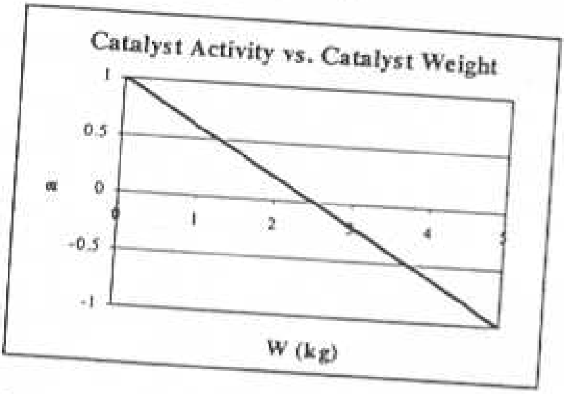
$$-\frac{da}{dW} = \frac{k_D}{U_s}$$

$$\int_1^a -da = \frac{k_D}{U_s}\int_0^W dW \quad \Rightarrow \quad 1 - a = \frac{k_D}{U_s}W$$

$$1 - 0 = \left(\frac{0.2\ \text{s}^{-1}}{U_s}\right)(5\ \text{kg}) \quad \Rightarrow \quad U_s = 1\ \text{kg/s}$$

(b) For $U_S = 0.5$ kg/s:

$$a = 1 - \frac{k_D}{U_S}W = 1 - \left(\frac{0.2\,s^{-1}}{0.5\,kg/s}\right)W = 1 - \left(0.4\,kg^{-1}\right)W$$



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 : $F_{A0}\frac{dX}{dW} = a(-r_A')$

Rate Law : $-r_A' = kC_AC_B$

Decay Law : $-\frac{da}{dW} = \frac{k_D}{U_S} = \frac{0.2\,s^{-1}}{0.5\,kg/s} = 0.4\,kg^{-1} \Rightarrow a = 1 - 0.4W$

Stoichiometry : (Assume $T = T_o, P = P_o$, and $\upsilon = \upsilon_o$)

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

Combine :

$$F_{A0}\frac{dX}{dW} = (1-0.4W)\left[kC_{A0}^2(1-X)^2\right]$$

$$\left(\frac{F_{A0}}{kC_{A0}^2}\right)\frac{dX}{(1-X)^2} = \left(1 - \frac{k_D}{U_S}W\right)dW \Rightarrow \left(\frac{F_{A0}}{kC_{A0}^2}\right)\frac{X}{(1-X)} = \left(W - \frac{k_D}{2U_S}W^2\right)$$

$$\frac{X}{(1-X)} = \frac{kC_{A0}^2}{F_{A0}}\left(W - \frac{k_D}{2U_S}W^2\right)$$

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 :

$$\frac{X}{(1-X)} = \frac{(1)(0.2)^2}{0.2}\left(2.5 - \frac{(0.2)}{2(0.5)}2.5^2\right) = 0.25$$

$X = 0.2$

CDP10-M (cont'd)

(d) To achieve 40% conversion:

$$\frac{X}{(1-X)}=\frac{kC_{A0}^2}{F_{A0}}\left(W-\frac{k_D}{2U_s}W^2\right)$$

$$\frac{0.40}{(1-0.40)}=0.2\left(5-\frac{0.2}{2U_s}5^2\right) \Rightarrow 0.667=1-\frac{2.5}{U_s}$$

$$U_s=7.5\,\text{kg/s}$$

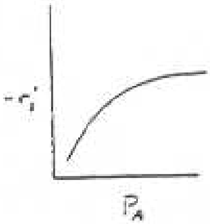
(e)

For $U_s=\infty$: $$\frac{X}{(1-X)}=\frac{kC_{A0}^2}{F_{A0}}\left(W-\frac{k_D}{2(\infty)}W^2\right) \Rightarrow \frac{X}{(1-X)}=\frac{kC_{A0}^2}{F_{A0}}(W)$$

$$\frac{X}{(1-X)}=(0.2)W=(0.2)(5)=1 \Rightarrow X=0.50$$

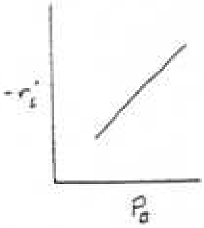
CDP10-N

(a)



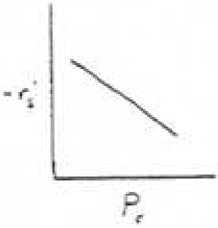
Runs 1,3,6,7

$$-r_s=\frac{P_A}{1+K_AP_A+\ldots}$$



Runs 1,2,4

$$-r_s=P_B+\ldots$$



Runs 4,5

$$-r_s=\frac{1}{1+K_CP_C+\ldots}$$

(b) Numerator: P_A and P_B

Denominator: P_A and P_C

Power of Denominator: 1

(c) Proposed Rate Law: $$-r_s=\frac{kP_AP_B}{1+K_AP_A+K_CP_C}$$

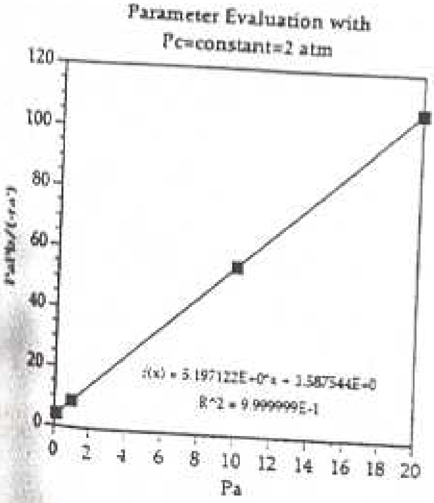
(d) To find the rate law parameters, rearrange the rate law so that it can be plotted as a line with the rate law parameters as the slope and intercept of the line.

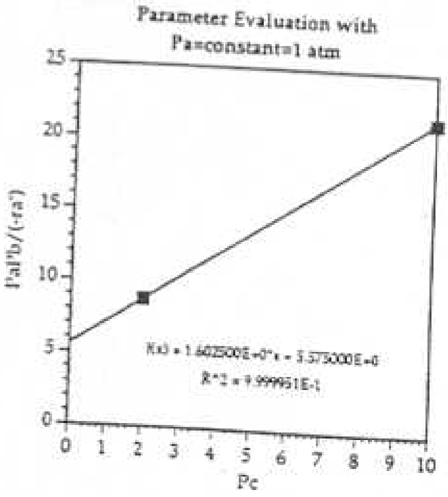
$$\frac{P_A P_B}{-r_S} = \frac{K_A}{k} P_A + \frac{K_C}{k} P_C + \frac{1}{k}$$

First, hold P_C constant and plot $\frac{P_A P_B}{-r_S}$ 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,

$$\text{Slope} = \frac{K_C}{k} = 1.6025, \quad y - \text{Intercept} = \frac{1 + K_A P_A}{k} = 5.575$$

Using the four equations above to solve for k, K_A, and K_C, we get:

$$k = 2.60 \frac{\text{mol}}{\text{gcat} \cdot \text{sec} \cdot \text{atm}^2}, \quad K_A = 13.52 \text{ atm}^{-1}, \quad K_C = 4.1665 \text{ atm}^{-1}$$

CDP10-N (cont'd)

(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, $C_V = \frac{C_T}{1 + K_A P_A + K_C P_C}$

Next, substitute the above equations into the reactions step to get

$$-r_S = \frac{k P_A P_B}{1 + K_A P_A + K_C P_C}$$

Because this is the same as the rate law in part c, the rate law and limiting step assumptions have been verified.

CDP10-N (cont'd)

(g) Ratio of sites of A to sites of B at 80% conversion:

$$\frac{C_{A\cdot S}}{C_{C\cdot S}} = \frac{K_A P_A C_v}{K_C P_C C_v} = \frac{K_A P_{A0}(1-X)}{K_C P_{A0} X} = \frac{(13.52)(0.20)}{(4.1665)(0.80)} = 0.81$$

Conversion at which the number of sites of A equal the number of sites of C:

$$\frac{C_{A\cdot S}}{C_{C\cdot S}} = \frac{K_A(1-X)}{K_C X} = \frac{(13.52)(1-X)}{(4.1665)(X)} = 1$$

$$X = 0.76$$

(Solution by J.T. Santini, Jr.)

CDP10-O

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

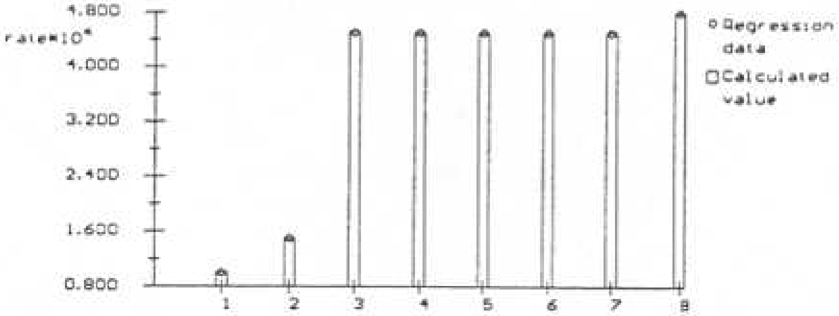
$$A \cdot S + B(g) \rightarrow C \cdot S$$

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 = 0.00044999 7                   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-P

$$\underset{(A)}{2\,C_2H_5OH} \rightarrow \underset{(E)}{C_2H_5OC_2H_5} + \underset{(W)}{H_2O}$$

$$A + S \rightleftarrows A\cdot S \qquad r_1 = k_1[P_A C_S - C_{A\cdot S}/K_1]$$

$$A\cdot S + A\cdot S \rightleftarrows E\cdot S + W\cdot S \qquad r_2 = k_2[C_{A\cdot S}^2 - C_{E\cdot S}C_{W\cdot S}/K_2]$$

$$E\cdot S \rightleftarrows E + S \qquad r_3 = k_3[C_{E\cdot S} - P_E C_S/K_3]$$

$$W\cdot S \rightleftarrows W + S \qquad r_4 = k_4[C_{W\cdot S} - P_W C_S/K_4]$$

At steady state $r = -\frac{dC_A}{dt} \Rightarrow \quad r = r_1 = 2r_2 = 2r_3 = 2r_4$

If surface reaction is controlling.

$$\frac{r_1}{k_1} \cong 0 \quad \Rightarrow C_{A\cdot S} = K_1 P_A C_S$$

$$\frac{r_3}{k_2} \cong 0 \qquad C_{E\cdot S} = \frac{P_E C_S}{K_3}$$

$$\frac{r_4}{k_4} \cong 0 \qquad C_{W\cdot S} = \frac{P_W C_S}{K_4}$$

$$C_T = C_S + C_{A\cdot S} + C_{W\cdot S} = C_S\left[1 + K_1P_A + \frac{P_E}{K_3} + \frac{P_W}{K_4}\right]$$

$$C_S = \frac{C_T}{1 + K_1P_A + \frac{P_E}{K_3} + \frac{P_W}{K_4}}$$

$$\therefore r = 2r_2 = \frac{2k_2\left[K_1^2 P_A^2 C_T^2 - \frac{P_E P_W C_T^2}{K_2 K_3 K_4}\right]}{\left[1 + K_1 P_A + \frac{P_E}{K_3} + \frac{P_W}{K_4}\right]^2} = \frac{k\left[P_A^2 - \frac{P_E P_W}{K_{eq}}\right]}{\left[1 + K_1 P_A + \frac{P_E}{K_3} + \frac{P_W}{K_4}\right]^2}$$

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 $\frac{K_1}{k}$

slope $= \sqrt{\frac{1}{k}} = 4.945 \qquad \therefore\ k = 0.0409$

intercept $= \frac{K_1}{\sqrt{k}} = 85.59 \qquad \therefore\ K_1 = 17.31$

CDP10-P (cont'd)

Using point 10, P = 0 $\therefore$ $K_4 = 0.0399$

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-Q

Design Equation : $N_{Bo}\dfrac{dX}{dt} = -r_A' aW$

Rate Law : $-r_B' = k' C_B^2$

Decay Law : $-\dfrac{da}{dt} = k_D = 0.05$

$$\int_1^a da = -0.05\int_0^t dt \quad \Rightarrow \quad a = 1 - 0.05t$$

From this we can see that the maximum reaction time is 20 min. We will find the conversion at this

Stoichiometry : (Assume constant volume)

$$C_B = C_{Bo}(1-X) = \frac{N_{Bo}}{V}(1-X)$$

Combine :

$$\frac{dX}{dt} = \frac{k'(1-0.05t)N_{Bo}^2(1-X)^2 W}{V^2 N_{Bo}} = \frac{k'WN_{Bo}}{V^2}(1-0.05t)(1-X)^2$$

$$\frac{dX}{(1-X)^2} = \frac{k'WN_{Bo}}{V^2}(1-0.05t)dt \quad \Rightarrow \quad \frac{X}{1-X} = \frac{k'WN_{Bo}}{V^2}(t-0.025t^2)$$

$$\frac{X}{1-X} = \frac{(0.01)(10)(1)}{(1)}\left(20-0.025(20)^2\right) = 1$$

$$X = 0.50$$

P10-R

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.

CDP10-R (cont'd)

```
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     -0.000878421
```

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.

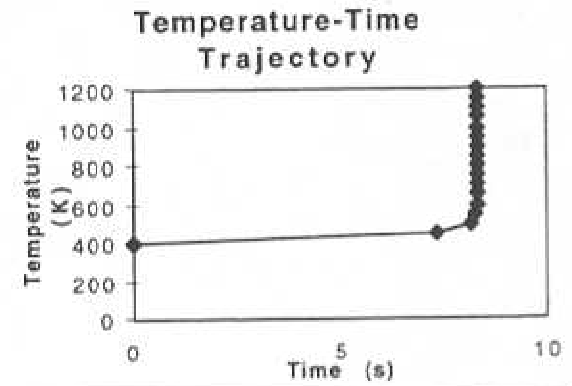
```
Variable      Initial value  Maximum value   Minimum value   Final value
w             0              100             0               100
fa            1              1               1.02629e-23     1.02629e-23
fb            0              0.524487        0               1.35042e-10
fc            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        -0.0716782      -9.56332e-12
```

c) To get the Time-Temperature trajectory we can use the following equation to create it:

CDP10-R (cont'd)

$$t = \frac{1-\exp\left[\frac{E_d}{R}\left(\frac{1}{T}-\frac{1}{400}\right)\right]}{k_{d0}\left(E_d / E_A\right)}$$

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.

$$\frac{dT}{dW} = \frac{(r_A')(\Delta H_{Rx}) + (r_B')(\Delta H_{Rx})}{C_{ps}U_S + C_p(F_A + F_B + F_C)}$$

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)
w0 = 0,    wf = 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
                                                            0.000739224
rc          0               0.00273258      0
rb          0.0265744       0.0265744       1.38516e-05     1.38516e-05
```

P11-1

No solution will be given.

Problem P11-2$_B$

Part (a)

No solution will be given.

Part (b)

No difference.

Part (c)

No difference except on physical property data.

Part (d)

The growing core model would have the same molar flux as the shrinking core

$$W_A = -\frac{De.C_{AO}}{\left(\frac{1}{R(t)} - \frac{1}{Ro}\right).r^2}$$

but R(t) , the radius of the carbon interface will increase with time rather than decrease.

The rate of appearance of carbon is equal to the flux of oxygen to the gas-carbon interface

$$r_c'' = -W_{AR}|_{r=R} = -\frac{De.C_{AO}}{\left(R - \frac{R^2}{Ro}\right)} \qquad \text{and} \qquad \frac{dR}{dt} = \frac{r_c''}{\phi_c.\rho_c}$$

$$\frac{dR}{dt} = -\frac{De.C_{AO}}{\phi_c.\rho_c}.\frac{1}{\left(R - \frac{R^2}{Ro}\right)}$$

as for the shrinking model but without the minus sign, because R increases with time.

P11-2 cont'd

Boundary conditions $t = 0$ $R = Ro$

$$\int_{Ro}^{R}\left(R-\frac{R^2}{Ro}\right)dR=\frac{De.C_{AO}}{\phi_c.\rho_c}\int_0^t dt$$

$$\frac{R^2-Ro^2}{2}-\frac{R^3-Ro^3}{3R_0}=\frac{De.C_{AO}}{\phi_c.\rho_c}t$$

Part (e)

Liquid phase : e.g. water $\mathrm{Re}=\frac{\rho.u.d}{\mu}=\frac{1000\times0.1\times0.05}{10e-3}=5000$

P11-2 cont'd

$$Sc = \frac{\mu}{\rho . D_{AB}} = \frac{10e-3}{1000 \times 10e-9} = 1000$$

single spheres

$$Sh = 2 + 0.6Re^{1/2}\, Sc^{1/3} = 2 + 0.6(5000)^{1/2}\,(1000)^{1/3} \sim 400$$

$$kc = \frac{Sh. D_{AB}}{dp} = \frac{400 \times 10e-9}{0.002} = 0.0002 m^2 / s$$

Gas phase : e.g. air

$$Re = \frac{\rho . u. d}{\mu} = \frac{1 \times 0.1 \times 0.05}{10e-5} = 500$$

$$Sc = \frac{\mu}{\rho . D_{AB}} = \frac{10e-5}{1 \times 10e-9} = 1$$

$$Sh = 2 + 0.6Re^{1/2}\, Sc^{1/3} = 2 + 0.6(500)^{1/2}\,(1)^{1/3} \sim 15$$

$$kc = \frac{Sh. D_{AB}}{dp} = \frac{15 \times 10e-5}{0.002} = 0.075 m^2 / s$$

Problem P11-3$_B$

Mol balance on oxygen : $F_{O_2} - 0 + r_{O_2} = 0$ constant liquid composition.

$F_{O_2} = C_{O_2} . \upsilon_o$ and $r_{O_2} = - k.C_{O_2}^{n}$ where n is the reaction order.

Assuming ideal gas law applies : $F_{O_2} = \frac{P.\upsilon_o}{R.T}$ 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 $F_{O_2} = C. \upsilon_o$

Assuming Henry's law applies (low pressures) $C_{O_2} = H.P_{O_2}$

where H is Henry's constant and P_{O_2} is the oxygen partial pressure

P11-3 cont'd

Substituting into the mol balance : $F_{O_2} = -r_{O_2}$

$$C.\upsilon_o = k.C_{O_2}^n = k.(H.P_{O_2})^n$$

$$\upsilon_o = P_{O_2}^n.\frac{k.H^n}{C}$$

$$\ln \upsilon_o = n.\ln P_{O_2} + \ln\frac{k.H^n}{C}$$

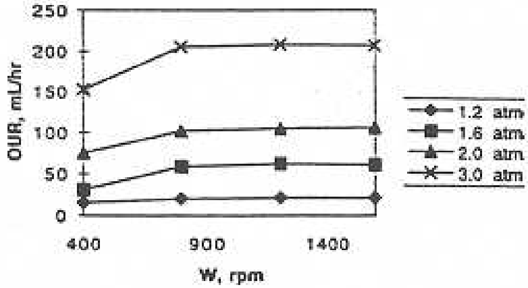
A plot of $\ln \upsilon_o$ vs $\ln P_{O_2}$ will give n as the gradient.

As the system pressure, P, given in the data is absolute : $P = P_x + P_{O_2}$

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

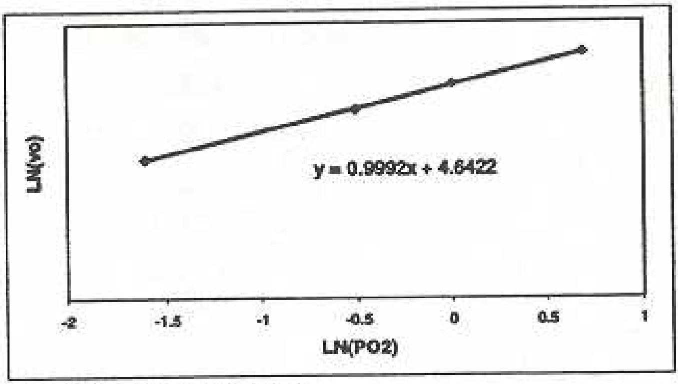
Hence using the system pressure data at 1600 rpm for the plot of $\ln \upsilon_o$ vs $\ln P_{O_2}$ will give n uninfluenced by diffusion.

$P_{O_2} = P - P_x = P - 1$

P11-3 cont'd

At 1600 rpm

υ_o, ml/hr	ln υ_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:

$$-r_{O2} = k.C_{O2}^{1}$$

Problem P11-4$_B$

Part (a & b) *Packed bed, mass tranfer limited, gas phase*

Mol balance :

$$-\frac{1}{Ac}\frac{dFa}{dz} + ra''.a_c = 0$$

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

P11-4 cont'd

Stoichiometry : Assume constant T, P, gas phase

$$Ca = \frac{Cao.(1-X)}{(1+\varepsilon.X)} \qquad \text{where } \varepsilon = yao.\delta = 0.05 \text{ x } 3 = 0.15$$

Combining :

$$\frac{U.Cao.dX}{dz} = ra''.a_c$$

$$Cao.Uo.\frac{dX}{dz} = a_c.kc.Ca$$

$$\frac{dX}{dz} = \frac{a_c.kc.(1-X)}{Uo.(1+0.15X)}$$

Use Thoenes & Kramers correlation for kc : $Sh' = (Re')^{1/2}(Sc')^{1/3}$

$$\frac{kc.dp}{Dab}\cdot\left(\frac{\phi}{1-\phi}\right)\cdot\frac{1}{\gamma} = \left[\frac{U.dp.\rho}{\mu.(1-\phi).\gamma}\right]^{1/2}\left[\frac{\mu}{\rho.Dab}\right]^{1/3}$$

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

$$Dab = \frac{0.001(773)^{1.75}\left[\frac{1}{84}+\frac{1}{2}\right]^{1/2}}{2\left[\left(\sum 122\right)^{1/3}+(7.07)^{1/3}\right]^2} = 0.857cm^2/s$$

P11-4 cont'd

$\phi = 0.4$

$$\gamma = \frac{2.\pi.\frac{d^2}{4} + \pi.d.l}{\pi.dp^2} = \frac{\frac{0.5^2}{2} + 0.5(0.5)}{0.572} = 1.146$$

$$Uo = \frac{\upsilon_o}{Ac} = \frac{60000}{\frac{\pi.dt^2}{4}.60} = 50.9 cm/s$$

$$U = Uo.(1 + \varepsilon.X) = 50.9(1 + 0.15X)$$

$$\rho = \frac{RMM.P}{R.T} = \frac{(84x0.05x2) + (2x0.95x2)}{0.0821x773} = 0.19 gm/l = 0.00019 g/cm^3$$

$\mu = 0.00017$ g/cm.s (H_2 , 500 K , 2 atm)

$$\text{Re}' = \frac{50.9(1 + 0.15X)0.572x0.00019}{0.00017(1 - 0.4)1.146} = 47.3(1 + 0.15X)$$

$$Sc' = \frac{0.00017}{0.00019x0.857} = 1.044$$

$$kc.\frac{0.572}{0.857}\left(\frac{0.4}{1 - 0.4}\right).\frac{1}{1.146} = 0.388.kc$$

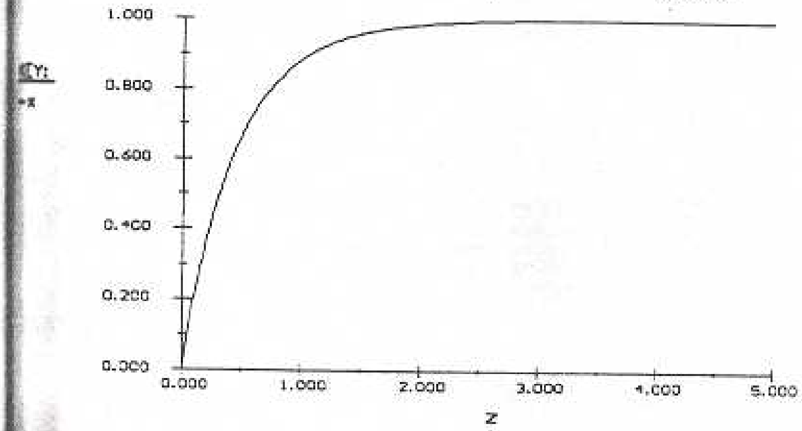
$$kc = \frac{1}{0.388}.[47.3(1 + 0.15X)]^{1/2}[1.044]^{1/3} = 17.98(1 + 0.15X)^{1/2}$$

$$a_c = \frac{6(1 - 0.4)}{0.572} = 6.29 cm^{-1}$$

$$\frac{dX}{dz} = 2.22\frac{(1 - X)}{(1 + 0.15X)^{1/2}} \qquad \text{POLYMATH}$$

```
Problem P11-4B part a/b
ations:
x)/d(z)=2.22*(1-x)/(1+.15*x)^.5                                Initial value
                                                               0
 = 0,    zf = 5

riable        Initial value  Maximum value  Minimum value  Final value
              0              5              0              5
              0              0.99997        0              0.99997
```



```
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.

P11-4 cont'd

Part (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:

$$dp=\left[\frac{6}{\pi}.Vp\right]^{1/3}=\left[\frac{6(0.25)^2 0.25}{4}\right]^{1/3}=0.286cm$$

$$\gamma=\frac{2.\pi.\frac{d^2}{4}+\pi.d.l}{\pi.dp^2}=\frac{\frac{0.25^2}{2}+0.25(0.25)}{0.286}=1.145$$

$$Re'=\frac{50.9(1+0.15X)0.286x0.00019}{0.00017(1-0.4)1.145}=23.68(1+0.15X)$$

$$kc.\frac{0.286}{0.857}\left(\frac{0.4}{1-0.4}\right).\frac{1}{1.145}=0.194.kc$$

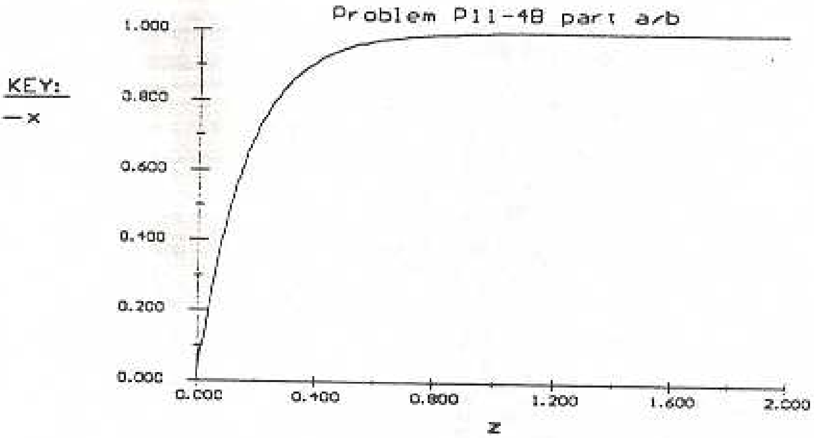
$$kc=\frac{1}{0.194}.\left[23.68(1+0.15X)\right]^{1/2}\left[1.044\right]^{1/3}=25.39(1+0.15X)^{1/2}$$

$$a_c=\frac{6(1-0.4)}{0.286}=12.59cm^{-1}$$

$$\frac{dX}{dz}=\frac{12.59x25.39(1+0.15X)^{1/2}}{50.9}.\frac{(1-X)}{(1+0.15X)}$$

$$\frac{dX}{dz}=6.28\frac{(1-X)}{(1+0.15X)^{1/2}}$$ POLYMATH

P11-4 cont'd



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.

Part (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 :

$$\rho = \frac{RMM.P}{R.T} = \frac{(84x2)}{0.0821x773} = 2.647gm/l = 0.00265g/cm^3$$

μ = ? g/cm.s (cyclohexane , 500 K , 2 atm)

Part (e)

This problem gives an indication as to how changes in parameters may affect a packed bed.

Problem P11-5$_B$

Mass transfer limited, rapid reaction, packed bed.

$X_1 = 0.632$ for d_p, L_b and υ_o

$X_2 = ?$ for $d_p/3$, $1.5\,L_b$ and $4\,\upsilon_o$

$$X = 1-\exp\left(-\frac{kc.a_c.L}{u}\right) \quad \text{or} \quad Ln\left(\frac{1}{1-X}\right)=\frac{kc.a_c.L}{u}$$

Thoenes and Kramers $Sh' = Re'^{1/2}\,Sc'^{1/3}$

$$Re' = \frac{Re}{(1-\phi)\gamma}=\frac{\rho u d_p}{\mu(1-\phi)}$$

assume spheres ($\gamma = 1$) and constant fluid properties, voidage.

$$Sc' = \frac{\mu}{\rho.D_{AB}} \qquad Sh' = \frac{Sh.\phi}{(1-\phi).\gamma}=\frac{kc.d_p.\phi}{D_{AB}(1-\phi)}$$

$$kc = \frac{D_{AB}.(1-\phi)}{d_p.\phi}\left(\frac{\rho.u.d_p}{1-\phi}\right)^{1/2} Sc^{1/3}$$

$$kc \propto \frac{u^{1/2}}{d_p^{1/2}} \qquad u = \frac{\upsilon_o}{A_b}$$

constant bed diameter $u \propto \upsilon_o$

$$a_c = \frac{6.(1-\phi)}{d_p} \qquad a_c \propto \frac{1}{d_p}$$

$$Ln\left(\frac{1}{1-X}\right) \propto \left(\frac{\upsilon_o}{d_p}\right)^{1/2}\frac{1}{d_p}L\frac{1}{\upsilon_o} \propto \frac{1}{\upsilon_o^{1/2}}.\frac{1}{d_p^{3/2}}.L$$

$$\frac{Ln\left(\frac{1}{1-0.632}\right)}{Ln\left(\frac{1}{1-X_2}\right)} = \frac{(4\upsilon_o)^{1/2}}{\upsilon_o^{1/2}}.\frac{\left(\frac{d_p}{3}\right)^{3/2}}{d_p^{3/2}}.\frac{L}{1.5L} = 2\left(\frac{\upsilon_o}{\upsilon_o}\right)^{1/2}\left(\frac{1}{3}\right)^{3/2}\left(\frac{d_p}{d_p}\right)^{3/2}\frac{1}{1.5}$$

$$= 0.257$$

$$Ln\frac{1}{1-X_2} = \frac{Ln\dfrac{1}{1-0.632}}{0.257} = 3.896$$

$X_2 = 0.98$

P11-5 cont'd

Proposed guidelines for optimum process conditions :

Use high T, so that the removal of chlorine is only mass transfer limited (i.e. rapid reaction rate cf diffusion).

Increasing υ (directly proportional to velocity u) , enhances the mass transfer coefficient but also acts to reduce conversion X. The latter dependency is more influential on X (raised to a higher power), so reduction of υ may be preferable (for constant packed bed properties). If conversion is already high enough, then a larger velocity may be preferable for a mass transfer limited reaction.

The mass transfer rate can be increased by increasing the concentration gradient achieved by increasing the bulk C_A.

Problem P11-6$_B$

Mass transfer limited, packed bed, reversible reaction.

Part (a)

Assume a Langmuir-Hinshelwood mechanism surface reaction

$$-r_{As}'' = \frac{k1.C_{As} - k2.C_{Bs}}{1 + k_A.C_{As} + k_B.C_{Bs}}$$

at high T weak adsorption $1 >> k_A.C_{As} + k_B.C_{Bs}$

$$-r_{As}'' = k1.C_{As} - k2.C_{Bs} = k1\left[C_{As} - \frac{C_{Bs}}{K}\right]$$

where equilibrium constant $K = \frac{k1}{k2}$

Mass transfer limited boundary conditions $W_A|_{surface} = k_A.(C_A - C_{As}) = -r_{As}''$

$W_B|_{surface} = k_B.(C_{Bs} - C_B) = -r_{As}''$

$$k1\left[C_{As} - \frac{C_{Bs}}{K}\right] = -r_{As}''$$

P11-6 cont'd

$$C_A - C_{As} = \frac{-r_{As}}{k_A} \qquad (1)$$

$$C_B - C_{Bs} = \frac{-r_{As}}{k_B} \qquad (2)$$

$$\left[C_{As} - \frac{C_{Bs}}{K}\right] = \frac{-r_{As}''}{k1} \qquad (3)$$

(1) + (3) eliminates C_{As}

$$-r_{As}''\left[\frac{1}{k_A} - \frac{1}{k1}\right] = C_A + \frac{C_{Bs}}{K}$$

$$-r_{As}''\left[\frac{1}{k_A} - \frac{1}{k1}\right].K = K.C_A + C_{Bs} \qquad (4)$$

(2) + (4) eliminates C_{Bs}

$$-r_{As}''\left[\left(\frac{1}{k_A} - \frac{1}{k1}\right).K + \frac{1}{k_B}\right] = K.C_A - C_B$$

$$-r_{As}''\left[\left(\frac{1}{k_A} - \frac{1}{k1}\right) + \frac{1}{K.k_B}\right] = C_A - \frac{C_B}{K}$$

But it is mass transfer limited so k1 is relatively large

$$-r_{As}''\left[\frac{1}{k_A} + \frac{1}{K.k_B}\right] = C_A - \frac{C_B}{K}$$

$$-r_{As}'' = \frac{C_A - \frac{C_B}{K}}{\left[\frac{1}{k_A} + \frac{1}{K.k_B}\right]}$$

Gives

$$-r_{As}'' = \frac{k_B\left[C_A - \frac{C_B}{K}\right]}{\frac{k_B}{k_A} + \frac{1}{K}}$$

Part (b)

$X_1 = X_2$ $$Ln\left(\frac{1}{1-X}\right) = \frac{kc.a_c.L}{u}$$

Thoenes and Kramers $Sh' = Re'^{1/2}\, Sc'^{1/3}$

$Sh' \propto kc$ and $Re' \propto u$

$$\frac{kc_1.a_{c1}.L_1}{u_1} = \frac{kc_2.a_{c2}.L_2}{u_2}$$

$$k_C = \frac{D_{AB}(1-\phi)}{d_p\phi}\left(\frac{\rho u d_p}{\mu(1-\phi)}\right)^{\frac{1}{2}}\left(\frac{\mu}{\rho D_{AB}}\right)^{\frac{1}{3}}$$

$k_A \propto u^{1/2}$ all other parameters are constant

$a_{c1} = a_{c2} =$ constant

$$\frac{L_1}{u_1^{1/2}} = \frac{L_2}{u_2^{1/2}}$$

if the flowrate is doubled and the diameter of the packed bed remains the same, then $u_2 = 2\,u_1$

$$L_2 = (2u_1)^{1/2}\frac{L_1}{u_1^{1/2}} = 1.41L_1$$

Hence the required catalyst weight W_2 will be 1.41 W_1, the original catalyst weight, if the strategy is to increase bed length rather than diameter.

$$X = 1 - \exp\left(-\frac{kc.a_c.L}{u}\right)$$ let

$$E = \left(\frac{k_C a_C L}{u}\right)$$

$$1 - \frac{1}{e^E} = X$$

E increases, e^E increases, $1/e^E$ decreases, X increases

P11-6 cont'd

If u ↑ then E and X ↓

Temperature, T, affects kc (via D_{AB}, μ and ρ)

$$kc \propto D_{AB}\left(\frac{\rho}{\mu}\right)^{1/2}\left(\frac{\mu}{\rho . D_{AB}}\right)^{1/3}$$ from T-K correlation

hence $E \propto \frac{D_{AB}^{2/3}\rho^{1/6}}{\mu^{1/6}}$

If T ↑ then μ ↓ but ρ and D_{AB} ↑ so kc, E and X ↑

Particle size, d_p, affects kc and a_c (not u if voidage remains the same)

$$kc \propto \frac{1}{d_p^{1/2}}$$ from T-K correlation

$$a_c \propto \frac{1}{d_p}$$

Hence $E \propto \frac{1}{d_p^{3/2}}$

If d_p ↑ then E and X↓

Problem P11-7$_B$

Mesh, gas phase

Mol balance : $\frac{dFa}{dV} = -kc.a_c.Ca$ $Fao\frac{dX}{dV} = kc.a_c.Ca$

Stoichiometry : constant T, P

$$Ca = Cao.\frac{(1-X)}{(1+\varepsilon.X)}$$ ε = yao.δ

P11-7 cont'd

$$\text{voidage},\ \varepsilon = 1-\pi.L.\frac{N^2 d}{4} = 1-\pi.\left[\frac{1}{250^2}+\left(\frac{0.044}{25.4}\right)\right]^{1/2} 250^2.\frac{0.044}{25.4x4} = 0.63$$

At STP (273 K, 1 atm) : 22.4 dm^3 – 1 mol gas

$$\text{Assume ideal gas law}: V2 = \frac{P1.V1.T2}{P2.T1} = \frac{1x22.4x500}{2x273} = 20.5 dm^3 / mol$$

Total molar flowrate, Fo = 8.44 x 10 = 84.4 mol/min

υ_0 = 20.5 Fo = 20.5 x 84.4 = 1731 dm^3 /min = 1731e3 cm^3 /min

$$Ac = \frac{\pi.d_{mesh}^2}{4} = \frac{\pi.10^2}{4} = 78.53 cm^2$$

$$u = \frac{\upsilon_0}{Ac} = \frac{1731e3}{78.53x60} = 367.4 cm/s$$

$$\mathrm{Re} = \frac{1.387.\dfrac{3.67}{0.63}0.044e-3}{2.7e-5} = 13.17$$

$$Sc = \left(\frac{\mu}{\rho.Dab}\right)$$

$D_{NH3,\ air}$ (295 K, 1 atm) = 0.247 cm^2 /s

$$D_{NH3,\ air}\ (500\ K,\ 2\ atm) = 0.247.\frac{1}{2}.\left(\frac{500}{295}\right)^{1.75} = 0.311 cm^2/s$$

$$Sc = \left(\frac{2.7e-5}{1.387x0.311e-4}\right) = 0.626$$

$$\mathrm{Sh} = \mathrm{Sc}^{1/3}.\mathrm{Re}.J_D = \frac{kc.d_w}{Dab}$$

$$kc = \frac{0.311}{0.0044}.0.626^{1/3}13.17\frac{0.94}{13.17^{0.717}} = 118 cm/s$$

P11-7 cont'd

For 1 mol NH_3 $\quad N_T = N_a + N_b = 1 + 1.25\frac{5}{4}\cdot\frac{1}{0.21} = 8.44$

$$y_{A0} = \frac{1-0.118}{8.44} \qquad \varepsilon = 0.118 \text{ x } 0.25 = 0.0295$$

$$C_{A0} = y_{A0}\frac{P}{RT} = \frac{0.118*2}{0.0821*500K} = 0.00575$$

$$F_{A0} = \frac{10}{60} = 0.167 mol/\min$$

a_g = total screen surface area per total volume of one screen

$$= \pi.L.N^2 = \pi.\left[\frac{1}{N^2} + d_w^2\right]^{1/2} N^2 \qquad N = \text{mesh size} = 250$$

$$= \pi.\left[\frac{1}{250^2} + \left(\frac{0.044}{25.4}\right)^2\right]^{1/2} 250^2 = 855 inch^{-1} = 337 cm^{-1}$$

Using Colburn J factor for kc :

$$J_D = \frac{Sh}{Sc^{1/3}\,\text{Re}} = \frac{0.94}{\text{Re}^{0.717}} \qquad \text{for mesh}$$

$$\text{Re} = \frac{\rho.u_i.d_w}{\mu}$$ but u_i is the actual velocity in the mesh

and $u_i = \frac{u}{\phi}$ where u is the superficial velocity

Assume ρ (air, 500 K, 2 atm) = 1.387 kg/m^3

μ (air, 500 K, 2 atm) = 2.7 e-5 kg/m.s

ChemCAD III physical properties database

P11-7 cont'd

Substituting into the mol balance:

$$\frac{dX}{dV} = k_C a_s \frac{1-X}{(1+0.03X)}$$

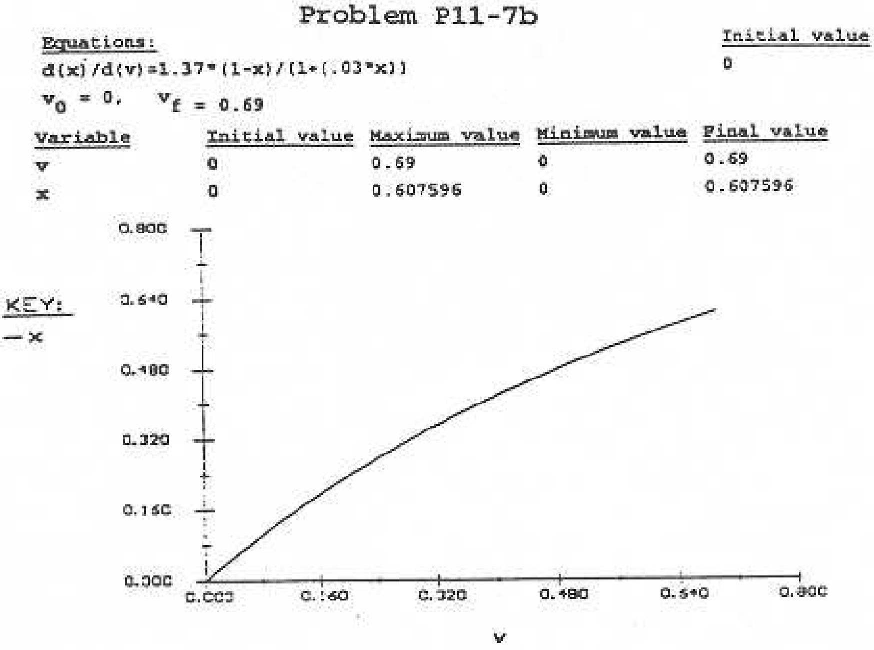
$$= 118 \times 337 \frac{0.00575e-3}{0.167} \frac{(1-X)}{(1+0.03X)}$$

$$= 1.37 \frac{(1-X)}{(1+0.03X)}$$

where

$$V_{screen} = \frac{\pi d_{screen}^2}{4} 2d_w = \frac{\pi \times 10^2 \times 2 \times 0.0044}{4} = 0.69 \text{ cm}^3$$

POLYMATH

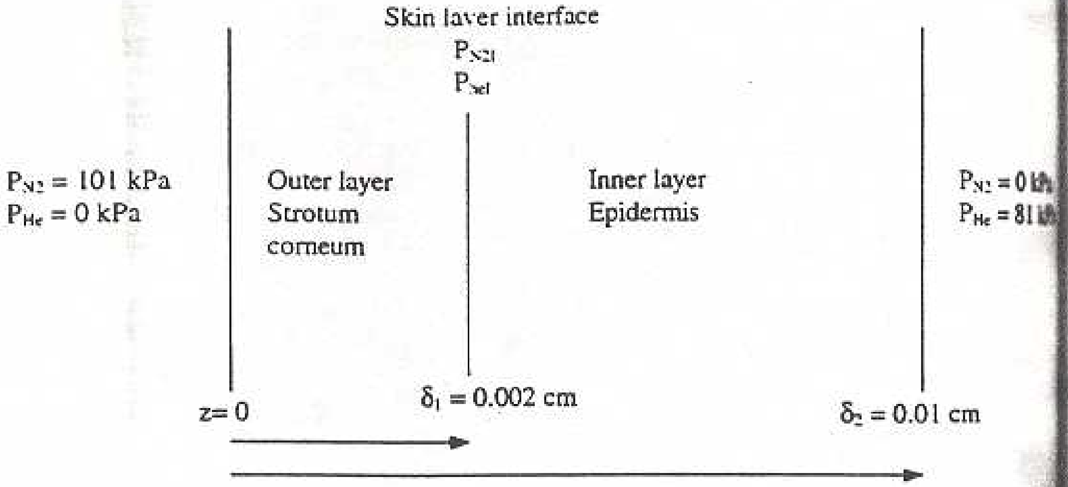


```
                     Problem P11-7b
Equations:                                                   Initial value
d(x)/d(v)=1.37*(1-x)/(1+(.03*x))                              0
v0 = 0,    vf = 0.69
Variable        Initial value   Maximum value   Minimum value   Final value
v               0               0.69            0               0.69
x               0               0.607596        0               0.607596
```

The results show that with a single screen, the final conversion is 60.7 % and is just sufficient for the requirement.

Problem P11-8$_C$

Diffusion in adjacent skin layers



Assuming dilute solution and constant total concentration in both layers gives:

$$\frac{d^2C_A}{dz^2}=0 \qquad \frac{dC_A}{dz}=K_1 \qquad C_A=K_1.z+K_2$$

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 $$C_A=C_{AI}.\left(\frac{\delta_2-z}{\delta_2-\delta_1}\right)$$

P11-8 cont'd

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*

$$P_A + P_B = P_A + P_B$$

$$1010 + 4000.z = 810 + 26000(0.01 - z)$$

$$1018 = 1018$$ correct!

Plot these two profiles across the skin from z = 0 to z = 0.01 cm

P11-8cont'd

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 $z = \delta_1$, $C_B = C_{BI}$

$z = 0$, $C_B = 0$

$$K_2 = 0 \qquad K_1 = \frac{C_{BI}}{\delta_1}$$

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. $W_{A1} = W_{A2}$

$$\frac{W_A}{\frac{D_{1N2}}{\delta_1}} = [C_{AO} - C_{AI}] \qquad \frac{W_A}{\frac{D_{2N2}}{\delta_2 - \delta_1}} = [C_{AI} - 0]$$

P11-8 cont'd

$$W_A.\left[\frac{1}{\frac{D_{1N2}}{\delta_1}}+\frac{1}{\frac{D_{2N2}}{\delta_2-\delta_1}}\right]=C_{AO}$$

Conversion of kPa to kg/cm*s^2
101kPa=101000Pa=101000kg/ms^2=1010kg/cms^2 ∴ 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 : $W_B=\frac{D_{1He}}{\delta_2}[C_{BI}-0]$

Inner layer : $W_B=\frac{D_{2He}}{\delta_2-\delta_1}.[C_{BO}-C_{BI}]$

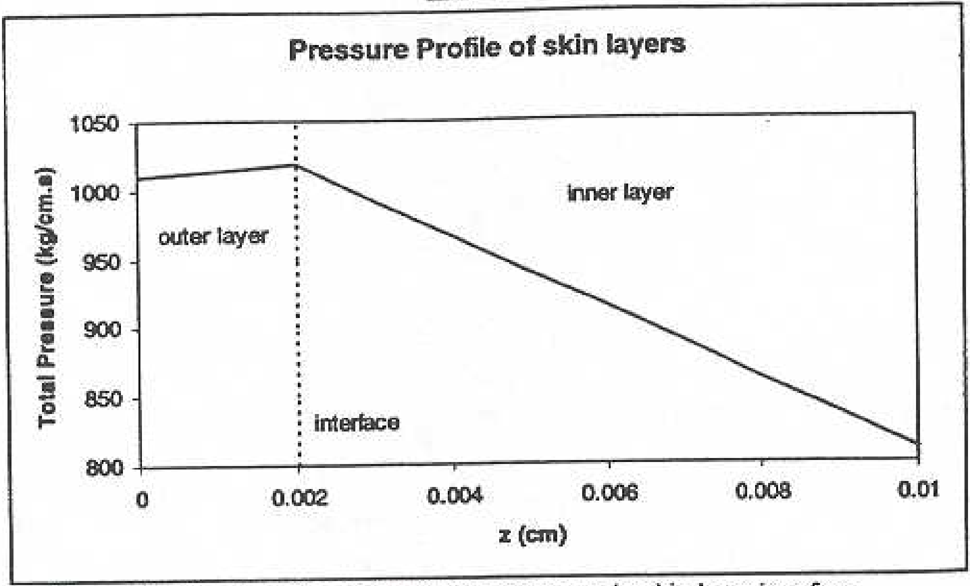
$$W_B.\left[\frac{1}{\frac{D_{1He}}{\delta_1}}+\frac{1}{\frac{D_{2He}}{\delta_2-\delta_1}}\right]=C_{BO}$$

$$W_B=\frac{C_{BO}}{\left[\frac{1}{\frac{D_{1He}}{\delta_1}}+\frac{1}{\frac{D_{2He}}{\delta_2-\delta_1}}\right]}=\frac{81x10}{\left[\frac{1}{\frac{10e-5}{0.002}}+\frac{1}{\frac{5x10e-7}{0.008}}\right]}=5x10e-2kg/cm^2s$$

Hence : $P_{AI}=\frac{W_A}{\frac{D_{2N2}}{\delta_2-\delta_1}}=\frac{1.89x10e-2}{\frac{1.5x10e-7}{0.008}}=1008kg/cm.s^2$

$$P_{BI}=\frac{W_B}{\frac{D_{2He}}{\delta_1}}=\frac{5x10e-2}{\frac{10e-5}{0.002}}=10kg/cm.s^2$$

P11-8 cont'd



The maximum sum of partial pressures occurs at the skin layer interface

$$z = 0.002 \text{ cm} \qquad P_{Total} = 1018 \text{ kg/cm.s}^2$$

$$P_{sat} = 101 \text{ kPa} = 1010 \text{ kg/cm.s}^2 < P_{Total} = 1018 \text{ kg/cm.s}^2$$

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.

Problem P11-9$_A$

Dissolution of monodisperse solid particles in excess solvent.

$$Di - D + \frac{1}{2D^*}(Di^2 - D^2) = \alpha.t$$

Define conversion in terms of volume dissolved : $X = \dfrac{\frac{\rho.\pi}{6}(Di^3 - D^3)}{\frac{\rho.\pi}{6}Di^3}$

gives $D = Di\,(1 - X)^{1/3}$

P11-9 cont'd

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

$$Di - \mathrm{Di}\,(1 - X)^{1/3} = \alpha.\mathrm{t}$$

$$1 - (1 - X)^{1/3} = \frac{\alpha.t}{Di}$$

Mass transfer controls : D* is small, term 1 is small cf term 2

$$\frac{1}{2D*}\left(Di^2 - \left[\mathrm{Di}\,(1 - X)^{1/3}\right]^2\right) = \alpha.t$$

$$\frac{Di}{2D*}(1-(1-X)^{2/3}) = \frac{\alpha.t}{Di}$$

Both regimes apparent : Term 1 and term 2 apply

$$\left[1 - (1 - X)^{1/3}\right] + \left[\frac{Di}{2D*}(1-(1-X)^{2/3})\right] = \frac{\alpha.t}{Di}$$

Problem P11-10$_C$

Part (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 : $kc = \frac{2.De}{D}$

$$-r_{As}'' = \frac{2.De}{D}.C_{AO}$$

P11-10cont'd

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

Part (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 $-r_{As}'' = -r_{Bs}''$

P11-10cont'd

$$\frac{dD}{dt} = -\left[\frac{2(-r''_{As})}{\rho}\right] = -\frac{2}{5}k_r C_{A0}$$

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, ρ = 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.

Part (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

$$W_{Ar} = kc.(C_A - C_{As}) = -r_{As}'' = \frac{kc.kr}{kc + kr}.C_A \quad \text{and} \quad kc = \frac{2.De}{D}$$

$$-r_{As}'' = \frac{kr}{1 + \frac{D}{D^*}}.C_A \quad \text{where} \quad D^* = \frac{2.De}{kr}$$

P11-10 cont'd

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 :

$$tc = \frac{1}{\alpha}\left[Di + \frac{Di^2}{2.D*}\right]$$

P11-10cont'd

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.

Part (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.

Problem P11-11$_B$

Irreversible, gas-phase, adiabatic, no pressure drop, packed bed.

Part (a) Isothermal

Mol balance : $F_{AO}.\frac{dX}{dW} = -r_A$ mol/gcat s

where $F_{AO} = C_{AO}.\upsilon_o$ = 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.

$W_A = kc.(C_A - C_{as}) = k'.C_{As}$

P11-11cont'd

$$C_{As} = \frac{kc.C_A}{kc + k'}$$

$$-r_{As} = \frac{k'.kc.C_A}{kc + k'} \qquad \frac{cm^3}{s.gcat}.\frac{mol}{cm^3}$$

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 $\varepsilon = y_{AO}.\delta = 0.5(1-1) = 0$

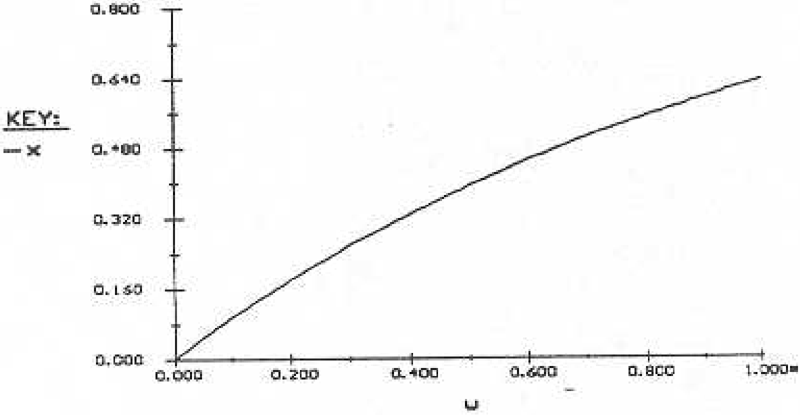
$C_A = C_{AO}(1 - X)$ and C_{AO} = 1 mol/dm^3 = 10e-3 mol/cm^3

POLYMATH

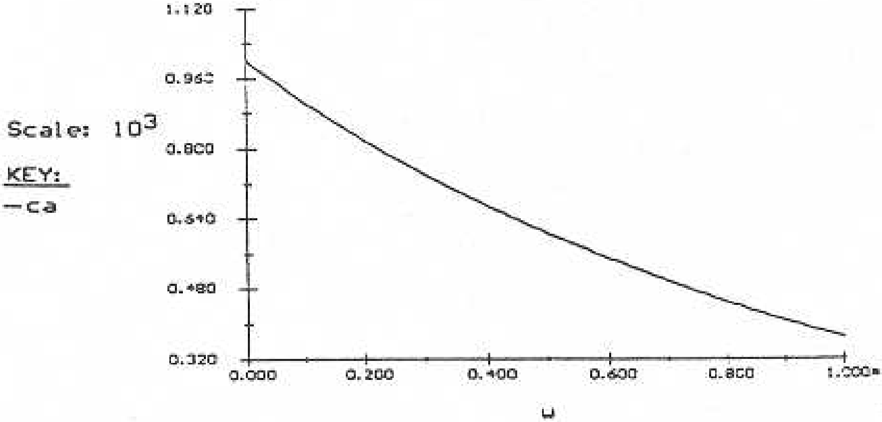
```
                 Problem P11-11B part a
                                                        Initial value
Equations:
d(x)/d(w)=-ra/fao                                       0
k=0.01
fao=10
kc=4242
cao=0.001
ca=cao*(1-x)
ra=-(k*kc*ca)/(k+kc)
w0 = 0,    wf = 1e+06
```

P11-11cont'd

```
                      Problem P11-11B part a
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 $X = 60\,\%$, $W_{cat} = 925$ kg



P11-11cont'd

Part (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 : $C_A = Cao.\left(\frac{1-X}{1+\varepsilon.X}\right)\frac{To}{T}$ where $\varepsilon = 0$ and To = 300 K

and C_{AO} = 10e-3 mol/cm^3

Energy balance : $$\frac{dF}{dt} = \frac{Q - W_S - \sum F_{io}C_{pi}(T - T_{io}) + F_{A0}X(-\Delta H_{RX}(T))}{\sum N_i C_{pi}} = 0$$

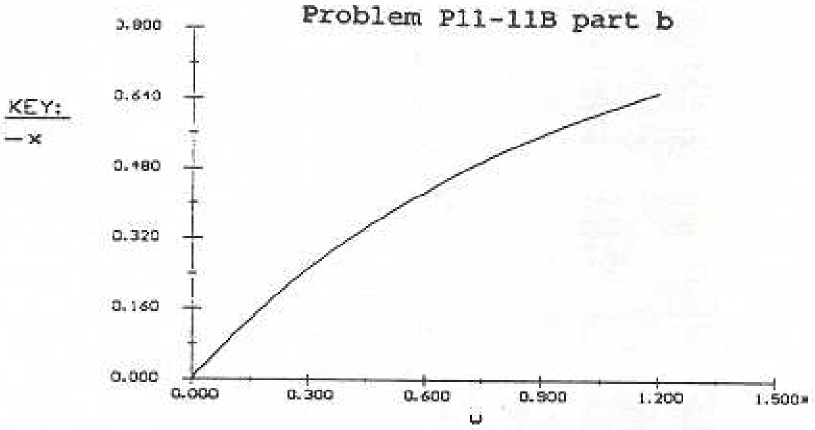
$$\sum Fio.Cpi.(T - Tio) = [10 \times 25\,(T - 300)] + [10 \times 75\,(T - 750)]$$
$$= 1000\,(T - 300)$$

$$-1000\,(T - 300) + 10.X.(10000) = 0$$

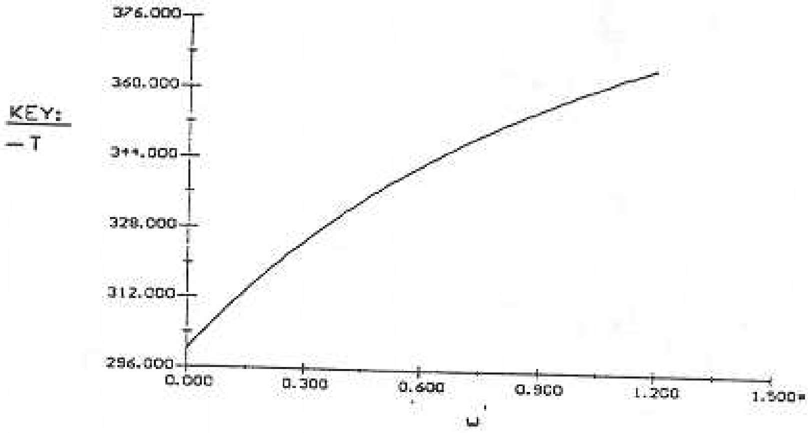
POLYMATH

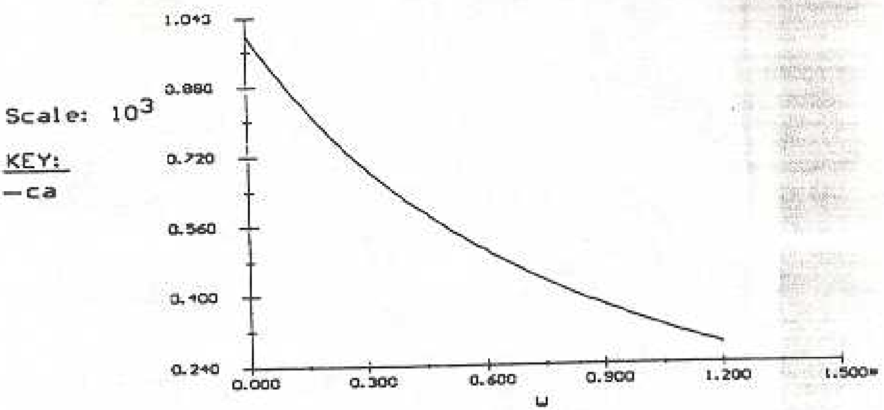
```
              Problem P11-11B part b
Equations:                                                        Initial value
d(x)/d(w)=-ra/fao                                                 0
k=0.01
fao=10
kc=4242
cao=0.001
To=300
T=(10*x*10000/1000)+To
ca=cao*(1-x)*(To/T)
ra=-(k*kc*ca)/(k+kc)
w0 = 0,    wf = 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-06   -2.8333e-06    -9.99998e-06   -2.8333e-06
```

P11-11 cont'd



For a conversion of X = 60 % , W_{cat} = 1020 kg





Part (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.

Problem P11-12$_C$

Dissolution of pills.

Part (a)

Complete dissolution.

P11-12 cont'd

$$C_B = \frac{W_{druginblood}}{W_{body}} \qquad C_A = \frac{W_{druginstomach}}{V_{stomach}}$$

$$\frac{dC_B}{dt} = k_A . C_A \frac{V_{stomach}}{W_{body}} \qquad \frac{g_{drug}}{g_{body}.\,\text{min}}$$

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 $t_1 = \dfrac{0.0354x(0.5^2 - 0.3^2)}{8x(6x10e-4)x1.0} = 1.18\,\text{min}$

Pill 2 : $D_2 = 4$ mm, $D_1 = 3$ mm

Time for outer layer to dissolve $t_1 = \dfrac{0.0354x(0.4^2 - 0.3^2)}{8x(6x10e-4)x1.0} = 0.52\,\text{min}$

Pill 3 : $D_2 = 3.5$ mm, $D_1 = 3$ mm

Time for outer layer to dissolve $t_1 = \dfrac{0.0354x(0.35^2 - 0.3^2)}{8x(6x10e-4)x1.0} = 0.24\,\text{min}$

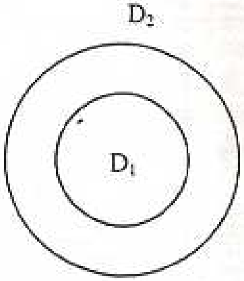
At $t = t_1$ mol balance on drug : $r_A''\pi . D_1^2 = \dfrac{dW_{druginstomach}}{dt}$ druginStomach

where $C_A = \dfrac{W_{druginstomach}}{V}$ and $r_A'' = k_c.S_{in}$ "$k_c S_{in}$"

$$\frac{dC_A}{dt} = \frac{k_c.S_{in}.\pi.D^2}{V} = \frac{2.D_{AB}.S_{in}.\pi.D^2}{D.V}$$

where W = mass of drug in stomach, g
V = volume stomach fluid , cm^3

and boundary conditions : $t = t_1$, $C_A = 0$
$t = t_2$, $C_A = C_{A0} = W_o/V = 0.5/1200 = 4.17x10e\text{-}4\ g/cm^3$



$D_2 = 4$ 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 $= \dfrac{500x10e-6}{\frac{\pi.(0.3)^3}{6}} = 0.0354 kg/cm^3$

$$S_{out} = 1.0\ \text{kg}/\text{cm}^3$$

$$\frac{dD}{dt} = -\frac{2.(-r_A'')}{\rho} = -\frac{2x2xD_{AB}.S_{out}}{D.\rho}$$

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

$$t_1 = \frac{0.0354x(0.4^2 - 0.3^2)}{8x(6x10e-4)x1.0} = 0.52\ \text{min}$$

P11-12cont'd

Inner core :

Boundary conditions : $t = 0,\ D = D_1$

$t = t_2,\ D = 0$

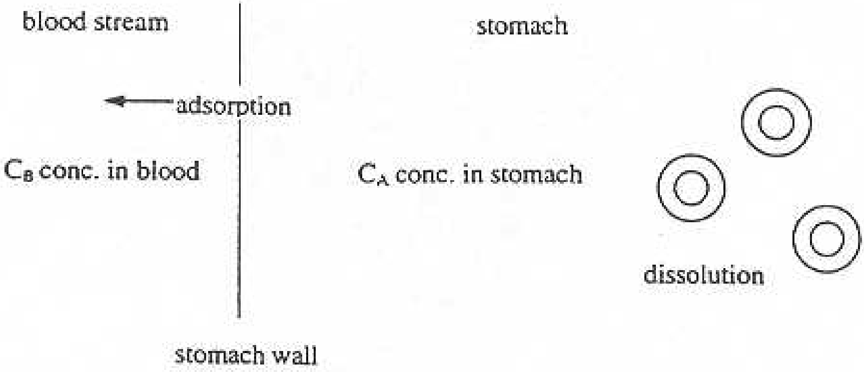
$$\frac{D_1^2}{2} = \frac{2x2.D_{AB}.S_m}{\rho}.t_2$$

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

Part (b)



Let rate of adsorption into bloodstream

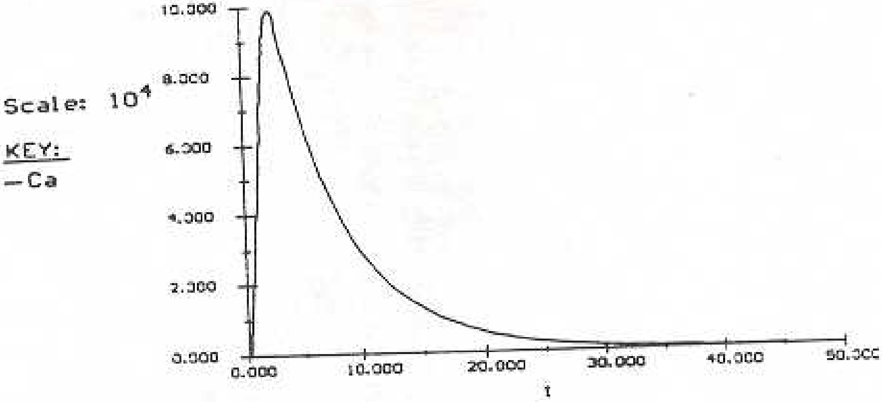
$$-r_A'' = k_A.C_A$$

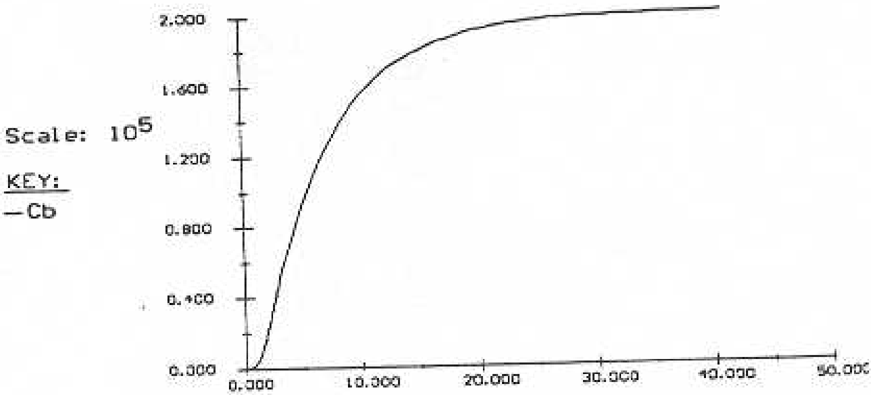
Relate concentration in stomach C_A , to concentration in blood C_B :

Mol balance on drug in bloodstream : $$-r_A'' = \frac{dC_B}{dt}$$

$$\frac{dC_B}{dt} = k_A.C_A$$

P11-12 cont'd





Part (c)

The graph of C_a 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.

P11-12cont'd

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.

P11-12C

```
Equations:
d(D1)/d(t)=if(t>0.24)then(if(D1>0.00001)then(-4*Dab*Sin/(    Initial value
   D1*rho))else(0))else(0)                                     0.3
d(Cb)/d(t)=ka*Ca*V/Wbody
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/(      0
   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)
d(D3)/d(t)=if(t>1.18)then(if(D3>0.00001)then(-4*Dab*Sin/(      0
   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)
t0 = 0,   tf = 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
```

P11-12cont'd

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.

P11-12C

```
Equations:                                                          Initial value
d(D1)/d(t)=if(t>0.24)then(if(D1>0.00001)then(-4*Dab*Sin/(    0.3
   D1*rho))else(0))else(0)
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/(    0.3
   D2*rho))else(0))else(0)
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/(    0.3
   D3*rho))else(0))else(0)
Dab=0.0006
Sin=400
rho=35.4
ka=0.166667
V=1200
Wbody=75000
Ca=Ca1+Ca2+Ca3-(Cb*Wbody/V)
t0 = 0,    tf = 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
```

P11-12cont'd

Part (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.

Problem P11-13$_B$

Part (a)

A possible reason is a reduction in the conversion of hydrazine in the packed bed.

$$X = 1 - \exp\left[-\frac{kc.a_c.L}{u}\right]$$

The two routes of investigation are :

1) Possible sabotage of the hydrazine / helium
2) Possible sabotage of the packed bed

Three logical questions may be :

1) What was the size of the packing particles used ? (affects kc and a_c)
2) What was the bed porosity ? (affects kc)
3) What was the composition of the fuel mixture ? (affects D_{AB})

Part (b)

Thoenes and Kramer's correlation $Sh' = (Re')^{1/2} (Sc)^{1/3}$

P11-13cont'd

$$kc = \frac{D_{AB}}{d_p} \cdot \frac{(1-\phi)}{\phi} \cdot \gamma \cdot \left[\frac{\rho . u . d_p}{\mu .(1-\phi). \gamma}\right]^{1/2} \left[\frac{\mu}{\rho . D_{AB}}\right]^{1/3}$$

$$kc = \frac{D_{AB}^{2/3}}{d_p} \cdot \frac{(1-\phi)^{1/2}}{\phi} \cdot \gamma^{1/2} \cdot \left[\frac{\rho . u . d_p}{\mu}\right]^{1/2} \left[\frac{\mu}{\rho}\right]^{1/3}$$

but $\gamma = \dfrac{2.r.\pi . L_p + 2.\pi . r^2}{\pi . d_p^2}$

$$kc = 2^{1/2} \frac{D_{AB}^{2/3}}{d_p^{1/2}} \cdot \frac{(1-\phi)^{1/2}}{\phi} \left[\frac{r.L_p + r^2}{d_p^2}\right]^{1/2} \left[\frac{\rho}{\mu}\right]^{1/6} u^{1/2}$$

$$kc = 2^{\frac{1}{2}} \frac{D_{AB}^{2/3}}{d_p^{3/2}} \cdot \frac{(1-\phi)^{1/2}}{\phi} \left[r.L_p + r^2\right]^{1/2} \left[\frac{\rho}{\mu}\right]^{1/6} u^{1/2}$$

$$D_{AB}(T) = D_{AB}(298\text{ K}) \left(\frac{T}{298}\right)^{1.75}$$

$$a_c = \frac{6.(1-\phi)}{d_p}$$

A reduction in the conversion X would mean that not all the fuel mixture decomposed and hence there would not be the required amount of energy or thrust released, causing the crash.

$$X = 1 - \exp\left[-\frac{kc.a_c.L}{u}\right]$$

and $$\frac{kc.a_c.L}{u} = \underbrace{6.(2)^{1/2} \frac{D_{AB}^{2/3}}{d_p^{5/2}} \cdot \frac{(1-\phi)^{3/2}}{\phi} \left[r.L_p + r^2\right]^{1/2} \left[\frac{\rho}{\mu}\right]^{1/6}}_{\text{Term 1}} \frac{L}{u^{1/2}}$$

P11-13cont'd

If term 1 decreases then X also decreases.

Possible reasons for the reduction in X could be :

- Increase in volume-average particle diameter, reduction in cylindrical radius and/or length of particle.

  d_p particularly has a large influence on X : $\frac{kc.a_c.L}{u} \propto \frac{1}{d_p^{5/2}}$

- Increase in porosity of bed, ϕ (due to change in packing shape), small effect on X.
- Change in fuel properties : decrease in ρ
  increase in μ

  small impact on X $\frac{kc.a_c.L}{u} \propto \left[\frac{\rho}{\mu}\right]^{1/6}$

- Change in fuel composition :
  probably insignificant effect on fluid properties
  increase in % hydrazine - diffusivity, D_{AB} possibly decreased
  decrease in % hydrazine - less energy release

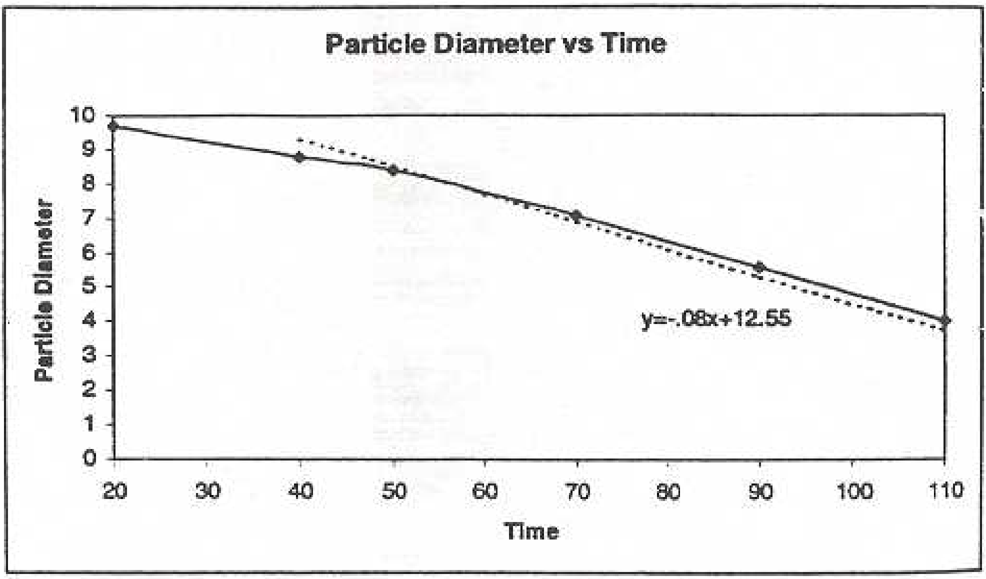
- Decrease in gas velocity, u (pump malfunction, wrong storage pressure)
  $\frac{kc.a_c.L}{u} \propto \frac{1}{u^{1/2}}$ if u > 1 m/s then X increases but if u < 1 then X decreases.

- Reduction in bed length, L $\frac{kc.a_c.L}{u} \propto L$
  an unlikely cause unless no packing is used.

- Wrong catalyst used in bed.
- Catalyst had become poisoned./deactivated - slower surface reaction may become limiting.
- Isothermal operation not achieved - failure of cooling system, may have caused a structural fault.
- Non-uniform physical properties of the packing inside the bed - plugging, channelling etc. will create hot/cold spots and uneven distribution of thrust.

Problem P11-14$_B$

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.

Problem 11-15$_B$

Mol balance on layer of earth control volume:

$$F_A|_z - F_A|_{z+\Delta z} = A_c.\Delta z.\frac{dC_A}{dt} \qquad \text{but } F_A = A_c.W_A$$

$$\frac{A_c.W_A|_{z+\Delta z} - A_c.W_A|_z}{A_c.\Delta z} = -\frac{dC_A}{dt}$$

$$z \to 0 \qquad \frac{dW_A}{dz} = -\frac{dC_A}{dt}$$

For dilute solution and constant total concentration : $W_A = -D_{AB}.\frac{dC_A}{dz}$

Gives : $$D_{AB}\frac{d^2C_A}{dz^2} = \frac{dC_A}{dt}$$

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), $\psi = 0$

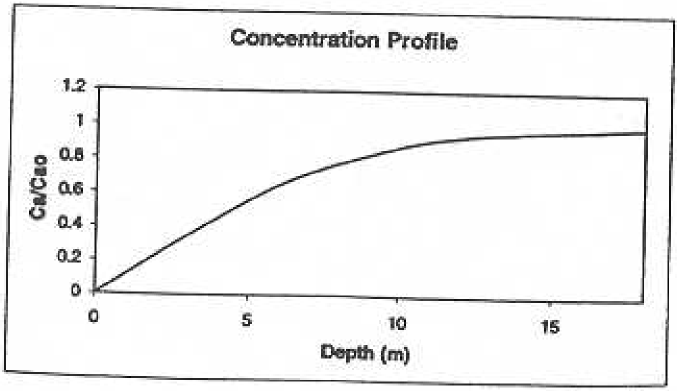
$z = \infty$, $\psi = 1$

$t = 0$ (end of glacial) , $z > 0$, $\psi = 1$

Gives the error function : $\psi = erf\frac{z}{\sqrt{4.D_{AB}.t}}$ let $\eta = \frac{z}{\sqrt{4.D_{AB}.t}}$

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) : $1.82 = \frac{\delta}{\sqrt{4.D_{AB}.t}}$



P11-15cont'd

But the graph gives at , $C_A = 0.01\ C_{AO}$ → $z = 0.4$ 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)

$$t = \left(\frac{17.6}{1.82}\right)^2 \frac{1}{2x2.64x10e-10} \cdot \frac{1}{3600x24x365} = 5616\, years$$

P12-1 No solution will be given

P12-2

a) The rate of reaction (mol/dm^3*s) would decrease since -ra = $\rho_c S_a(-r_a'')$. Using equation (12-32_ we see that decreasing the surface area would decrease the Thiele modulus and thus increase η.

b) It really depends on the reaction order. If n is much larger than n', then the catalyst weight will be underdesigned since $-r_{sf} < -r_A$ and $dW/dx = F_{A0}/-r_A$ in a PFR the weight will be smaller. Another problem is the dependence on temperature and activation energies which could become very destructive.

c) If the gas velocity were to increase the catalyst weight required would increase

$$W = \frac{v_0}{\Omega k S_a} \ln \frac{1}{1-X}$$

the length would then increase by the same factor:

$$L = \frac{W}{A_c \rho_b}$$

Increasing temperature would change the specific reaction rates which would cause the weight to decrease and the length to decrease.

d)In example 12-4, the reactor is 5m in diameter and 22m high whereas the reactor in example 12-6 is only 2 m^3 in volume. The charge is much different. In 12-4 the charge is 100 kg/m^3 whereas 12-6 it is only 3.9 kg.m^3.

e) No solution will be given.

f)

$$C_{wp} = \frac{-r_A \rho_c R^2}{D_e C_{As}} = \frac{k S_a \rho_c C_{NO} R^2}{D_e C_{As}}$$

$$= \frac{(4.42 * 10^{-10})(530)(3 * 10^{-3})(0.0004)}{(1.89 * 10^{-8})(0.02)} = 20$$

P12-2 cont'd

$C_{wp} > 1$ so it is internal diffusion limited

$$\frac{k\rho_b S_a R n}{k_c C_{Ab}} = \frac{\left(4.42*10^{-10}\right)\left(1.6*10^{6}\right)(530)\left(3*10^{-3}\right)(.0004)}{\left(6*10^{-5}\right)(0.02)}$$

$$= .33$$

0.33 > 0.15 so it is also external diffusion limited.

$$\left|\frac{-\Delta H\left(kS_A C_{NO}\right)\rho_b R E}{hT^2 R_g}\right| =$$

$$\frac{(104.67)\left(4.42*10^{-10}\right)(530)(0.004)\left(1.4*10^{6}\right)\left(3*10^{-3}\right)(83.76)}{(105.5)(1651.73)^2(.008314)}$$

$$= 4.37*10^{-5}$$

$4.37*10^{-5} < 0.15$ so the bulk temperature is the same as the temperature of the surface of the pellet.

g) 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.

h) No solution will be given

i) No solution will be given

j) No solution will be given.

k) If the diameter of the catalyst pellet were decreased, the value of the Thiele modulus would decrease, but β would not.

P12-3

(a) Yes.

(b) All T, F_{T0} = 10 g moles/hr. the rate of reaction changes with flow rate and increases linearly with temperature.

(c) Yes.

(d) T < 367 K; F_{T0} = 1000 g mole/hr , 5000 gmole/hr

T < 362 K; F_{T0} = 100 g mole/hr.

(e) Yes.

P12-3 cont'd

(f) $T > 367$ K: $F_{T0} = 1000$ g mole/hr , 5000 gmol/hr

$T > 362$ K: $F_{T0} = 100$ g mole/hr.

(g) $$\Omega = \frac{\text{actual rate of reaction}}{\text{ideal rate of reaction}} = \frac{-r'_A\,(\text{at } 362\text{ K}, F_{T0} = 10\text{ g mol/hr})}{-r'_A\,(\text{at } 362\text{ K}, F_{T0} = 5000\text{ g mol/hr})}$$

$$\Omega = \frac{0.26}{0.70} = 0.37$$

(h) At $F_{T0} = 5000$ g mole/hr , there is no external diffusion limitation, so the external effectiveness factor is one.

$$\eta = \frac{\text{actual rate of reaction (at 362 K, } F_{T0} = 5000\text{ g mol/hr)}}{\text{extrapolated rate of reaction (at 362 K, } F_{T0} = 5000\text{ g mol/hr)}}$$

$$\eta = \frac{1.2}{1.4} = 0.86$$

(i) $$\eta = \frac{3\left[\phi \cosh \phi - 1\right]}{\phi^2} = 0.86$$

By iterative solution, $\phi = 1.60$

$$\varphi = \frac{C_A}{C_{AS}} = \left(\frac{1}{\lambda}\right)\frac{\sinh(\phi\lambda)}{\sinh\phi}$$

P12-4 No solution will be given

P12-5

Curve A is reaction-rate limited. This is so because of the way the curve bends implying an exponential function which is also the equation for k of a reaction with respect to temperature.

Curve B is inter-diffusion limited. This is because it has a dependence on temperature, but not a real significant

Curve C is outer-diffusion limited. This has a much larger dependence on temperature.

P12-6

$$\text{If } \varphi = \frac{C_A}{C_{AS}},\ \lambda = \frac{r}{R},\ \phi_n^2 = \frac{k_n R^2 S_a \rho_b C_{AS}^{n-1}}{D_e}$$

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 $C_{AS} = 1 \times 10^{-3} \frac{\text{mole}}{1}$

$R = 1 \times 10^{-3}\ \text{cm}^{1}$

$D_C = 0.1\ \text{cm}^2/\text{sec}$

(a) $\lambda = \frac{7 \times 10^{-4}}{1 \times 10^{-3}} = 0.7$

$$\varphi = \left(\frac{1}{\lambda}\right)\left(\frac{\sin h\, \phi_1 \lambda}{\sin h\, \phi_1}\right)$$

At $\lambda = \frac{1}{2}$, $\varphi = 0.1$: $0.1 = 2\left[\frac{\sin h(\phi_1/2)}{\sin h(\phi_1)}\right] \Rightarrow \phi_1 = 6.0$

$$\therefore \quad \varphi = \frac{1}{0.7}\left[\frac{\sin h(6 \times 0.7)}{\sin h\, 6}\right]$$

$$\frac{C_A}{1 \times 10^{-3}} = \frac{1}{0.7}\left[\frac{e^{4.2} - e^{-4.2}}{e^{6} - e^{-6}}\right]$$

$$C_A = 2.36 \times 10^{-4}\ \frac{\text{g mol}}{1}$$

P12-6 cont'd

(b) $$\eta = \frac{3}{\phi_1^2}\left[\phi_1 \cos h\, \phi_1 - 1\right] = 0.80 \Rightarrow \phi_1 = 2.04$$

$$\phi_1^2 = \frac{k R^2 S_A \rho_B}{D_e}$$

At $\lambda = \frac{1}{2}$, $\varphi = 0.1$: $\phi_1 = 6$ (see part (a))

12-7

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 $\quad C_{A0} = C_2$

$$C_A = \frac{k}{2D_e}z^2 - \frac{kL}{D_e}z + C_{A0}$$

(b) $\eta = \dfrac{\text{rate of reaction with diffusion}}{\text{rate of reaction without diffusion}}$

$$\eta = \frac{\dfrac{2D(C_A - C_{A0})}{z(z-2L)}}{k} = \frac{2D(C_A - C_{A0})}{k\,z(z-2L)}$$

(c) Boundary conditions: $\quad C_A = 0$ at $z = L$

$$0 = \frac{kL}{D}\left(\frac{L}{2} - L\right) + C_{A0}$$

$$C_{A0} = \frac{kL^2}{2D}$$

P12-7 cont'd

$$L = \sqrt{\frac{2D\,C_{A0}}{k}} = \sqrt{\frac{2(3.6\times10^{-6}\ \text{cm}^2/\text{s})(4.36\times10^{-5}\ \text{mol/cm}^3)}{(2.3\times10^{-15}\ \text{mol/s})/(3\times10^{-10}\ \text{cm}^2)(L\ \text{cm})}}$$

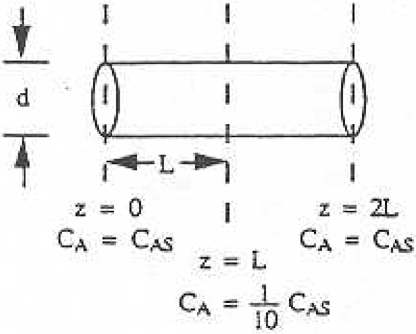
$$L^{1/2} = 0.0640$$

$$L = 0.0041\ \text{cm} = 41\ \mu\text{m}$$

(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: $-\frac{\pi}{d}d^2\left(\frac{dW_A}{dz}\right) + \pi\,d\,r_A^{-} = 0$

$$\frac{d}{4}D\left(\frac{d^2C_A}{dz^2}\right) - k\,C_A = 0$$

$$\frac{C_{AS}}{L^2}\left(\frac{d^2\psi}{d\lambda^2}\right) - \left(\frac{4\,k}{D\,d}\right)C_{AS}\,\psi = 0$$

$$\Rightarrow \phi^2 = \left(\frac{4k\,L^2}{D\,d}\right)$$

Concentration distribution: $C_A = C_{AS}\left(\dfrac{\cos h\left[\phi\left(1-\frac{z}{L}\right)\right]}{\cos h\,\phi}\right)$

$L = 10^{-3}$ cm, $2L = 2\times10^{-3}$ cm

$C_{AS} = 10^{-3}$ g mole/l

$D = 0.1$ cm^2/sec

At $z = L$, $C_A = \dfrac{1}{10}C_{AS} = C_{AS}\left(\dfrac{\cos h\left[\phi\left(1-\frac{L}{L}\right)\right]}{\cos h\,\phi}\right)$

$$\frac{1}{10} = \frac{1}{\cos h\,\phi}$$

$$\phi = 2.9932$$

(a) At $z = 1/2$ L: $C_A = C_{AS}\left(\dfrac{\cos h\left[\phi\left(1-\frac{0.5L}{L}\right)\right]}{\cos h\,\phi}\right)$

$$C_A = (0.001)\left(\frac{\cos h\,[2.9932(0.5)]}{\cos h\,(2.9932)}\right)$$

$$C_A = 2.345\times10^{-4}\text{ g mol/l}$$

(b) $\phi = 2L\sqrt{\dfrac{k}{D\,d}} \Rightarrow \phi\;\alpha\;(2L)$

$$\eta_{old} = \frac{\tan h\,\phi_{old}}{\phi_{old}} = \frac{\tan h\,(2.9932)}{2.9932} = 0.3324$$

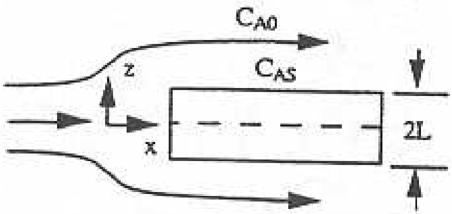
$$\eta_{new} = 0.8 = \frac{\tan h\,\phi_{new}}{\phi_{new}} \Rightarrow \phi_{new} = 0.8880$$

$$2L_{new} = 2L_{old}\left(\frac{\phi_{new}}{\phi_{old}}\right) = (2\times10^{-3})\left(\frac{0.8880}{2.9932}\right) = 5.993\times10^{-4}\text{ cm}$$

(c) At $z = L$, $C_A = \dfrac{C_{AS}}{\cos h\,\phi_{new}} = \dfrac{0.001}{\cos h\,(0.8880)} = 7.038\times10^{-4}$ 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.

P12-9



Define $W_A > 0$ in direction of increasing z.

Material balance:

$$W_A A_P \big|_z - W_A A_P \big|_{z+\Delta z} + -r_A'' a A_P \Delta_z = 0$$

$-r_A'' = k C_A$; $W_A = -D_e \dfrac{dC_A}{dz} + C_A V \cong -D_e \dfrac{dC_A}{dz}$ for small C_A

Taking $\Delta z \to 0$: $-A_P \dfrac{dW_A}{dz} + r_A'' a A_P = 0$

$$A_P \frac{d}{dz}\left(D_e \frac{dC_A}{dz}\right) - k C_A a A_P = 0$$

For constant D_e ; $D_e \dfrac{d^2 C_A}{dz^2} - k C_A a = 0$

Boundary conditions: $z = L \quad C_A = C_{AS}$

$z = 0 \quad \dfrac{dC_A}{dz} = 0$ by symmetry

$\dfrac{d^2 C_A}{dz^2} - \alpha^2 C_A = 0$ where $\alpha^2 = \dfrac{k a}{D_e}$

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 $z = L$: $C_{AS} = A_1 e^{-\alpha L} + A_2 e^{\alpha L}$

$\dfrac{dC_A}{dz}\Big|_{z=0} = 0 = -\alpha A_1 + \alpha A_2 = 0$

$\therefore \quad A_1 = A_2$

From above: $A_1 = \dfrac{C_{AS}}{e^{-\alpha L} + e^{\alpha L}}$

$$C_A = C_{AS}\left(\frac{e^{-\alpha L} + e^{\alpha L}}{e^{-\alpha L} + e^{\alpha L}}\right)$$

12-9

P12-9 cont'd

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: $$\frac{\Omega}{\eta} = \frac{C_{AS}}{C_{A0}}$$

$$-W_A A_P = k_C A_P (C_{A0} - C_{AS}) = \alpha A_P D_e C_{AS}\tan h\,(\alpha L)$$

$$C_{A0} = C_{AS}\left[1 + \frac{\alpha D_e}{k_C}\tan h\,(\alpha L)\right]$$

$$\frac{C_{AS}}{C_{A0}} = \left[\frac{1}{1 + \frac{\alpha D_e}{k_C}\tan h\,(\alpha L)}\right]$$

$$\Omega = \frac{\eta}{1 + \frac{\alpha D_e}{k_C}\tan h\,(\alpha L)} = \frac{\left(\sqrt{\frac{D_e}{k a}}\,\frac{1}{L}\right)\tan h\left(\sqrt{\frac{k a}{D_e}}\,L\right)}{1 + \sqrt{\frac{k a D_e}{k_C}}\tan h\left(\sqrt{\frac{k a}{D_e}}\,L\right)}$$

P12-10

Start with the mole balance:

$$W_{Az}A\big|_z - W_{Az}A\big|_{z+\Delta z} + r_A A\Delta z = 0$$

Divide by (-AΔz) and take the limit as Δz approaches zero.

$$\frac{dW_{Az}}{dz} - r_A = 0$$

Then find the equation for the flux:

$$W_{Az} = -D_e\frac{dC_A}{dt}$$

Combine and get the correct differential equation:

$$\frac{d}{dz}\left(-D_e\frac{dC_A}{dz}\right) + k = 0$$

$$\frac{d^2C_A}{dz^2} - \frac{k}{D_e} = 0$$

The boundary conditions are as follows:

B.C. 1: $dC_A/dz = 0$ @ $z = 0$

B.C. 1: $C_A = C_{As}$ @ $z = L$

We are then able to solve the equation:

$$\frac{dC_A}{dz} = \frac{kz}{D_e} + C_1$$

$$0 = C_1$$

$$C_A = \frac{kz^2}{2D_e} + C_2$$

$$C_{As} = \frac{kL^2}{2D_e} + C_2$$

P12-10cont'd

$$C_A = C_{As} + \frac{kz^2}{2D_e} - \frac{kL^2}{2D_e}$$

$$\frac{C_A}{C_{As}} = 1 + \frac{\Phi_0^2}{2}\left(\frac{z^2}{L^2}\right) - \frac{\Phi_0^2}{2} = 1 + \frac{\Phi_0^2}{2}\left(\frac{z^2}{L^2} - 1\right)$$

b) $\Phi_o = 1.414$ $\qquad$ $\Phi_o^2 = 2$

$$0 = 1 + 1\left(\frac{z^2}{L^2} - 1\right)$$

$$z = 0$$

$\Phi_o = 4$ $\qquad$ $\Phi_o^2 = 16$

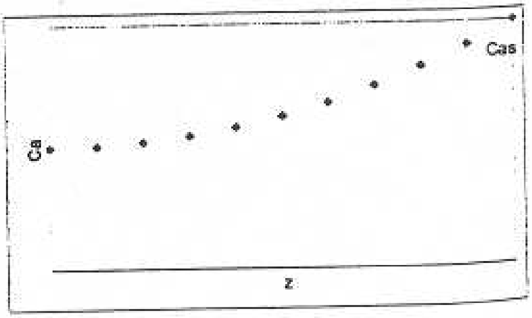
$$0 = 1 + 8\frac{z^2}{L^2} - 8$$

$$7 = 8\frac{z^2}{L^2}$$

$$z = 0.935L$$

c)

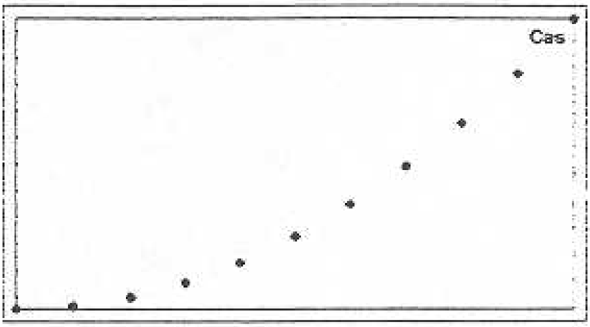
$$\frac{C_A}{C_{AS}} = 1 + \frac{\Phi_0^2}{2}\left[\left(\frac{z}{L}\right)^2 - 1\right]$$



for $\Phi_o^2 < 2$

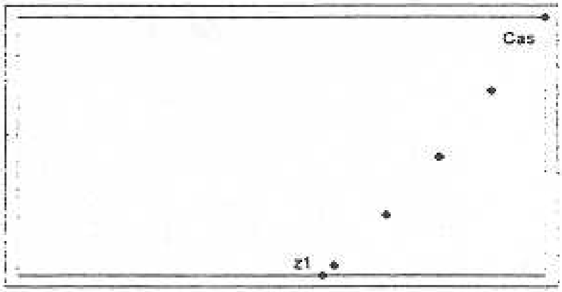
P12-10cont'd

for $\Phi_o^2 = 2$



for $\Phi_o^2 > 2$

where $z_1 = L\sqrt{1-\frac{2}{\Phi_o^2}}$



$$\eta = \frac{\int_{z_1}^{L} -r_A A_C dz}{-r_{AS} A_C L}$$

when Φ_o^2 □ 2 then $z_1 = 0$. Then $\eta = 1$.

When $\Phi_o^2 > 2$ then $z_1 = L\sqrt{1-\frac{2}{\Phi_o^2}}$

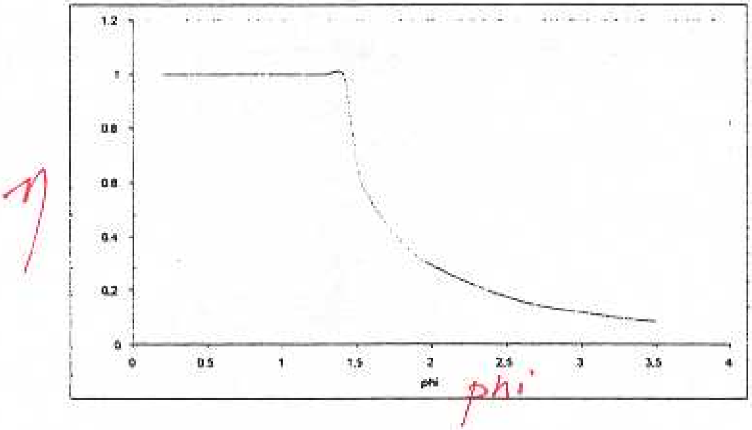
Then the integration goes like this:

P12-10cont'd

$$\eta = \frac{-r_A A_C L + r_A A_C L\left(1-\frac{2}{\Phi_0^2}\right)^{\frac{1}{2}}}{-r_A A_C L}$$

$$= 1-\left(1-\frac{2}{\Phi_0^2}\right)^{\frac{1}{2}}$$

d)



e) Start with the mole balance:

$$W_{Ar}4\pi r^2\Big|_r - W_{Ar}4\pi r^2\Big|_{r+\Delta r} - r_A 4\pi r^2 = 0$$

Then divide by -4πΔr and take the limit as Δr approaches zero.

$$\frac{dW_{Ar}r^2}{dr} - r_A r^2 = 0$$
$$W_{Ar} = -D_e\frac{dC_A}{dr}$$

P12-10cont'd

Then find the equation for the flux:

$$\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right)=\frac{k}{D_e}r^2$$

$$\int_0^r d\left(r^2\frac{dC_A}{dr}\right)=\int_0^r\frac{k}{D_e}r^2dr$$

$$r^2\frac{dC_A}{dr}\bigg|_{r=r}-r^2\frac{dC_A}{dr}\bigg|_{r=0}=\frac{k}{D_e}\frac{r^3}{3}$$

$$\frac{dC_A}{dr}=\frac{kr}{3D_e}$$

$$\int_{C_{AS}}^{C_A}dC_A=\frac{k}{3D_e}\int_R^r rdr$$

$$C_A-C_{AS}=\frac{kR^2}{6D_e}\left(1-\left(\frac{r}{R}\right)^2\right)$$

$$\frac{C_A}{C_{AS}}=1+\frac{\Phi_0^2}{6}\left[\left(\frac{r}{R}\right)^2-1\right]$$

$$\text{where } \Phi_0^2=\frac{kR^2}{D_eC_{AS}}$$

$\Phi_0 = 1.414$ $\quad\quad$ $\Phi_0^2 = 2$

$$0=1+\frac{2}{6}\left[\left(\frac{r}{R}\right)^2-1\right]$$

$$\left(\frac{r}{R}\right)^2=-2$$

This is not possible so C_A is going to finite non-zero everywhere.

$\Phi_0 = 4$ $\quad\quad$ $\Phi_0^2 = 16$

$$0=1+\frac{16}{6}\left[\left(\frac{r}{R}\right)^2-1\right]$$

$$\left(\frac{r}{R}\right)^2=-\frac{6}{16}+1=\frac{5}{8}$$

P12-10cont'd

Hence $C_A = 0$ at $r = R\sqrt{\frac{5}{8}}$

For $\Phi_0^2 \le 6$

$$\eta = \frac{\int_{z_1}^{R} -r_A A_C dz}{-r_{AS} A_C R} \qquad \text{where } z_1 = 0$$

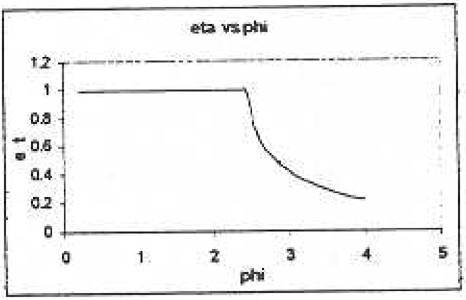
$$\eta = 1$$

For $\Phi_0^2 > 6$

$$\eta = \frac{\int_{z_1}^{R} -r_A A_C dz}{-r_{AS} A_C R}$$

$$= \frac{-r_A A_C R + r_A A_C R\left(1 - \frac{6}{\Phi_0^2}\right)^{\frac{1}{2}}}{-r_{AS} A_C R}$$

$$= 1 - \left(1 - \frac{6}{\Phi_0^2}\right)^{\frac{1}{2}}$$



P12-10cont'd

f) For cylinder

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dC_A}{dr}\right)=\frac{k}{D_e}$$

$$\int_0^r \frac{d}{dr}\left(r\frac{dC_A}{dr}\right)=\frac{k}{D_e}\int_0^r r dr$$

$$r\frac{dC_A}{dr}\bigg|_{r=r}-r\frac{dC_A}{dr}\bigg|_{r=0}=\frac{kr^2}{2D_e}$$

$$\frac{dC_A}{dr}=\frac{kr}{2D_e}$$

$$\int_{C_{AS}}^{C_A} dC_A=\frac{k}{2D_e}\int_0^r r dr$$

$$C_A-C_{AS}=\frac{kR^2}{4D_e}\left[\left(\frac{r}{R}\right)^2-1\right]$$

$$\frac{C_A}{C_{AS}}=1+\frac{kR^2}{4D_eC_{AS}}\left[\left(\frac{r}{R}\right)^2-1\right]$$

$$\frac{C_A}{C_{AS}}=1+\frac{\Phi_0^2}{4}\left[\left(\frac{r}{R}\right)^2-1\right]$$

where $\Phi_0^2=\frac{kR^2}{D_eC_{AS}}$

$\Phi = 1.414$ $\Phi_0^2 = 2$

$$0=1+\frac{2}{4}\left[\left(\frac{r}{R}\right)^2-1\right]$$

$$\left(\frac{r}{R}\right)^2=-1$$

This is not possible so C_A will never be zero.

$\Phi = 4$ $\Phi_o^2 = 16$

$$0 = 1 + \frac{16}{4}\left[\left(\frac{r}{R}\right)^2 - 1\right]$$

$$\left(\frac{r}{R}\right)^2 = \frac{3}{4}$$

$$r' = R\sqrt{\frac{3}{4}}$$

For $\Phi_o^2 \le 4$

$$\eta = \frac{\int_{z_1}^{R} -r_A A_C dz}{-r_{AS} A_C R} \qquad \text{where } z_1 = 0$$

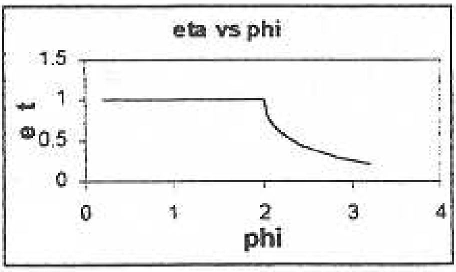
$$\eta = 1$$

For $\Phi_o^2 > 4$

$$\eta = \frac{\int_{z1}^{R} -r_A A_C dz}{-r_{AS} A_C R}$$

$$= \frac{-r_A A_C R + r_A A_C R\left(1 - \frac{4}{\Phi_0^2}\right)^{\frac{1}{2}}}{-r_{AS} A_C R} \qquad \text{where } z_1 = \left(1 - \frac{4}{\Phi_0^2}\right)^{\frac{1}{2}}$$

$$= 1 - \left(1 - \frac{4}{\Phi_0^2}\right)^{\frac{1}{2}}$$



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: equation (11-65) from the text.

$$D_{AB}\frac{d^2 C_A}{dz^2} - U\frac{dC_A}{dz} + r_A' \rho_B = 0$$

$$D_{AB}\frac{d^2 C_A}{dz^2} - U\frac{dC_A}{dz} - \Omega k S_A \rho_B C_A^2 = 0$$

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 $z = L$: $$\frac{1}{C_{A0}} = \left(\frac{1}{1-X} - 1\right) = \left(\frac{-2\rho_B k S_A}{U}\right) L$$

$$L = \left(\frac{U}{\Omega \rho_B k S_A C_{A0}}\right)\left(\frac{1}{1-X} - 1\right)$$

Internal effective factor: $\eta = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{\varphi_n}$ where $n = 2$

$$\phi_2 = R\sqrt{\frac{k S_A \rho_B C_{A0}}{D_e}}$$

P12-11cont'd

$$\phi_2 = 0.2 \times 10^{-2}\ \mathrm{m}\sqrt{\frac{\left(50\ \frac{\mathrm{m}^2}{\mathrm{g\ s\ mol}}\right)\left(400\ \frac{\mathrm{m}^2}{\mathrm{g}}\right)\left(2 \times 10^6\ \frac{\mathrm{g}}{\mathrm{m}^2}\right)\left(0.115\ \frac{\mathrm{g\ mol}}{\mathrm{l}}\right)\left(\frac{10^3\ \mathrm{l}}{\mathrm{m}^3}\right)}{2.66 \times 10^{-8}\ \frac{\mathrm{m}^2}{\mathrm{s}}}}$$

$\phi_2 = 2.63 \times 10^7$ 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: $\Omega = \eta = 9.313 \times 10^{-8}$

Reactor length:

$$L = \frac{3\ \mathrm{m/s}\left(\frac{1}{1-0.8} - 1\right)}{\left(9.313 \times 10^{-8}\right) 2 \times 10^6\ \frac{\mathrm{g}}{\mathrm{m}^3}\left(50\ \frac{\mathrm{m}^6}{\mathrm{g\ s\ mol}}\right)\left(400\ \frac{\mathrm{m}^2}{\mathrm{g}}\right)\left(115\ \frac{\mathrm{g\ mol}}{\mathrm{m}^3}\right)}$$

$L = 2.80 \times 10^{-5}\mathrm{m}$

P12-12

a) Start with the mole balance taken on a shell

$$W_{Ar} 2\pi r l\Big|_z - W_{Ar} 2\pi r l\Big|_{z+\Delta z} + r_A' \rho_c 2\pi r l \Delta r = 0$$

Divide by $-2\pi l \Delta r$ 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:

$$\frac{d\left(r\left(-D_e \, {}^{dC_A}\!/_{dr}\right)\right)}{dr} - r_A' \rho_c r = 0$$

P12-12 cont'd

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:

$$\varphi=C_1I_0(\Phi\lambda)+C_2K_0(\Phi\lambda)$$

Boundary Conditions:

$$\varphi=1@\lambda=1$$

$$\frac{d\varphi}{d\lambda}=0@\lambda=0$$

$$\frac{d\varphi}{d\lambda}=\Phi[C_1I_1(\Phi\lambda)-C_2K_1(\Phi\lambda)]$$

$$I_1(0)=0$$

$$K_1(0)=\infty$$

as $\left.\frac{d\varphi}{d\lambda}\right|_{\lambda=0}\to 0\Rightarrow C_2=0$

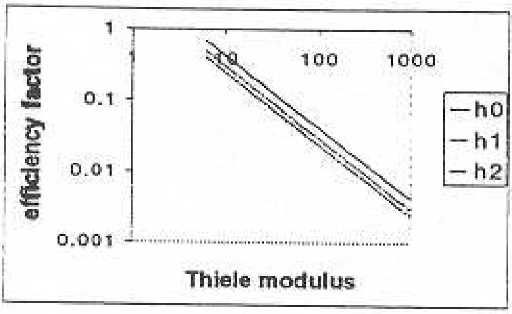
$$\varphi=C_1I_0(\Phi\lambda)$$

$$1=C_1I_0(\Phi)\Rightarrow C_1=\frac{1}{I_0(\Phi)}$$

$$\varphi=\frac{I_0(\Phi\lambda)}{I_0(\Phi)}$$

P12-13

As can be seen by this graph, all of the lines do not coalesce into one line, but are in fact three different lines

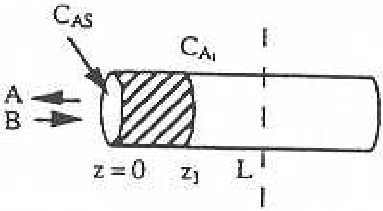


P12-14 No solution will be given

P12-15 No solution will be given

P12-16 No solution will be given

P12-17



Given: A ↔ B on the walls of a cylindrical catalyst pore.

z_1 = length of poisoned section

$-r_A' = k\,C_A$

P12-17cont'd

(a) In the poisoned section:

$$W_A \pi r^2 \big|_z - W_A \pi r^2 \big|_{z+\Delta z} + r_A'' P \Delta z = 0$$

For $0 \le z \le z_1$, $r_A'' = 0$, since this area is poisoned.

$$W_A \pi r^2 \big|_z - W_A \pi r^2 \big|_{z+\Delta z} = 0 \quad \text{or} \quad \frac{-dW_A}{dz} = 0$$

$$W_A = -CD_{AB}\frac{dX_A}{dz} + X_A(W_A + W_B)$$

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 $z = 0$, $X_A = \frac{C_{AS}}{C}$: $K_2 = \frac{C_{AS}}{C}$

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 $W_A = -C D_{AB}\frac{dX_A}{dz} = -D_{AB}\frac{dC_A}{dz}(C_{A1} - C_{AS})$

(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 :

$$(L - z)\left(\frac{2k''}{r D_{AB}}\right)^{1/2} = \left(1 - \frac{z}{L}\right)\phi_1 \text{, i.e., } \eta = \frac{\tan h\left[\phi_1\left(1 - \frac{z}{L}\right)\right]}{\phi_1\left(1 - \frac{z}{L}\right)}$$

P12-17 cont'd

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 $W_A \pi r^2 = \eta' 2\pi r L C_{AS} k''$

$$\eta' = \eta\left(1 - \frac{z_1}{L}\right)\left(1 - \frac{2\eta' L^2 C_{AS} k'' z_1}{r D_{AB} L}\right)$$

$$\eta' = \eta\left(1 - \frac{z_1}{L}\right)\left(1 - \eta'\left(\frac{z_1}{L}\right)\phi^2\right)$$

$$\eta' = \frac{\eta\left(1 - \frac{z_1}{L}\right)}{1 + \phi_1^2 \eta\left(1 - \frac{z_1}{L}\right)\left(\frac{z_1}{L}\right)} = \frac{\left(1 - \frac{z_1}{L}\right)\left[\frac{\tanh\left\{\phi_1\left(1 - \frac{z}{L}\right)\right\}}{\phi_1\left(1 - \frac{z}{L}\right)}\right]}{1 + \phi_1^2 \eta\left(1 - \frac{z_1}{L}\right)\left(\frac{z_1}{L}\right)\left[\frac{\tanh\left\{\phi_1\left(1 - \frac{z}{L}\right)\right\}}{\phi_1\left(1 - \frac{z_1}{L}\right)}\right]}$$

$$\eta' = \frac{\tanh\left\{\phi_1\left(1 - \frac{z}{L}\right)\right\}}{\phi_1 + \phi_1^2\left(\frac{z_1}{L}\right)\tanh\left\{\phi_1\left(1 - \frac{z}{L}\right)\right\}}$$

P12-18 The reaction is $A \rightarrow \frac{1}{2} A_2$

(a) $\delta = \frac{1}{2} - 1 = -\frac{1}{2}$; $\varepsilon = y_{A0}\,\delta = -0.5$

$$C_A = \frac{C_{A0}(1 - X)}{(1 - 0.5X)} \quad \text{where} \quad C_{A0} = \frac{P}{RT} = \frac{8.2 \text{ atm}}{\frac{0.082 \text{ l atm}}{\text{g mol °K}}(227 + 273 \text{ K})} = 0.2\ \frac{\text{g mol}}{\text{l}}$$

P12-18cont'd

$$y_A = \frac{F_A}{F_A + F_{A2}} = \frac{F_A}{F_A + \frac{1}{2}(F_{A0} - F_A)} = \frac{2F_A}{F_A + F_{A0}}$$

$$\frac{1}{y_A} = \frac{1}{2} + \frac{1}{2}\frac{F_{A0}}{F_A}$$

$$\frac{F_{A0}}{F_A} = 2\left(\frac{1}{y_A} - \frac{1}{2}\right) \quad \text{or} \quad \frac{F_A}{F_{A0}} = \frac{1}{\frac{2}{y_A} - 1} = \frac{y_A}{2 - y_A}$$

$$X = 1 - \frac{F_A}{F_{A0}} = 1 - \frac{y_A}{2 - y_A} = \frac{2 - 2y_A}{2 - y_A}$$

$$r_A' = \frac{F_{A0}\,X}{W} \quad \text{where } W = 4 \times 40\text{g} = 160\text{ g} = 0.16\text{ kg}$$

$$r_A' = k\,C_A^{\alpha}$$

$$\ln\left(-r_A'\right) = \ln k_0 + \alpha \ln C_A$$

Let $M = \ln\left(-r_A'\right)$; $A_0 = \ln k_0$; $A_1 = \alpha$; 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_{T0}	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:

$$17.196 = 6A_0 - 14.338\,A_1$$

$$-39.266 = -14.338\,A_0 + 35.513\,A_1$$

P12-18cont'd

$$\therefore \quad A_0 = 6.36 = \ln k_0 \rightarrow k_0 = 578.25$$

$$A_1 = 1.46 \cong 1.5 = \alpha$$

$$\text{At } T_1 = 237\text{ C} = 510\text{ K}: \; k_1 = \frac{-r_A'}{C_A^{1.5}}$$

$$-r_A' = \frac{F_{A0}X}{W} \quad \text{where } X = \frac{2 - 2(0.097)}{2 - 0.097} = 0.9490$$

$$-r_A' = \frac{(9)(0.9490)}{0.16} = 53.38 = k_1\, C_A^{1.5} \quad \text{where:}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{8.2}{0.082(510)} = 0.196\,\frac{\text{g mol}}{\text{l}}$$

$$C_A = \frac{0.196\,(1 - 0.9490)}{1 - 0.5(0.9490)} = 0.019\,\frac{\text{g mol}}{\text{l}}$$

$$k_1 = \frac{53.38}{(0.019)^{1.5}} = 2.035 \times 10^4$$

$$k_1 = k_0 \exp\left\{\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)\right\}$$

$$2.035 \times 10^4 = 578.25 \exp\left\{\frac{E\,(\text{J/mole})}{8.314}\left(\frac{1}{500} - \frac{1}{510}\right)\right\}$$

$$\therefore \quad E = 7.55 \times 10^5\,\frac{\text{J}}{\text{g mol}}$$

(b) $n_{true} = 2n_{app} - 1 = 2(1.5) - 1 = 2$: second order

$$E_{true} = 2E_{app} = 15.1 \times 10^5\,\frac{\text{J}}{\text{mol}}$$

(c) $$\phi_2 = R\sqrt{\frac{k\,S_a\,\rho_b\,C_{A0}}{D_e}} = \sqrt{\frac{\left(1 \times 10^{-2}\right)^2 \left(2.035 \times 10^4\right) 49 \left(2.3 \times 10^6\right) 0.196}{0.23 \times 10^{-4}}}$$

$$\phi_2 = 1.40 \times 10^6$$

$$\eta = \left(\frac{2}{n+1}\right)^{1/2}\left(\frac{3}{\phi_n}\right) = \left(\frac{2}{2+1}\right)^{1/2}\left(\frac{3}{1.40 \times 10^6}\right) = 1.75 \times 10^{-6}$$

(d) To make the catalyst more effective, we should use smaller diameter.

P12-18cont'd

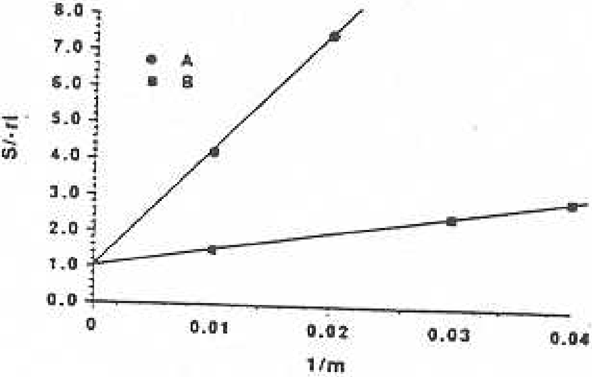
(e) $C_A = 0.01 \frac{g\ mol}{l}$; T = 527 C = 800 K

$$k = k_0 \exp\left\{\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right\} = 578.25 \exp\left\{\frac{7.55 \times 10^5}{8.314}\left(\frac{1}{500} - \frac{1}{800}\right)\right\}$$

$$k = 2.19 \times 10^{32}$$

$$-r_A' = k C_A^{1.5} = 2.19 \times 10^{32} (0.01)^{1.5} = 2.19 \times 10^{29} \frac{g\ mole}{l\ s}$$

P12-19 (a) $\frac{-S}{r_L'} = \frac{1}{k_b\, a_b} + \frac{1}{k\eta}\frac{1}{m}$



$$\text{Slope A} = \frac{7.5 - 4.2}{0.01} = 330 = \frac{1}{k\eta_A}$$

$$\text{Slope B} = \frac{3 - 2.5}{0.01} = 50 = \frac{1}{k\eta_B}$$

Therefore, catalyst size A has smaller effectiveness factor than catalyst size B, since the k's are equal.

(b) From the figure above, r_{cr} depends on particle size, which means surface reaction rate does not control. Diffusion is the major resistance for particle size A.

$$\frac{1}{m} = \frac{1\ \text{dm}^3}{50\ \text{g}} = 0.02\ \frac{\text{dm}^3}{\text{g}}$$

intercept A = r_b = 0.9 min.

$$\%\ \text{gas absorption} = \frac{0.9}{7.5} \times 100\% = 12\%$$

$$\%\ \text{internal diffusion} = \frac{7.5 - 0.9}{7.5} \times 100\% = 88\%$$

Since internal diffusion is the controlling step, if a more efficient sparger were used, a significant increase in reaction would not be obtained.

(c)

$$\frac{\left(\frac{S}{-r_1'}\right) - r_b}{\left(\frac{S}{-r_L'}\right)} \times 100\% = 50\%$$

From the graph above, intercept r_b = 1 min.

$$\frac{\left(\frac{S}{-r_2'}\right) - 1}{\left(\frac{S}{-r_2'}\right)} \le 0.5 \qquad \therefore \left(\frac{S}{-r_2'}\right) \le 2\ \text{min}$$

$$2\ \text{min} = 50\frac{1}{m} + 1\ \text{min}$$

$$\frac{1}{m} = 0.02\ \frac{\text{dm}^3}{\text{g}} \quad \text{or} \quad m = 50\ \frac{\text{g}}{\text{dm}^3}$$

The minimum catalyst charge is $50\ \frac{\text{g}}{\text{dm}^3}$

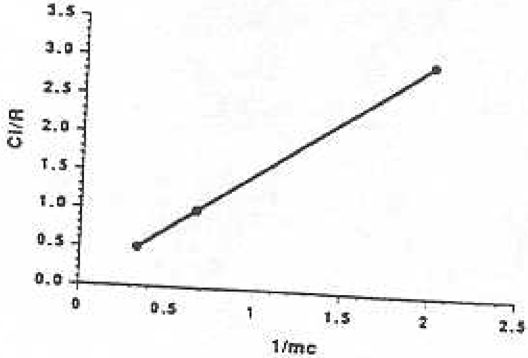
P12-20

$$\frac{C_i}{R} = \frac{1}{k_b\, a_b} + \frac{1}{m_0}\left[\frac{1}{k_c\, a_c} + \frac{1}{\eta k}\right]$$

species i representing H_2

P12-20cont'd

Run	P_i (atm)	C_i (gmol/dm^3)	R (gmol/ dm^3 min)	m_c (g/dm^3)	1/mc (dm^3/g)	C_i / R (min.)	d_p (μm)
1	3	0.007	0.014	3.0	0.333	0.5	12
2	18	0.042	0.014	0.5	2.000	3.0	50
3	3	0.007	0.007	1.5	0.667	1.0	50



For run 1, 2, and 3 $\frac{C_i}{R}$ vs $\frac{1}{m_c}$ plot has intercept $= 0$

(a) Therefore:

- No resistance to gas absorption and the reaction rate is independent of particle diameter.
- Installing a more efficient sparager will not help the overall reaction rate.
- Increasing stirring rate would not help.

(b) This is the case of reaction rate limited. $\frac{1}{k_c a_c} = 0$, $\eta = 1$

$$\text{slope} = \frac{1}{k} \quad \text{or} \quad k = 0.667 \frac{\text{dm}^3}{\text{min gm cat}}$$

(c) For run 4 slope $= 6 = \frac{1}{k_c a_c} + \frac{1}{\eta k}$

$$\eta = \frac{3}{\phi} = \frac{3}{9} = 0.333$$

$$a_c = \frac{6}{d_p \rho_p} = \frac{6}{(0.075\ \text{cm})(2 \times 10\ \text{g/cm}^3)} = 40 \frac{\text{cm}^2}{\text{gm}} = 0.4 \frac{\text{dm}^2}{\text{gm}}, \quad \rho = 2\ \text{g/cm}^3$$

P12-20cont'd

$$6\ \frac{\text{gm min}}{\text{dm}^3} = \frac{1}{0.4\ k_c} + \frac{1}{(0.333)(0.667)} = \frac{1}{0.4\ k_c} + 4.5$$

$$k_c = \frac{1}{(6 - 4.5)\,400} = 1.666\ \frac{\text{dm}}{\text{min}}$$

$$r_c = \frac{1}{(k_c\, a_c)} = \frac{1}{\left(1.666\ \frac{\text{dm}}{\text{min}}\right)\left(0.4\ \frac{\text{dm}^2}{\text{gm}}\right)} = 1.5\ \frac{\text{gm min}}{\text{dm}^3}$$

$$r_{\text{overall}} = (r_{cr})\left(\frac{1}{m_c}\right) + r_b = \left(6\ \frac{\text{gm min}}{\text{dm}^3}\right)\left(\frac{1\ \text{dm}^3}{2\ \text{gm}}\right) + 0$$

$$r_{\text{overall}} = 3\ \text{min}$$

Resistance of external mass - transfer $= \frac{1}{m_c}\, r_c = \frac{1\ \text{dm}^3}{2\ \text{gm}} \times 1.5\ \frac{\text{gm min}}{\text{dm}^3} = 0.75\ \text{min}$

% external mass-transfer resistance $= \frac{0.75}{3} \times 100\% = 25\%$

P12-21

$$r_A = \frac{C_i}{\frac{1}{k_b\, a_b} + \frac{1}{mk_c\, a_c} + \frac{1}{mk\eta\, C_{org}}}$$

Resistance due to the first term:

$$\frac{1}{k_b\, a_b} = \frac{1}{0.3\ \text{s}^{-1}} = 3.33\ \text{sec}$$

Resistance due to the first term:

$$a_c = \frac{6}{\rho_p\, d_p} = \frac{6}{1500\ \frac{\text{kg}}{\text{m}^3}\left(1 \times 10^{-4}\ \text{m}\right)} = 40\ \frac{\text{m}^2}{\text{kg}}$$

$$m = 0.1\ \text{kg} / \text{m}^3$$

$$\frac{1}{mk_c\, a_c} = \frac{1}{\left(0.1\ \frac{\text{kg}}{\text{m}^3}\right)\left(0.005 \times 10^{-2}\ \frac{\text{m}}{\text{s}}\right)\left(40\ \frac{\text{m}^2}{\text{kg}}\right)} = 5000\ \text{sec}$$

Resistance due to the third term:

$$C_{org} = C_{org,\,0}\,(1 - X)$$

Assuming reaction occurs in well-mixed CSTR and concentration on the surface equals bulk concentration.

P12-21 cont'd

$$C_{org,0} = 2.5 \text{ k mol/m}^3$$

Assume that tortuosity = 1.5 and constriction = 0.8

$$D_0 = D_L \frac{\sigma \varepsilon_p}{\tau} = \frac{(10^{-9})(0.8)(0.4)}{(1.5)} = 2.133 \times 10^{-10} \frac{\text{m}^2}{\text{s}}$$

$$\phi = R\sqrt{\frac{k\rho_p C_{org}}{D_c}} = \frac{1 \times 10^{-4}}{2} \text{m} \sqrt{\frac{0.048 \dfrac{\text{m}^6}{\text{kg kmol s}} \times 1500 \dfrac{\text{kg}}{\text{m}^3} \times 2.5 \dfrac{\text{kmol}}{\text{m}^3}(1 - X)}{2.133 \times 10^{-10} \dfrac{\text{m}^2}{\text{s}}}}$$

$$\phi = 45.93 \sqrt{1 - X}$$

$$\eta = \frac{3}{\phi} = \frac{0.065}{\sqrt{1 - X}}$$

$$\frac{1}{m\eta k C_{org}} = \frac{1}{\left(0.1 \dfrac{\text{kg}}{\text{m}^3}\right)\left(\dfrac{(0.065)}{\sqrt{1 - X}}\right)\left(0.048 \dfrac{\text{m}^6}{\text{kg kmol s}}\right)\left(2.5 \dfrac{\text{k mol}}{\text{m}^3}\right)(1 - X)}$$

$$\frac{1}{m\eta k C_{org}} = \frac{1282}{\sqrt{1 - X}} \text{ sec}$$

Let $X = 0.80 \Rightarrow \dfrac{1}{\mu\eta k C_{org}} = 2867$ sec

Gathering all the resistance terms, at $X = 0.80$

Step	Resistance (sec)	Percent
Gas absorption	3.33	0.04
Transport to catalyst surface	5000	63.53
Internal diffusion & reaction	2867	36.43
Total	7870.33	100%

(b) Assume the system behaving as a batch reactor.

$$\frac{dN_A}{dt} = r_A V$$

Rate law: $$r_A = \frac{C_i}{\dfrac{1}{k_b a_b} + \dfrac{1}{mk_c a_c} + \dfrac{1}{mk\eta C_A}}$$

Stoichiometry:

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

P12-21 cont'd

$$\frac{d}{dt}(C_A V) = r_A V \quad \text{where V is constant}$$

$$\frac{dC_A}{dt} = \frac{C_i}{\frac{1}{k_b a_b} + \frac{1}{mk_c a_c} + \frac{1}{mk\eta C_A}}$$

$$\frac{dX}{dt} = \frac{\left(\frac{C_i}{C_{A0}}\right)}{\frac{1}{k_b a_b} + \frac{1}{mk_c a_c} + \frac{1}{mk\eta C_{A0}(1 - X)}}$$

$$\frac{dX}{dt} = \frac{\left(\frac{0.01 \text{ kmol}/\text{m}^3}{2.5 \text{ kmol}/\text{m}^3}\right)}{5.33 + 5000 + \frac{1282}{\sqrt{(1 - X)}}} = \frac{0.004}{5003.33 + \frac{1282}{\sqrt{(1 - X)}}}$$

CDP12-A No solution will be given

CDP12-B No solution will be given

CDP12-C No solution will be given

CDP12-D No solution will be given

CDP12-E No solution will be given

CDP12-F No solution will be given

CDP12-G

Part (c) is done first.

(c) Only the gas phase resistances are determined here. The assumption of pseudo first order kinetics means that gas phase resistances are much larger than the liquid phase resistances and are rate controlling. In part (d) where the other assumption is made, liquid phase resistances are determined.

CDP12-G cont'd

$$-r_A = \frac{\dfrac{C_{H_2}}{H}}{\dfrac{(1-\varepsilon)\rho_p}{Hk_g\,a_i} + \dfrac{(1-\varepsilon)\rho_p}{k_l\,a_i} + \dfrac{1}{k_c\,a_c} + \dfrac{1}{\eta k\,C_{org,s}}}$$

We need to evaluate parameters in the above equation. The first term:

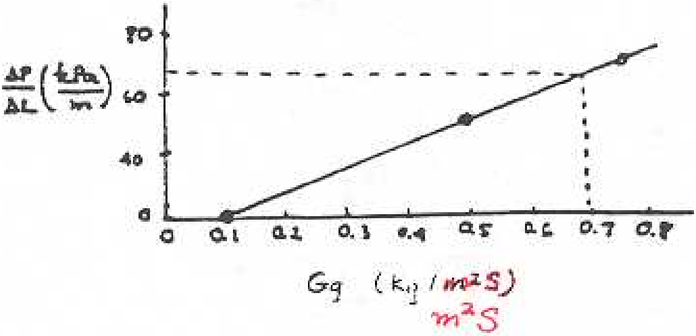
$$k_g\,a_i = 2 + 0.91E_g^{2/3} \qquad E_g = \frac{\Delta P}{\Delta L}U_g$$

$$\upsilon_0 = 36\,\frac{\text{mol}}{\text{s}} \times 0.0224\,\frac{\text{m}^3}{\text{mol}} \times \frac{1\text{ atm}}{2\text{ atm}} \times \frac{400\text{ K}}{273\text{ K}} = 0.5907\,\frac{\text{m}^3}{\text{s}}$$

$$A_c = \frac{\pi D^2}{4} = \frac{\pi}{4}(1\text{ m})^2 = 0.785\text{ m}^2$$

$$U_g = \frac{\upsilon_0}{A_c} = \frac{0.5907\text{ m}^3/\text{s}}{0.785\text{ m}^2} = 0.7526\text{ m/s}$$

$$G_g = \frac{m_g}{A_c} = 36\,\frac{\text{mol}}{\text{s}} \times \frac{(2+28)\text{ g}}{2\text{ mol}} \times \frac{1\text{ kg}}{1000\text{ g}} \times \frac{1}{0.785\text{m}^2} = 0.69\,\frac{\text{kg}}{\text{m}^2\text{ s}}$$



From the graph above: $\frac{\Delta P}{\Delta L} = 65\,\frac{\text{kPa}}{\text{m}}$ at $0.69\,\frac{\text{kg}}{\text{m}^2\text{ s}}$

$$E_g = \left(65\,\frac{\text{kPa}}{\text{m}}\right)\left(0.7526\,\frac{\text{m}}{\text{s}}\right) = 48.919\,\frac{\text{kPa}}{\text{s}} = 1025\,\frac{\text{ft lb}_f}{\text{ft}^3\text{ s}}$$

$$k_g\,a_i = 2 + 0.91\,(1025)^{2/3} = 94.53\text{ s}^{-1}$$

CDP12-G cont'd

Solubility: $H' = 0.004 \, \frac{\text{k mol K}}{\text{m}^3 \text{ atm}}$

$$H = \frac{1}{RTH'} = \frac{1}{\frac{0.082 \text{ m}^3 \text{ atm}}{\text{k mol K}} \times 400 \text{ K} \times 0.004 \frac{\text{kmol}}{\text{m}^3 \text{ atm}}} = 7.62$$

$$R_g = \frac{(1 - \varepsilon_p)\,\rho_p}{H \, (k \, g \, a_i)}$$

$$R_g = \frac{(1 - 0.45)\left(1600 \frac{\text{kg}}{\text{m}^3}\right)}{(7.62)\,(94.53 \text{ s}^{-1})} = 1.22 \, \frac{\text{kg s}}{\text{m}^3}$$

The second term: $R_l = \frac{(1 - \varepsilon)\,\rho_p}{k_c \, a_i}$

$$k_l \, a_i = D_L \left[16.8 \, \frac{R_e^{1/4}}{G_a^{0.22}} \, S_c^{1/2} \right]$$

$$R_e = \frac{G_L \, d_p}{\mu_L} = \frac{\left(5 \frac{\text{kg}}{\text{m}^2 \text{ s}}\right)(0.40 \text{ cm})\left(\frac{1 \text{ m}}{100 \text{ cm}}\right)}{0.0031 \frac{\text{kg}}{\text{m s}}} = 6.45$$

$$G_a = \frac{d_p^3 \, \rho_L^2 \, g}{\mu_L^2} = \frac{(0.4 \times 10^{-2} \text{ m})^3 \, (700 \text{ kg/m}^3)^2 \, (9.8 \text{ m/s}^2)}{\left(0.0031 \frac{\text{kg}}{\text{m s}}\right)^2} = 31{,}980$$

$$S_c = \frac{\mu_L}{\rho_L \, D_L} = \frac{0.0031 \frac{\text{kg}}{\text{m s}}}{(700 \text{ kg/m}^3)\left(7 \times 10^{-9} \frac{\text{m}^2}{\text{s}}\right)} = 632.65$$

$$k_l \, a_i = \left(7 \times 10^{-9} \frac{\text{m}^2}{\text{s}}\right)\left[\frac{(16.8)(6.45)^{1/4}(632.65)^{1/2}}{(31980)^{0.22}}\right] \text{cm}^2 = 4.81 \times 10^{-3} \text{ s}^{-1}$$

$$R_L = \frac{(1 - 0.45)(1600 \text{ kg/m}^3)}{4.81 \times 10^{-3} \text{ s}^{-1}} = 1.8288 \times 10^5 \, \frac{\text{kg s}}{\text{m}^3}$$

The third term: $R_e = \frac{1}{k_c \, a_e}$

$$a_c = \frac{6}{\rho_p \, d_p} = \frac{6}{\left(1600 \frac{\text{kg}}{\text{m}^3}\right) 0.4 \times 10^{-2} \text{ m}} = 0.9375 \, \frac{\text{m}^2}{\text{kg}}$$

$$Sh = 0.266 \, R_e^{1.15} \, S_c^{1/3} = (0.266)(6.45)^{1.15}(632.65)^{1/3} = 19.5$$

CDP12-G cont'd

$$Sh = 0.266\, R_e^{1.15}\, S_c^{1/3} = (0.266)(6.45)^{1.15}(632.65)^{1/3} =$$

$$19.5 \quad k_C = \frac{Sh\, D_L}{d_p} = \frac{(19.5)\left(7 \times 10^{-9}\ \mathrm{m^2/s}\right)}{0.4 \times 10^{-2}\ \mathrm{m}} = 3.41 \times 10^{-5}\ \frac{\mathrm{m}}{\mathrm{s}}$$

$$R_c = \frac{1}{\left(3.41 \times 10^{-5}\ \frac{\mathrm{m}}{\mathrm{s}}\right)\left(0.9375\ \frac{\mathrm{m^2}}{\mathrm{kg}}\right)} = 3.13 \times 10^{4}\ \frac{\mathrm{kg\ s}}{\mathrm{m^3}}$$

The fourth term: $\dfrac{1}{\eta k\, C_{org,s}} = \dfrac{1}{\eta k'}$ where $k' = 2.5 \times 10^{-5}\ \dfrac{\mathrm{m^3}}{\mathrm{kg\ s}}$

Assume $\tau = 1.5$, $\sigma = 0.8$

$$D_C = D_C \frac{\sigma\, \varepsilon_p}{\tau}$$

$$\phi = R_p \sqrt{\frac{k\rho_p}{D_c}} = 2 \times 10^{-3} \sqrt{\frac{(1600)\left(2.5 \times 10^{-5}\right)(1.5)}{\left(7 \times 10^{-4}\right)(0.8)(0.45)}} = 9.759\ ;\ \eta = \frac{3}{\phi} = 0.307$$

$$\frac{1}{\eta k'} = \frac{1}{(0.307)\left(2.5 \times 10^{-5}\ \frac{\mathrm{m^3}}{\mathrm{kg\ s}}\right)} = 1.3 \times 10^{5}\ \frac{\mathrm{kg\ s}}{\mathrm{m^3}}$$

Bringing together the resistance terms:

Step	Resistance $\left(\frac{\mathrm{kg\ s}}{\mathrm{m^3}}\right)$	Percent resistance
Bulk gas - gas interface	1.222	0
Interface - bulk-liquid	1.8288×10^5	53.1
Bulk-liquid - catalyst surface	3.13×10^4	9.1
Diffusion - reaction in pellet	1.3×10^5	37.8
Total = R_T	3.442×10^5	100%

(a) Calculate catalyst weight:

$$(1 + \varepsilon) \ln \frac{1}{1 - X} - \varepsilon X = \frac{k_{vg}}{v_0}\left(W - \frac{\beta}{2} W^2\right) \qquad \text{(E - 12-3.7)}$$

$$k_{vg} = \frac{1}{H\, R_T} = \frac{1}{(7.62)\left(3.442 \times 10^5\right)} = 3.813 \times 10^{-7}\ \frac{\mathrm{m^3}}{\mathrm{kg\ s}}$$

$$\frac{k_{vg}}{v_0} = \frac{3.813 \times 10^{-7}}{0.5907} = 6.455 \times 10^{-7}\ \mathrm{kg^{-1}}$$

CDP12-G cont'd

$$\beta = \frac{\alpha}{A_c P_0 \rho (1-\varepsilon_b)} = \frac{\frac{65}{101.3}\frac{\text{atm}}{\text{m}}}{(0.785\text{m}^2)(2\text{ atm})(1600\text{ kg/m}^3)(0.6)} = \frac{4.257\times10^{-4}}{\text{kg}}$$

Substitution yields:

$$(1-0.5)\ln\frac{1}{1-0.55}-[(-0.5)\,0.55] = 6.455\times10^{-7}\left(W-\frac{4.257\times10^{-4}}{2}W^2\right)$$

The equation above yields no solution for W.

(b) If P = 100 atm, then:

$$\upsilon_0 = 0.5907\frac{\text{m}^3}{\text{g}}\left(\frac{2\text{ atm}}{100\text{ atm}}\right) = 1.1814\times10^{-2}\frac{\text{m}^3}{\text{s}}$$

$$U_g = \frac{1.1814\times10^{-2}\frac{\text{m}^3}{\text{s}}}{0.785\text{ m}^2} = 1.5050\times10^{-2}\text{ m/s}$$

$$E_g = \left(65\frac{k\rho_a}{\text{m}}\right)\left(1.5050\times10^{-2}\text{ m/s}\right) = 0.9782\frac{k\rho_a}{\text{s}} = 20.50\frac{\text{ft lb}_f}{\text{ft}^3\text{ s}}$$

$$R_g = \frac{(1-0.45)(1600)}{7.62\left[2+(0.91)(20.50)^{2/3}\right]} = 13.10\frac{\text{kg s}}{\text{m}^3}$$ still very small, does not affect R_T

$$\frac{k\upsilon_g}{\upsilon_0} = \frac{3.813\times10^{-7}}{1.1814\times10^{-2}} = 3.2275\times10^{-5}\text{ kg}^{-1}$$

$$\beta = 4.257\times10^{-4}\left(\frac{2}{100}\right) = 8.514\times10^{-6}\text{ kg}^{-1}$$

$$(1-0.5)\ln\frac{1}{(1-0.55)}-[(-0.5)\,0.55] = 3.2275\times10^{-5}\left(W-\frac{8.514\times10^{-6}}{2}W^2\right)$$

$$W^2 = 2.349\times10^5\,W + 4.907\times10^9 = 0$$

$$W = 23174\text{ kg}$$

The operating condition is P = 100 atm, T = 400°K

(d) By definition:

$$-r_A = \frac{(C_{Ag}/H)}{\left[R_3+\frac{1}{\eta_A k C_{B_s}}\right]} = k_{\upsilon g}(C_{Ag})$$

$$-r_B = \frac{C_{B_l}}{\left[R_{C_l}+\frac{1}{\eta_B k C_{AS}}\right]} = k_{\upsilon l} C_{B_l}$$

In general, C_{Bl} will vary significantly, so that $k_{\upsilon g}$, thus C_{AS} will vary significantly. Hence, k_{υ_l} will also vary significantly as a function of conversion. C_{Ag} will vary significantly only if the pressure drop is significant. The Δp factor α is proportional to $\frac{G^2}{\rho D_p}$ all else constant (assuming turbulent). Between the present case and part (b), G/ρ = constant, $G^2 / G^1 = 2/15$ (because $\overline{M}_1 = 15$, $\overline{M}_2 = 2$) and $D_{p_2}/D_{p_1} = 1/4$, so $\alpha_2 = \alpha_1 (8/2.5) = 5 \times 10^{-8}\ kg^{-1}$. Assuming a liberal $w = 5 \times 10^4$ kg, $P_f = P_0(1 - \alpha w) = 99.75$ atm. Thus, C_{Ag} is essentially constant.

Let $R_3 = R_g + R_l + R_{C_l}$

$$-r_A = k\, C_{A_s} C_{B_s} = -r_B$$

Let $= C_{A_l} \dfrac{C_{Ag}}{H}$

$$k\, C_{A_s} C_{B_s} \eta = \frac{C_{Al}}{R_3 + \dfrac{1}{\eta\, k\, C_{B_s}}} = \frac{C_{Bl}}{\left[R_{C_l} + \dfrac{1}{\eta\, k\, C_{A_s}}\right]}$$

$$\text{Then,}\quad C_{A_s} = \frac{C_{Al}}{[1 - R_3\, k\, \eta\, C_{B_s}]}\ ;\ C_{B_s} = \frac{C_{Bl}}{[1 + R_{C_l}\, k\, \eta\, C_{A_s}]}$$

$$\text{Let}\ Q_2 = R_3\, k\, \eta\, C_{B_s},\ Q_1 = R_{C_l}\, k\, \eta\, C_{A_s},\ C_A^* = \frac{C_{A_s}}{C_{Al}},\ C_B^* = \frac{C_{B_s}}{C_{Bl}}$$

$$C_A^* = \frac{1}{1 + Q_2\, 2C_B^*}\ ,\ C_B^* = \frac{1}{1 + Q_1\, C_A^*},\ C_A^* = \frac{1}{1 + Q_2\left(\dfrac{1}{1 + Q_1\, C_A^*}\right)}$$

Substituting for C_B^*:

$$C_A^* = \frac{1 + Q_1\, C_A^*}{1 + Q_2 + Q_1\, C_A^*}$$

$$C_A^* + Q_1\, C_A^{*2} + Q_2\, C_A^* = 1 + Q_1\, C_A^*$$

$$Q_1\, C_A^{*2} + (1 + Q_2 - Q_1)\, C_A^* - 1 = 0$$

This allows C_{AS} to be calculated from C_{AC}, C_{Bl}, and constant parameters k, η, R_3, R_{C_2}. Given C_{AS}, $-r_B$ can be calculated. For an overall material balance:

$$F_{B_0} \frac{dX}{dW} = k_{\upsilon l}\, C_{B_0}(1 - X)$$

CDP12-G cont'd

$$\frac{dX}{dW} = \frac{1}{F_{B_0}} \frac{C_{B_0}(1-X)}{R_{C_2} + \frac{1}{k\eta\, C_{AS}(X)}}$$

Where $C_{AS}(X)$ is C_{AS} evaluated at $C_{B1} = C_{B_0}(1-X)$

$$\frac{dX}{dW} = \frac{1}{F_{B_0}} \frac{C_{B_0}(1-X)k\eta C_{A1}C_A^*}{R_{C_2}k\eta\, C_{A1}C_A^* + 1} = \frac{(1-X)(Q_1/R_{C_2})C_A^*}{Q_1 C_A^* + 1}\frac{C_{B1_0}}{F_{B_0}}$$

$$\frac{dX}{dW} = \frac{C_{B_0}}{R_{C_2}F_{B_0}} = \frac{Q_1 C_A^*(X)}{Q_1 C_A^*(X) + 1}(1-X)$$

Let W = total weight, $\omega = \frac{w}{W}$

$$\frac{dX}{dW} = \frac{C_{B_0}W}{F_{B_0}R_{C_2}} = \frac{Q_1 C_A^*(X)}{Q_1 C_A^*(X)+1}(1-X) = \frac{Q_3 Q_1 C_A^*}{Q_1 C_A^* + 1}(1-X) = \frac{dX}{dW}$$

$$Q_1 = R_{C_2}k\eta\, C_{A1},\ Q_2 = R_3 k\eta\, C_{B_0},\ Q_3 = \frac{C_{B_0}W}{F_{B_0}R_{C_2}}$$

$$\eta = \frac{3}{\phi^2}(\phi\cosh\phi - 1) \text{ where } \phi = \left[\frac{k\delta^2(C_{AS}+C_{BS})}{D}\right]^{1/2}$$

When $C_{AS} >> C_{BS}$ this becomes correct for pseudo-first-order kinetics in C_{BS}. Similarly, $C_{BS} >> C_{AS}$ gives η applied to pseudo-first-order kinetics in C_{AS}. When $C_{AS} = C_{BS}$, for large ϕ, this definition of ϕ gives $\frac{1}{\sqrt{2}}$ times the first order η, which is close to the (proper) 2nd order η. So, our definition of ϕ is an approximation, but one which is simple, correct in the limits, and nearly correct in intermediate behavior. Therefore, we must guess η, solve for C_{AS}, C_{BS}, calculate a revised η, and recalculate C_{AS}, C_{BS}, etc. This introduces two more dimensionless groups, $\frac{k\delta^2 C_{A1}}{D}$ and $\frac{k\delta^2}{D}C_{B_0}$.

Numerically,

$R_3 = 230811.3$ kg s/m³

$R_{C_2} = 19130$ kg s/m³

$\delta = 0.5 \times 10^{-3}$ m

$D_H = 7 \times 10^{-9}$ m²/s

$D_{org} = 2.5 \times 10^{-9}$ m²/s

$k = 9.142857 \times 10^{-6} \frac{m^6}{\text{kg kmol s}}$

CDP12-G cont'd

$C_{B_0} = 2.734 \text{ kmol/m}^3$

$C_{AI} = 0.39981 \text{ kmol/m}^3$

$F_{B_0} = 1.53398 \times 10^{-2} \text{ kmol/s}$

$\tau = 1.5$

$\sigma = 0.8$

$\varepsilon_p = 0.45$

$\rho_C = 1600 \text{ kg/m}^3$

$$Q_1 = R_{C_2} k C_{AI}(19130)\left(9.142857 \times 10^{-6}\right)(0.39981) = 6.9927 \times 10^{-2}$$

$$Q_2 = R_3 k C_{B_0}(230811.3)\left(9.142857 \times 10^{-6}\right)(2.734) = 5.7695$$

$$Q_3 = \frac{k\delta^2 C_{AI} \tau \rho_C}{D_H \sigma \varepsilon_p} = \frac{\left(9.142857 \times 10^{-6}\right)\left(5 \times 10^{-4}\right)^2 (0.39981)(1.5)(1600)}{\left(7 \times 10^{-9}\right)(0.8)(0.45)} = 0.87033$$

$$Q_4 = \frac{k\delta^2 C_{B_0} \tau \rho_C}{D_{org} \sigma \varepsilon_p} = \frac{\left(9.142857 \times 10^{-6}\right)\left(5 \times 10^{-4}\right)^2 (2.734)(1.5)(1600)}{\left(2.5 \times 10^{-9}\right)(0.8)(0.45)} = 16.664$$

$$Q_5 = \frac{C_{B_0} W}{F_{B_0} R_{C_2}} = \frac{(2.734)\,W}{\left(1.53398 \times 10^{-2}\right)(1.9130)} = \left(9.3167 \times 10^{-3} \text{ kg}^{-1}\right)(W \text{ kg})$$

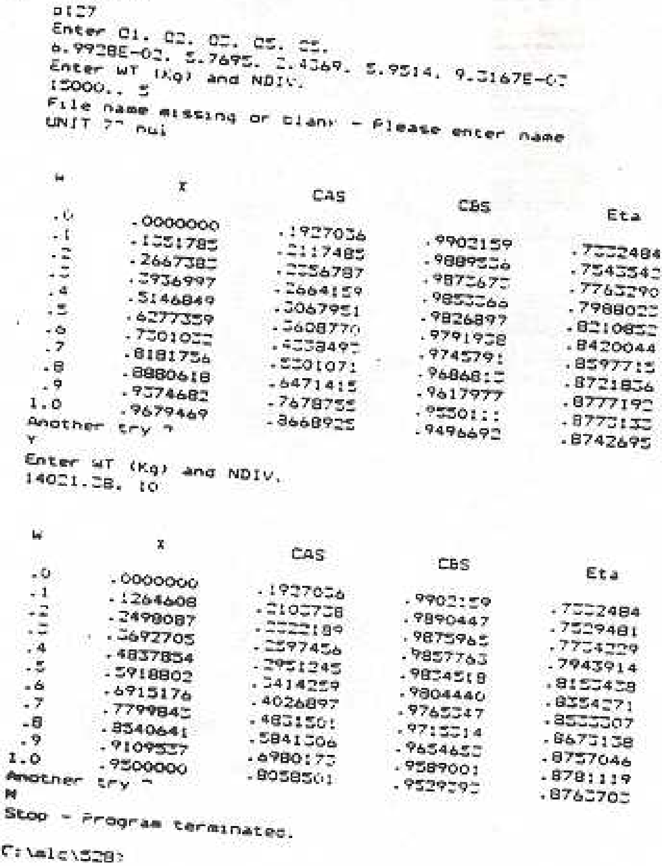
Using the constants in a computer program to solve for W, we get W = 18450 kg catalyst. Note that the 18450 is wrong due to complete error. Also, the D's in Q_3 and Q_4 should be switched. Thus:

$$Q_3 = \frac{k\delta^2 C_{AI} \tau \rho_C}{D_{org} \sigma \varepsilon_p} = 2.4369$$

$$Q_4 = \frac{k\delta^2 C_{B_0} \tau \rho_C}{D_H \sigma \varepsilon_p} = 5.9514$$

This results in W = 14021.38 kg. If you assume $C_{AS} = C_{AI}$ and $C_S \gg C_A$ to calculate a constant k_{ul} and solve for $W = \frac{F_{B_0}}{C_{B_0} k_{ul}} \ln\left(\frac{1}{1-X}\right)$, one gets W = 6523.4 kg. If one assumes $C_B \gg C_A$ but $C_{AS} = 0.1927\, C_{AI}$, then one gets W = 32372.4 kg. These results show that it is necessary to consider the coupling.

CDP12-G cont'd



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D137
Enter C1, C2, C3, C5, C6.
6.9928E-03, 5.7695, 3.4369, 5.9514, 9.3167E-03
Enter WT (Kg) and NDIV.
15000., 5
File name missing or blank - Please enter name
UNIT 7? nul

 W        X             CAS             CBS             Eta
 .0      .0000000      .1937036        .9903159        .7332484
 .1      .1351785      .2117485        .9889536        .7543543
 .2      .2667383      .2356787        .9873673        .7763290
 .3      .3936997      .2664159        .9853366        .7988033
 .4      .5146849      .3067951        .9826897        .8210853
 .5      .6277359      .3608770        .9791938        .8420044
 .6      .7301033      .4338493        .9745791        .8597715
 .7      .8181736      .5301071        .9686813        .8721836
 .8      .8880618      .6471415        .9617977        .8777193
 .9      .9374683      .7678735        .9550111        .8773133
1.0      .9679469      .8668925        .9496693        .8742695
Another try ?
Y
Enter WT (Kg) and NDIV.
14021.38, 10

 W        X             CAS             CBS             Eta
 .0      .0000000      .1937036        .9903159        .7332484
 .1      .1264608      .2103738        .9890447        .7529481
 .2      .2498087      .2333189        .9875965        .7734229
 .3      .3692705      .2597456        .9857763        .7943914
 .4      .4837854      .2951245        .9834518        .8153438
 .5      .5918802      .3414259        .9804440        .8354271
 .6      .6915176      .4026897        .9765347        .8533307
 .7      .7799843      .4831501        .9713314        .8673138
 .8      .8540641      .5841306        .9654653        .8757046
 .9      .9109537      .6980173        .9589001        .8781119
1.0      .9500000      .8058501        .9529393        .8763703
Another try ?
N
Stop - Program terminated.

C:\mlc\528>
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(e) Plug flow model works $\frac{L}{d_p} > \frac{20}{P_e} n \ \ln\left(\frac{1}{1-X}\right)$

$$L = 1235 \text{ kg} \frac{\text{m}^3}{1600 \text{ kg}} \left(\frac{1}{0.785 \text{ m}^2}\right) = 0.98 \text{ m}$$

$$U_C = \frac{5 \text{ kg/m}^2 \text{ s}}{700 \text{ kg/m}^3} = 0.007143 \frac{\text{m}}{\text{s}}$$

$$P_e = \frac{U_C d_p}{D_{AX}} = \frac{\left(0.007143 \frac{\text{m}}{\text{s}}\right)\left(0.1 \times 10^{-2} \text{ m}\right)}{0.38 \times 10^{-4} \frac{\text{m}^2}{\text{s}}} = 0.188$$

$$\frac{L}{d_p} = \frac{0.98 \text{ m}}{0.1 \times 10^{-2} \text{ m}} = 980$$

CDP12-G cont'd

$$\frac{20}{P_e} n \ln \frac{1}{1 - X} = \frac{20}{0.188} \ln \frac{1}{1 - 0.95} = 318.7$$

Yes, plug flow model is a good assumption.

CDP12-H No solution will be given

CDP12-I No solution will be given

CDP12-J

Part (b) is done first.

(b) Let B = organic. Then the liquid phase resistance is:

$$-r_B = \frac{1}{\dfrac{1}{k_C\, a_C} + \dfrac{1}{\eta k\, C_{H_2,S}}} C_B$$

The first term:

$$a_C = \frac{6}{\rho_p\, d_p} = \frac{6}{\left(1500 \dfrac{kg}{m^3}\right)\left(1/8 \text{ in}\left(\dfrac{2.54 \times 10^{-2} \text{ m}}{1 \text{ in}}\right)\right)} = \frac{6}{\left(1500 \dfrac{kg}{m^3}\right)\left(3.175 \times 10^{-3} \text{ m}\right)}$$

$$a_C = 1.260 \frac{m^2}{kg}$$

$$Sh = 0.266\, R_{e_L}^{1.15}\ Sc^{1/3}$$

$$R_{e_L} = \frac{G_L\, d_p}{\mu_L} = \frac{(8 \text{ kg/m}^2 \text{ s})(3.175 \times 10^{-3} \text{ m})}{3.0 \times 10^{-3} \text{ kg/m s}} = 8.47$$

$$Sc = \frac{\mu}{\rho D_{AB}} = \frac{(3 \times 10^{-3} \text{ kg/m s})}{(900 \text{ kg/m}^3)\, 6 \times 10^{-11} \text{ m}^2\text{/s}} = 55555$$

$$S_h = (0.266)(8.47)^{1.15}(55{,}555)^{1/3} = 118.45 = \frac{k_C\, d_p\, \alpha}{D_L}$$

$$k_C = \frac{(118.45)\, 6 \times 10^{-11} \text{ m}^2\text{/s}}{3.175 \times 10^{-3} \text{ m}} = 2.238 \times 10^{-6} \text{ m/s} \quad (\text{assuming } \alpha = 1)$$

$$\frac{1}{k_C\, a_C} = \left[(2.238 \times 10^{-6} \text{ m/s})(1.260 \text{ m}^2\text{/kg})\right]^{-1} = 3.546 \times 10^{5} \text{ kg s/m}^3$$

The second term:

$$\frac{n_{H_2}}{n_{N_2}} = \frac{\dfrac{0.2 \text{ kg/m}^2 \text{ s}}{2 \text{ g/gmol}}}{\dfrac{0.05 \text{ kg/m}^2 \text{ s}}{2.8 \text{ g/gmol}}} = 5.6$$

CDP12-I cont'd

$$y_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{N_2}} = \frac{1}{1 + \frac{n_{N_2}}{n_{H_2}}} = \frac{1}{1 + \frac{1}{5.6}} = 0.85$$

$$P_{H_2} = (50\text{ atm})(0.85) = 42.5\text{ atm}$$

$$C_{H_2,S} = (42.5\text{ atm})\left(0.0068\ \frac{\text{mol}}{\text{dm}^3\text{ atm}}\right) = 0.289\ \frac{\text{g mol H}_2}{\text{dm}^3\text{ liquid}}$$

$$k' = kC_{H_2,S} = \left(2\times 10^{-5}\ \frac{\text{m}^6}{\text{k mol kg s}}\right)\left(0.289\ \frac{\text{k mol}}{\text{m}^3}\right) = 5.78\times 10^{-6}\ \frac{\text{m}^3}{\text{kg s}}$$

$$D_e = D_L\frac{\sigma\varepsilon_p}{\tau} = \left(6\times 10^{-11}\ \frac{\text{m}^2}{\text{s}}\right)\frac{(0.8)(0.5)}{(3.8)} = 6.316\times 10^{-12}\ \frac{\text{m}^2}{\text{s}}$$

$$\phi = R\sqrt{\frac{k'\rho_p}{D_e}} = \frac{3.175\times 10^{-3}}{2}\sqrt{\frac{(5.78\times 10^{-6})1500}{6.316\times 10^{-12}}} = 58.8$$

$$\eta = \frac{3}{\phi} = 0.051$$

$$\frac{1}{\eta kC_{H_2,S}} = \frac{1}{\eta k'} = \frac{1}{(0.051)(5.78\times 10^{-6})} = 3.392\times 10^{6}\text{ kg s/m}^3$$

<u>Liquid Resistance</u>

Step	Resistance	Percent
Bulk liquid to catalyst surface	3.546×10^5	9.5
Diffusion/reaction	3.392×10^6	90.5
Total	3.746×10^6	100%

Gas phase resistance: $$-r_A' = \frac{1/H}{\frac{(1-\varepsilon)\rho_p}{H\,k_g a_i} + \frac{(1-\varepsilon)\rho_p}{k_l a_i} + \frac{1}{k_l a_C} + \frac{1}{\eta\, k\, C_{org,\,s}}}C_{H_2}\quad\text{(gas)}$$

The first term: $k_g a_i = 2 + 0.91\,E_G^{2/3}$

$$E_G = \frac{\Delta P}{\Delta L}U_g$$

CDP12-I cont'd

Assuming ideal gas behavior: $\rho_g = \frac{PM}{RT} = \frac{50\,(2)}{0.082\,(373)} = 3.2695\,\frac{kg}{m^3}$

$$U_g = \frac{G_g}{\rho_g} = \frac{0.2\ kg/m^2\,s}{3.2695\ kg/m^3} = 0.06117\,\frac{m}{s}$$

$$E_g = \left(30\,\frac{kP_a}{m}\right)\left(0.06117\,\frac{m}{s}\right) = 1.8352\,\frac{kP_a}{s} = 38.46\,\frac{ft\ lb_f}{ft^3\ s}$$

$$k_g\,a_i = 2 + 0.91\,(38.46)^{2/3} = 12.37\ s^{-1}$$

$$H = \frac{1}{RTH'} = \frac{1}{\frac{0.082\ m^3\ atm}{k\,mol\ K}\,(373K)\,\frac{0.0068\ kmol}{m^3\ atm}} = 4.81$$

$$\frac{(1-\varepsilon)\,\rho_p}{H\,k_g\,a_i} = \frac{(0.5)(1500\ kg/m^3)}{(4.81)(12.37\ s^{-1})} = 12.605\,\frac{kg\ s}{m^3}$$

The second term: $\frac{k_l\,a_i}{D_L} = 16.8\,\frac{R_{e_L}^{\ 1/4}}{G_a^{\ 0.22}}\,S_C^{\ 1/2}$

$$S_C = \frac{\mu_L}{\rho_L\,D_{H_2}} = \frac{0.0031\ kg/m\ s}{(900\ kg/m^3)(8\times10^{-9}\ m^2/s)} = 430.56$$

$$G_a = \frac{d_p^3\,\rho_L^2\,g}{\mu_L^2} = \frac{(3.175\times10^{-3}\ m)^2\,(900\ kg/m^3)^2\,(9.8\ m/s^2)}{(0.0031\ kg/m\ s)^2} = 2.6437\times10^4$$

$$\frac{k_l\,a_i}{D_{H_2}} = (16.8)\,\frac{(8.47)^{1/4}\,(430.56)^{1/2}}{(2.6437\times10^4)^{0.22}} = 63.30$$

$$k_l\,a_i = 63.30\,(8\times10^{-7}) = 5.064\times10^{-5}\ sec^{-1}$$

$$\frac{(1-\varepsilon)\,\rho_p}{k_l\,a_i} = \frac{(0.5)(1500\ kg/m^3)}{5.064\times10^{-5}\ s^{-1}} = 1.481\times10^7\,\frac{kg\ s}{m^3}$$

The third term:

$$Sh' = 0.266\,R_e^{\ 1.15}\,S_C^{\ 1/3} = 0.266\,(8.47)^{1.15}\,(430.56)^{1/3} = 23.44$$

$23.44 = \frac{k_C\,d_p}{D_{H_2}}\,\alpha$ Assuming $\alpha = 1.0$

CDP12-I cont'd

$$k_C = \frac{(23.44)\left(8 \times 10^{-9}\right)}{3.175 \times 10^{-3}} = 5.906 \times 10^{-5} \text{ m/s}$$

$$k_C a_C = \left(5.906 \times 10^{-5} \text{ m/s}\right)\left(1.260 \text{ m}^2/\text{kg}\right) = 7.442 \times 10^{-5} \text{ m}^3/\text{kg s}$$

$$\frac{1}{k_C a_C} = 1.344 \times 10^4 \text{ kg s/m}^3$$

The last term:

$$\frac{1}{\eta k C_{org}} = \frac{1}{(0.051)\left(2 \times 10^{-5} \frac{\text{m}^6}{\text{kmol kg s}}\right)\left(0.07 \frac{\text{kmol}}{\text{m}^3}\right)} = 1.40 \times 10^7 \frac{\text{kg s}}{\text{m}^3}$$

Gathering up the resistances in gas phase:

Step	Resistance	Percent
Bulk gas - gas interface	12.605	0.0
Interface - bulk liquid	1.481×10^7	51.4
Bulk liquid - catalyst surface	1.344×10^4	0.0
Diffusion - reaction in pellet	1.40×10^7	48.6
Total	2.882×10^7	100%

(a) Mole balance, plug flow model: $-\frac{dF_B}{dW} = -r_B$

Rate Law: $r_B' = k_{ul} C_B$

Stoichiometry: $C_B = C_{B0}(1 - X_B)$

Combine: $\frac{dX_B}{dW} = \frac{C_{B0}}{F_{B0}} k_{ul}(1 - X_B)$

$$\frac{dX_B}{1 - X_B} = \frac{C_{B0}}{F_{B0}} k_{ul}\, dW$$

$$k_{ul} = \frac{1}{R_T} = \frac{1}{3.746 \times 10^6} = 2.67 \times 10^{-7} \frac{\text{m}^3}{\text{kg s}}$$

$$C_{B0} = 0.07 \frac{\text{kmol}}{\text{m}^3}$$

CDP12-I cont'd

$$F_{B0} = \frac{(8\ \text{kg/m}^2\ \text{s})\frac{\pi}{4}(1\ \text{m})^2}{(900\ \text{kg/m}^3)\left(0.07\ \frac{\text{kmol}}{\text{m}^3}\right)} = 9.973 \times 10^{-2}\ \frac{\text{kmol}}{\text{s}}$$

$$\frac{dX_B}{(1 - X_B)} = \frac{\left(0.07\ \frac{\text{kmol}}{\text{m}^3}\right)}{9.973 \times 10^{-2}\ \frac{\text{kmol}}{\text{s}}}\left(2.67 \times 10^{-7}\ \frac{\text{m}^3}{\text{kg s}}\ dW\right) \quad \text{W in kgs}$$

$$\frac{dX_B}{(1 - X_B)} = 1.874 \times 10^{-7}\ dW$$

$$\ln\frac{1}{(1 - X_B)} = 1.874 \times 10^{-7}\ W$$

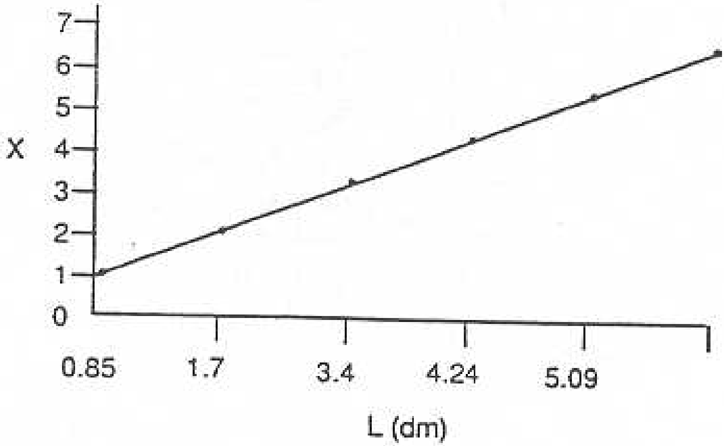
$$W_{max} = \left[\frac{\pi}{4}(1\ \text{m})^2\right](6\ \text{m})\ 0.5\left(1500\ \frac{\text{kg}}{\text{m}^3}\right) = 3534\ \text{kg}$$

$$\ln\frac{1}{(1 - X_{B\ max})} = 6.623 \times 10^{-4}$$

$$X_{B\ max} = 6.621 \times 10^{-4}$$

This choice of η and k gives a rather low total conversion. Since diffusion-reaction resistance is the largest by far, W coefficient is almost linear in it.

W (kg)	L (m)	X_B
500	0.85	9.369×10^{-5}
1000	1.70	1.874×10^{-4}
1500	2.55	2.811×10^{-4}
2000	3.40	3.747×10^{-4}
2500	4.24	4.684×10^{-4}
3000	5.09	5.620×10^{-4}
3500	5.94	6.557×10^{-4}



(c) For all the conditions used in this problem, the diffusion into pellet and reaction resistances were dominate for both liquid and gas.

At 50 atm total pressure with 80% H_2 in the gas feed. The equilibrium H_2 solubility is 0.289 gmol/l vs organic maximum concentration of 0.07 gmol/l. Also, the molar flow rate of H_2 is higher than the flow rate of organics.

For these reasons, cutting gas flow rate could have no effect on the conversion provided the same inlet pressure is maintained. There will still be a huge excess of the H_2 and the system will behave as a quasi first-order reaction modeled as a plug flow reactor. The H_2 concentration at all points will be essentially the equilibrium saturation liquid concentration.

Answer: No change in conversion.

CDP12-K

a) The Orcutt model agrees with Kunii-Levenspeil in believing all the bubbles are uniform throughout the reactor and both also agree that transfer from bubble phase to emulsion phase is by two superimposed independent mechanisms. However they differ in that in K-L believes that transfer from emulsion and cloud-wake is different from Orcutt's belief is the same as bubble to emulsion transfer. A disadvantage of the Orcutt model is that the mass transfer parameter is over estimated making the model incorrect

The Rowe and Partridge model assumes that bubble size changes as well as the velocities which K-L does not do. However due to the model they used, the cloud area gets overestimated and does not correlate to the bed cross-sectional area.

The Kato and Wen model assumes that the bubble phase includes clouds and voids. K-L only includes clouds. It also assumes that each phase is perfectly mixed which K-L also agrees with. But interphase transfer uses a different mechanism. This model gives the lowest F factor, but the dense phase profile and outlet reactant concentrations were over predicted.

b) $K_{ce}=\frac{6.4}{D_p}=\frac{6.4}{4.87}=1.31$

Solving for K_R:

$$K_R=0.01+\frac{1}{0.017+\frac{1}{0.187+\frac{1}{\frac{1}{2.28}+0.065}}}=2.11$$

Then finding the conversion:

$$X=1-\exp\left(-\frac{K_R k_{cat} h}{U_b}\right)=0.18$$

CDP12-L

a)

$$\langle \varepsilon_B \rangle = 5.4 * 10^{-2} (U - U_{mf})^{0.4} = 0.11$$

$$D_B = 5.3 * 10^{-3} U y + 2.1$$

At a height of y = 0.5H

y = 30 cm.

D_B = 3.4 cm

$$f = 1.15 * 10^3 \langle \varepsilon_B \rangle D_B^{-1.45} = 21.7$$

$$U_B = 13 * A_B^{0.35}$$

$$A_B = \frac{\pi D_B^2}{4} = 6.74 cm^2$$

$$U_B = 25.4 cm$$

b) We now must find the conversion:

$$K_{ce} = 6.77 \left(\frac{\varepsilon_{mf} D_{AB} U_B}{D_B^3} \right)^{0.5} = 0.89$$

$$K_{bc} = 4.5 \left(\frac{1.48}{3.4} \right) + 5.85 \left(\frac{D_{AB}^{0.5} g^{0.25}}{D_B^{1.25}} \right) = 7.5$$

$$\gamma_c = (1 - \varepsilon_{mf}) \left[\frac{3(u_{mf} / \varepsilon_{mf})}{u_b - (u_{mf} / \varepsilon_{mf})} + \alpha \right] = 0.24$$

$$\delta = \frac{u - u_{mf}}{u_b - u_{mf}(1 + \alpha)} = 0.28$$

$$\gamma_e = (1 - \varepsilon_{mf}) \frac{1 - \delta}{\delta} - \gamma_c - \gamma_b = 0.632$$

$$K_R = \gamma_b + \cfrac{1}{\cfrac{k_{cat}}{K_{bc}} + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{1}{\gamma_e} + \cfrac{k_{cat}}{K_{ce}}}}} = 0.48$$

$$X = 1 - \exp\left(- \frac{K_R k_{cat} h}{U_b} \right) = 0.093$$

Much smaller than that obtained in the example.

CDP12-M

$$u_{ms} = \frac{(\psi d_p)^2 \eta \varepsilon_{mf}^2}{150\mu(1-\varepsilon_{mf})}$$

$$\frac{u_{mf2}}{u_{mf1}} = \frac{\mu_1}{\mu_2} = \left(\frac{T_1}{T_2}\right)^{1/2}$$

Since $\mu_{gas} \; \alpha \; T^{1/2}$

$$\frac{u_{mf2}}{u_{mf1}} = \left(\frac{273}{546}\right)^{1/2} = \left(\frac{1}{2}\right)^{1/2} = \frac{1}{1.4}$$

The minimum fluidization velocity will decrease by a factor of 1.4 (b)(b).

CDP12-N

Start with the equation for the rate law:

$$-r_A = \Omega k C_{Ae} \qquad \text{at top}$$

Then find the concentrations

$$C_{A0} = y_{A0}\frac{P_0}{RT_0} = .1\frac{\frac{840}{760}}{82.06 * 523} = 2.575 * 10^{-6}\,\frac{gmol}{cc}$$

$$C_{Ae} = 0.939 * C_{AC} = 0.939(0.961 * C_{Ab})$$

At top

$$C_{Ab} = 0.8 * C_{A0}$$

$$C_{Ae} = (0.939)(0.961)(0.8)2.575 * 10^{-6}$$

$$C_{Ae} = 1.859 * 10^{-6}\,\frac{gmol}{cc}$$

$$\Omega = 2.28$$

Finding the rate:

$$-r_A = 2.28\frac{\text{cc of cat}}{\text{cc of bubble}} * 0.0858\frac{\text{cc of gas}}{\text{cc of cat sec}} * 1.859 * 10^{-6}\,\frac{gmol}{cc}$$

$$-r_A = 3.64 * 10^{-7}\;\frac{\text{gmol}}{\text{cc of bubbles * sec}}$$

CDP12-Q

a) Assume a ψ of 0.6 and then find ε_{mf}.

$$\varepsilon_{mf} = \left(\frac{0.071}{\psi}\right)^{1/3} = 0.49$$

Next find the equation for the diameter of the particle and another for the porosity.

$$d_p = \sqrt{\frac{150u_{mf}\mu(1-\varepsilon_{mf})}{0.36\eta\varepsilon_{mf}^3}}$$

$$\varepsilon_{mf} = \frac{0.586 * \mu^{0.058} * d_p^{0.087}}{0.6^{0.7}\rho_g^{0.008}\eta^{0.029}\rho_c^{0.021}}$$

Assume 290K and 760 mmHg: $\mu = 1.89*10^{-4}$ cp; $\rho_c = 0.001204$ g/cm^3.

Guess a value for the density of the catalyst and plug into the equations for d_p and ε_{mf} until $\varepsilon_{mf} = 0.5$

$d_p = 0.27$ cm

b) Find the diameter of the column:

$$A_c = 314.16 = \pi r^2$$
$$r = 10cm$$
$$D = 20cm$$

Find the maximum and minimum diameters of the bubbles:

$$d_{bm} = 0.652(314.16(10-2))^{0.4} = 14.9$$
$$d_{b0} = 0.00376(8)^2 = 0.24$$

Find the height of the column:

$$\frac{d_{bm} - d_b}{d_{bm} - d_{b0}} = e^{-0.3h/D}$$
$$h = 73cm$$

CDP12-O cont'd

c) Find u_b

$$0.106 = \frac{10-2}{u_b - 2.8}$$

$$u_b = 78.3 cm/s$$

Then find the conversion achieved at the height of the tower.

$$73 = \frac{78.3}{k_{cat}K_R}\ln\frac{1}{1-X}$$

$$X = 0.26$$

CDP12-P

$$h = \frac{U_b}{k_{cat}K_e}\ln\frac{1}{1-X}$$

$$\frac{h_2}{h_1} = \frac{U_{b2}}{U_{b1}}\frac{K_{R1}}{K_{R2}}\frac{\ln {}^{1}\!/\!_{(1-X_2)}}{\ln {}^{1}\!/\!_{(1-X_1)}}$$

$$h_2 = h_1$$

$$\varepsilon_{mf2} \equiv \varepsilon_{mf1}$$

$$u_{01} = 2u_{mf1}$$

$$u_{02} = 2u_{01} = 4u_{mf1}$$

a) For reaction limitation

$$K_R = (1-\varepsilon_{mf})\frac{u_b}{u_0 - u_{mf}}$$

$$1 = \frac{(u_0 - u_{mf})_2}{(u_0 - u_{mf})_1}\frac{\ln {}^{1}\!/\!_{(1-X)}}{1.0}$$

$$u_{mf2} = u_{mf1}\left(\frac{1}{2}\right)^2$$

$$u_{mf2} = \frac{1}{4}u_{mf1}$$

$$\ln\frac{1}{1-X} = \frac{(u_0 - u_{mf})_2}{(u_0 - u_{mf})_1} = \frac{2u_{mf1} - u_{mf1}}{4u_{mf1} - {}^{1}\!/\!_{4}\,u_{mf1}} = \frac{1}{3.75}$$

$$X_2 = 0.23$$

CDP12-P cont'd

b) For mass transfer

$$K_R = \frac{K_{bc}}{k_{cat}}$$

$$K_{bc} \cong 4.5\frac{u_{mf}}{d_b}$$

$$\frac{h_2}{h_1} = \left(\frac{d_{b2}}{d_{b1}}\right)^{3/2} \frac{u_{mf1}}{u_{mf2}} \frac{\ln {}^{1}\!/_{(1-X)}}{\ln {}^{1}\!/_{(1-X)}}$$

$$d_b \propto \left(u_0 - u_{mf}\right)^{0.4}$$

$$\ln\frac{1}{1-X_2} = \left(\frac{u_{mf2}}{u_{mf1}}\right)\left(\frac{\left[u_0 - u_{mf}\right]_1}{\left[u_0 - u_{mf}\right]_2}\right)^{0.6}$$

$$= \frac{1}{4}\frac{u_{mf1}}{u_{mf1}}\left[\frac{u_{mf1}}{3.75u_{mf1}}\right]^{0.6} = \frac{.45}{4}$$

$$X_2 = 0.11$$

CDP12-Q

$$h = \frac{U_b}{k_{cat}K_R}\ln\frac{1}{1-X}$$

$$\frac{h_2}{h_1} = \frac{U_{b2}}{U_{b1}}\frac{k_{cat1}}{k_{cat2}}\frac{K_{R1}}{K_{R2}}$$

a) For mass transfer:

$$\frac{\varepsilon_{mf2}}{\varepsilon_{mf1}} = \left(\frac{\mu_2}{\mu_1}\right)^{0.058}\left(\frac{\rho_{g1}}{\rho_{g2}}\right)^{0.029}\left(\frac{\eta_1}{\eta_2}\right)^{0.029}\left(\frac{\rho_{g2}}{\rho_{g1}}\right)^{0.021}$$

Assume $\eta_1 = \eta_2$

$$\frac{\varepsilon_{mf2}}{\varepsilon_{mf1}} = \left[\left(\frac{T_2}{T_1}\right)^{1/2}\right]^{0.058}\left(\frac{T_2}{T_1}\right)^{0.029}\left(\frac{T_1}{T_2}\right)^{0.021} = 0.988$$

$$\frac{u_{mf2}}{u_{mf1}} = \frac{\mu_1}{\mu_2}\left(\frac{\varepsilon_{mf2}}{\varepsilon_{mf1}}\right)^3\frac{1-\varepsilon_{mf1}}{1-\varepsilon_{mf2}} = 1.13$$

CDP12-Q cont'd

Now the mass transfer coefficient:

$$K_R = \frac{K_{bc}}{k_{cat}}$$

$$K_{bc} \cong 4.5\frac{u_{mf}}{d_b}$$

$$d_b \propto \left(u_0 - u_{mf}\right)^{0.4}$$

$$\frac{h_2}{h_1} = \left(\frac{\left[u_0 - u_{mf}\right]_1}{\left[u_0 - u_{mf}\right]_2}\right)^{0.6} \frac{u_{mf2}}{u_{mf1}} = \left(\frac{u_{mf1}}{1.13u_{mf1}}\right)^{0.6} \frac{1.13u_{mf1}}{u_{mf1}}$$

$$\frac{h_2}{h_1} = 1.05$$

b) Reaction rate limited:

$$\frac{h_2}{h_1} = \frac{k_{cat1}}{k_{cat2}}$$

$$k_{cat2} = k_{cat1} * \exp\left[\frac{19870}{1.987}\left(\frac{1}{700} - \frac{1}{500}\right)\right] = 0.0033k_{cat1}$$

$$\frac{h_2}{h_1} = \frac{1}{0.0033} = 303.2$$

CDP12-R

We first need the viscosity and density of the gas which is said to have air-like properties so looking up the two values at this temperature and atmospheric pressure we find that:

$\mu = 215.39*10^{-6}$ g/cm*s

$\rho = 9.5*10^{-4}$ g/cm^3

b) We must find η

$$\eta = g\left(\rho_c - \rho_g\right) = 980\left(2 - 9.5*10^{-4}\right) = 1959.069$$

We can then find ε_{mf}

$$\varepsilon_{mf} = 0.586*(0.6)^{-0.72}\left(\frac{\left(215.39*10^{-6}\right)^2}{\left(9.5*10^{-6}\right)1959.069(.01)^3}\right)^{0.029}\left(\frac{9.5*10^{-4}}{2}\right)^{0.021}$$

$$\varepsilon_{mf} = 0.648$$

CDP12-R cont'd

a) We can then find u_{mf}

$$u_{mf} = \frac{(\psi d_p)^2}{150\mu} \eta \frac{\varepsilon_{mf}^3}{1-\varepsilon_{mf}}$$

$$= \frac{(0.6 * 0.01)^2}{150 * 215.39 * 10^{-6}} * 1959.069 * \frac{0.648^3}{1-0.648}$$

$$\doteq 1.69 \text{ cm/s}$$

c) The diameter of the bed:

$$5 * 1.69 = \frac{2277 * 4}{\pi * D_t^2}$$

$$D_t = 18.6 cm$$

d) By trial and error we have to determine what the entrainment velocity is:

$$u_t = \frac{\eta d_p^2}{18\mu} = \frac{1959.069 * 0.01^2}{18 * 215.39 * 10^{-6}} = 50 cm/s$$

$$\mathrm{Re} = \frac{\rho u_o D}{\mu} = 2.2$$

This is not correct because the Reynold's number is > 0.4.

$$u_t = \left(\frac{1.78 * 10^{-2} \eta^2}{\rho_g \mu}\right)^{1/3} d_p = 69.4$$

$$\mathrm{Re} = 3.06$$

This is correct because 0.4 < Re < 500.

e) Minimum bubble diameter:

$$d_{b0} = 0.00376 (u_0 - u_{mf})^2 = 3.24 cm$$

CDP12-R cont'd

f) Maximum bubble diameter:

$$d_{bm} = 0.652\left[A_c\left(u_0 - u_{mf}\right)\right]^{0.4} = 13.1cm$$

g) Bubble velocity

Guess a bubble diameter of 12.7 cm.

$$u_b = u_0 - u_{mf} + (0.71)\left(gd_p\right)^{1/2} = 85.9cm/s$$

h) No solution will be given

i) Fraction of the bed occupied by the bubble:

$$\delta = \frac{u_0 - u_{mf}}{u_b - u_{mf}(1+\alpha)} = 0.080$$

j) Fraction of the bed occupied by the wake:

$$\alpha\delta = 0.032$$

k) Velocity of the solids:

$$u_s = \frac{\alpha\delta u_b}{1-\delta-\alpha\delta} = \frac{(0.032)(85.9)}{1-0.08-0.032} = 3.09cm/s$$

l) Velocity of the rise in the emulsion phase:

$$u_e = \frac{u_{mf}}{\varepsilon_{mf}} - u_s = \frac{1.67}{0.648} - 3.13 = -0.55cm/s$$

m) I can't come up with the final equaiton

n) K_{BC}

$$K_{BC} = 4.5\left(\frac{u_{mf}}{d_b}\right) + 5.85\left(\frac{D_{AB}^{0.5}g^{0.25}}{d_b^{1.25}}\right) = 1.45$$

CDP12-R cont'd

o) K_{ce}

$$K_{ce} = 6.77\left(\frac{\varepsilon_{mf} D_{AB} u_b}{d_b^3}\right)^{0.5} = 0.71$$

p) γ_c

$$\gamma_c = \left(1-\varepsilon_{mf}\right)\left[\frac{3\left(u_{mf}/\varepsilon_{mf}\right)}{u_b-\left(u_{mf}/\varepsilon_{mf}\right)}+\alpha\right] = 0.15$$

γ_e

$$\gamma_e = \left(1-\varepsilon_{mf}\right)\frac{1-\delta}{\delta} - \gamma_c - \gamma_b = 3.89$$

q) K_R

$$K_R = \gamma_b + \cfrac{1}{\cfrac{k_{cat}}{K_{bc}} + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{1}{\gamma_e} + \cfrac{k_{cat}}{K_{ce}}}}} = 0.15$$

r) Find the necessary concentration to give 90% conversion

$$0.9 = \frac{0.5 - C_A}{0.5}$$
$$C_A = 0.05$$

Solving the differential equation:

$$\frac{dC_{Ab}}{C_{Ab}} = -k_{cat} K_R dt$$
$$\ln C_{Ab}\Big|_{0.5}^{0.05} = -(5*0.15)*t\Big|_0^t$$
$$t = 3.07s$$

CDP12-R cont'd

Solve for the hieght:

$$h = tu_b = 3.07 * 85.9 = 263.7cm$$

s) The catalyst weight is then:

$$W = \rho_c A_c h(1-\varepsilon_{mf})(1-\delta) = 31541g$$

t) Diameter of the bubbles halfway up the reactor:

$$\frac{d_{bm}-d_b}{d_{bm}-d_{b0}} = e^{-0.3*h/D}$$

$$d_{b0.5} = 12.9cm$$

u) No solution will be given

CDP12-S No solution will be given

CDP12-T No solution will be given

CDP12-U

(a)

Mole Balance: $\frac{dF_A}{dW} = r_A' \quad \Rightarrow \quad F_{Ao}\frac{dX}{dW} = -r_A'$

Rate Law: $-r_A' = k_{vg}C_A$

$$k_{vg} = \frac{1/H}{R_T}$$

Stoichiometry: $C_A = C_{Ao}\left(\frac{1-X}{1+\varepsilon X}\right)\frac{P}{P_o}$

$$\varepsilon = y_{Ao}\delta = (0.80)(0-0-1) = -0.8$$

$$C_A = C_{Ao}\left(\frac{1-X}{1-0.8X}\right)\frac{P}{P_o}$$

CDP12-U (cont'd)

Pressure Drop: $$\frac{d(P/P_o)}{dW}=\frac{-\alpha}{P_oA_c(1-\varepsilon_b)\rho_p}$$

Evaluate Parameters:

Solubility -

$$H'=0.0068\ \text{mol/dm}^3$$

$$H=\frac{1}{RTH'}=\frac{1}{\left(0.0082\ \frac{\text{dm}^3\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(373\ \text{K})\left(0.0068\ \frac{\text{mol}}{\text{dm}^3\cdot\text{atm}}\right)}=48.08$$

Internal Diffusion and Reaction -

$$R_r=\frac{1}{\eta k}$$

$$\phi=R\sqrt{\frac{k\rho_c}{D_e}}$$

$$D_e=D_L\frac{\sigma\varepsilon_p}{\tau}=\left(8\times10^{-9}\ \text{m}^2/\text{s}\right)\frac{(0.8)(0.5)}{(3.8)}=8.42\times10^{-10}\ \text{m}^2/\text{s}$$

$$\phi=0.0015875\ \text{m}\sqrt{\frac{\left(2\times10^{-5}\ \text{m}^3/\text{kg}\cdot\text{s}\right)\left(1500\ \text{kg/m}^3\right)}{\left(8.42\times10^{-10}\ \text{m}^2/\text{s}\right)}}=9.476\ \text{m}^2/\text{s}$$

$$\eta=\frac{3}{\phi}=\frac{3}{9.476}=0.317$$

$$R_R=\frac{1}{(0.317)\left(2\times10^{-5}\ \text{m}^3/\text{kg}\cdot\text{s}\right)}=1.2\times10^5\ \frac{\text{kg}\cdot\text{s}}{\text{m}^3}$$

Gas Absorption -

$$R_g=\frac{(1-\varepsilon_b)\rho_c}{Hk_ga_i}$$

$$k_ga_i=2+0.91E_g^{2/3}\quad\Rightarrow\quad E_g=\frac{\Delta P}{\Delta L}U_g$$

$$U_g=\left(\frac{0.25\ \text{kg}}{\text{m}^2\cdot\text{s}}\right)\left(\frac{8.206\times10^{-5}\ \text{m}^3\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)\left(\frac{373\ \text{K}}{50\ \text{atm}}\right)\left(\frac{1\ \text{mol}}{0.0072\ \text{kg}}\right)=0.0212\ \text{m/s}$$

$$E_g=(30\ \text{kPa/m})(0.0212\ \text{m/s})=0.638\ \text{kPa/s}=13.32\ \frac{\text{ft}\cdot\text{lb}_f}{\text{ft}^3\cdot\text{s}}$$

$$k_ga_i=2+0.91(13.32)^{2/3}=7.11\ \text{s}^{-1}$$

$$R_g=\frac{(1-0.35)\left(1500\ \text{kg/m}^3\right)}{(48.08)\left(7.11\ \text{s}^{-1}\right)}=2.85\ \frac{\text{kg}\cdot\text{s}}{\text{m}^3}$$

Transport from gas - liquid interface to bulk liquids -

$$R_l = \frac{(1-\varepsilon_b)\rho_p}{k_l a_i}$$

$$Re_L = \frac{Gd_p}{\mu_L} = \frac{(8\ \text{kg/m}^2\cdot\text{s})(0.003175\ \text{m})}{0.003\ \text{kg/m}\cdot\text{s}} = 8.467$$

$$Ga = \frac{d_p^3\rho_L^2 g}{\mu_L^2} = \frac{(0.003175\ \text{m})^3(900\ \text{kg/m}^3)^2(9.8\ \text{m/s}^2)}{(0.003\ \text{kg/m}\cdot\text{s})^2} = 28{,}096$$

$$Sc = \frac{\mu_L}{\rho_L D_L} = \frac{(0.003\ \text{kg/m}\cdot\text{s})}{(900\ \text{kg/m}^3)(8\times10^{-9}\ \text{m}^2\text{/s})} = 416.67$$

From the correlation for organic liquids,

$$k_l a_i = D_L\left(16.8\frac{Re_L^{1/4}Sc^{1/2}}{Ga^{0.22}}\right) = 8\times10^{-5}\ \text{cm}^2\text{/s}\left[\frac{(16.8)(8.467)^{1/4}(416.67)^{1/2}}{(28{,}096)^{0.22}}\right] = 4.915\times10^{-3}\ \text{s}^{-1}$$

$$R_l = \frac{(1-0.35)(1500\ \text{kg/m}^3)}{4.915\times10^{-3}\text{s}^{-1}} = 2.32\times10^5\ \frac{\text{kg}\cdot\text{s}}{\text{m}^3}$$

Resistance from bulk liquid to catalyst -

$$R_c = \frac{1}{k_c a_p}$$

$$a_p = \frac{6}{\rho_c d_p} = \frac{6}{(1500\ \text{kg/m}^3)(0.003175\ \text{m})} = 1.26\ \text{m}^2\text{/kg}$$

$$Sh = 0.266Re^{1.15}Sc^{1/3} = (0.266)(8.467)^{1.15}(416.67)^{1/3} = 19.69$$

$$k_c = \frac{ShD_L}{d_p} = \frac{(19.69)(8\times10^{-9}\ \text{m}^2\text{/s})}{(0.003175\ \text{m})} = 4.96\times10^{-5}\ \text{m/s}$$

$$R_c = \frac{1}{(4.96\times10^{-5}\ \text{m/s})(1.26\ \text{m}^2\text{/kg})} = 0.16\times10^5\ \frac{\text{kg}\cdot\text{s}}{\text{m}^3}$$

Total Resistance:

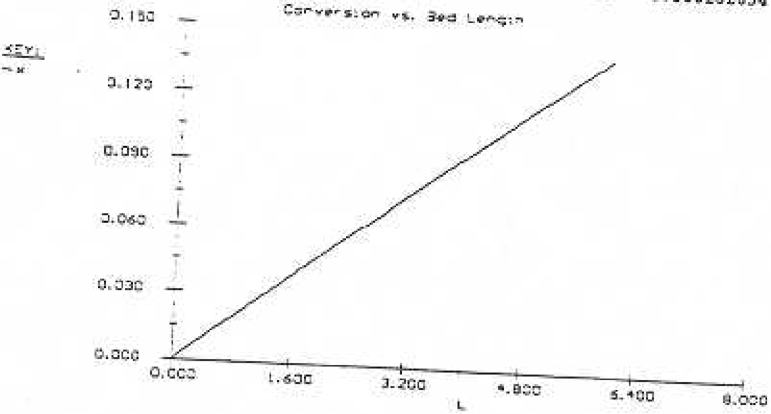
$$R_T = R_c + R_l + R_g + R_R = 0.16\times10^5 + 2.32\times10^5 + 2.85 + 1.2\times10^5 = 3.68\times10^5\ \frac{\text{kg}\cdot\text{s}}{\text{m}^3}$$

Use these equations in POLYMATH to generate the following program and desired graph:

CDP12-U (cont'd)

```
CDP12-U  Trickle Bed Reactor
Equations:                                                    Initial value
d(x)/d(w)=-ra/fao                                             0
d(P)/d(w)=-a/Po/Ac/(1-eb)/rho                                 50
H=48.08
Rt=3.68E5
cao=70
a=0.296
Po=50
Ac=0.785
eb=0.35
rho=1500
fao=8*Ac
ca=cao*((1-x)/(1-0.5*x))*P
kvg=1/H/Rt
L=w/(1-eb)/rho/Ac
ra=-kvg*ca
w0 = 0,    wf = 4600
```

```
CDP12-U  Trickle Bed Reactor
Variable     Initial value   Maximum value   Minimum value   Final value
w            0               4600            0               4600
x            0               0.139475        0               0.139475
P            50              50              49.9644         49.9644
H            48.08           48.08           48.08           48.08
Rt           368000          368000          368000          368000
cao          70              70              70              70
a            0.296           0.296           0.296           0.296
Po           50              50              50              50
Ac           0.785           0.785           0.785           0.785
eb           0.35            0.35            0.35            0.35
rho          1500            1500            1500            1500
fao          6.28            6.28            6.28            6.28
ca           3500            3500            3235.32         3235.32
kvg          5.65181e-08     5.65181e-08     5.65181e-08     5.65181e-08
L            0               6.01013         0               6.01013
ra           -0.000197813    -0.000182854    -0.000197813    -0.000182854
```



CDP12-U (cont'd)

(b)

Percentages :

$$\text{Gas Absorption} = \frac{2.85}{3.68\times10^{5}} = 7.74\times10^{-6} = 7.74\times10^{-6} = 7.74\times10^{-4}\%$$

$$\text{Bulk liquid to catalyst} = \frac{0.16}{3.68} = 0.0435 = 4.35\%$$

$$\text{Internal diffusion and reaction} = \frac{1.2}{3.68} = 0.3261 = 32.61\%$$

$$\text{Gas interface to bulk liquid} = \frac{2.32}{3.68} = 0.6304 = 63.04\%$$

(c) Changing the gas flow rate effects only the resistance due to gas absorption. Since the percent resistance of this step is so small, the total resistance is essentially the same and the conversion will be virtually unaffected.

(d) Decreasing the flow of liquid, increasing the initial pressure, and increasing the initial concentration of aromatics in the feed all cause an increase in conversion.

Problem P13-1

No solution will be given.

P13-2_A

Part (a) No solution will be given.

Part (b) See p 905

Part (c)

The conversions of the asymmetric distributions in both models are greater than the corresponding conversions in the bimodal distributions

The average primary reactant exit concentrations $C_A$bar and $C_B$bar are greater in both models for the asymmetric distribution results over the bimodal whereas the average product exit concentrations $C_C$bar, $C_D$bar and $C_E$bar are lower.

The selectivities of both models are greater in the asymmetric distribution results over the bimodal ones with the exception of S_{CD} in the maximum mixedness model.

Comparison of the asymmetric distribution results with the bimodal distribution results for both the segregation and maximum mixedness models yield similar outcomes except the values are slightly different.

Hence the generalisation may be made that if one model is used (segregation or maximum mixedness) and results are obtained for the different RTD's (asymmetric and bimodal in this Example) then these results will be similar for the other model. Comparison between results from different RTD's is model independent.

Part (d)

Liquid phase, third order, maximum mixedness model

Rate law :

$$-r_A = k.C_A^3$$

$$C_A = C_{AO}.(1-x)$$

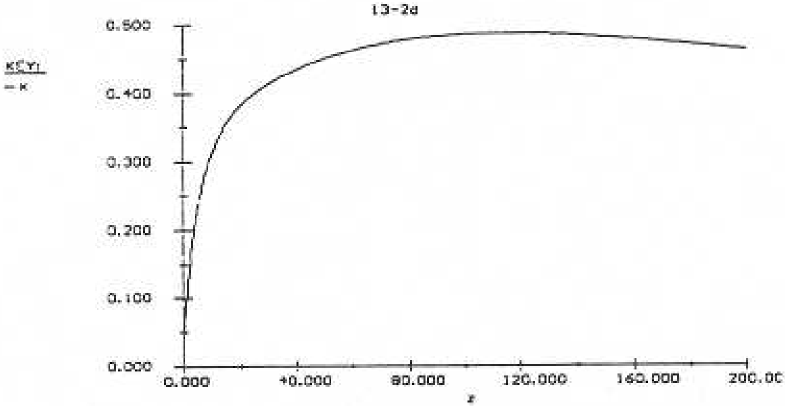
$$r_A = -k.C_{AO}^3.(1-x)^3$$

$$\frac{r_A}{C_{AO}} = -k.C_{AO}^2.(1-x)^3$$ where $k.C_{AO}^2 = 0.08$ /min

P13-2 cont'd

```
13-2d                                                                    Initial value
Equations:                                                               0
d(x)/d(z)=-(-.08*(1-x)^3)-(E/(1-F)*x)
lam=200-z
E1=4.44658e-10*lam^4-1.1802e-7*lam^3+1.35358e-5*lam^2-.00
   0865652*lam+.028004
E2=-2.64e-9*lam^3+1.3618e-6*lam^2-.00024069*lam+.015011
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
F2=-(-9.30769e-8*lam^3+5.02846e-5*lam^2-.00941*lam+.61823
   1-1)
E=if(lam<=70)then(E1)else(E2)
F=if(lam<=70)then(F1)else(F2)
EF=E/(1-F)
z0 = 0,   zf = 200
```

```
13-2d
Variable        Initial value   Maximum value   Minimum value   Final value
z               0               200             0               200
x               0               0.48673         0               0.461431
lam             200             200             0               0
E1              0.163598        0.163598        0.00287273      0.028004
E2              0.000225        0.015011        0.000225        0.015011
F1              5.63334         5.63334         0               0
F2              0.997           0.997           0.381769        0.381769
E               0.000225        0.028004        0.000225        0.028004
F               0.997           0.997           0               0
EF              0.075005        0.075005        0.0220679       0.028004
```



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.

P13-2 cont'd

Part (e)

Liquid phase, half order, maximum mixedness model

Rate law :

$$-r_A = k.C_A^{1/2}$$

$$C_A = C_{A0}.(1-x)$$

$$r_A = -k.C_{A0}^{1/2}.(1-x)^{1/2}$$

$$\frac{r_A}{C_{A0}} = -k.C_{A0}^{-1/2}.(1-x)^{1/2} \qquad \text{where } k.C_{AO}^{-1/2} = 0.08\ /\text{min}$$

```
13-2d
Variable     Initial value  Maximum value  Minimum value  Final value
z            0              200            0              200
x            0              0.641149       0              0.599649
lam          200            200            0              0
E1           0.163598       0.163598       0.00287273     0.028004
E2           0.000225       0.015011       0.000225       0.015011
F1           5.63334        5.63334        0              0
F2           0.997          0.997          0.381769       0.381769
E            0.000225       0.028004       0.000225       0.028004
F            0.997          0.997          0              0
EF           0.075005       0.075005       0.022068       0.028004
```

At z = 200 , i.e. $\lambda = 0$ (exit) , conversion x = 60.0 %

The decrease in reaction order from 2nd to 1/2 has the effect of increasing the exit conversion by 4 %. 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.

Part (f) No solution will be given.

Part (g) No solution will be given.

Part (h)

First order, liquid phase, adiabatic, irreversible, completely segregated.

Design equation for a batch globule, constant volume :

$$\frac{dX}{dt} = k.(1-X)$$

P13-2 cont'd

where $k(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right] = 0.1\exp\left[\frac{30000}{8.314}\left(\frac{1}{320} - \frac{1}{T}\right)\right]$

and $T(K) = To + \left(\frac{-\Delta Hrx}{Cp_A}\right).X = 320 + 150X$

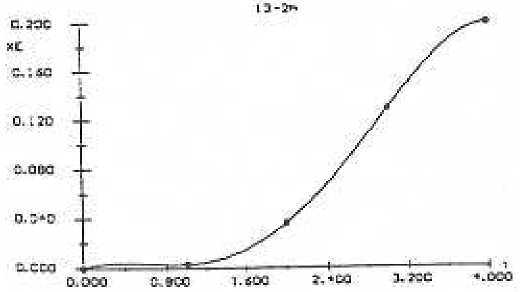
Use POLYMATH for X(t,T) for t = 1 to 14 mins.

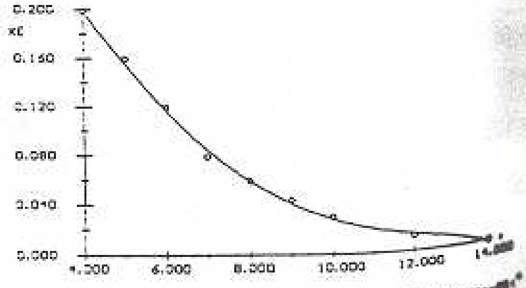
t (min)	E(t) (/min)	X(t,T)	E(t).X(t,T) (/min)
0	0.000	0.000	0.000
1	0.020	0.132	0.003
2	0.100	0.359	0.036
3	0.160	0.799	0.128
4	0.200	0.998	0.199
5	0.160	1.000	0.160
6	0.120	1.000	0.120
7	0.080	1.000	0.080
8	0.060	1.000	0.060
9	0.044	1.000	0.044
10	0.030	1.000	0.030
12	0.012	1.000	0.012
14	0.000	1.000	0.000

E(t) for t = 1 to 14 min obtained from Example 13-1, gives X(t,T).E(t) (min^{-1}) and evaluating the integral :

$$\overline{X} = \int_0^\infty X(t,T).E(t)dt$$ gives the mean conversion

The equation of the curve X(t,T).E(t) may be found by individual polynomial fitting for the rising and falling limbs of the curve and hence the integral can be evaluated reasonably accurately.





P(t) = 0.389124 -0.0401039 t -0.00415685 t^2 +0.000696904 t^3 -2.40[illegible]

P(t) = -3.14108e-15 +0.0249167 t -0.0494583 t^2 +0.0320833 t^3 -0.00541667 t^4

P13-2 cont'd

```
13-2h
Equations:                                                          Initial value
d(x)/d(t)=k*(1-x)                                                   0
d(xbar)/d(t)=if(t<=4)then(E1)else(E2)                               0
E1=0.0241679*t-.0494583*t^2+.0320833*t^3-.00454167*t^4
E2=.389124-.0401033*t-.00415685*t^2+.000696906*t^3-2.4096
   4e-5*t^4
T=320+(150*x)
k=.1*exp((30000/8.314)*((1/320)-(1/T)))
t0 = 0,   tf = 14
```

```
13-2h
Variable        Initial value  Maximum value  Minimum value  Final value
t               0              14             0              14
x               0              1              0              1
xbar            0              0.891414       0              0.891414
E1              0              0.196086       -95.7917       -95.7917
E2              0.389124       0.389124       -0.000442038   -0.000442038
T               320            470            320            470
k               0.1            3.65534        0.1            3.65534
```

The mean conversion Xbar, the integral, is estimated to be 89 %.

The reaction is adiabatic and exothermic as the temperature increases to a maximum of 470 K once the batch conversions within the globules has reached 100% which occurs after only ~ 3 minutes. Hence, the adiabatic increase in temperature considerably increases the rate at which conversion increases with time and hence also the final value. It is noted that the isothermal batch and mean conversion only reach 75% and 38% respectively after 14 minutes, much less than the respective conversions in the adiabatic exothermic case.

Part (i) No solution will be given.

Part (j) No solution will be given for Example 13-8

See Part (h) except :

$$T(K) = To + \left(\frac{-\Delta Hrx}{Cp_A}\right) X = 320 - 100X$$

P13-2 cont'd

```
13-2h
Variable        Initial value  Maximum value  Minimum value   Final value
t               0              14             0               14
x               0              0.41027        0               0.41027
xbar            0              0.245657       -0.000736912    0.245657
E1              0              2.12301        -0.00140392     2.12301
E2              0.0257813      0.0482985      -0.000115754    -0.000115754
T               320            320            278.973         278.973
k               0.1            0.1            0.0190458       0.0190458
```

The mean conversion Xbar, the integral, is estimated to be 25 %.

The reaction is adiabatic and endothermic as the temperature decreases to a minimum of 279 K after 14 minutes by which time the batch conversions within the globules have reached 41 %. Hence the decrease in temperature considerably decreases the rate at which conversion increases with time and hence also the final value. It is noted that the isothermal batch and mean conversion reach 75 % and 38 % respectively after 14 minutes, much more than the respective conversions in the adiabatic endothermic case.

Part (k)

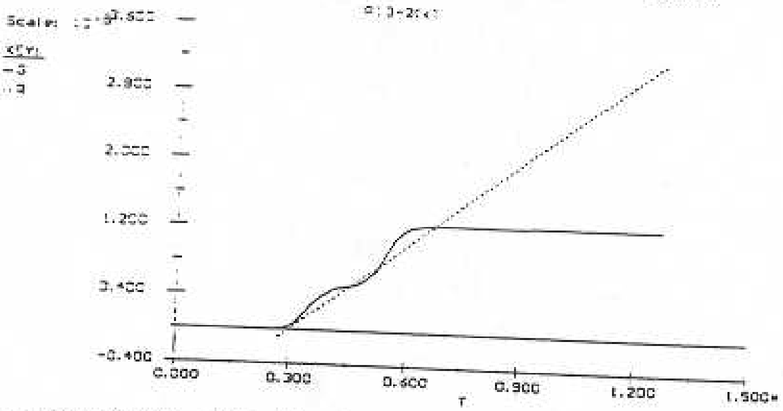
See Example 8-12 for solution and Table E8-12.1 for POLYMATH equations.

Let t_m = 1.26 s

```
P13-2(k)                                                    Initial value
Equations:                                                  273
d(T)/d(t)=2
Cp=200
cao=.3
To=283
tau=0.021
Dh1=-55000
Dh2=-71500
vo=1000
E2=27000
E1=9900
UA=40000
Ta=330
k2=4.58*exp((E2/1.987)*((1/500)-(1/T)))
k1=3.3*exp((E1/1.987)*((1/300)-(1/T)))
ca=cao/(1+(tau*k1))
kappa=UA/(vo*cao)/Cp
G=-tau*k1/(1+k1*tau)*Dh1-k1*tau*k2*tau*Dh2/((1+tau*k1)*(1
    +tau*k2))
Tc=(To+kappa*Ta)/(1+kappa)
Cb=tau*k1*ca/(1+k2*tau)
R=Cp*(1+kappa)*(T-Tc)
Cc=cao-ca-Cb
F=G-R
t0 = 0.   tf = 500
```

P13-2 cont'd

```
P13-2(k)
Variable     Initial value   Maximum value   Minimum value   Final value
t            0               500             0               500
T            273             1273            273             1273
Cp           200             200             200             200
cao          0.3             0.3             0.3             0.3
To           283             283             283             283
tau          0.021           0.021           0.021           0.021
Dh1          -55000          -55000          -55000          -55000
Dh2          -71500          -71500          -71500          -71500
vo           1000            1000            1000            1000
E2           27000           27000           27000           27000
E1           9900            9900            9900            9900
UA           40000           40000           40000           40000
Ta           330             330             330             330
k2           7.02951e-10     6.72612e+07     7.02951e-10     6.72612e+07
k1           0.638507        1.07516e+06     0.638507        1.07516e+06
ca           0.296031        0.296031        1.32865e-05     1.32865e-05
kappa        0.666667        0.666667        0.666667        0.666667
G            727.718         126494          727.718         126494
Tc           301.8           301.8           301.8           301.8
Cb           0.00396937      0.284642        2.12382e-07     2.12382e-07
R            -9600           323733          -9600           323733
Cc           5.86111e-14     0.299987        5.86111e-14     0.299987
F            10327.7         19689.2         -197239         -197239
```



With a t_m = 1.26 s (0.021 min) rather than 0.01 min it is clear that only three steady states exist rather than five.

SS	T	C_A	C_B	C_C
1	462	0.012	0.285	0.003
2	530	0.003	0.207	0.09
3	677	0.0004	0.0025	0.2974

Problem P13-3$_C$

Maximum mixedness model :

$$\frac{dC_A}{d\lambda} = k.C_A + \frac{E(\lambda)}{1-F(\lambda)}(C_A - C_{AO})$$

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 integrating factor :

$$\frac{d\left[\frac{C_A}{C_{AO}} e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda}\right]}{d\lambda} = -\frac{E(\lambda)}{1-F(\lambda)} e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda}$$

$$\frac{C_A}{C_{AO}} e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda} = -\int_\infty^\lambda \left[\frac{E(\lambda)}{1-F(\lambda)} e^{-\int\left[k+\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda}\right]d\lambda$$

$$\frac{C_A}{C_{AO}} e^{-\lambda.k} e^{-\int\left[\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda} = -\int_\infty^\lambda \left[\frac{E(\lambda)}{1-F(\lambda)} e^{-k.\lambda} e^{-\int\left[\frac{E(\lambda)}{1-F(\lambda)}\right]d\lambda}\right]d\lambda$$

But $E(\lambda)\,d(\lambda) = dF(\lambda)$

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 variable from λ to t in the RHS integral :

$$\frac{C_A}{C_{AO}} e^{-k\lambda}(1-F(\lambda)) = \int_\lambda^\infty \left[\frac{E(t)}{1-F(t)} e^{-kt}(1-F(t))\right]dt$$

$$C_A = \frac{C_{AO}.e^{\lambda.k}}{1-F(\lambda)} \int_\lambda^\infty E(t)e^{-k.t}dt \qquad (1)$$

Exit concentration is when $\lambda = 0$, $F(0) = 0$ hence eqn (1) becomes :

$$C_A = C_{AO}\int_0^\infty E(t)e^{-k.t}dt$$

which is the same expression as for the exit concentration for the segregation model.

Problem P13-4$_C$

Part (a)

CSTR

$$\upsilon.(C_{AO} - C_A) = k.C_A^n V$$

$$= k.C_{AO}^n (1 - X)^n V$$

$$= k.C_{AO}.C_{AO}^{n-1}(1 - X)^n V$$

$$X = k.C_{AO}^{n-1}(1-X)^n \frac{V}{\upsilon}$$

$$\frac{X}{(1-X)^n} = k.\tau.C_{AO}^{n-1} \qquad \text{for CSTR}$$

PFR

$$\upsilon.C_{AO}\frac{dX}{dV} = k.C_A^n$$

$$\frac{dX}{dV} = \frac{k.C_{AO}^n}{\upsilon.C_{AO}}(1-X)^n$$

$$\int_0^X \frac{dX}{(1-X)^n} = \frac{k.C_{AO}^{n-1}}{\upsilon}\int_0^V dV = k.\tau.C_{AO}^{n-1}$$

Now evaluating $\int_0^X \frac{dX}{(1-X)^n}$ put $y = 1 - X$, $dy = - dX$; limits $X = 0, y = 1$; $X = X , y = y$

$$-\int_1^y \frac{1}{y^n}dy = -\left[\frac{y^{1-n}}{1-n}\right]_1^y = \left[\frac{(1-X)^{1-n}}{1-n}\right]_X^0 = \frac{1}{1-n}\left[1-(1-X)^{1-n}\right]$$

$$\frac{1}{1-n}\left[1-(1-X)^{1-n}\right] = k.\tau.C_{AO}^{n-1} \qquad \text{for PFR}$$

Equating

$$\frac{X_{CSTR}}{(1-X_{CSTR})^n} = \frac{1}{1-n}\left[1-(1-X_{PFR})^{1-n}\right]$$

For n < 1 the conversion is greater for CSTR.

Part (b)

See CD-ROM for full length answer.

For an nth order reaction $-r_A = k_n C_A^n$

$$\left.\frac{\delta^2(-r_A)}{\delta C_A^2}\right|_{C_A=C_{AT}} = n(n-1)k_n C_{AT}^{n-2}$$

The maximum mixedness model will give greater conversion as compared to the segregation model if

$$n(n-1) < 0$$

$$\Rightarrow n \in (0,1)$$

Similarly, the segregation model will give greater conversion as compared to the maximum mixedness model if

$$n(n-1) > 0$$

$$\Rightarrow \text{either } n < 0 \text{ or } n > 1$$

Both models will give the same conversion if

$$n(n-1) = 0$$

$$\Rightarrow \text{either } n = 0 \text{ or } n = 1$$

Problem P13-5$_B$ (old manual solution)

The tracer experiment for the poor operation indicate that initially there is channelling in the bed, corresponding to the rapid peak in concentration. After the peak the concentration falls as the tracer flow is hindered by compacted packing in the other parts of the bed.

Part (a), (b)

The mean conversion for RTD analysis is $\bar{X} = \int_0^\infty (1-e^{-kt}).E(t).dt$

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)}$$

Using E(t) data from the flow conditions we get the following mean conversion after evaluating the above integral.

X_A values for different operations

Flow condition	$k_1 = 0.1\ hr^{-1}$	$k_2 = 2\ hr^{-1}$
Poor operation	0.1	0.364
Good operation	0.4	0.518

Part (c)

Results point to the importance of flow condition in achieving high conversion.

Problem P13-6$_B$

Irreversible liquid phase, half order, segregation model.

Mean conversion $\overline{X} = \int_0^{\infty} X(t).E(t)dt = 0.1$

Assume a normal distribution for E(t) :

$$E(t) = \frac{1}{\sigma\sqrt{2.\pi}}\exp\left[-\frac{(t-\tau)^2}{2.\sigma^2}\right] = \frac{1}{3\sqrt{2.\pi}}\exp\left[-\frac{(t-5)^2}{2x3^2}\right]$$

$$\frac{dX}{dt} = k\frac{C_{AO}^{1/2}}{C_{AO}}(1-X)^{1/2} \qquad \text{and } C_{AO} = 1 \text{ mol/dm}^3$$

By integrating for X at values of k_1 and inserting into the integral for mean conversion, along with the E(t) function will yield Xbar = 0.1 for some value of k_1. This is a trial and error method to estimate k_1 .

Using POLYMATH : $k_1 = 0.0205\ mol^{1/2}/dm^{1/6}.s$

P13-6 cont'd

```
Equations:                                                   Initial value
d(x)/d(t)=k*((1-x)^(1/2))                                    0
d(xbar)/d(t)=x*E                                             0
k=0.0205
sigma=3
tau=5
E=(1/(sigma*((23.14)^(1/2))))*exp(-((t-tau)^2)/(2*(sigma^
   2)))
t0 = 0,   tf = 120

Variable      Initial value  Maximum value  Minimum value  Final value
t             0              97.5607        0              97.5607
x             0              1              0              1
xbar          0              0.0521924      0              0.0521924
k             0.0205         0.0205         0.0205         0.0205
sigma         3              3              3              3
tau           5              5              5              5
E             0.0172787      0.0691952      1.34602e-208   1.34602e-208
```

Problem P13-7$_B$ (old manual solution)

Cumulative exit age distribution function : $F(t) = \int_0^t E(t).dt$

For a negative step
$$F(t) = \int_0^t -\frac{d}{dt}\left[\frac{C(t)}{Co}\right]dt = 1 - \frac{C(t)}{Co}$$

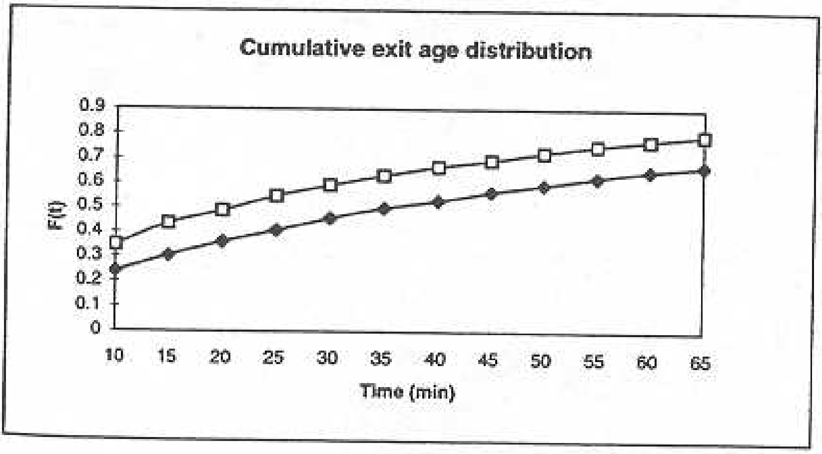
$$I(t) = \frac{\upsilon}{V}(1 - F(t)) = \frac{\upsilon}{V}\frac{C(t)}{Co}$$

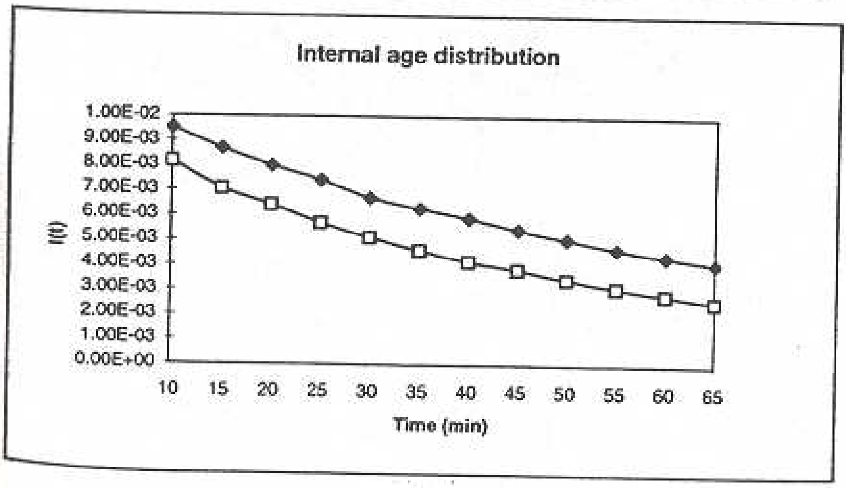
$$\upsilon = 1.15 \text{ gal/min} = 4.35 \text{ l/min}$$

$$V = \frac{\pi}{4}D^2L = \frac{\pi}{4}(30)^2(30)in^3 = 347.35 litres$$

P13-7 cont'd

Time (min)	Cumulative exit age distribution F(t)		Internal age I(t)	
	170 rpm	100 rpm	170 rpm	100 rpm
10	0.239	0.347	9.51E-03	8.16E-03
15	0.305	0.434	8.69E-03	7.07E-03
20	0.361	0.487	7.99E-03	6.41E-03
25	0.408	0.546	7.40E-03	5.67E-03
30	0.457	0.591	6.70E-03	5.11E-03
35	0.498	0.631	6.28E-03	4.60E-03
40	0.528	0.667	5.90E-03	4.16E-03
45	0.564	0.693	5.45E-03	3.84E-03
50	0.593	0.724	5.08E-03	3.45E-03
55	0.624	0.752	4.70E-03	3.10E-03
60	0.65	0.774	4.38E-03	2.83E-03
65	0.671	0.795	4.11E-03	2.56E-03





P13-7 cont'd

The tracer fraction leaving the tank which has been in the tank for time t is always greater in the 100 rpm tank than the 170 rpm tank. Consequently the tracer fraction inside the tank which has been inside the tank for time t is always greater for the 170 rpm tank. This suggests that the tank operated at 100 rpm has dead zones and the tracer bypasses.

Part (b) *second order, completely segregated model*

Batch reactor eqn for a second order reaction

$$\frac{dC_A}{dt} = r_A \qquad \frac{dX}{dt} = -\frac{r_A}{C_{A0}}$$

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

$$\int_0^X \frac{dX}{(1-X)^2} = \int_0^t k.C_{A0}.dt \qquad \frac{X}{1-X} = k.C_{A0}.t$$

$$X = \frac{k.C_{A0}.t}{1+k.C_{A0}.t}$$

where $k.C_{AO} = 0.05$ /min

mean conversion $\overline{X} = \int_0^\infty X(t,T).E(t)dt$

	170 rpm	100 rpm
mean conversion	0.63	0.58

Part (c) *second order, maximum mixedness model*

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)}.X$$

Rate law : $-r_A = k.C_A^2$

$$C_A = C_{A0}.(1-x)$$

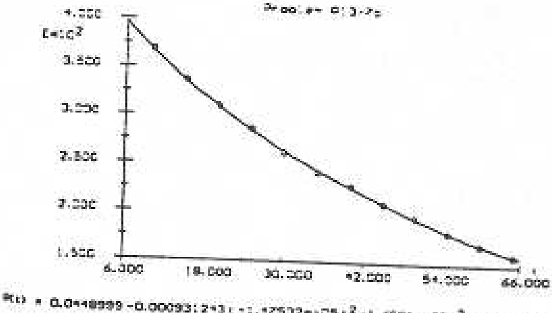
$$r_A = -k.C_{A0}^2.(1-x)^2$$

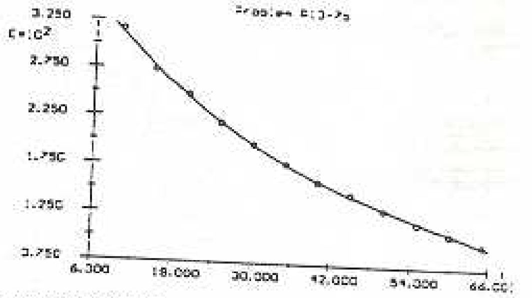
P13-7 cont'd

$$\frac{r_A}{C_{AO}} = -k.C_{AO}\ .(1-x)^2$$ where $k.C_{AO} = 0.05$ /min

$$E(\lambda) = \frac{C(\lambda)}{\int_0^{\infty} C(\lambda)d\lambda} \qquad \frac{dF}{d\lambda} = E(\lambda) \qquad \lambda = 65 - t$$

E(λ) is found using POLYMATH polynomial fitting





100 rpm : $E(\lambda) = 0.04045 - 0.001028\lambda + 1.366e\text{-}5\lambda^2 - 7.833e\text{-}8\lambda^3$

170 rpm : $E(\lambda) = 0.0449 - 0.000931\lambda + 1.475e\text{-}5\lambda^2 - 1.659e\text{-}7\lambda^3 + 8.28e\text{-}10\lambda^4$

	170 rpm	100 rpm
conversion	0.47	0.45

```
Problem P13-7c
Equations:                                                   Initial value
d(X)/d(t)=(kCao*((1-X)^2))-((E*X)/(1-F))                     0
d(F)/d(t)=-E                                                 0.999
kCao=0.05
lam=65-t
E=0.0449-(0.000931*lam)+((1.475e-5)*(lam^2))-((1.659e-7)*
   (lam^3))+((8.28e-10)*(lam^4))
t0 = 0,   tf = 65
```

```
Problem P13-7c
Variable         Initial value  Maximum value  Minimum value  Final value
t                0              65             0              65
X                0              0.474937       0              0.474937
F                0.999          0.999          -0.754792      -0.754792
kCao             0.05           0.05           0.05           0.05
lam              65             65             0              0
E                0.0159238      0.0449         0.0159238      0.0449
```

P13-7 cont'd

Part (d)

As in Part (b) segregation model, second order: except adiabatic

As in Part (c) maximum mixedness model , second order : except adiabatic

where $$k(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To}-\frac{1}{T}\right)\right] = 0.05\exp\left[\frac{5000}{1.987}\left(\frac{1}{320}-\frac{1}{T}\right)\right]$$

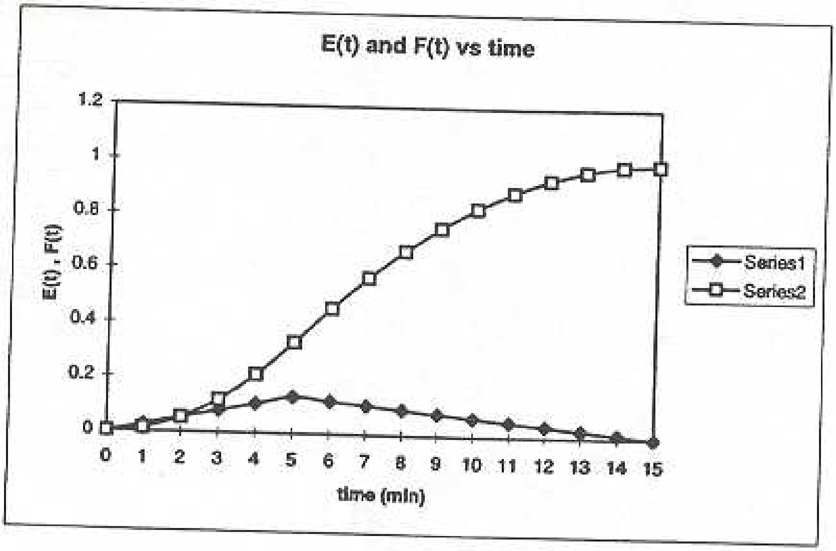
and $$T(K) = To + \left(\frac{-\Delta Hrx}{Cp_A}\right)X = 320+80X$$

C_{AO} = ?

Problem P13-8_B

Part (a)

t (min)	C (10e-6 mol)	E(t)	F(t)	t.E(t)
0	0	0	0	0
1	0.1	0.026667	0.013333	0.026667
2	0.2	0.053333	0.053333	0.106667
3	0.3	0.08	0.12	0.24
4	0.4	0.106667	0.213333	0.426667
5	0.5	0.133333	0.333333	0.666667
6	0.45	0.12	0.46	0.72
7	0.4	0.106667	0.573333	0.746667
8	0.35	0.093333	0.673333	0.746667
9	0.3	0.08	0.76	0.72
10	0.25	0.066667	0.833333	0.666667
11	0.2	0.053333	0.893333	0.586667
12	0.15	0.04	0.94	0.48
13	0.1	0.026667	0.973333	0.346667
14	0.05	0.013333	0.993333	0.186667
15	0	0	1	0
int C =	3.75E-06 mol.s/dm3		int t.E(t) =	6.666667
int E(t) =	0.9999975			



Part (b)

Mean residence time , $t_m = \int_0^\infty t.E(t) = 6.67$ min (see table)

Volume $V = t_m * \upsilon = 6.667 * 150 = 1000$ gal.

Part (c)

PFR , second order $$\upsilon.C_{AO}\frac{dX}{dV} = k.C_A^2$$

$$\int_0^X \frac{dX}{(1-X)^2} = \frac{k.C_{AO}}{\upsilon}\int_0^V dV$$

where V = 1000 gal, υ = 150 gal/min, $k.C_{AO} = 1.2$ /min

$$\frac{X}{1-X} = 1.2.\frac{1000}{150}$$

gives X = 0.889 by iteration

P13-8 cont'd

Part (d)

CSTR , second order

$$\upsilon.(C_{AO} - C_A) = k.C_A^2 V$$

$$\frac{(C_{AO} - C_A)}{C_A} = \frac{V}{\upsilon} k.C_{AO}.(1 - X)^2$$

$$\frac{X}{(1 - X)^2} = \frac{V}{\upsilon} k.C_{AO}$$

where V = 1000 gal, υ = 150 gal/min, k.C_{AO} = 1.2 /min

gives X = 0.703 by iteration

Part (e)

Completely segregated

Batch reactor eqn :

$$\frac{dC_A}{d\lambda} = kC_A^2$$

$$\frac{dX}{d\lambda} = -kC_{A0}(1 - X)^2$$

$$\overline{X} = \int_0^\infty -X(\lambda)E(\lambda)d\lambda$$

where E(t) = if (t <= 5) then (0.1333 / 5) * t) else (0.2 - (0.13333 / 10) * t)

```
Problem P13-8e                                                    Initial value
Equations:
d(X)/d(t)=kCao*(1-X)^2                                            0
d(xbar)/d(t)=E*X                                                  0
kCao=1.2
E=if(t<=5)then(0.0266667*t)else(0.2-(0.013333*t))
lam=15-t
t0 = 0,   tf = 15
Problem P13-8e
Variable        Initial value   Maximum value   Minimum value   Final value
t               0               15              0               15
X               0               0.947368        0               0.947368
xbar            0               0.860399        0               0.860399
kCao            1.2             1.2             1.2             1.2
E               0               0.133322        0               5e-06
lam             15              15              0               0
```

P13-8 cont'd

Using POLYMATH gives mean conversion xbar = 0.86 at t = 15 min

Part (f)

Maximum mixedness

$$\frac{dX}{d\lambda}=\frac{r_A}{C_{AO}}+\frac{E(\lambda)}{1-F(\lambda)}.X$$

Rate law : $-r_A = k.C_A^2$

$$C_A = C_{AO}.(1-x)$$

$$r_A = -k.C_{AO}^2.(1-x)^2$$

$$\frac{r_A}{C_{AO}} = -k.C_{AO}\ .(1-x)^2$$ where $k.C_{AO} = 1.2$ /min

$$\frac{dF}{d\lambda} = E(\lambda) \qquad \lambda = 15 - t$$

where E(λ) = if (λ >= 5) then (0.3999 - (0.1333 / 5) * λ) else ((0.13333 / 10) * t)

```
Problem P13-8f
Equations:                                                        Initial value
d(F)/d(t)=-E                                                      0.9999
d(X)/d(t)=(kCao*((1-X)^2))-(E*X/(1-F))                            0
kCao=1.2
lam=15-t
E=if(lam>=10)then(0.39999-(0.026667*lam))else(0.013333*la
   m)
t0 = 0,   tf = 15

Problem P13-8f
Variable       Initial value  Maximum value  Minimum value  Final value
t              0              15             0              15
F              0.9999         0.9999         -1.24957e-05   -1.24957e-05
X              0              0.853917       0              0.853917
kCao           1.2            1.2            1.2            1.2
lam            15             15             0              0
E              -1.5e-05       0.133318       -1.5e-05       0
```

Using POLYMATH gives X = 0.854

P13-8 cont'd

Part (g)

$$k(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right] = ko.\exp\left[\frac{30000}{8.314}\left(\frac{1}{325} - \frac{1}{T}\right)\right]$$

and $$T(K) = To + \left(\frac{-\Delta Hrx}{Cp_A}\right).X = 320 + 150X$$

But k(325K) = ? and C_{AO} = ?

Part (h)

$$k(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right] = ko\exp\left[\frac{10000}{1.987}\left(\frac{1}{325} - \frac{1}{T}\right)\right]$$

and $$T(K) = To + \left(\frac{-\Delta Hrx}{Cp_A}\right).X = 325 - 500X$$

But k(325K) = ? and C_{AO} =

Problem P13-9$_A$

3rd order
Part (a)

PFR Design equation

$$\upsilon_0 C_{AO}\frac{dX}{dV} = k.C_A.C_B^2$$

$$C_A = C_{AO}(1-X)$$
$$C_B = C_{BO}(1-X)$$

$$\int_0^X \frac{dX}{(1-X)^3} = k.C_{BO}^2\frac{V}{\upsilon}$$

Let $y = 1 - X$, $dy = -dX$

$$\int -\frac{dy}{y^3} = \left[\frac{1}{2y^2}\right] = \left[\frac{1}{2(1-X)^2}\right]_0^X = k.C_{BO}^2.\frac{V}{\upsilon_0}$$

$$\frac{1}{(1-X)^2}-1=2.k.C_{BO}^2.\frac{V}{\upsilon}$$

$$1-2X+X^2=\frac{1}{1+2.k.C_{BO}^2.\frac{V}{\upsilon}}$$

Using the quadratic solution $X=\dfrac{2\pm\sqrt{4-4\left[1-\dfrac{1}{1+2.k.C_{BO}^2.\frac{V}{\upsilon}}\right]}}{2}$

Substituting the values $X=1\pm\sqrt{\left[\dfrac{1}{1+2.k.C_{BO}^2.\frac{V}{\upsilon}}\right]}=1-0.168=0.832$

The conversion for a PFR X = 83.2 %

CSTR Design equation

$$\upsilon_O.(C_{AO}-C_A)=-r_A.V$$

$$-r_A=k.C_A.C_B^2$$

$$C_A=C_{AO}(1-X)$$
$$C_B=C_{BO}(1-X)$$

$$\frac{C_{AO}-C_A}{C_{AO}}=X$$

$$X=k.C_{BO}^2.(1-X)^3\frac{V}{\upsilon}$$

Substituting the values and iteration gives:

The conversion for a CSTR X = 66.2 %

Laminar flow , completely segregated

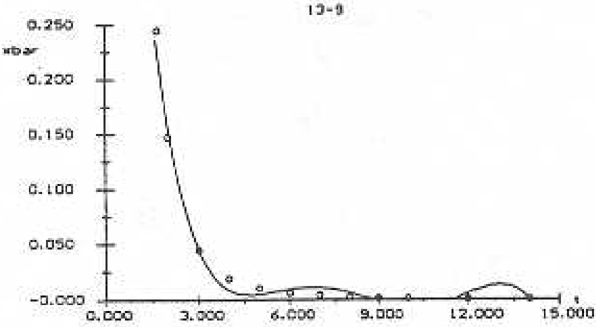
$$E(t) = 0 \quad \text{for} \quad t < \tau/2$$
$$= \tau^2/2t^3 \quad \text{for} \quad t \geq \tau/2$$

$$\tau = V/\upsilon = 1000/10 = 100 \text{ s} = 1.67 \text{ min}$$

$$\bar{X} = \int_0^\infty X(t).E(t)dt$$

where

$$X(t) = 1 - \sqrt{\frac{1}{1+2.k.C_{BO}^2.t}}$$



```
P(t) = 0.910432 -0.635652 t +0.169362 t^2 -0.0215654 t^3 +0.00130028 t^4
     -2.99258e-05 t^5
variance = 0.000148111
```

The integral xbar gives mean conversion = 22 %

Part (b)

Segregated model

$$-\frac{dN_A}{dt} = -r_A.V$$

Batch reactor $\quad N_A = N_{AO}(1-X)$

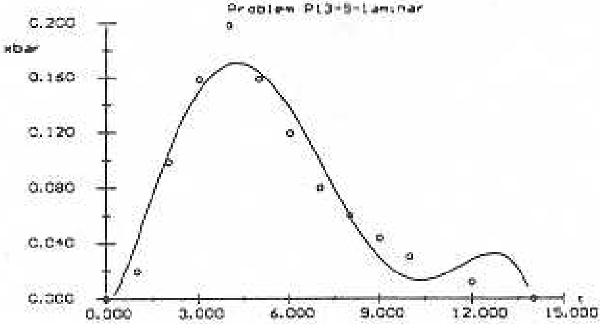
$$N_{AO}\frac{dX}{dt} = k.C_A.C_B^2.V$$
$$C_A = C_{AO}(1-X)$$
$$C_B = C_{BO}(1-X)$$

P13-9 cont'd

$$\int_0^X \frac{dX}{(1-X)^3} = k.C_{BO}^2.t$$

Similarly $$X(t) = 1 - \sqrt{\left[\frac{1}{1+2.k.C_{BO}^2.t}\right]}$$

$$\overline{X} = \int_0^\infty X(t).E(t)dt$$ and E(t) from the given data.



```
P(t) = -0.0111381 +0.039064 t +0.020792 t^2 -0.00720741 t^3 +0.00068036 t^4
    -2.04051e-05 t^5
variance = 0.000439956
```

Evaluation of the integral givesmean conversion for the segregation model

xbar = 90 %

Maximum mixedness

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{AO}} + \frac{E(\lambda)}{1-F(\lambda)}.X$$

Rate law : $$-r_A = k.C_A.C_B^2$$

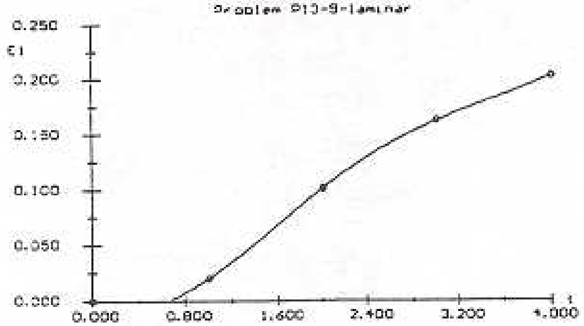
$$C_A = C_{AO}.(1-x) \qquad C_B = C_{BO}.(1-x)$$

$$r_A = -k.C_{AO}.C_{BO}^2.(1-x)^3$$ where k = 10500 $dm^6/mol^2.min$

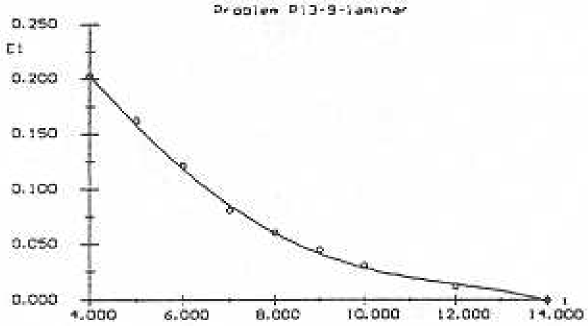
$$\frac{r_A}{C_{AO}} = -k.C_{BO}^2.(1-x)^3$$

$$\frac{dF}{d\lambda} = E(\lambda) \qquad \lambda = 14 - t$$

P13-9 cont'd



$P(t) = 5.92497e-15 - 0.057553t + 0.108335t^2 - 0.0338547t^3 + 0.00338547t^4$



$P(t) = 0.409357 - 0.0472613t - 0.00313845t^2 + 0.000631035t^3 - 2.25042e-05t^4$

variance = 1.58574e-05

where $E(\lambda) =$ if ($\lambda >= 10$)
then ($4.52e\text{-}15 - 0.05755\lambda + 0.10833\lambda^2 - 0.03385\lambda^3 + 0.003385\lambda^4$) else
($0.40936 - 0.04726\lambda - 0.003138\lambda^2 + 0.000631\lambda^3 - 2.2504e\text{-}5\lambda^4$)

```
13-9
Equations:                                                      Initial value
d(F)/d(t)=-E                                                    0.9999
d(x)/d(t)=(k*(cbo^2)*((1-x)^3))-(E*x/(1-F))                     0
k=10500
cbo=0.313
lam=15-t
E1=(4.526e-15)-(0.05755*lam)+(0.10833*(lam^2))-(.03385*(l
   am^3))+(.003385*(lam^4))
E2=.4093-(.04726*lam)-(.003138*(lam^2))+(.000631*(lam^3))
   -((2.25046e-5)*(lam^4))
E=if(lam>=10)then(E1)else(E2)
t0 = 0,    tf = 14
```

P13-9 cont'd

```
13-9
Variable      Initial value    Maximum value    Minimum value    Final value
t             0                14               0                14
F             0.9999           0.9999           -185.199         -185.199
x             0                0.989531         0                0.98881
k             10500            10500            10500            10500
cbo           0.313            0.313            0.313            0.313
lam           15               15               1                1
E1            80.6329          80.6329          0.020315         0.020315
E2            -0.0153204       0.35951          -0.0153204       0.35951
E             80.6329          80.6329          0.028854         0.35951
```

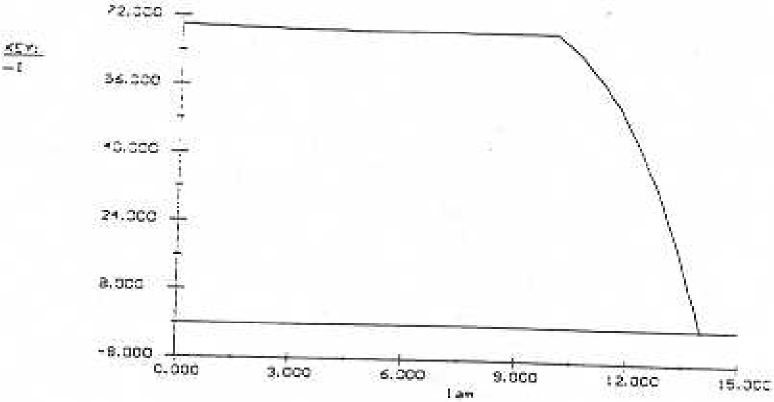
The exit conversion as estimated by the maximum mixedness model is X = 92.7 %

Part (c)

$$\int_0^t E(t)dt = F(t) \Rightarrow \frac{dF(t)}{dt} = E(t)$$

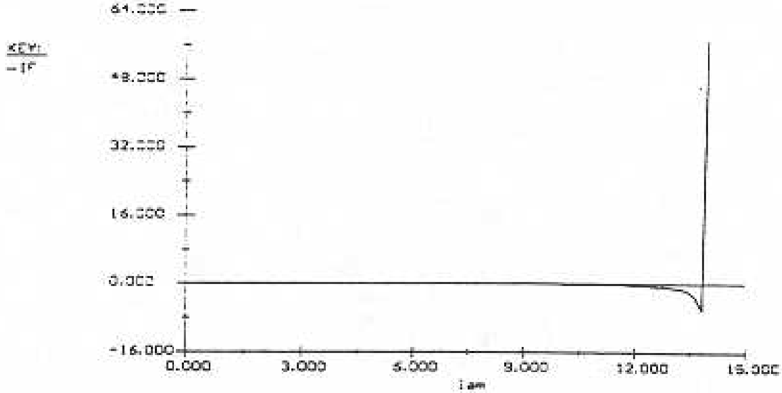
where E(t) is obtained from the polynomial fit in Part (b).

Let α = age $$I(\alpha) = \frac{v}{V}[1 - F(\alpha)]$$



P13-9 cont'd

Intensity function
$$\Lambda\lambda = \frac{E(\lambda)}{1-F(\lambda)}$$



Part (d)

Segregation model

$$\frac{dX}{dt} = k.C_{BO}^2(1-X)^3$$

where $k(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To}-\frac{1}{T}\right)\right] = 10500\exp\left[\frac{30000}{8.314}\left(\frac{1}{320}-\frac{1}{T}\right)\right]$

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.

Evaluating X(t, T) using ODE solver and then evaluating the integral xbar using polyfitting gives

xbar = 98 %

Maximum mixedness model

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{AO}} + \frac{E(\lambda)}{1-F(\lambda)}.X$$

$$\frac{r_A}{C_{AO}} = -k.C_{BO}^2.(1-x)^3$$

P13-9 cont'd

where $k(T) = ko.\exp\left[\frac{E}{R}\left(\frac{1}{To} - \frac{1}{T}\right)\right] = 10500\exp\left[\frac{30000}{8.314}\left(\frac{1}{320} - \frac{1}{T}\right)\right]$

and $T(K) = To + \left(\frac{-\Delta Hrx}{Cp_A}\right).X = 320 + 150X$

gives X = 99 %

Problem P13-10$_B$(old manual solution)

Irreversible, first order, long tubular reactor, constant volume , isothermal.

For a PFR $$\frac{dF_A}{dV} = -r_A$$

$$F_{AO}\frac{dX}{dV} = k.C_{AO}.(1-X)$$

$$\int_0^X \frac{dX}{1-X} = \frac{k}{\upsilon_o}\int_0^V dV$$

$$X = 1 - e^{-k.\tau}$$

For X = 0.865 ⇒ $k.\tau = 2.0$

For laminar flow with negligible diffusion, the mean conversion is given by

$$\overline{X} = \int_0^\infty X(t,T).E(t)dt = \int_{\tau/2}^\infty X(t).E(t).dt$$

X(t) used for batch = $1 - e^{-k.\tau}$

E(t) for laminar flow reactor $= \frac{\tau^2}{2t^3}$ where $t \geq \frac{\tau}{2}$

Therefore $$\overline{X} = \int_{\tau/2}^\infty (1 - e^{-k.\tau})\frac{\tau^2}{2t^3}dt = 1 - \int_{\tau/2}^\infty \frac{e^{-k.\tau}\tau^2}{2t^3}dt$$

$$\overline{X} = 1 - \frac{\tau^2}{2}\int_{\tau/2}^\infty \frac{e^{-k.\tau}\tau^2}{t^3}dt$$

P13-10 cont'd

Integrate by parts :

$$u = e^{-k.\tau} \qquad du = -k.\, e^{-k.\tau}dt$$

$$dv = \frac{dt}{t^3} \qquad v = -\frac{1}{2t^2}$$

$$\overline{X} = 1 - \frac{\tau^2}{2}\left\{\frac{e^{-k.\tau}}{2t^2}\right\}\Bigg|_{\tau/2}^{\infty} - \int_{\tau/2}^{\infty} k.\frac{e^{-k.t}}{2t^2}dt$$

$$\overline{X} = 1 - \frac{\tau^2}{2}\left\{0 + \frac{2e^{-k.\tau/2}}{t^2} - \frac{k}{2}\int_{\tau/2}^{\infty}\frac{e^{-k.\tau}}{t^2}dt\right\}$$

Integrate again by parts :

$$u = e^{-k.\tau} \qquad du = -k.\, e^{-k.\tau}dt$$

$$dv = \frac{dt}{t^2} \qquad v = -\frac{1}{t}$$

$$\overline{X} = 1 - e^{-k.\tau/2} + \frac{k.\tau^2}{4}\left\{\frac{e^{-k.\tau}}{t}\Bigg|_{\tau/2}^{\infty} - \int_{\tau/2}^{\infty}\frac{k.e^{-k.\tau}}{t}dt\right\}$$

$$\overline{X} = 1 - e^{-k\tau/2} + \frac{k\tau^2}{4}\left\{0 - \frac{2e^{-k\tau/2}}{\tau} - k\int_{\tau/2}^{\infty}\frac{e^{-kt}}{t^2}dt\right\} \qquad (1)$$

From the CRC Handbook of Physics and Chemistry :

$$\int_{\infty}^{1}\frac{e^{-yu}}{u}du = \gamma + Lny - y + \frac{y^2}{2.2!} - \frac{y^3}{3.3!} + \frac{y^4}{4.4!} - \ldots.$$

where $\gamma = 0.577$

To solve $\displaystyle\int_{\tau/2}^{\infty}\frac{e^{-k.t}}{t}dt$ let $k.t = \phi$ $\Rightarrow$ $\phi_o = \dfrac{k.\tau}{2}$

$$dt = \frac{d\phi}{k}$$

At $t = \dfrac{\tau}{2}$, $\phi = \phi_o = \dfrac{k.\tau}{2} = 1$

P13-10 cont'd

Substituting :

$$\int_{\tau/2}^{\infty} \frac{e^{-k.t}}{t} dt = \int_{1}^{\infty} \frac{e^{-\phi}}{(\phi / k)} \frac{1}{k} d\phi = \int_{1}^{\infty} \frac{e^{-\phi}}{\phi} d\phi = -\int_{\infty}^{1} \frac{e^{-\phi}}{\phi} d\phi$$

Here y = 1

$$\int_{\tau/2}^{\infty} \frac{e^{-kt}}{t} dt \cong -\left[\gamma + \ln(y) - y + \frac{y^2}{2 * 2!} - \frac{y^3}{3 * 3!} + \frac{y^4}{4 * 4!}\right]$$

Note: Series is truncated after y^4

$$\int_{\tau/2}^{\infty} \frac{e^{-k.t}}{t} dt \cong -\left[0.577 + 0 - y + \frac{1}{4} - \frac{1}{18} + \frac{1}{96}\right] = 0.218$$

Equation (1) becomes :

$$\overline{X} = 1 - e^{-k.\tau/2} + \frac{k.\tau}{2} e^{-k.\tau/2} - \frac{k^2.\tau^2}{4}(0.218)$$

$$\overline{X} = 1 - e^{-1} + e^{-1} - 0.218$$

$$\therefore \overline{X} = 1 - 0.218 = 0.782$$

Problem P13-11$_B$(old manual solution)

Turbulent velocity profile is given by :

$$u = u_{\max}\left(1 - \frac{r}{R}\right)^{1/7}$$

Fraction of fluid between r and r + dr : $\frac{dv}{vo} = \frac{2.\pi.r}{vo} r.dr.u(r)$

To find E(t) which is the fraction of fluid between time t and t + dt, we need to relate r and t:

$$u_{avg} = \frac{\int_0^R 2\pi.r.u(r).dr}{\int_0^R 2\pi.r.dr} = \frac{2.\pi \int_0^R r.u_{\max}\left(1 - \frac{r}{R}\right)^{1/7} dr}{\pi.R^2}$$

P13-11 cont'd

Let $X = 1 - r/R \Rightarrow r = (1 - X)R \qquad dr = -R\,dX$

At $r = 0 \quad X = 1$
$r = R \quad X = 0$

$$u_{avg} = \frac{2}{R^2}.u_{\max}\int_1^0 X^{1/7}R(1-X)(-R)dX = -2.u_{\max}\int_1^0 (X^{1/7} - X^{8/7})dX$$

$$u_{avg} = 2.u_{\max}\left[\frac{7}{8}X^{8/7} - \frac{7}{15}X^{15/7}\right]_1^0 = (2.u_{\max})(7)\left(\frac{15-8}{120}\right) = \frac{49}{60}u_{\max}$$

But $u_{avg} = \dfrac{\upsilon_o}{\pi.R^2}$

$$u_{\max} = \frac{60}{49}\frac{\upsilon_o}{\pi.R^2}$$

then $u(r) = \dfrac{60}{49}\dfrac{\upsilon_o}{\pi.R^2}\left(1 - \dfrac{r}{R}\right)^{1/7}$

$$t = \frac{L}{u(r)} = \frac{49}{60}\frac{\pi.R^2L}{\upsilon_o}\frac{1}{\left(1-\frac{r}{R}\right)^{1/7}} = \frac{49}{60}\frac{\tau}{\left(1-\frac{r}{R}\right)^{1/7}}$$

where $\tau = \dfrac{\pi.R^2L}{\upsilon_o}$

$$dt = \frac{49}{60}\tau\left[-\frac{1}{7}\frac{1}{\left(1-\frac{r}{R}\right)^{8/7}}\right]\left(-\frac{1}{R}\right)dr = \frac{7}{60}\frac{\tau}{R}\frac{1}{\left(1-\frac{r}{R}\right)^{8/7}}dr$$

$$dt = \frac{7}{60}\frac{\tau}{R}\left[\frac{1}{\left(1-\frac{r}{R}\right)^{8/7}}\left(\frac{49}{60}\tau\right)^8\right]\left(\frac{60}{49.\tau}\right)^8 = \frac{0.5896}{R\tau^7}t^8dr$$

P13-11 cont'd

Also

$$\left(1-\frac{r}{R}\right)^{1/7}=\frac{49}{60}\frac{\tau}{R}$$

or

$$r=R\left[1-\left(\frac{49}{60}\frac{\tau}{R}\right)^{7}\right]$$

Substituting

$$\frac{dv}{v_0}=\frac{2\pi}{v_0}\left(\frac{L}{t}\right)^{8}\left[1-\left(\frac{49}{60}\frac{\tau}{t}\right)^{7}\right]\frac{R\tau^{7}}{0.5896t^{8}}dt$$

$$E(t)=3.392213\frac{\tau^{8}}{t^{9}}\left[1-\left(\frac{49}{60}\frac{\tau}{t}\right)^{7}\right]$$

Checking : $\int_0^\infty E(t)dt=\int_{\frac{49}{60}\tau}^{\infty}E(t)dt$

Let $X=\frac{49}{60}\frac{\tau}{t}\Rightarrow t=\frac{49}{60}\frac{\tau}{X}$ and $t=\frac{49}{60}\tau\rightarrow X=1$

$dt=-\frac{49}{60}\frac{\tau}{X^{2}}dX$ $t=\infty\rightarrow X=0$

$$\therefore\int_0^\infty E(t)dt=\int_1^0 339213\frac{\tau^{8}}{\left(\frac{49}{60}\frac{\tau}{X}\right)^{9}}\left[1-X^{7}\right]-\left(\frac{49}{60}\frac{\tau}{X^{2}}\right)dX$$

$$\int_0^\infty E(t)dt=-3.39213\left(\frac{60}{49}\right)^{8}\int_1^0 X^{7}(1-X^{7})dX$$

$$\int_0^\infty E(t)dt=-3.39213\left(\frac{60}{49}\right)^{8}\left[\frac{X^{8}}{8}-\frac{X^{15}}{15}\right]_1^{10}=-3.39213\left(\frac{60}{49}\right)^{8}\left(-\frac{7}{120}\right)$$

$$\int_0^\infty E(t)dt=1.00$$

P13-11 cont'd

We have $u_{\max} = \frac{60}{49}\frac{\upsilon_0}{\pi.R^2} \Rightarrow \upsilon_0 = \frac{49\pi.R^2}{60}u_{\max}$

$$\upsilon_0 = \frac{49\pi.(10dm)^2}{60}(10dm/s) = 2565.63dm^3/s$$

$$\tau = \frac{\pi R^2 L}{\upsilon_0} = \frac{(\pi)(10dm)^2(100dm)}{2565\!\!\diagup_{63}dm^3/s} = 12.245s$$

PFR

$$\frac{dC_A}{dt} = -k.C_A$$

$$Ln\frac{C_A}{C_{AO}} = -k.t$$

$$1-X = \frac{C_A}{C_{AO}} = e^{-k.t}$$

$$X = 1-e^{-k.t} = 1-e^{-0.1t}$$

$$\overline{X} = \int_0^\infty X(t)E(t)dt = 3.39213(12.245)^8\int_{\frac{49}{60}12.245}^{\infty}\left\{1-\left[\frac{(49)(12.245)}{(60)tt^9}\right]^7\right\}\frac{(1-e^{-0.1t})}{t^9}dt$$

$$\overline{X} = 1.7145e9\int_{10}^{\infty}\left\{1-\left[\frac{10}{t}\right]^7\right\}\frac{(1-e^{-0.1t})}{t^9}dt = 0.70$$

Problem P13-12$_B$(old manual solution)

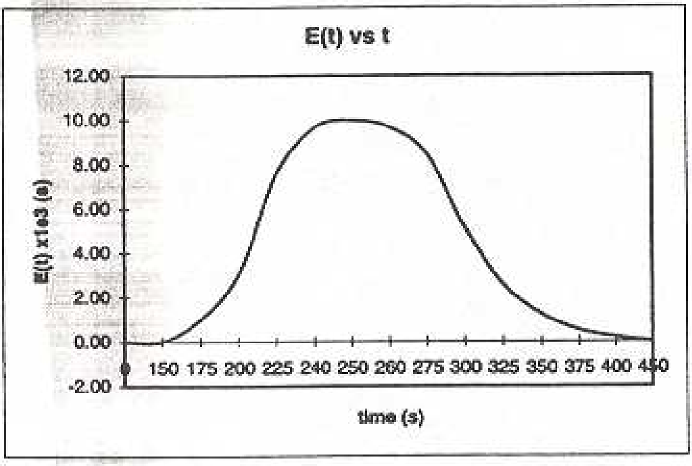
t	C (x1000)	E(t) (x1000)	F(t)	t.E(t) (x1000)	(t-tm)^2 (x1000)	E(t) (t-tm)^2	1 - (e^ k.t)	(1-(e^ k.t))E(t)	t/(1+k.Co. t)	E(t).X(t)
sec	g/l	sec						(x1000)		
150	0	0	0	0	-	0	0	0	0	0
175	1	1.03		180.25	7.482	7.71	0.866	0.982	134	0.318
200	3	3.08	0.06	616	3.78	11.64	0.9	2.772	148	0.456
210	4.5	4.62		970.2	2.65	12.24	0.91	4.204	153	0.71
220	6.3	6.47		1423.4	1.72	11.13	0.92	5.952	159	1.03
230	8.5	8.74		2010.2	0.99	8.65	0.93	8.128	163	1.43
240	9.4	9.66		2318.4	0.462	4.46	0.94	9.080	169	1.63
250	9.7	9.97		2492.5	0.132	1.32	0.944	9.412	174	1.73
260	9.4	9.66	0.324	2511.6	0.002	0.02	0.95	9.177	178	1.72
270	8.6	8.44	0.422	2278.8	0.072	0.61	0.955	8.060	183	1.62
280	7.6	7.81		2186.8	0.342	2.67	0.96	7.498	188	1.47
290	6.3	6.47	0.768	1876.3	0.812	5.25	0.964	6.237	192	1.24
300	5	5.14	0.826	1542	1.482	7.62	0.968	4.976	196	1.01
325	2.5	2.57		835.25	4.03	10.36	0.976	2.508	207	0.532
350	1.2	1.23	0.976	430.5	7.83	9.63	0.982	1.208	217	0.266
400	0.2	0.21		84	19.18	4.03	0.99	0.208	235	0.049
450	0	0	1	0	-	0	-	0	-	0

13·33

Problem P13-12$_B$(old manual solution)

Part (a)

$$\int_0^{\infty} C(t)dt = 0.973 gm.s/dm^3$$



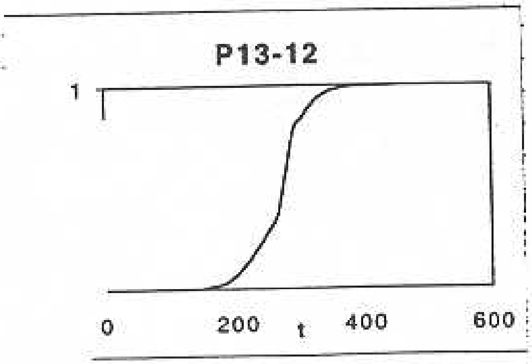
Part (b)

To find the fraction spending between 230 and 270 s, use Simpson's rule for points between 230 and 270 s :

$$\int_{230}^{270} E(t)dt = \frac{10}{3}[8.74 + 4(9.66 + 9.66) + 2(9.97) + 8.84] x10e-3$$

$$\int_{230}^{270} E(t)dt = 0.382$$

Part (c)



P13-12 cont'd

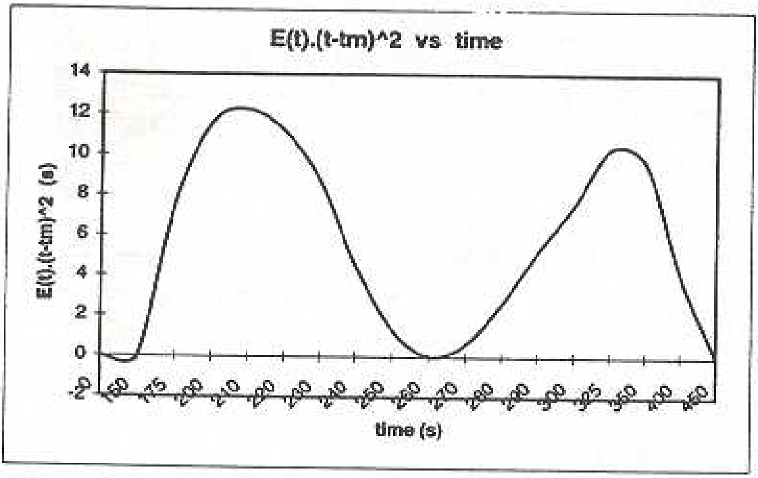
Part (d)

The fraction spending less than 250 s is o.422

Part (e)

Mean residence time $= t_m = \int_0^{\infty} t.E(t)dt = 273$ s from polynomial fitting

Part (f)



Part (g)

$$\sigma^2 = \int_0^{\infty} (t - t_m)^2 E(t)dt = 1832 \text{ by polynomial fitting}$$

The standard deviation = 42.81 s

Part (h)

The E(t) graph demonstrates good symmetry about the mean time t_m = 260 s. The model suggested the reactor is a plug flow reactor with $\tau = 250$ s.

Part (I)

For segregation model : $\bar{X} = \int_0^{\infty} X(t)E(t)dt$

For first order $X(t) = 1 - e^{-k.t}$ with $k = 0.0115$ /s

Gives xbar = 94.5 %

Part (j)

For second order reaction : $\frac{dC}{dt} = -k.C^2 \Rightarrow -\frac{1}{C} + \frac{1}{Co} = -k.t$

$$\frac{1}{C} = \frac{1}{Co} + k.t$$

$$C = \frac{Co}{1 + k.Co.t}$$

$$1 - X = \frac{1}{1 + k.Co.t}$$

$$X = \frac{k.Co.t}{1 + k.Co.t}$$

$$\overline{X} = k.Co\int_0^{\infty} \frac{t}{1 + k.Co.t} E(t)$$

where Co = 0.01 mol/dm^3 k = 10.55/60 = 0.1758 mol/dm^{3}s

gives xbar = 0.313

Problem P13-13$_B$

The elementary gas phase reaction : A + B → C in a CSTR

$F_C = 20$ kg/s ; $V_O = 1$ m^3 ; $C_{AO} = 0.4$ mol/dm^3 ; $\upsilon_O = 10$ dm^3/s ;

$k_d = 0.06$ /s ; $k = 0.03$ dm^6/mol.s.g ; $\tau_c = 200/20 = 10$ s

Second order decay : $\frac{da}{dt} = -k_d.a^2 \Rightarrow a = \frac{1}{1 + k_d.t}$

P13-13 cont'd

Part (a)

Mean activity exisiting in the reactor : $\bar{a} = \int_0^\infty a(t).E(t)dt$

$$\bar{a} = \frac{1}{\tau}\int_0^\infty \frac{e^{-t/\tau}}{1+k_d.t}dt = \frac{1}{10}\int_0^\infty \frac{e^{-t/10}}{1+0.06t}dt$$

t	$\frac{e^{-t/10}}{1+0.06t}$
0	1
5	0.467
10	0.229
15	0.117
20	0.0615
25	0.0328
30	0.0178
35	0.0097
40	0.0054
45	0.0030
50	0.0017
55	0.00095
60	0.00054
65	0.00031

Ude Simpson's rule to evaluate the integral : $\bar{a} = \frac{6.9219}{10} = 0.6922$

Part (b)

The mean activity of the catalyst in the reactor is the same as that at the exit. In the case of non-linear rate problem the mean activity calculated from residence time distribution will give an upper bound for order greater than unity and lower bound for order less than unity.

The actual value of mean activity can be calculated using population balance technique. (see Joshi, P.A., PhD thesis, Dept Chemical Engineering, IIT, Bombay, 1985)

P13-13 cont'd

Part (c)

Assuming micromixing : $$W = \frac{F_{AO}X}{-r_{AO}.\overline{a}}$$

or $$\upsilon_o.X = k.C_{AO}\frac{(1-X)^2}{(1+\varepsilon.X)^2}\overline{a}.W$$

$$\varepsilon = -0.5$$

Checking units : $dm^3/s = dm^6/mol.s.g \text{ x } mol.g/dm^3$

$dm^3/s = dm^3/s$ OK

$$10X = \frac{(0.03).(0.04).(1-X)^2(0.6922).(2x10^5)}{(1-0.5X)^2}$$

eqn (1)

$$X = 16.613\frac{(1-X)^2}{(1-0.5X)^2} \Rightarrow X = 0.87$$

Part (d)

Assuming segregation model :

$$-r_A = -\frac{1}{W}\frac{dN_A}{dt} = \frac{N_{AO}}{W}\frac{dX}{dt} = k.C_{AO}{}^2\frac{(1-X)^2}{(1+\varepsilon.X)^2}a(t)$$

$$\frac{C_{AO}.V_o}{W}\frac{dX}{dt} = k.C_{AO}{}^2\frac{(1-X)^2}{(1+\varepsilon.X)^2}.\frac{1}{1+k_d.t}$$

$$\int_0^X \frac{(1-X)^2}{(1+\varepsilon.X)^2}\frac{dX}{dt} = \frac{k.C_{AO}.W}{k_d.V_o}Ln(1+k_d.t)$$

$$2\varepsilon(1+\varepsilon)Ln(1-X)+\varepsilon^2X+\frac{(1+\varepsilon.)^2X}{(1-X)} = \frac{k.C_{AO}.W}{k_d.V_o}Ln(1+k_d.t)$$

$$-0.5Ln(1-X)+0.25X+\frac{0.25X}{1-X} = 4Ln(1-0.06t)$$

P13-13 cont'd

$$\overline{X} = \int_0^\infty X(t)E(t)dt$$

Do it numerically.

Part (e)

X = 0.75 Use eqn (1) where W is unknown :

$$(10)(0.75) = \frac{(0.03).(0.04).(1-(0.75))^2(0.6922).(W)}{(1-0.5(0.75))^2}$$

$$W = 56{,}432g$$

Part (f)

$\tau = 2$ s

$$\overline{a} = \frac{1}{2}\int_0^\infty \frac{e^{-t/2}}{1+0.06t}dt = \frac{1}{2}\int_0^\infty f(t)dt \qquad \text{where } \frac{e^{-t/2}}{1+0.06t}$$

t	f(t)
0	1
1	0.5722
2	0.3285
3	0.1891
4	0.1091
5	0.06314
6	0.03661
7	0.02127
8	0.01238
9	0.00721
10	0.00421

Use Simpson's rule to evaluate the integral :

$$\overline{a} = \frac{1.7964}{2} = 0.8982$$

$$10X = \frac{(0.03).(0.04).(1-X)^2(0.8982).(2x10^5)}{(1-0.5X)^2}$$

<u>P13-13</u> cont'd

$$X = 21.56\frac{(1-X)^2}{(1-0.5X)^2}$$

$$X = 0.89$$

does not change very much.

Part (g)

For first order decay :

$$\frac{da}{dt} = -k_d.a$$

$$a = ao.e^{-k_d.t}$$

$$\overline{a} = \frac{1}{\tau c}\int_0^\infty e^{-k_d.t}e^{t/\tau c}dt = -\frac{1}{\tau c}\left[\frac{\exp\left\{-\left(k_d+\frac{1}{\tau c}\right)t\right\}}{k_d+\frac{1}{\tau c}}\right]_0^\infty$$

$$\overline{a} = \frac{1}{1+k_d.\tau c} = \frac{1}{1+(0.06).(10)} = 0.625$$

$$10X = \frac{(0.03).(0.04).(1-X)^2(0.625).(2x10^5)}{(1-0.5X)^2}$$

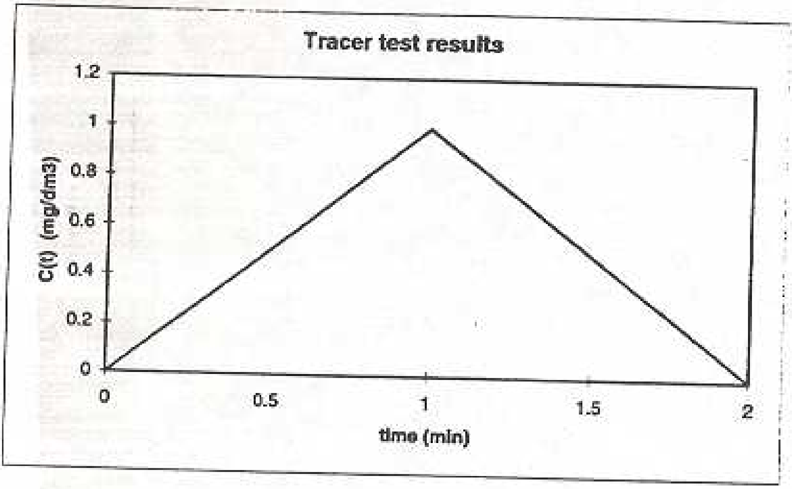
$$X = 15\frac{(1-X)^2}{(1-0.5X)^2}$$

$$X = 0.86$$

$$(10)(0.75) = \frac{(0.03).(0.04).(1-0.75)^2(0.625).(W)}{(1-0.5(0.75))^2}$$

$$W = 62{,}500g$$

Problem P13-14



Part (a)

Liquid phase, segregation model, secondorder, non ideal GSTR, adiabatic

$$\overline{X} = \int_0^\infty X(t,T).E(t)dt = 0.67$$

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} \qquad \text{but} \qquad \int_0^\infty C(t)dt = 1mg.\text{min}/\ dm^3$$

E(t) = IF (t ≤ 1) THEN (t) ELSE (IF (t ≥ 2) THEN (0) ELSE (2 - t))

For a batch globule : $C_{AO}\dfrac{dX}{dt} = -r_A$

$$-r_A = k.C_A^2$$

$$C_A = C_{AO}(1-X)$$

$$\frac{dX}{dt} = k.C_{AO}.(1-X)^2$$

where $C_{AO} = 2 \text{ mol} / \text{dm}^3$

$$k(T) = 0.5.\exp\left[\frac{Ea}{8.314}\left(\frac{1}{300}-\frac{1}{T}\right)\right]$$

P13-14 cont'd

$$T = To + \frac{-\Delta Hrx.X}{Cps + \Delta Cp.X}$$

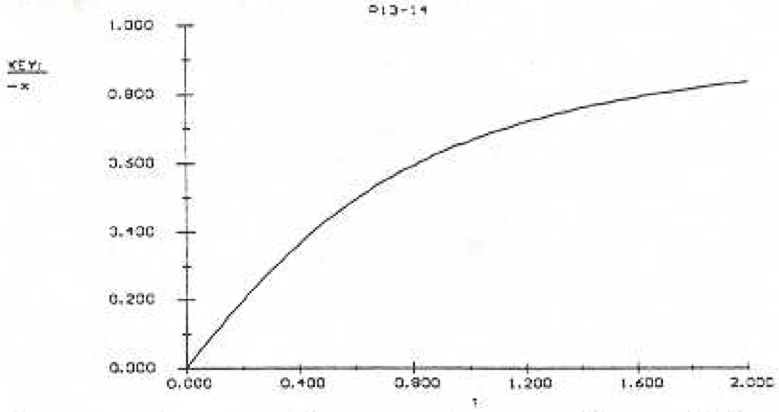
where Cps = ΣθiCpi = Cpa + 0 = 50 J/mol.K
ΔCp = 1/2 Cpb - Cpa = 100/2 - 50 = 0

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 $\overline{X} = \int_0^\infty X(t,T).E(t)dt = 0.67$

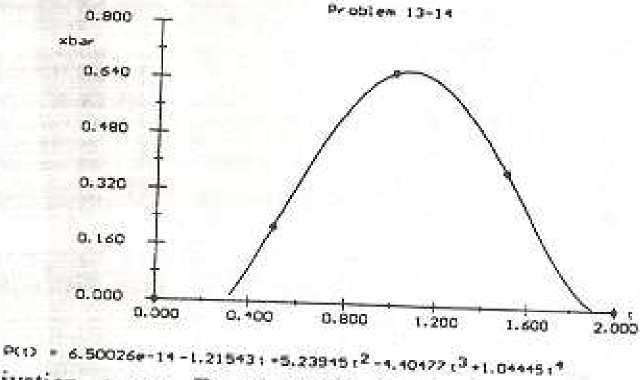
When the evaluated integral xbar = 0.67 then the Ea is correct.

```
P13-14
Equations:                                              Initial value
d(x)/d(t)=k*cao*((1-x)^2)                               0
cao=2
T=300+(150*x)
E1=t
E2=2-t
Ea=10000
k=.5*exp((Ea/8.314)*((1/300)-(1/T)))
E=if(t<=1)then(E1)else(E2)
t0 = 0,   tf = 2
```



```
#        t        C        E        x        xbar
1        0        0        0        0        0
2      0.5      0.5      0.5  0.43366  0.21683
3        1        1        1   0.6637   0.6637
4      1.5      0.5      0.5   0.7741  0.38705
5        2        0        0   0.8336        0
```

P13-14 cont'd



An activation energy Ea of 10000 J/mol gives approximately the correct mean conversion, xbar = 0.67. Inaccuracy lies in the polynomial fit and hence the integral area.

Part (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

$$\frac{dC_{Abar}}{dt} = C_AE(t)$$

$$\frac{dC_{Bbar}}{dt} = C_BE(t)$$

$$\frac{dC_{Cbar}}{dt} = C_CE(t)$$

E(t) = IF (t ≤ 1) THEN (t) ELSE (IF (t ≥ 2) THEN (0) ELSE (2 - t))

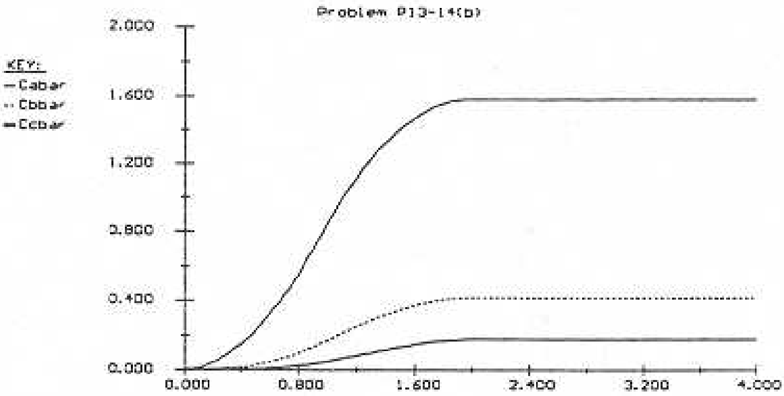
P13-14 cont'd

selectivity $S = \frac{C_{Bbar}}{C_{Cbar}}$ (= 2.38)

Iteration with k_{2C} until S = 2.38 gives $k_{2C} = 0.3755\ dm^3/mol.min$

```
Problem P13-14(b)
Equations:                                                   Initial value
d(Ca)/d(t)=(-k1a*(Ca^2))+(k2a*Ca*Cb)                         2
d(Cb)/d(t)=(k1a*(Ca^2))-(k2a*Ca*Cb)                          0
d(Cc)/d(t)=k2a*Ca*Cb                                         0
d(Cabar)/d(t)=Ca*E                                           0
d(Cbbar)/d(t)=Cb*E                                           0
d(Ccbar)/d(t)=Cc*E                                           0
k1a=0.2
k2a=0.3755
E=if(t<=1)then(t)else(if(t>=2)then(0)else(2-t))
S=Cbbar/(Ccbar+0.000001)
t0 = 0,   tf = 4
```

```
Problem P13-14(b)
Variable     Initial value  Maximum value  Minimum value  Final value
t            0              4              0              4
Ca           2              2              1.32783        1.32783
Cb           0              0.672165       0              0.672165
Cc           0              1.1095         0              1.1095
Cabar        0              1.58256        0              1.58256
Cbbar        0              0.417439       0              0.417439
Ccbar        0              0.175374       0              0.175374
k1a          0.2            0.2            0.2            0.2
k2a          0.3755         0.3755         0.3755         0.3755
E            0              1              0              0
S            0              33.117         0              2.38027
```



Problem P13-16$_B$

Multiple parallel reactions, isothermal

$E(t) = 0.0279693 - 0.0008527\,t + 1.2778e\text{-}5\,t^2 - 1.0661e\text{-}7\,t^3 + 4.5747e\text{-}10\,t^4 - 7.73108e\text{-}13\,t^5$

k1 = 5.0 $m^6/kmol^2min$, k2 = 2.0 $m^3/kmol.min$, k3 = 10 $m^6/kmol^2min$, k4 = 5.0 $m^2/kmol^{2/3}min$

Part (a)

Segregated model

$$\frac{dC_A}{dt} = -k_1.C_A.C_B^2 - k_2.C_A.C_B - \frac{2}{3}k_4.C_C.C_A^{2/3}$$

$$\frac{dC_B}{dt} = -1.25k_1.C_A.C_B^2 - 0.75k_2.C_A.C_B - k_3.C_B.C_C^2$$

$$\frac{dC_C}{dt} = k_1.C_A.C_B^2 - 2k_3.C_C^2.C_B - k_4.C_C.C_A^{2/3}$$

$$\frac{dC_D}{dt} = 1.5k_1.C_A.C_B^2 + 1.5k_2.C_A.C_B + k_4.C_C.C_A^{2/3}$$

$$\frac{dC_E}{dt} = 0.5k_2.C_A.C_B + \frac{5}{6}k_4.C_C.C_A^{2/3}$$

$$\frac{dC_F}{dt} = 2k_3.C_C^2.C_B$$

$$\frac{d\overline{C}_A}{dt} = C_A.E(t) \qquad \frac{d\overline{C}_B}{dt} = C_B.E(t) \qquad \frac{d\overline{C}_C}{dt} = C_C.E(t)$$

$$\frac{d\overline{C}_D}{dt} = C_B.E(t) \qquad \frac{d\overline{C}_E}{dt} = C_E.E(t) \qquad \frac{d\overline{C}_F}{dt} = C_F.E(t)$$

$$S_{CD} = \frac{\overline{C}_C}{\overline{C}_D} \qquad S_{DE} = \frac{\overline{C}_D}{\overline{C}_E} \qquad S_{EF} = \frac{\overline{C}_E}{\overline{C}_F}$$

P13-16 cont'd

```
Problem P13-16
Equations:                                                          Initial value
d(Ca)/d(t)=(-k1*Ca*(Cb^2))-(k2*Ca*Cb)-((2/3)*k4*Cc*(Ca^(2           0.05
   /3)))
d(Cb)/d(t)=(-1.25*k1*Ca*(Cb^2))-(0.75*k1*Ca*Cb)-(k3*Cb*(C           0.05
   c^2))
d(Cc)/d(t)=(k1*Ca*(Cb^2))-(2*k3*Cb*(Cc^2))-(k4*Cc*(Ca^(2/            0
   3)))
d(Cd)/d(t)=(1.5*k1*Ca*(Cb^2))+(1.5*k2*Ca*Cb)+(k4*Cc*(Ca^(            0
   2/3)))
d(Ce)/d(t)=(0.5*k2*Ca*Cb)+((5/6)*k4*Cc*(Ca^(2/3)))                    0
d(Cf)/d(t)=(2*k3*Cb*(Cc^2))                                           0
d(Cabar)/d(t)=E*Ca                                                    0
d(Cbbar)/d(t)=E*Cb                                                    0
d(Ccbar)/d(t)=E*Cc                                                    0
d(Cdbar)/d(t)=E*Cd                                                    0
d(Cebar)/d(t)=E*Ce                                                    0
d(Cfbar)/d(t)=E*Cf                                                    0
k1=5
k2=2
k4=5
k3=10
E=0.0279693-(0.000852735*t)+((1.2778e-5)*(t^2))-((1.0661e
   -7)*(t^3))+((4.5747e-10)*(t^4))-((7.73108e-13)*(t^5))
Scd=Ccbar/(Cdbar+0.000000001)
Sde=Cdbar/(Cebar+0.000000001)
Sef=Cebar/(Cfbar+0.00000000001)
t0 = 0,   tf = 200
```

```
Problem P13-16
Variable        Initial value   Maximum value   Minimum value   Final value
t               0               200             0               200
Ca              0.05            0.05            0.0217543       0.0217543
Cb              0.05            0.05            1.7211e-09      1.7211e-09
Cc              0               0.000418278     0               1.42227e-18
Cd              0               0.0423686       0               0.0423686
Ce              0               0.0141226       0               0.0141226
Cf              0               4.49497e-07     0               4.49497e-07
Cabar           0               0.0263679       0               0.0263679
Cbbar           0               0.00826231      0               0.00826231
Ccbar           0               6.95492e-05     0               6.95492e-05
Cdbar           0               0.0355547       0               0.0355547
Cebar           0               0.0118166       0               0.0118166
Cfbar           0               4.15583e-07     0               4.15583e-07
k1              5               5               5               5
k2              2               2               2               2
k4              5               5               5               5
k3              10              10              10              10
E               0.0279693       0.0279693       0.00021974      0.00021974
Scd             0               0.0703057       0               0.00195612
Sde             0               3.35056         0               3.00888
Sef             0               206571          0               28433.1
```

P13-16 cont'd

Exit concentrations :

$\overline{C}_A = 0.026 mol / dm^3$

$\overline{C}_B = 0.008$

$\overline{C}_C = 6.955e-5$

$\overline{C}_D = 0.036$

$\overline{C}_E = 0.012$

$\overline{C}_F = 4.156e-7$

Selectivities

$S_{CD} = 0.00196$

$S_{DE} = 3.009$

$S_{EF} = 28433$

Part (b)

Maximum mixedness model

E(t) = 0.0279693 - 0.0008527λ + 1.2778e-5λ^2 - 1.0661e-7λ^3 + 4.5747e-10λ^4 - 7.73108e-13λ^5

and $\lambda = t_f - z$, where z = t, t_f = 200 min (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 the other species.

$$\frac{dF(\lambda)}{dz} = -E(\lambda) \qquad \text{gives } F(\lambda)$$

```
Problem P13-16
Equations:                                                          Initial value
d(Ca)/d(z)=((-k1*Ca*(Cb^2))-(k2*Ca*Cb)-((2/3)*k4*Cc*(Ca^(   0.05
   2/3))))-((Ca-Cao)*E/(1-F))
d(Cb)/d(z)=((-1.25*k1*Ca*(Cb^2))-(0.75*k1*Ca*Cb)-(k3*Cb*(   0.05
   Cc^2)))-((Cb-Cbo)*E/(1-F))
d(Cc)/d(z)=((k1*Ca*(Cb^2))-(2*k3*Cb*(Cc^2))-(k4*Cc*(Ca^(2   0
   /3))))-(Cc*E/(1-F))
d(F)/d(z)=-E                                                        0.99999
d(Cd)/d(z)=((1.5*k1*Ca*(Cb^2))+(1.5*k2*Ca*Cb)+(k4*Cc*(Ca^   0
   (2/3))))-(Cd*E/(1-F))
d(Ce)/d(z)=((0.5*k2*Ca*Cb)+((5/6)*k4*Cc*(Ca^(2/3))))-(Ce*   0
   E/(1-F))
d(Cf)/d(z)=((2*k3*Cb*(Cc^2)))-(Cf*E/(1-F))                  0
k3=10
k1=5
k2=2
k4=5
```

P13-16 cont'd

```
Cao=0.05
Cbo=0.05
lam=200-z
Scd=Cc/(Cd+0.0000000001)
Sde=Cd/(Ce+0.000000001)
Sef=Ce/(Cf+0.0000000001)
E=0.02797-(0.000852735*lam)+((1.2778e-5)*(lam^2))-((1.066
    1e-7)*(lam^3))+((4.5747e-10)*(lam^4))-((7.73108e-13)*(
    lam^5))
z0 = 0,   zf = 200
```

```
Problem P13-16
Variable        Initial value  Maximum value  Minimum value  Final value
z               0              200            0              200
Ca              0.05           0.05           0.0262434      0.0282525
Cb              0.05           0.05           0.00690604     0.0101378
Cc              0              0.000318211    0              2.9267e-05
F               0.99999        0.99999        -0.00157133    -0.00157133
Cd              0              0.035635       0              0.0326212
Ce              0              0.0118713      0              0.0108591
Cf              0              2.10543e-07    0              7.98503e-09
k3              10             10             10             10
k1              5              5              5              5
k2              2              2              2              2
k4              5              5              5              5
Cao             0.05           0.05           0.05           0.05
Cbo             0.05           0.05           0.05           0.05
lam             200            200            0              0
Scd             0              0.0736547      0              0.000897176
Sde             0              3.3725         0              3.00404
Sef             0              1.34311e+06    0              1.34311e+06
E               0.00022044     0.02797        0.00022044     0.02797
```

Exit selectivites :

$C_A = 0.028 mol / dm^3$

$C_B = 0.010$

$C_C = 2.927e-5$

$C_D = 0.033$

$C_E = 0.011$

$C_F = 7.985e-9$

Selectivites :

$S_{CD} = 0.0009$

$S_{DE} = 3.004$

$S_{EF} = 1343110$

Part (c)

Ideal CSTR

$$t_m = \tau \quad \text{and} \qquad E(t) = \frac{e^{-t/\tau}}{\tau}$$

P13-16 cont'd

Mol balances :

$$\frac{dF_A}{dt} = F_{AO} - (-r_A) \qquad \text{where} \quad r_A = -k_1 . C_A . C_B^2 - k_2 . C_A . C_B - \frac{2}{3} k_4 . C_C . C_A^{2/3}$$

$$F_{AO} = C_{AO} . \upsilon_O = 0.05 * 10 = 0.5 \text{ mol/min} = F_{BO}$$

and so on for the other species.

$$C_A = C_{TO} \frac{F_A}{F_T} \rightarrow etc...$$

$$C_{TO} = C_{AO} + C_{BO} = 0.05 + 0.05 = 0.1$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_f$$

```
Problem P13-16
Equations:                                                    Initial value
d(Fa)/d(t)=0.5+((-k1*Ca*(Cb^2))-(k2*Ca*Cb)-((2/3)*k4*Cc*(    0.5
   Ca^(2/3))))
d(Ff)/d(t)=((2*k3*Cb*(Cc^2)))                                0
d(Fb)/d(t)=0.5+((-1.25*k1*Ca*(Cb^2))-(0.75*k1*Ca*Cb)-(k3*    0.5
   Cb*(Cc^2)))
d(Fc)/d(t)=((k1*Ca*(Cb^2))-(2*k3*Cb*(Cc^2))-(k4*Cc*(Ca^(2    0
   /3))))
d(Fd)/d(t)=((1.5*k1*Ca*(Cb^2))+(1.5*k2*Ca*Cb)+(k4*Cc*(Ca^    0
   (2/3))))
d(Fe)/d(t)=((0.5*k2*Ca*Cb)+((5/6)*k4*Cc*(Ca^(2/3))))         0
k1=5
k2=2
k4=5
k3=10
E=0.0279693-(0.000852735*t)+((1.2778e-5)*(t^2))-((1.0661e
   -7)*(t^3))+((4.5747e-10)*(t^4))-((7.73108e-13)*(t^5))
  Cao=0.05
  Cbo=0.05
  Ft=Fa+Fb+Fc+Fd+Fe+Ff
  Ca=0.1*Fa/Ft
  Cb=0.1*Fb/Ft
  Cc=0.1*Fc/Ft
  Cd=0.1*Fd/Ft
  Ce=0.1*Fe/Ft
  Cf=0.1*Ff/Ft
  Scd=if(t<1)then(Cc/(Cd+0.00001))else(Cc/Cd)
  Sde=if(t<1)then(Cd/(Ce+0.00001))else(Cd/Ce)
  Sef=if(t<1)then(Ce/(Cf+0.00001))else(Ce/Cf)
  t0 = 0,   tf = 200
```

P13-16 cont'd

```
Problem P13-16
Variable      Initial value   Maximum value   Minimum value   Final value
t             0               200             0               200
Fa            0.5             99.3967         0.5             99.3967
Ff            0               6.07003e-07     0               6.07003e-07
Fb            0.5             98.5159         0.5             98.5159
Fc            0               0.112878        0               0.112878
Fd            0               1.65498         0               1.65498
Fe            0               0.49522         0               0.49522
k1            5               5               5               5
k2            2               2               2               2
k4            5               5               5               5
k3            10              10              10              10
E             0.0279693       0.0279693       0.00021974      0.00021974
Cao           0.05            0.05            0.05            0.05
Cbo           0.05            0.05            0.05            0.05
Ft            1               200.176         1               200.176
Ca            0.05            0.05            0.0496547       0.0496547
Cb            0.05            0.05            0.0492147       0.0492147
Cc            0               5.63893e-05     0               5.63893e-05
Cd            0               0.000826763     0               0.000826763
Ce            0               0.000247393     0               0.000247393
Cf            0               3.03235e-10     0               3.03235e-10
Scd           0               0.0719365       0               0.0682049
Sde           0               3.36287         0               3.3419
Sef           0               4.99062e+06     0               815844
```

Exit concentrations :

$C_A = 0.050 mol / dm^3$

$C_B = 0.049$

$C_C = 5.639e-5$

$C_D = 0.0008$

$C_E = 0.0002$

$C_F = 3.03e-10$

Selectivites :

$S_{CD} = 0.068$

$S_{DE} = 3.342$

$S_{EF} = 815844$

Ideal PFR

$t_m = \tau$ and RTD function $E(t) = \delta(t - \tau)$

$$\frac{dF_A}{dV} = (-r_A) \qquad r_A = -k_1.C_A.C_B^2 - k_2.C_A.C_B - \frac{2}{3}k_4.C_C.C_A^{2/3}$$

and so on for the other species.

P13-16 cont'd

$$C_A = C_{T0}\frac{F_A}{F_T} \rightarrow etc...$$

$$C_{T0} = C_{A0} + C_{B0} = 0.05 + 0.05 = 0.1$$

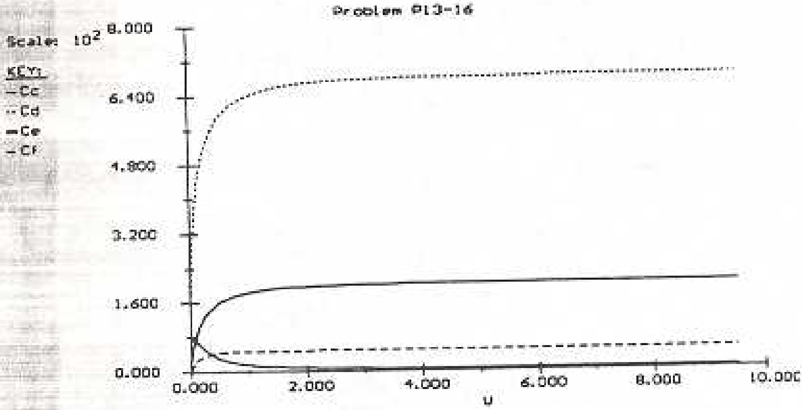
$$F_T = F_A + F_B + F_C + F_D + F_E + F_F$$

```
Problem P13-16
Equations:                                              Initial value
d(Ff)/d(V)=-2*r3b                                       0
d(Fa)/d(V)=r1a+r2a+2*r4c/3                              0.5
d(Fb)/d(V)=1.25*r1a+0.75*r2a+r3b                        0.5
d(Fc)/d(V)=-r1a+2*r3b+r4c                               0
d(Fd)/d(V)=-1.5*r1a-1.5*r2a-r4c                         0
d(Fe)/d(V)=-0.5*r2a-5*r4c/6                             0
Ft=Fa+Fb+Fc+Fd+Fe+Ff
r1a=-5*8*(Fa/Ft)*(Fb/Ft)^2
r2a=-2*4*(Fa/Ft)*(Fb/Ft)
r4c=-5*3.175*(Fc/Ft)*(Fa/Ft)^(2/3)
r3b=-10*8*(Fc/Ft)^2*(Fb/Ft)
Ca=0.1*Fa/Ft
Cb=0.1*Fb/Ft
Cc=0.1*Fc/Ft
Cd=0.1*Fd/Ft
Ce=0.1*Fe/Ft
Cf=0.1*Ff/Ft
Scd=Cc/(Cd+0.00001)
Sde=Cd/(Ce+0.00001)
Sef=Ce/(Cf+0.00001)
V0 = 0,    Vf = 10
```

```
Problem P13-16
Variable   Initial value   Maximum value   Minimum value   Final value
V          0               9.5             0               9.5
Ff         0               0.0518155       0               0.0518155
Fa         0.5             0.5             4.37412e-08     4.37412e-08
Fb         0.5             0.5             0.0716595       0.0716595
Fc         0               0.0812645       0               0.00305004
Fd         0               0.75            0               0.75
Fe         0               0.222567        0               0.222567
Ft         1               1.0992          1               1.09909
r1a        -5              -6.767e-09      -5              -6.767e-09
r2a        -2              -2.0758e-08     -2              -2.0758e-08
r4c        -0              -0              -0.554504       -5.1352e-07
r3b        -0              -0              -0.144083       -4.01674e-05
Ca         0.05            0.05            3.97976e-09     3.97976e-09
Cb         0.05            0.05            0.00651988      0.00651988
Cc         0               0.00779971      0               0.000277506
Cd         0               0.0682381       0               0.0682381
```

P13-16 cont'd

```
Ce      0     0.0202501     0     0.0202501
Cf      0     0.00471439    0     0.00471439
Scd     0     0.366108      0     0.00406613
Sde     0     7.03231       0     3.36811
Sef     0     8.0226        0     4.28629
```



Exit concentrations :

$C_A = 3.98e-9 mol/dm^3$

$C_B = 0.0065$

$C_C = 0.000277$

$C_D = 0.068$

$C_E = 0.0202$

$C_F = 0.0047$

Selectivites :

$S_{CD} = 0.004$

$S_{DE} = 3.368$

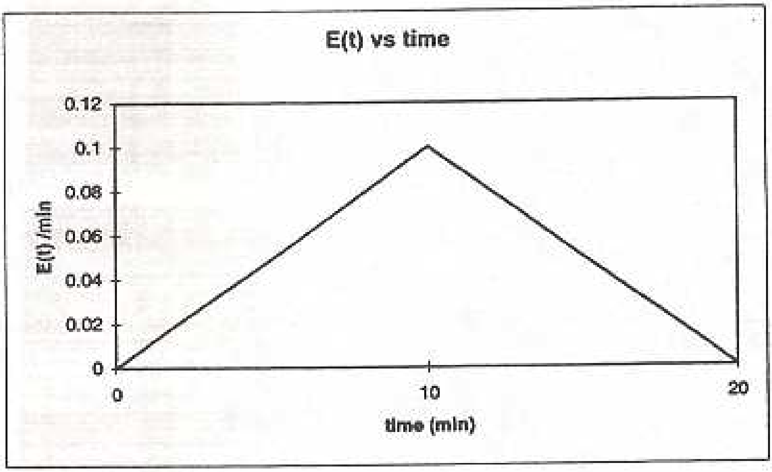
$S_{EF} = 4.286$

Segregation	Maximixmum M	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 cont'd

Part (d)



E(t) = IF (t ≤ 10) THEN (0.01 t) ELSE (IF (t ≥ 20) THEN (0) ELSE (0.2 - 0.01 t))

Segregation	Maximum M	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).

Problem P13-17$_B$

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 cont'd

Part (a)

Segregated model

$$\frac{dC_A}{dt} = -k_{D1}.C_A.C_B^2 - 3k_{E2}.C_A.C_D$$

$$\frac{dC_B}{dt} = -2k_{D1}.C_A.C_B^2 - k_{F3}.C_B.C_C^2$$

$$\frac{dC_C}{dt} = k_{D1}.C_A.C_B^2 + k_{E2}.C_A.C_D - 2k_{F3}.C_B.C_C^2$$

$$\frac{dC_D}{dt} = k_{D1}.C_A.C_B^2 - 2k_{E2}.C_A.C_D + k_{F3}.C_B.C_C^2$$

$$\frac{dC_E}{dt} = k_{E2}.C_A.C_D$$

$$\frac{dC_F}{dt} = k_{F3}.C_B.C_C^2$$

$$\frac{d\overline{C}_A}{dt} = C_A.E(t) \qquad \frac{d\overline{C}_C}{dt} = C_C.E(t) \qquad \frac{d\overline{C}_E}{dt} = C_E.E(t)$$

$$\frac{d\overline{C}_B}{dt} = C_B.E(t) \qquad \frac{d\overline{C}_D}{dt} = C_D.E(t) \qquad \frac{d\overline{C}_F}{dt} = C_F.E(t)$$

$$S_{CD} = \frac{\overline{C}_C}{\overline{C}_D} \qquad S_{DE} = \frac{\overline{C}_D}{\overline{C}_E} \qquad S_{EF} = \frac{\overline{C}_E}{\overline{C}_F}$$

P13-17 cont'd

```
Problem P13-17
Equations:                                                               Initial value
d(Ca)/d(t)=(-kd1*Ca*(Cb^2))-(3*ke2*Ca*Cd)                                1.5
d(Cb)/d(t)=-(2*kd1*Ca*(Cb^2))-(kf3*Cb*(Cc^2))                            2
d(Cd)/d(t)=(kd1*Ca*(Cb^2))-(2*ke2*Ca*Cd)+(kf3*Cb*(Cc^2))                 0
d(Cc)/d(t)=(kd1*Ca*(Cb^2))+(ke2*Ca*Cd)-(2*kf3*Cb*(Cc^2))                 0
d(Ce)/d(t)=ke2*Ca*Cd                                                     0
d(Cabar)/d(t)=Ca*E                                                       1e-05
d(Cf)/d(t)=kf3*Cb*(Cc^2)                                                 0
d(Cbbar)/d(t)=Cb*E                                                       1e-05
d(Ccbar)/d(t)=Cc*E                                                       1e-05
d(Cdbar)/d(t)=Cd*E                                                       1e-05
d(Cebar)/d(t)=Ce*E                                                       1e-05
d(Cfbar)/d(t)=Cf*E                                                       1e-05
kd1=0.25
ke2=0.1
kf3=5
E2=(-2.104*(t^4))+(17.037*(t^3))-(50.247*(t^2))+(62.964*(
   t))-27.402
E1=(-2.104*(t^4))+(4.167*(t^3))-(1.596*(t^2))+(0.353*(t))
   -0.004
Scd=Ccbar/Cdbar
Sde=Cdbar/Cebar
Sef=Cebar/Cfbar
E=if(t<=1.26)then(E1)else(E2)
t0 = 0,   tf = 2.416
```

```
Problem P13-17
Variable     Initial value   Maximum value   Minimum value   Final value
t            0               2.416           0               2.416
Ca           1.5             1.5             0.579486        0.579486
Cb           2               2               0.511616        0.511616
Cd           0               0.674325        0               0.674325
Cc           0               0.197054        0               0.135425
Ce           0               0.106456        0               0.106456
Cabar        1e-05           0.818879        -2.17501e-05    0.818879
Cf           0               0.286089        0               0.286089
Cbbar        1e-05           0.767019        -3.22628e-05    0.767019
Ccbar        1e-05           0.162801        9.89375e-06     0.162801
Cdbar        1e-05           0.59962         9.89383e-06     0.59962
Cebar        1e-05           0.0529211       9.99996e-06     0.0529211
Cfbar        1e-05           0.198527        9.99999e-06     0.198527
kd1          0.25            0.25            0.25            0.25
ke2          0.1             0.1             0.1             0.1
kf3          5               5               5               5
E2           -27.402         0.95674         -27.402         -3.135e-05
E1           -0.004          0.958623        -21.3885        -21.3885
Scd          1               1               0.271507        0.271507
Sde          1               46.651          0.989386        11.3304
Sef          1               1               0.154929        0.266568
E            -0.004          0.958623        -0.004          -3.135e-05
```

P13-17 cont'd

Exit concentrations :

$\overline{C}_A = 0.819 mol/dm^3$

$\overline{C}_B = 0.767$

$\overline{C}_C = 0.163$

$\overline{C}_D = 0.600$

$\overline{C}_E = 0.053$

$\overline{C}_F = 0.199$

Selectivities :

$S_{CD} = 0.272$

$S_{DE} = 11.330$

$S_{EF} = 0.267$

Part (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).

$$\frac{dC_A}{d\lambda} = -\sum r_{iA} + (C_A - C_{AO})\frac{E(\lambda)}{1-F(\lambda)}$$

$$\frac{dC_A}{d\lambda} = -(-k_{D1}.C_A.C_B^2 - 3k_{E2}.C_A.C_D) + \left((C_A - C_{AO})\frac{E(\lambda)}{1-F(\lambda)}\right)$$

The same applies to the equations for the other species as in Part (a).

```
Problem P13-17
Equations:                                                          Initial value
d(Ca)/d(t)=((-kd1*Ca*(Cb^2))-(3*ke2*Ca*Cd))-((Ca-Cao)*E/(          1.5
    1-F))
d(Cb)/d(t)=(-(2*kd1*Ca*(Cb^2))-(kf3*Cb*(Cc^2)))-((Cb-Cbo)          2
    *E/(1-F))
d(Cd)/d(t)=((kd1*Ca*(Cb^2))-(2*ke2*Ca*Cd)+(kf3*Cb*(Cc^2))          0
    )-((Cd-Cdo)*E/(1-F))
d(F)/d(t)=-E                                                        0.999
d(Cc)/d(t)=((kd1*Ca*(Cb^2))+(ke2*Ca*Cd)-(2*kf3*Cb*(Cc^2))          0
    )-((Cc-Cco)*E/(1-F))
d(Ce)/d(t)=(ke2*Ca*Cd)-((Ce-Ceo)*E/(1-F))                           0
d(Cf)/d(t)=(kf3*Cb*(Cc^2))-((Cf-Cfo)*E/(1-F))                       0
kd1=0.25
ke2=0.1
Cao=1.5
kf3=5
Cbo=2
```

P13-17 cont'd

```
Cdo=0
Cco=0
Ceo=0
Cfo=0
Sef=Ce/(Cf+0.00001)
Scd=Cc/(Cd+0.00001)
Sde=Cd/(Ce+0.00001)
lam=2.416-t
E2=(-2.104*(lam^4))+(17.037*(lam^3))-(50.247*(lam^2))+(62
   .964*(lam))-27.402
E1=(-2.104*(lam^4))+(4.167*(lam^3))-(1.596*(lam^2))+(0.35
   3*(lam))-0.004
E=if(lam<=1.26)then(E1)else(E2)
t0 = 0,   tf = 2.416
Problem P13-17
Variable          Initial value  Maximum value  Minimum value  Final value
t                 0              2.416          0              2.416
Ca                1.5            1.5            0.846576       0.846576
Cb                2              2              0.824205       0.824205
Cd                0              0.576213       0              0.576213
F                 0.999          0.999          0.00932193     0.00932193
Cc                0              0.169878       0              0.161736
Ce                0              0.0538424      0              0.0538424
Cf                0              0.192001       0              0.192001
kd1               0.25           0.25           0.25           0.25
ke2               0.1            0.1            0.1            0.1
Cao               1.5            1.5            1.5            1.5
kf3               5              5              5              5
Cbo               2              2              2              2
Cdo               0              0              0              0
Cco               0              0              0              0
Ceo               0              0              0              0
Cfo               0              0              0              0
Sef               0              0.70501        0              0.280412
Scd               0              1.00008        0              0.280683
Sde               0              690.225        0              10.6999
lam               2.416          2.416          0              0
E2                -3.135e-05     0.95674        -27.402        -27.402
E1                -21.3885       0.958963       -21.3885       -0.004
E                 -3.135e-05     0.958963       -0.004         -0.004
```

Exit concentrations :

$C_A = 0.847 mol / dm^3$

$C_B = 0.824$

$C_C = 0.162$

$C_D = 0.576$

$C_E = 0.054$

$C_F = 0.192$

Selectivities :

$S_{CD} = 0.281$

$S_{DE} = 10.7$

$S_{EF} = 0.280$

P13-17 cont'd

Part (c)

Ideal CSTR

$$t_m = \tau \quad \text{and} \quad E(t) = \frac{e^{-t/\tau}}{\tau}$$

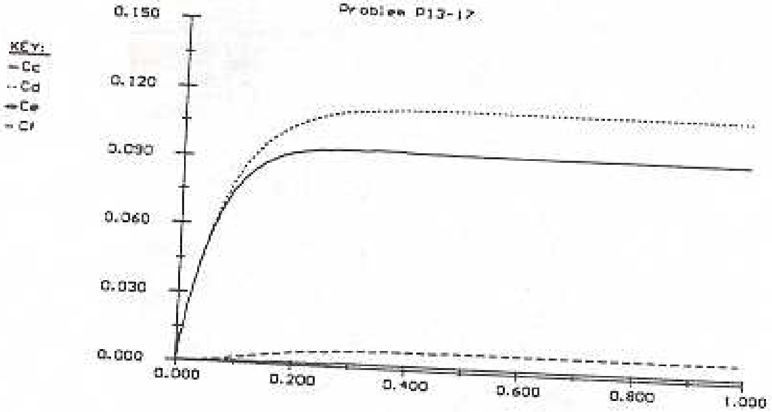
$$\frac{dC_A}{dt} = \upsilon.(C_{AO} - C_A) + r_A \qquad \text{where} \quad \begin{aligned} r_A &= (-k_{D1}.C_A.C_B^2 - 2k_{E2}.C_A.C_D) \\ \upsilon_O &= \upsilon \end{aligned}$$

and so on for the other species.

```
Problem P13-17
Equations:                                                              Initial value
d(Ca)/d(t)=(vo*(Cao-Ca))+((-kd1*Ca*(Cb^2))-(3*ke2*Ca*Cd))               1.5
d(Cb)/d(t)=(vo*(Cbo-Cb))+(-(2*kd1*Ca*(Cb^2))-(kf3*Cb*(Cc^               2
   2)))
d(Cd)/d(t)=(vo*(Cdo-Cd))+((kd1*Ca*(Cb^2))-(2*ke2*Ca*Cd)+(               0
   kf3*Cb*(Cc^2)))
d(Cc)/d(t)=(vo*(Cco-Cc))+((kd1*Ca*(Cb^2))+(ke2*Ca*Cd)-(2*               0
   kf3*Cb*(Cc^2)))
d(Ce)/d(t)=(vo*(Ceo-Ce))+(ke2*Ca*Cd)                                    0
d(Cf)/d(t)=(vo*(Cfo-Cf))+(kf3*Cb*(Cc^2))                                0
vo=10
Cao=1.5
kd1=0.25
ke2=0.1
Cbo=2
kf3=5
Cdo=0
Cco=0
Ceo=0
Cfo=0
tau=5
Sef=Ce/(Cf+0.00001)
Scd=Cc/(Cd+0.00001)
Sde=Cd/(Ce+0.00001)
E=exp(-t/tau)/tau
t0 = 0,   tf = 1
```

P13-17 cont'd

```
Problem P13-17
Variable    Initial value   Maximum value   Minimum value   Final value
t           0               1               0               1
Ca          1.5             1.5             1.38621         1.38621
Cb          2               2               1.77393         1.77393
Cd          0               0.113856        0               0.113856
Cc          0               0.0949571       0               0.0947184
Ce          0               0.00157803      0               0.00157803
Cf          0               0.00795718      0               0.00795718
vo          10              10              10              10
Cao         1.5             1.5             1.5             1.5
kd1         0.25            0.25            0.25            0.25
ke2         0.1             0.1             0.1             0.1
Cbo         2               2               2               2
kf3         5               5               5               5
Cdo         0               0               0               0
Cco         0               0               0               0
Ceo         0               0               0               0
Cfo         0               0               0               0
tau         5               5               5               5
Sef         0               0.728226        0               0.198067
Scd         0               1.00009         0               0.831842
Sde         0               682.717         0               71.6961
E           0.2             0.2             0.163746        0.163746
```



Exit concentrations :

$C_A = 1.386 mol/dm^3$

$C_B = 1.774$

$C_C = 0.095$

$C_D = 0.114$

$C_E = 0.002$

$C_F = 0.008$

$S_{CD} = 0.832$

$S_{DE} = 71.100$

$S_{EF} = 0.198$

P13-17 cont'd

Ideal PFR

$t_m = \tau$ and RTD function $E(t) = \delta(t - \tau)$

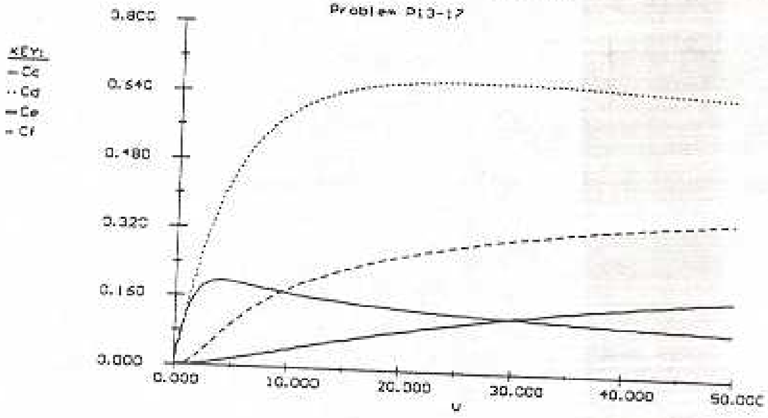
$$\frac{dC_A}{dV} = \frac{r_A}{\upsilon} \qquad \text{where} \qquad r_A = (-k_{D1}.C_A.C_B^2 - 2k_{E2}.C_A.C_D)$$

$$\upsilon_0 = \upsilon$$

and so on for the other species.

```
Problem P13-17
Equations:                                                      Initial value
d(Ca)/d(V)=((-kd1*Ca*(Cb^2))-(3*ke2*Ca*Cd))/vo                  1.5
d(Cb)/d(V)=(-(2*kd1*Ca*(Cb^2))-(kf3*Cb*(Cc^2)))/vo              2
d(Cd)/d(V)=((kd1*Ca*(Cb^2))-(2*ke2*Ca*Cd)+(kf3*Cb*(Cc^2))       0
   )/vo
d(Cc)/d(V)=((kd1*Ca*(Cb^2))+(ke2*Ca*Cd)-(2*kf3*Cb*(Cc^2))       0
   )/vo
d(Ce)/d(V)=(ke2*Ca*Cd)/vo                                       0
d(Cf)/d(V)=(kf3*Cb*(Cc^2))/vo                                   0
kf3=5
kd1=0.25
ke2=0.1
vo=10
Sef=Ce/(Cf+0.00001)
Scd=Cc/(Cd+0.00001)
Sde=Cd/(Ce+0.00001)
V0 = 0,   Vf = 50
Problem P13-17
Variable      Initial value  Maximum value  Minimum value  Final value
V             0              50             0              50
Ca            1.5            1.5            0.310006       0.310006
Cb            2              2              0.338482       0.338482
Cd            0              0.67513        0              0.651626
Cc            0              0.197055       0              0.105508
Ce            0              0.180102       0              0.180102
Cf            0              0.362141       0              0.362141
kf3           5              5              5              5
kd1           0.25           0.25           0.25           0.25
ke2           0.1            0.1            0.1            0.1
vo            10             10             10             10
Sef           0              0.71031        0              0.497311
Scd           0              1.00004        0              0.161912
Sde           0              695.865        0              3.6179
```

P13-17 cont'd



Exit concentrations :

$C_A = 0.310 mol / dm^3$
$C_B = 0.338$
$C_C = 0.106$
$C_D = 0.652$
$C_E = 0.180$
$C_F = 0.362$

Selectivites :

$S_{CD} = 0.162$
$S_{DE} = 3.618$
$S_{EF} = 0.497$

Segregated	Maximum M	CSTR	PFR
$S_{CD} = 0.272$	$S_{CD} = 0.281$	$S_{CD} = 0.832$	$S_{CD} = 0.162$
$S_{DE} = 11.330$	$S_{DE} = 10.7$	$S_{DE} = 71.100$	$S_{DE} = 3.618$
$S_{EF} = 0.267$	$S_{EF} = 0.280$	$S_{EF} = 0.198$	$S_{EF} = 0.497$

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.

P14-1

No soulution will be given.

Problem P14-2$_B$

Part (a)

The correlations between Re and Da show what flow conditions (characterised by Re) gives the greatest or smallest Da and hence dispersion. To minimise dispersion an Re of ~ 10 - 20 or Re > 10^5 gives the lowest value for Da. $Re = \frac{\rho . u . d}{\mu}$ the design of the vessel could be altered (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 the Re.

Part (b)

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 eqn 14-40, which can be tested experimentally by recording tracer concentrations with time and using the tanks in series model for a conversion comparison.

Part (c)

Verify when both models are equivalent , i.e. when the relation $B_O = 2\ (n-1)$ is valid, should give similar results.

Part (d)

Closed vessel dispersion model :

q is probably the most important term :

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = \sqrt{1 + \frac{4\tau k D_a}{UL}}$$

so the most important group of parameters is $\frac{k}{UL}$ wrt conversion.

For the ideal plug flow, tank in series and ideal CSTR models, k is the parameter to which conversion is most sensitive.

Part (e)

V = constant = $\pi.R^2L = 3.14*5^2*636 = 49951$ cm^3

gives $L = \dfrac{49951}{\pi * R^2}$

Figure 14-5 from the text book 3rd edn :

$$\text{Re}.Sc = \frac{u.D_t}{D_{AB}}$$

for values of Re.Sc > 10 :

Fig 14-5 gives dispersion coefficent $D_a = \dfrac{u^2 D_t^2}{192 * D_{AB}}$

$$Pe = \frac{U.L}{D_a}$$

1st order reaction : Damkohler no. Da = $\tau k = 5.15 * 0.25 = 1.288$

$$X = 1 - \frac{4q\exp\left(\frac{Pe_r}{2}\right)}{\left[(1+q)^2\exp\left(\frac{Pe_r q}{2}\right)\right] - \left[(1-q)^2\exp\left(\frac{-Pe_r q}{2}\right)\right]}$$

where $q = \sqrt{1 + \dfrac{4Da}{Pe_r}}$

P14-2 cont'd

Using Excel spreadsheet :

V (cm3)	U (cm/s)						
49951.28	0.01						
D_t(cm)	L(cm)	(Re)(Sc)	D_a (cm2/s)	Pe	Da	q	x
1	63600	1000	0.05	5.21	1.288	1.410	0.666
5	2544	5000	1.30	26.04	1.288	1.094	0.708
10	636	10000	5.21	52.08	1.288	1.048	0.716
20	159	20000	20.83	104.17	1.288	1.024	0.720
30	70.67	30000	46.88	156.25	1.288	1.016	0.721
40	39.75	40000	83.33	208.33	1.288	1.012	0.722
50	25.44	50000	130.21	260.42	1.288	1.010	0.722
60	17.67	60000	187.50	312.50	1.288	1.008	0.723
70	12.98	70000	255.21	364.58	1.288	1.007	0.723
80	9.94	80000	333.33	416.67	1.288	1.006	0.723
90	7.85	90000	421.88	468.75	1.288	1.005	0.723
100	6.36	100000	520.83	520.83	1.288	1.005	0.723

A velocity of 0.1 cm/s gives very large Pe values > 1000, and hence conversion cannot be calculated.

However a velocity of 0.01 cm/s gives a full range of results for 1 to 100 cm tube diameters.

It is clear that conversion increases with diameter, because the dispersion increases, better mixing. There is no diameter which provides a maximum or minimum conversion in this range except at the extreme values of 1 cm to 100 cm.

Part (f)

Open vessel : $\dfrac{\sigma^2}{t_m^{\,2}} = \dfrac{2}{Pe_r} + \dfrac{8}{Pe_r^{\,2}}$

from data : $\tau = \int_0^\infty tE(t)dt = 5.15\,\text{min}$

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)dt = \int_0^\infty t^2 E(t)dt - \tau^2 = 32.63 - 5.15^2 = 6.10\,\text{min}^2$$

<u>P14-2</u> cont'd

but $$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

$$\frac{\sigma^2}{\left(1 + \frac{2}{Pe_r}\right)^2 \tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^{\,2}}$$

Iterating gives $Pe_r = 5$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}}$$

$Da = \tau k = 5.15 * 0.25 = 1.2875$

$q = 1.425$

$$X = 1 - \frac{4q\exp\left(\frac{Pe_r}{2}\right)}{\left[(1+q)^2 \exp\left(\frac{Pe_r q}{2}\right)\right] - \left[(1-q)^2 \exp\left(\frac{-Pe_r q}{2}\right)\right]}$$

$$= 1 - \frac{4 * 1.425 * \exp\left(\frac{5}{2}\right)}{\left[(1+1.425)^2 \exp\left(\frac{5 * 1.425}{2}\right)\right] - \left[(1-1.425)^2 \exp\left(\frac{-5 * 1.425}{2}\right)\right]}$$

$= 0.665$

Closed model : $X = 68\ \%$

Open model : $X = 67\ \%$

Part (g)

$\alpha = 0.75$ $\beta = 0.15$

$V_s + V_d = V = 1.0\ \text{m}^3$

$\upsilon_o = \upsilon_s + \upsilon_b = 0.1\ \text{m}^3/\text{min}$

P14-2 cont'd

$$\alpha = \frac{V_s}{V} = 0.75$$

$$\beta = \frac{\upsilon_b}{\upsilon_o} = 0.15$$

$$V_s = \alpha V = 0.75 * 1 = 0.75 m^3$$

$$\upsilon_s = \upsilon_o - \upsilon_b = \upsilon_o - \upsilon_o\beta = 0.1 - (0.1*0.15) = 1-0.015 = 0.085\ m^3/min$$

$$\tau_s = \frac{V_s}{\upsilon_s} = \frac{0.75}{0.085} = 8.82\,\text{min}$$

$k = 0.28\ m^3kmol.min$, $C_{AO} = 2\ kmol/m^3$

$$C_{AS} = \frac{\sqrt{1+4\tau_s k C_{AO}}-1}{2\tau_s k} = 0.72 kmol/m^3$$

$$C_A = \frac{\upsilon_o - \upsilon_s}{\upsilon_o} C_{AO} + \frac{\upsilon_s}{\upsilon_o} C_{As} = \frac{0.1-0.085}{0.1} * 2 - \frac{0.085}{0.1} * 0.72 = 0.912$$

$X = 1 - \frac{0.912}{2.0} = 0.54$ cf o.51 as before.

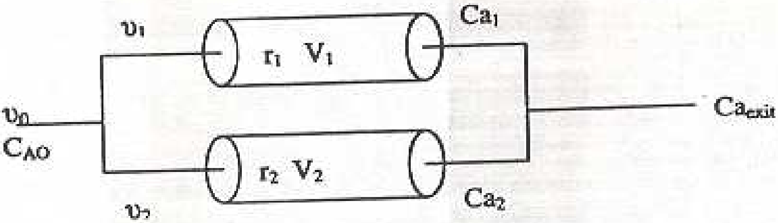
Part (h)

The model in Fig 14-14a, assumes a "faster" (channelling) reactor and a "slower" uniform reactor. There is a 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 14-14b 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 F9t) of the CSTR, giving a combined F(t).

$\theta_1 = \frac{\alpha}{\beta} = 0.5$ $\theta_2 = \frac{1-\alpha}{1-\beta} = 1.5$

P14-2 cont'd



$$\alpha = \frac{V_1}{V} \qquad \beta = \frac{\upsilon_1}{\upsilon} \qquad \tau = \frac{V}{\upsilon} = 5\,\text{min}$$

PFR mol balance : $\frac{dX}{dV} = -\frac{r_A}{F_{AO}}$

rate law : $-r_A = k.C_A^2$

Stoichiometry : liquid phase $C_A = C_{AO}(1 - X)$

2nd order PFR : $$\frac{V}{\upsilon} = \frac{1}{k.C_{AO}^2}\left[2\varepsilon(1+\varepsilon)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon^2)X}{1-X}\right]$$

$\varepsilon = y_{AO}.\delta$ $\qquad \delta = \frac{c}{a} + \frac{b}{a} - 1 = \frac{1}{2} + \frac{1}{2} - 1 = 0$

$\varepsilon = 0$

Determining α and β :

$$\frac{\alpha}{\beta} = \frac{V_1}{V}\frac{\upsilon_0}{\upsilon_1} = 0.5 \quad \rightarrow \quad V_1 = 2.5\,\upsilon_1$$

$$1 - \frac{V_1}{V} = 1.5\left(1 - \frac{\upsilon_1}{\upsilon}\right)$$

$$1 - 2.5\frac{\upsilon_1}{V} = 1.5 - 1.5\frac{\upsilon_1}{\upsilon}$$

$$V - 2.5\upsilon_1 = 1.5V - 7.5\upsilon_1$$

$$0.5V = 5\,\upsilon_1$$

$$V = 10\,\upsilon_1$$

gives $$\alpha = \frac{2.5\upsilon_1}{10\upsilon_1} = 0.25$$

$$\beta = \frac{V_1/2.5}{V/5} = \frac{5\alpha}{2.5} = 0.5$$

Now $$\tau = \frac{\tau_1 + \tau_2}{2} = \frac{V_1/\upsilon_1 + V_2/\upsilon_2}{2} = 5\,\text{min}$$

hence $$V_1/\upsilon_1 + V_2/\upsilon_2 = 10$$

but $V_1 = 2.5\,\upsilon_1$ → $V_2 = 7.5\,\upsilon_2$

gives $\tau_1 = 2.5$ min $\tau_2 = 7.5$ min

substituting into $$\frac{V}{\upsilon} = \frac{1}{k.C_{AO}^2}\left[2\varepsilon(1+\varepsilon)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon^2)X}{1-X}\right]$$

Reactor 1 : $$2.5 = \frac{1}{0.1 * 2^2}\left[\frac{X_1}{1-X_1}\right]$$

$$1 = \left[\frac{X_1}{1-X_1}\right] \quad \rightarrow \quad X_1 = 0.5$$

$$C_{A1} = C_{AO}(1 - X_1) = 2\,(1 - 0.5) = 1\ \text{mol/dm}^3$$

Reactor 2 : $$7.5 = \frac{1}{0.1 * 2^2}\left[\frac{X_2}{1-X_2}\right]$$

$$3 = \left[\frac{X_2}{1-X_2}\right] \quad \rightarrow \quad X_2 = 0.75$$

$$C_{A2} = C_{AO}(1 - X_2) = 2\,(1 - 0.75) = 0.5\ \text{mol/dm}^3$$

$$C_{Aexit} = \frac{C_{A1} + C_{A2}}{2} = \frac{1 + 0.5}{2} = 0.75 mol/dm^3$$

$$X = \frac{C_{AO} - C_A}{C_{AO}} = \frac{2 - 0.75}{2} = 0.625$$

Problem P14-3$_B$

Using the tank in series model :

second order reaction $X = \dfrac{2Da + 1 - \sqrt{4Da + 1}}{2Da}$ where $Da = k\tau C_{AO}$

$$C_A = C_{AO}(1 - X) \qquad X = \frac{C_{AO} - C_A}{C_{AO}}$$

Assume that $\tau = \tau_t$ and that in reactors modelled as more than one tank, that $\tau = \dfrac{\tau_t}{n}$

Number of tanks $n = \dfrac{\tau^2}{\sigma^2}$ 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 greates conversion.

Part (b)

Try :

Green & white and Maze & blue : $X_1 = 0.61$, $C_{A1} = 0.39 \rightarrow X_2 = 0.34$, $C_{A2} = 0.26 \rightarrow$
$X = 0.74$

P14-3 cont'd

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.

Problem 14-4$_B$

1st order, $k_1 = 0.0167$ /s, $\varepsilon = 0.5$, $d_p = 0.1$ cm,

$\nu = \frac{\mu}{\rho} = 0.01 cm^2 / s$ L = 10 cm, U = 1 cm/s

$\mathrm{Re} = \frac{\rho U d_p}{\mu} = \frac{1*0.1}{0.01} = 10$ $Sc = \frac{\nu}{D_{AB}}$ no data concerning D_{AB}

From packed bed correlation for D_a , and liquid phase region of graph,

gives $\frac{D_a \varepsilon}{U d_p} = 2$ approx. $\rightarrow$ $D_a = \frac{2 U d_p}{\varepsilon} = \frac{2*1*0.1}{0.5} = 0.4 cm^2 / s$

$$Pe_r = \frac{UL}{D_a} = \frac{1*10}{0.4} = 25$$

$$X = 1 - \frac{4q \exp\left(\frac{Pe_r}{2}\right)}{\left[(1+q)^2 \exp\left(\frac{Pe_r q}{2}\right)\right] - \left[(1-q)^2 \exp\left(\frac{-Pe_r q}{2}\right)\right]}$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}}$$

$Da = \tau k$ and $\tau = \frac{L}{U} = \frac{10}{1} = 10s$ $\rightarrow$ $Da = 10 * 0.0167 = 0.167$

$\rightarrow$ $q = 1.013$

P14-4 cont'd

$$X = 1 - \frac{4 * 1.013 * \exp\left(25/2\right)}{\left[(1+1.013)^2 \exp\left(25 * 1.013/2\right)\right] - \left[(1-1.013)^2 \exp\left(-25 * 1.013/2\right)\right]} = 0.15$$

Conversion X = 15 %

Problem P14-5$_A$

Part (a)

Assuming the Peclet-Bodenstein relation : $n = \frac{Bo}{2} + 1$

where $Bo = \frac{UL}{D_a}$

To estimate Bo, $\mathrm{Re} = \frac{du}{\nu} = \frac{5 * 2}{0.01} = 1000$

$$Sc = \frac{\nu}{D_{AB}} = \frac{0.01}{0.005} = 2$$

From gas phase dispersion correlation chart, $\frac{D_a}{u.d_t} = 8$

gives $D_a = 8*2*5 = 80\ \mathrm{cm}^2/\mathrm{s}$

$$Bo = \frac{2 * 200}{80} = 5$$

$$n = \frac{5}{2} + 1 = 3.5$$

Part (b)

Using individual reactor material balances :

Reactor 1 :

mol balance : $X = -\frac{r_A . V}{F_{AO}}$

P14-5 cont'd

rate law : $-r_A = k.C_A^2$

stoichiometry : $C_A = C_{AO}(1 - X_1)$ $\delta = 0$ and $\varepsilon = 0$ hence no volume change

$$X_1 = \frac{k.C_{AO}^2(1-X_1)^2}{\upsilon.C_{AO}} = \frac{25*0.01}{0.039}(1-X_1)^2$$

$X_1 = 6.366\,(1 - X_1)^2 \rightarrow$ 0.674

$C_{A1} = C_{AO}(1 - X_1) = 0.00326$ mol/dm^3

Reactor 2 : $$X_2 = \frac{k.C_{A1}\,(1-X_2)^2}{\upsilon} \rightarrow \frac{X_2}{(1-X_2)^2} = \frac{25*0.00326}{0.039} = 2.0897$$

$X_2 = 0.507$

$C_{A2} = C_{A1}(1 - X_2) = 0.00326\,(1 - 0.507) = 0.001607$ mol/dm^3

Reactor 3 : $$X_3 = \frac{k.C_{A2}\,(1-X_2)^2}{\upsilon} \rightarrow \frac{X_3}{(1-X_3)^2} = \frac{25*0.001607}{0.039} = 1.0302$$

$X_3 = 0.387$

$C_{A3} = C_{A2}(1 - X_3) = 0.001607\,(1 - 0.387) = 0.000985$ mol/dm^3

Reactor 4 : $$X_4 = \frac{k.C_{A3}\,(1-X_4)^2}{\upsilon} \rightarrow \frac{X_4}{(1-X_4)^2} = \frac{25*0.000985}{0.039} = 0.6315$$

$X_4 = 0.305$

$C_{A4} = C_{A3}(1 - X_4) = 0.000985\,(1 - 0.305) = 0.000685$ mol/dm^3

Bounds on conversion 3 tanks $$X = \frac{C_{AO} - C_{A3}}{C_{AO}} = 0.9015$$

4 tanks $$X = \frac{C_{AO} - C_{A4}}{C_{AO}} = 0.9315$$

Part (c)

Let U = 0.1 cm/s

Re = 50 Sc = 2

P14-5 cont'd

From gas phase dispersion correlation chart, $\frac{D_a}{u.d_t} = 0.5$

gives $D_a = 0.5*0.1*5 = 0.25\ cm^2/s$

$$Bo = \frac{0.1*200}{0.25} = 80$$

$n = \frac{80}{2} + 1 = 41$ probably giving a conversion ~ 99.99 %

Let $U = 100$ cm/s

Re = 50000 Sc = 2

From gas phase dispersion correlation chart, $\frac{D_a}{u.d_t} = 0.21$

gives $D_a = 0.21*100*5 = 105\ cm^2/s$

$$Bo = \frac{100*200}{105} = 190.5$$

$n = \frac{190.5}{2} + 1 = 96$ probably giving a conversion ~ 99.99 %

Part (d)

$$\mathrm{Re} = \frac{d_p u}{\nu} = \frac{0.2*4}{0.01} = 80$$

From packed bed disperaion correlation chart, $\frac{D_a \varepsilon}{u.d_p} = 0.55$

$$D_a = \frac{0.55*4*0.2}{0.4} = 1.1$$

$$Bo = \frac{4*200}{1.1} = 727$$

$n = \frac{727}{2} + 1 = 364.5$ probably giving a conversion ~ 99.99 %

P14-5 cont'd

Part (e)

Part (a)

$$\mathrm{Re} = \frac{du\rho}{\mu} = \frac{5*4*0.001}{0.1} = 0.2$$

$$Sc = \frac{\nu}{D_{AB}} = \frac{100}{5e-6} = 2*10^7$$

This is off the scale of the graph for liquid phase dispersion, hence D_a cannot be evaluated.

Problem P14-6$_A$

a) Closed:

$$\frac{\sigma^2}{tm^2} = \frac{2}{Pe_r} = \frac{2}{Pe_r^2}\left(1-e^{-Pe_r}\right)$$
$$= 7.54$$

Open:

$$\frac{\sigma^2}{tm^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2} = 11.68$$

b)

$$\tau = \frac{tm}{1+2/Pe_r} = 4.40$$
$$V_S = \tau * v_0 = 263.8dm^3$$
$$V_D = V - V_S = 156.2dm^3$$
$$\%deadvolume = \frac{156.2}{420} = 37.2\%$$

P14-6 cont'd

c)

$$X = 1 - \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2\exp(-Pe_r q/2)} = 0.570 dispersion$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = 1221$$

$$Da = k\tau = 0.927$$

$$n = \frac{\tau^2}{\sigma^2} = 4.35$$

$$x = 1 - \frac{1}{(1+\tau_i K)^n} = 0.568, \text{ tanks in series}$$

$$\text{PFR}: X = 1 - e^{-\tau k}$$

$$\text{CSTR}: X = 0.481$$

Part (d)

Tanks in series model : $n = \frac{\tau^2}{\sigma^2} = \frac{4.43^2}{2.4^2} = 3.407$

1st order reaction, so n can be a non-integer : $X = 1 - \frac{1}{(1+\tau k)^n}$

P14-6 cont'd

$$X = 1 - \frac{1}{\left(1 + \frac{\tau}{n}k\right)^{n}} = 1 - \frac{1}{\left(1 + \frac{4.43}{3.407}0.18\right)^{3.407}} = 0.51$$

PFR : $X = 1 - e^{-\tau k} = 1 - e^{-Da} = 1 - e^{-0.797} = 0.55$

CSTR : $X = \frac{\tau k}{1+\tau k} = \frac{0.797}{1+0.797} = 0.44$

	X
Dispersion	53 %
Tank in series	51 %
PFR	55 %
CSTR	44 %

Problem P14-7$_A$

1st order , irreversible, pulse tracer test $\rightarrow \sigma^2 = 65\ s^2$ and $t_m = 10$ s

For a 1st order reaction, PFR : $X = 1 - e^{-\tau k} = 0.98$

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.

Therefore assume closed vessel dispersion model :

$$t_m = \tau = 10\ s$$

$$k = -\frac{\ln(1-X)}{\tau} = -\frac{\ln(1-0.98)}{10} = 0.39 s^{-1}$$

$$\frac{\sigma^2}{t_m{}^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r{}^2}\left(1 - e^{Pe_r}\right) = \frac{65}{10^2} = 0.65$$

P14-7 cont'd

iterating → $Pe_r = 1.5$

$$X = 1 - \frac{4q\exp\left(\frac{Pe_r}{2}\right)}{\left[(1+q)^2\exp\left(\frac{Pe_r q}{2}\right)\right] - \left[(1-q)^2\exp\left(\frac{-Pe_r q}{2}\right)\right]}$$

$Da = \tau k = 10 * 0.39 = 3.9$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = \sqrt{1 + \frac{4 * 3.9}{1.5}} = 3.376$$

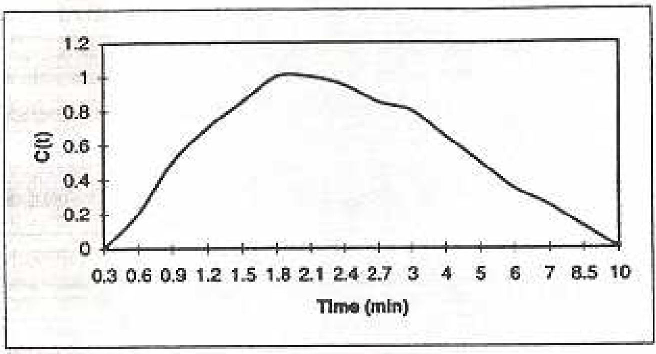
$$X = 1 - \frac{4 * 3.376\exp\left(\frac{1.5}{2}\right)}{\left[(1+3.376)^2\exp\left(\frac{1.5 * 3.376}{2}\right)\right] - \left[(1-3.375)^2\exp\left(\frac{-1.5 * 3.376}{2}\right)\right]} = 0.88$$

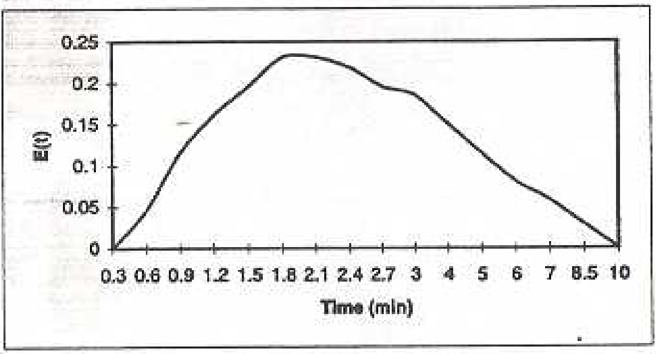
Conversion for the real reactor assuming the closed dispersion model is some what less than for the ideal PFR.

Problem P14-8_B

t (min)	C(t)	E(t)	t.E(t)	(t - tm)^2.E(t)
0.3	0	0	0.000	0.000
0.6	0.2	0.046	0.028	0.444
0.9	0.5	0.115	0.104	0.907
1.2	0.7	0.161	0.193	1.013
1.5	0.85	0.196	0.294	0.956
1.8	1	0.231	0.416	0.841
2.1	1	0.231	0.485	0.597
2.4	0.95	0.219	0.526	0.375
2.7	0.85	0.196	0.529	0.199
3	0.8	0.185	0.555	0.093
4	0.65	0.15	0.600	0.013
5	0.5	0.115	0.575	0.192
6	0.35	0.081	0.486	0.426
7	0.25	0.058	0.406	0.629
8.5	0.125	0.029	0.247	0.666
10	0	0	0.000	0.000

P14-8 cont'd





$$E(t) = \frac{C9t)}{\int_0^\infty C(t)dt} = \frac{C(t)}{4.335}$$

$$t_m = \int_0^\infty t.E(t).dt = 3.708\,\text{min}$$

Part (b)

Choosing the tanks in series model :

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t).dt = 4.144\,\text{min}^2$$

$$n = \frac{t_m^2}{\sigma^2} = \frac{3.708^2}{4.144} = 3.318\tan ks.$$

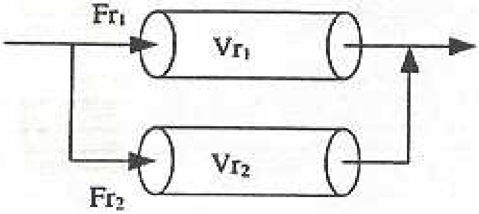
P14-8 cont'd

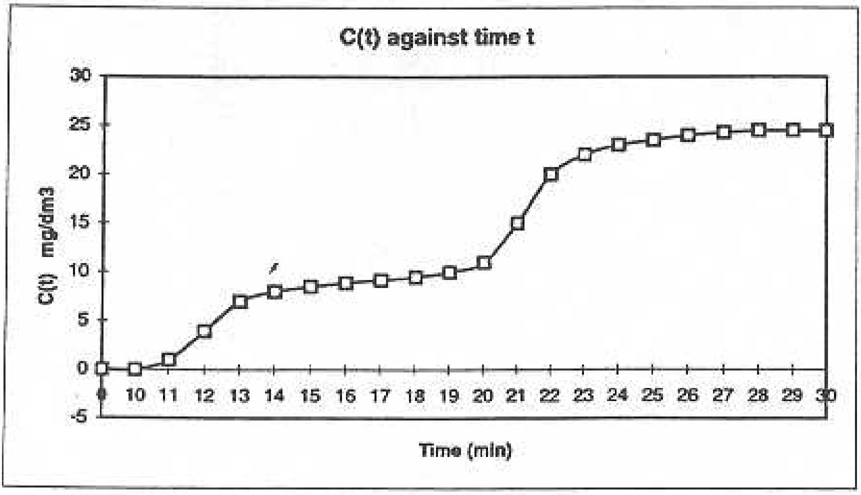
Part (c) No solution will be given.

Problem P14-9$_C$

Part (a)

Plug flow reactors in parallel.





P14-9 cont'd

time (min)	C(t)	E(t)	X(t)	X(t)E(t)	F(t)	tE(t)	t^2E(t)
0	0	0	0	0.0000	0	0	0
10	0	0	0.5	0.0000	0	0	0
11	1	0.0034	0.52	0.0018		0.0374	0.4114
12	4	0.0138	0.5454	0.0075		0.1656	1.9872
13	7	0.0241	0.5652	0.0136	0.03097	0.3133	4.0729
14	8	0.0276	0.5833	0.0161		0.3864	5.4096
15	8.5	0.0293	0.6	0.0176		0.4395	6.5925
16	8.9	0.0307	0.6154	0.0189	0.1251	0.4912	7.8592
17	9.2	0.0317	0.6296	0.0200		0.5389	9.1613
18	9.5	0.0327	0.6429	0.0210		0.5886	10.5948
19	10	0.0345	0.6552	0.0226	0.2327	0.6555	12.4545
20	11	0.0379	0.6667	0.0253		0.758	15.16
21	15	0.0517	0.6774	0.0350		1.0857	22.7997
22	20	0.0689	0.6875	0.0474	0.3866	1.5158	33.3476
23	22	0.0758	0.697	0.0528		1.7434	40.0982
24	23	0.0793	0.7059	0.0560		1.9032	45.6768
25	23.5	0.081	0.7143	0.0579	0.6434	2.025	50.625
26	24	0.0827	0.7222	0.0597		2.1502	55.9052
27	24.3	0.838	0.7297	0.6115		22.626	610.902
28	24.5	0.0845	0.7368	0.0623	0.9206	2.366	66.248
29	24.5	0.0845	0.7436	0.0628		2.4505	71.0645
30	24.5	0.0845	0.75	0.0634	1	2.535	76.05

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} = \frac{C(t)}{290.1} \qquad F(t) = \int_0^t E(t)dt$$

Part (b)

$$\frac{V_{r1}}{V_{total}} = \frac{\upsilon\int_0^{20} C(t)dt}{\upsilon\int_{10}^{30} C(t)dt} = \frac{71.5}{290.1} = 0.25$$

$V_{r1} = 0.25\ V_{total}$

$$\frac{F_{r1}}{F_{total}} - \frac{\upsilon C_{r1}}{\upsilon C_{total}} = \frac{9.0}{24.5} = 0.37$$

$F_{r1} = 0.37\ F_{total}$

Part (c)

PFR :

$$\frac{dC_A}{dt} = -k.C_A^2$$

$$\frac{1}{C_A} - \frac{1}{C_{AO}} = kt$$

$$\frac{1}{C_{AO}}\left(\frac{1}{1-X} - 1\right) = kt$$

$$X = 1 - \frac{1}{1+kC_{AO}t} = \frac{kC_{AO}t}{1+kC_{AO}t}$$

$$X = 1 - \frac{1}{1+\frac{(0.1\,\text{min})(1m^3)}{(0.06m^3/\text{min})}} = 0.625$$

Part (d)

Segregation model : $\overline{X} = \int_0^{\infty} X(t)E(t)$

$$X(t) = \frac{kC_{AO}t}{1+kC_{AO}t}$$

$$\overline{X} = 0.69$$

Part (e)

Maximum mixedness model :

Using Euler's method for numerical integration. Start with $\lambda = 30$ min and X = 0

λ (min)	X
30	0
28	0.2
25	0.2557
22	0.3357
19	0.4228
16	0.4782
13	0.5242
10	0.5921

P14-9 cont'd

$$X_{i+1} = X_i + (\Delta\lambda)\left[\frac{X(\lambda_i)}{1-F(\lambda_i)}X_i - k.C_{AO}(1-X_i)^2\right]$$

$X = 0.59$

Part (f)

Dispersion model : $\int_0^\infty E(t)dt = 23.1307$ $\quad \tau = \frac{V}{\upsilon} = \frac{1m^3}{0.06m^3/\min} = 16.7\min$

$$\int_0^\infty t^2 E(t)dt = 557.969$$

$\sigma^2 = 557.969 - (23.1307)+2+ = 22.94$

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r^2}\left[Pe_r - 1 + e^{-Per}\right] = \frac{22.94}{16.7^2} = 0.08258$$

$Pe_r = 23$

$Da = k.C_{AO}.\tau = 0.1*23.1307 = 2.313$

$$q = \sqrt{1+\frac{4Da}{Pe_r}} = \sqrt{1+\frac{4*2.312}{23}} = 1.18$$

$$\frac{Pe_r q}{2} = \frac{23*1.18}{2} = 13.6$$

$$X = 1 - \frac{4q\exp\left(Pe_r/2\right)}{\left[(1+q)^2\exp\left(Pe_r q/2\right)\right] - \left[(1-q)^2\exp\left(-Pe_r q/2\right)\right]}$$

$$X = 1 - \frac{4*1.18*\exp\left(23/2\right)}{\left[(1+1.18)^2\exp(13.6)\right] - \left[(1-1.18)^2\exp(-13.6)\right]}$$

$X = 0.88$

Summary :

	Conversion
PFR with bypass	0.63
Segregation	0.69
Maximum mixedness	0.59
Dispersion	0.88

Problem P14-11$_B$

Given : 2nd order irreversible reaction, isothermal, $V = 1000\ dm^3$ $\upsilon_O = 1\ dm^3/s$ $k = 0.005\ dm^3/mol.s$ $C_{AO} = 10\ mol/dm^3$

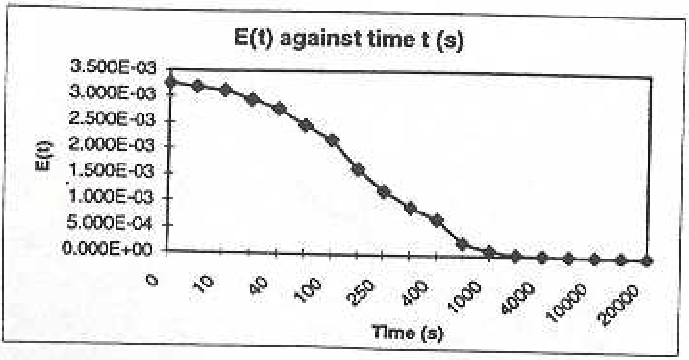
Part (a)

(1) Maximum segregation :

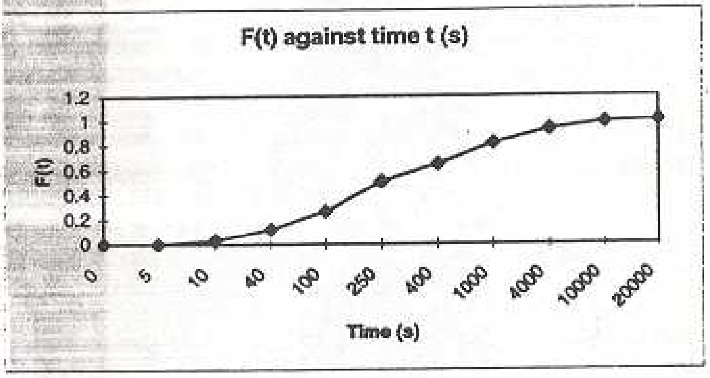
$$X = \frac{kC_{Ao}t}{1+kC_{Ao}t} = \frac{0.005*10*t}{1+(0.005*10*t)}$$

$$\overline{X} = \int_0^\infty X(t)E(t)dt = 0.868$$

t	E(t) (/s)	X(t)	X(t)E(t)	F(t)	tE(t)	t^2E(t)
0	3.250E-03	0.000	0.00E+00		0.000E+00	0.00
5	3.187E-03	0.200	6.37E-04		1.594E-02	0.08
10	3.124E-03	0.333	1.04E-03	0.032	3.124E-02	0.31
25	2.945E-03	0.556	1.64E-03		7.363E-02	1.84
40	2.776E-03	0.667	1.85E-03	0.118	1.110E-01	4.44
70	2.468E-03	0.778	1.92E-03		1.728E-01	12.09
100	2.194E-03	0.833	1.83E-03	0.265	2.194E-01	21.94
175	1.637E-03	0.897	1.47E-03		2.865E-01	50.13
250	1.224E-03	0.926	1.13E-03	0.51	3.060E-01	76.50
325	9.184E-04	0.942	8.65E-04		2.985E-01	97.01
400	6.913E-04	0.952	6.58E-04	0.648	2.765E-01	110.61
700	2.366E-04	0.972	2.30E-04		1.656E-01	115.93
1000	9.755E-05	0.980	9.56E-05	0.818	9.755E-02	97.55
2500	2.691E-05	0.992	2.67E-05		6.728E-02	168.19
4000	1.839E-05	0.995	1.83E-05	0.928	7.356E-02	294.24
7000	8.689E-06	0.997	8.66E-06		6.082E-02	425.76
10000	4.104E-06	0.998	4.10E-06	0.984	4.104E-02	410.40
15000	1.176E-06	0.999	1.17E-06		1.764E-02	264.60
20000	3.369E-07	0.999	3.37E-07	1	6.738E-03	134.76



P14-11 cont'd



(2) Maximum mixedness : $F(t)=\int_0^{\infty} E(t)dt$

$$X_{i+1}=X_i+(\Delta\lambda)\left[\frac{X(\lambda_i)}{1-F(\lambda_i)}X_i-k.C_{A0}(1-X_i)^2\right]$$

When t is small, the plot E(t) vs t is very much a straight line. Therefore we can interpolate to obtain intermediate values of E(t).

t	E(t)	F(t)
0	3.25e-3	
5	3.187e-3	
10	3.124e-3	0.032
15	3.064e-3	
20	3.005e-3	0.062
25	2.945e-3	
30	2.889e-3	0.091
35	2.832e-3	
40	2.776e-3	0.118
45	2.766e-3	
50	2.673e-3	0.143
55	2.622e-3	
60	2.570e-3	0.169
65	2.519e-3	
70	2.468e-3	0.194

P14-11 cont'd

λ	X
70	0
60	0.5
50	0.61
40	0.67
30	0.70
20	0.72
10	0.74
0	0.75

$X = 0.75$

Part (b)

Tanks in series : $n = \frac{\tau^2}{\sigma^2}$ $\tau = \frac{V}{\upsilon_0} = \frac{1000}{1} = 1000s$

$$\int_0^\infty tE(t)dt = 995$$

$$\int_0^\infty t^2E(t)dt = 5.656e6$$

$$n = \frac{\tau^2}{\sigma^2} = \frac{(10^3)^2}{4.666e6} = 0.214$$

$$X = 1 - \frac{1}{(1+\tau_i k)^n} = 1 - \frac{1}{\left(1+\frac{\tau}{n}k\right)^n} = 1 - \frac{1}{\left(1+\frac{1000}{0.214}0.005\right)^{0.214}}$$

$X = 0.495$

Part (c)

Two CSTR's in parallel

Assume the two CSTR's are equal in volume

$$V = \frac{F_{A0}X}{-r_A} = \frac{\upsilon_0 X}{k.C_{A0}(1-X)^2}$$

P14-11 cont'd

with $V_1 = V_2 = \frac{V}{2}$ and $\upsilon_{01} = \upsilon_{02} = \frac{\upsilon_0}{2}$, the conversion X, will be the same as for one CSTR with volume V and flowrate υ_O .

$$V = \frac{\upsilon_0 X}{k.C_{A0}(1-X)^2}$$

$$\frac{X}{(1-X)^2} = \frac{VkC_{A0}}{\upsilon_0} = \frac{1000)0.005*10}{1} = 50$$

gives X = 0.868 but iteration (or could solve the quadratic)

Part (d)

For a CSTR $V = \frac{\upsilon_0 X}{k.C_{A0}(1-X)^2}$

From Part (c) X = 0.868

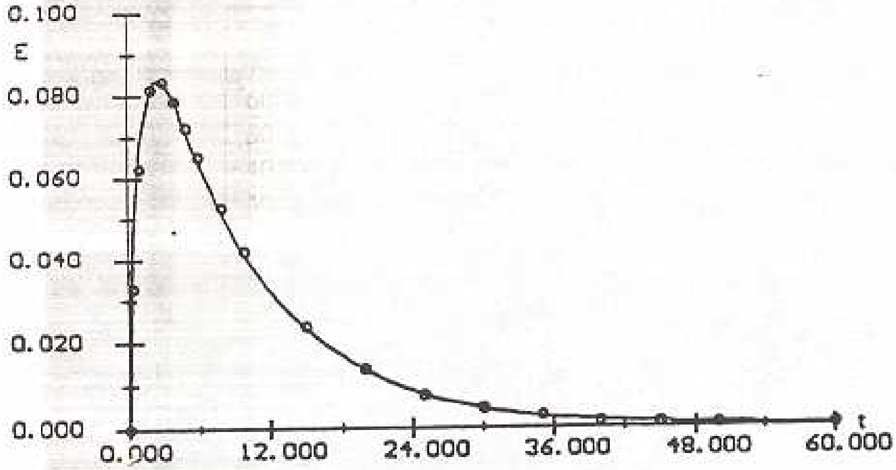
For a PFR : $X = \frac{kC_{A0}t}{1+kC_{A0}t}$ For $t = \tau$, $X_{CSTR} = 0.868$, $X_{PFR} = 0.980$

Summary :

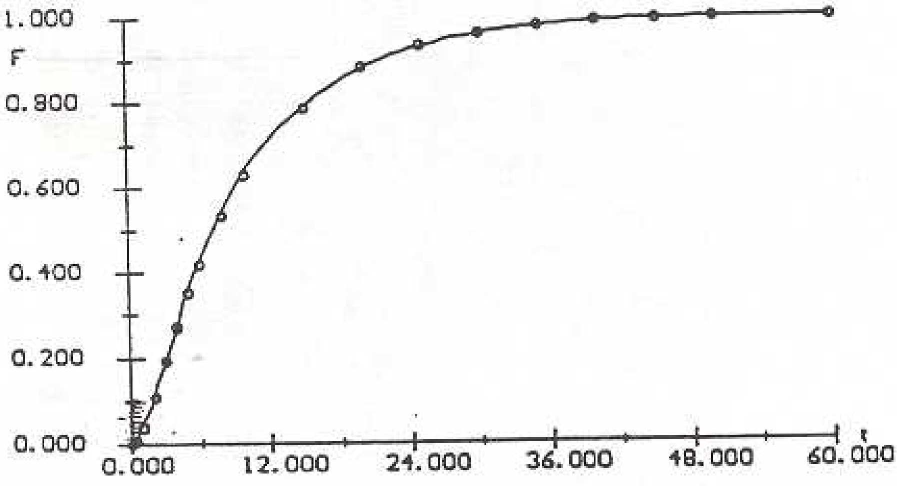
	Conversion, X
Maximum segregation	0.868
Minimum segregation	0.75
Tanks in series	0.5
2 CSTR's in parallel	0.868
Single CSTR	0.868
Single PFR	0.980

(a) Plot E(t) vs t

P14-13

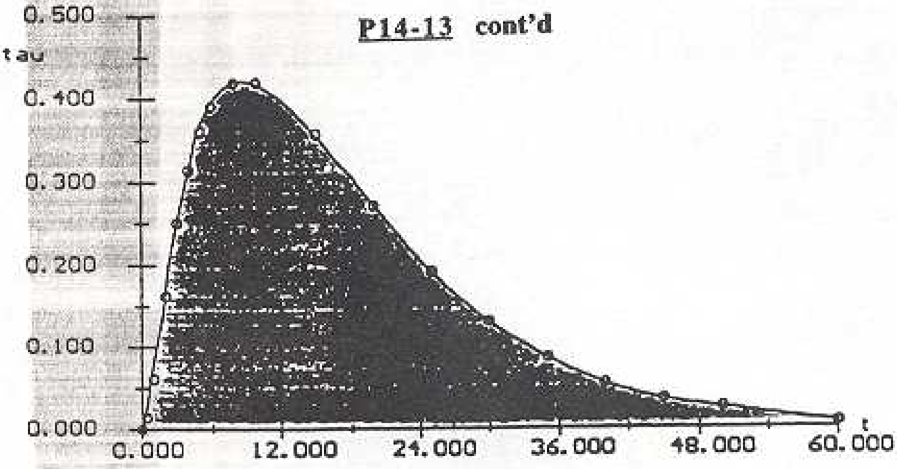


(b) Plot F(t) vs t



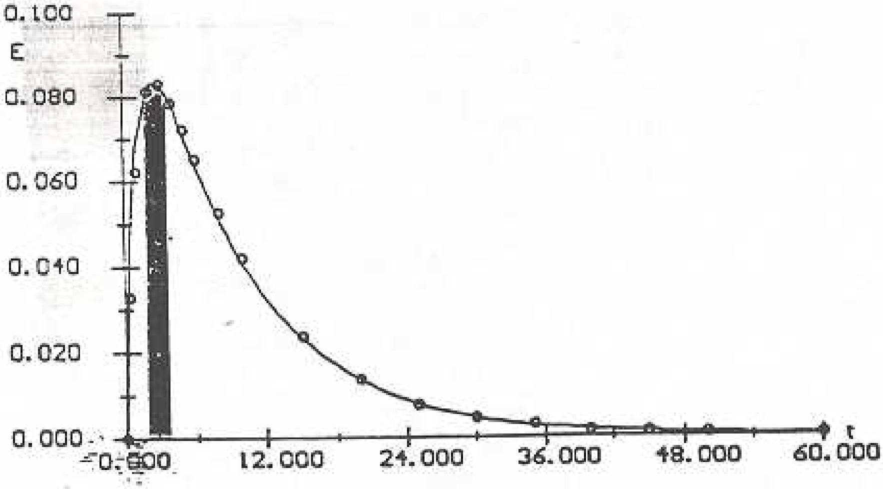
(c) Find t_m

P14-13 **cont'd**



$$t_m = \tau = \int_0^\infty tE(t)dt = 9.95$$

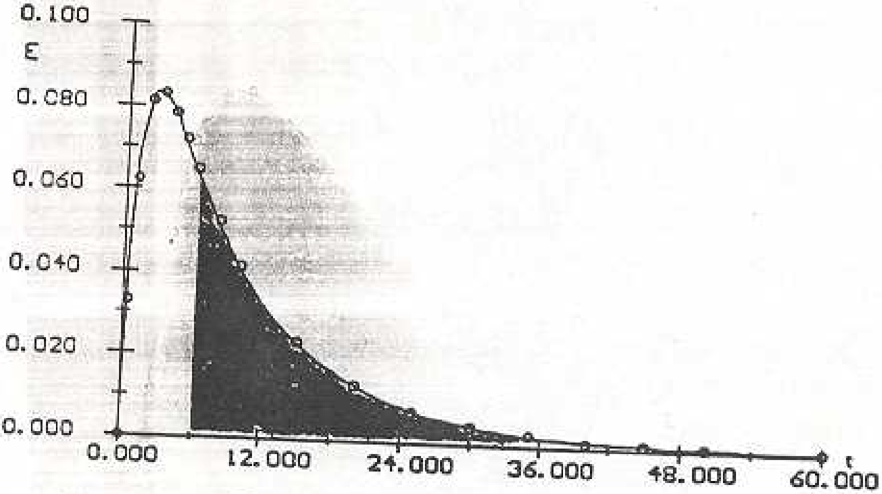
(d) Fraction that spends between 2 and 4 minutes



$$Fract = \int_2^4 tE(t)dt = 16.3\%$$

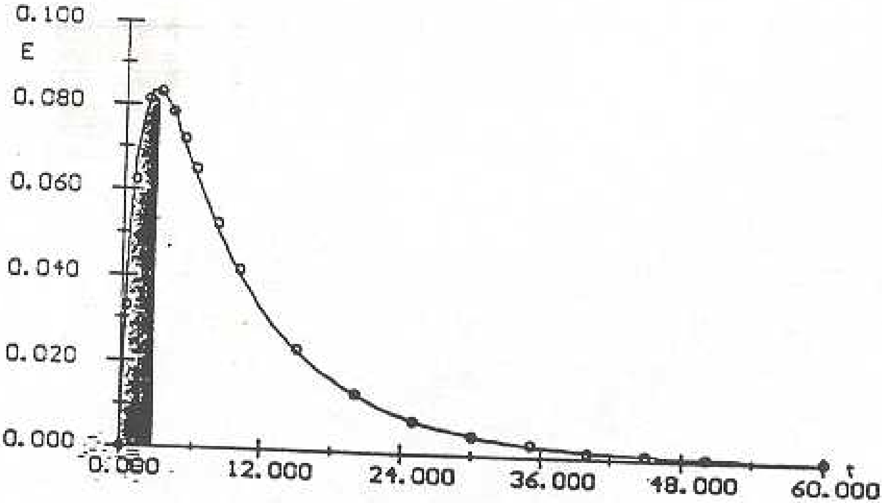
(e) Fraction that spends longer than 6 minutes

P14-13 **cont'd**



$$Fract = \int_{6}^{\infty} tE(t)dt = 58.3\%$$

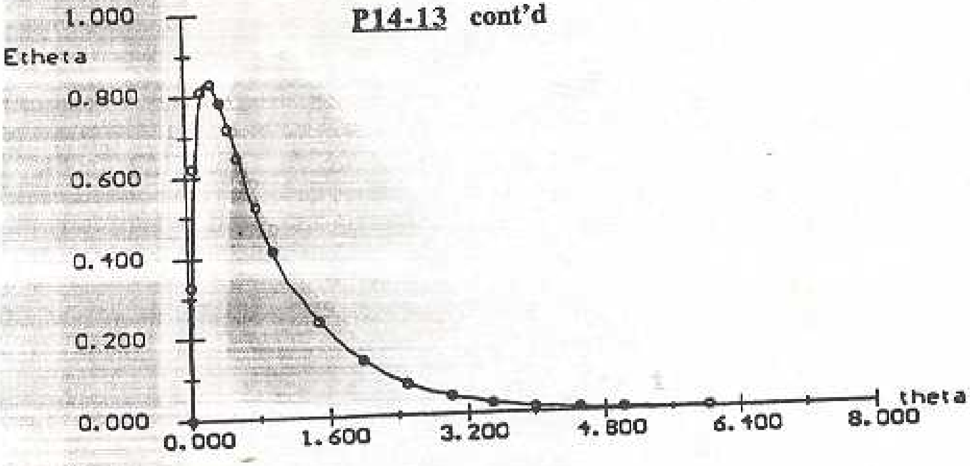
(f) Fraction that spends less than 3 minutes

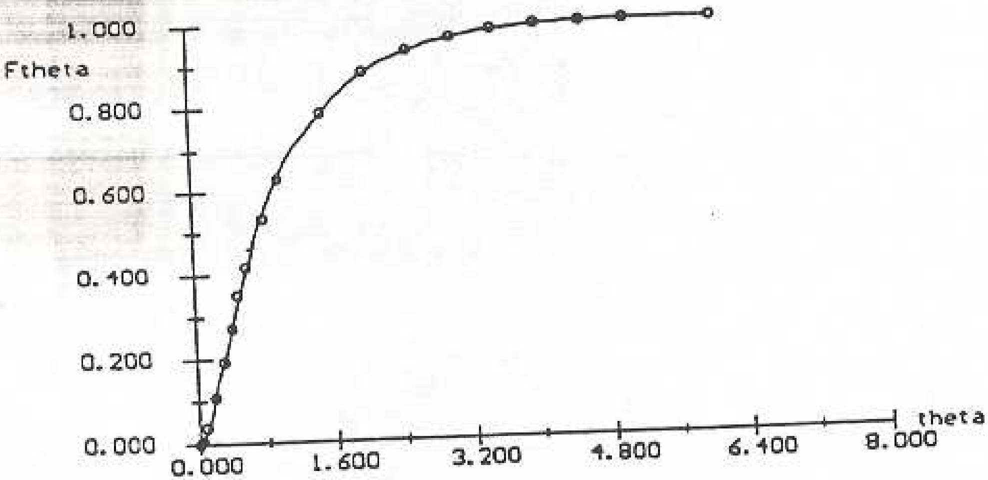


$$Fract = \int_{0}^{3} tE(t)dt = 19.4\%$$

(g) E(Θ) and F(Θ) vs. Θ

P14-13 cont'd



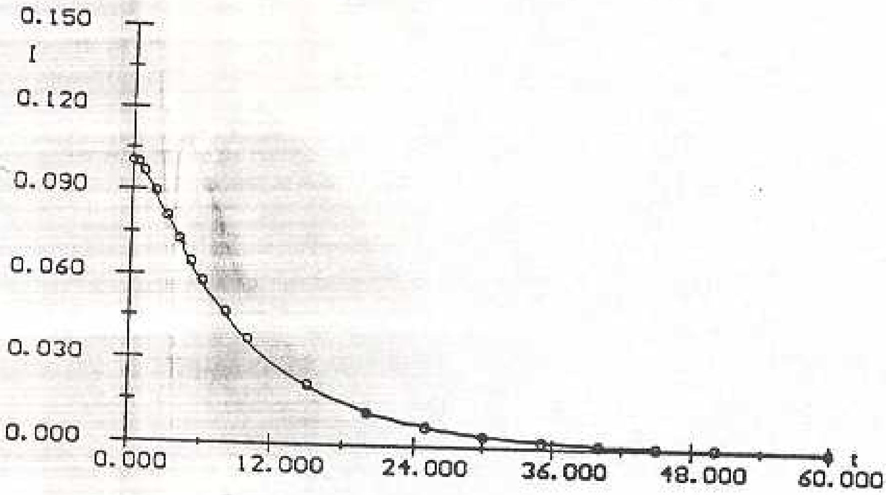


(h) Reactor Volume:

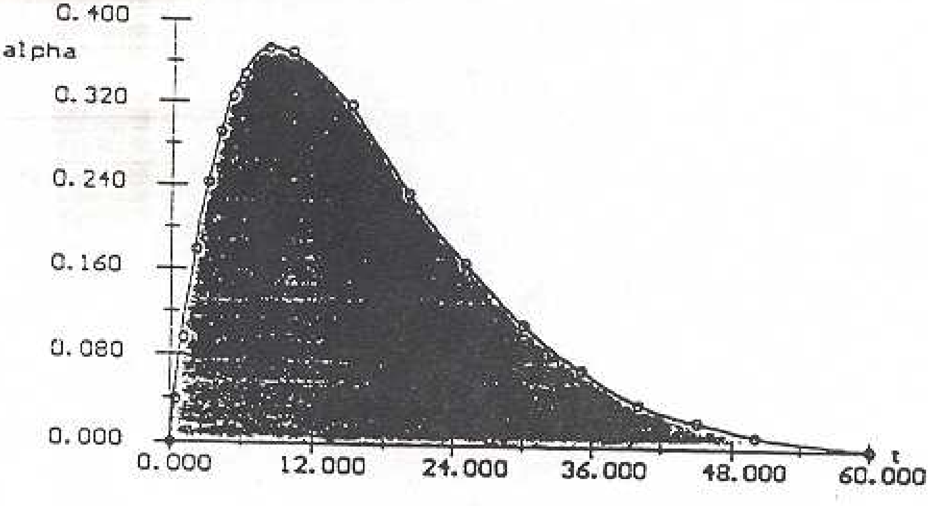
$$V = v\tau$$

$$V = \left(10\frac{dm^3}{\min}\right)(9.95\min) = 99.5dm^3$$

(j) Plot I(t) vs. t



(j) Find α_m



$$\alpha_m = \int_0^\infty tI(t)dt = 8.63$$

(k) Plot $\Delta(t)$ vs. t

P14-13 cont'd

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

$$-r_A = kC_A^2$$

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

$$V = \frac{X}{\dfrac{kC_{A0}(1-X)^2}{v}}$$

$$\frac{X}{(1-X)^2} = 1$$

$$X = 38.2\%$$

(p) Find the conversion for a segregation model.

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

$$-r_A = kC_A^{\ 2}$$

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

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

$$\frac{dX}{dt} = kC_{A0}(1-X)^2$$

$$\int_0^X \frac{dX}{(1-X)^2} = \int_0^t 0.1dt$$

$$\frac{1}{1-X} - 1 = 0.1t$$

$$X = 1 - \frac{1}{1+0.1t}$$

$$\overline{X} = \int_{\frac{\tau}{2}}^{\infty} X(t)E(t)dt = 42.3\%$$

P14-13 cont'd

(q) Find the conversion for a maximum mixedness model.

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)}(X)$$

$$-r_A = kC_A^2$$

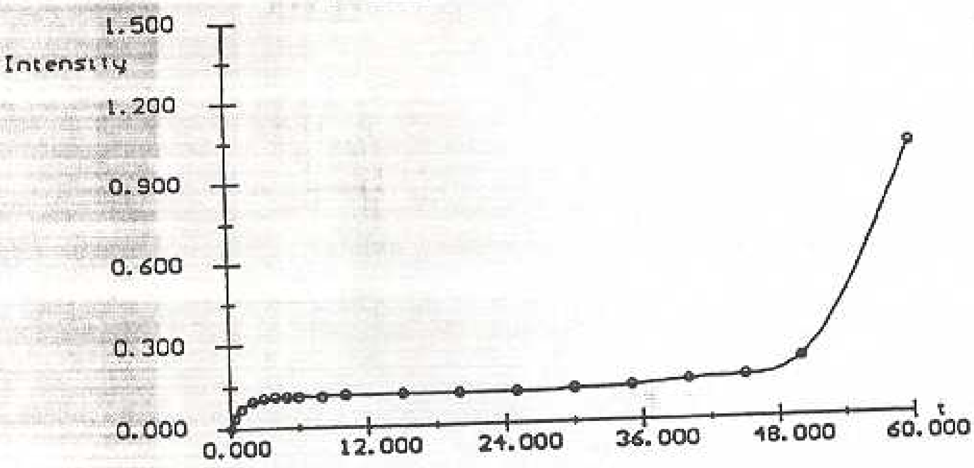
$$C_A = C_{A0}(1-X)$$

Integrate from $\lambda = \infty \rightarrow 0$ using POLYMATH

```
                              Maximum Mixedness Model
Equations
                                                                    Initial values
 d(x)/d(z)=-(ra/cao+EF*x)                                           0
 d(F)/d(z)=-E                                                       0.99
 cao=1
 k=.1
 lam=60-z
 ca=cao*(1-x)
 E1=-.0011721*lam^4+.0113999*lam^3-.0476813*lam^2+.0999015*lam
 E2=2.79737e-8*lam^4-4.94398e-6*lam^3+.000326287*lam^2-.00968055
    *lam+.111693
 ra=-k*ca^2
 E=if (lam<=3) then (E1) else (E2)
 EF=E/(1-F)
 z0 = 0,   zf = 60
```

$X = 40.4\%$

P14-13 cont'd



(l) Find the mean catalytic activity with a second order decay law

$$-\frac{da}{dt} = k_D a^2$$

where

$$k_D = 0.1 s^{-1}$$

$$-\int_1^a \frac{da}{a^2} = \int_0^t 6 \min^{-1} dt$$

$$-\frac{1}{a}\Big|_1^a = 6t\Big|_0^t$$

$$\frac{1}{a} - 1 = 6t$$

$$a = \frac{1}{6t+1}$$

$$\bar{a} = \int_0^\infty a I(\alpha) d\alpha$$

$$\bar{a} = 0.0725$$

P14-13 cont'd

(m) Find the conversion for a PFR with a second order reaction where $kC_{A0} = 0.1\,\text{min}^{-1}$

$$\frac{dX}{dV} = \frac{-r_A}{F_{Ao}}$$

$$-r_A = kC_A^2$$

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

$$\frac{dX}{dV} = \frac{kC_{A0}(1-X)^2}{v} = \frac{(0.1)(1-X)^2}{10}$$

$$\int_0^X \frac{dX}{(1-X)^2} = \int_0^{99.5} 0.01\,dV$$

$$\left.\frac{1}{1-X}\right|_0^X = 0.995$$

$$X = 50\%$$

(n) Find the conversion for a laminar flow reactor.

$$E(t) = 0 \qquad t < \frac{\tau}{2}$$

$$E(t) = \frac{\tau^2}{2t^3} \qquad t \ge \frac{\tau}{2}$$

$$t_m = \int_{\frac{\tau}{2}}^{\infty} tE(t)\,dt = \tau$$

With a second order reaction occurring,

$$X = 1 - \frac{1}{1+0.1t}$$

The mean conversion for the system is

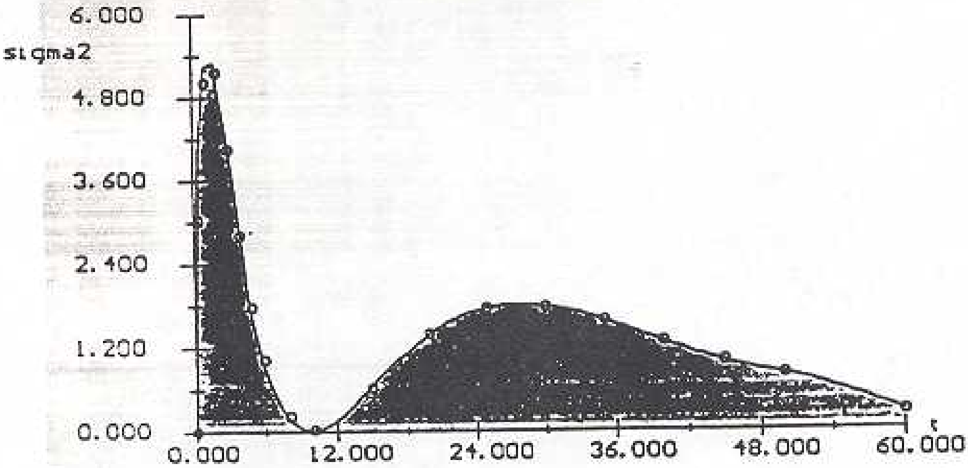
$$\bar{X} = \int_{\frac{\tau}{2}}^{\infty} X(t)E(t)\,dt = 44.3\%$$

(o) Find the conversion for a CSTR.

P14-13 cont'd

(r) How many tanks are needed to represent this reactor in a tanks-in-series model? Find the conversion for a first order reaction where

$k = 0.1\,\text{min}^{-1}$



$$\sigma^2 = \int_0^\infty E(t)(t - t_m)^2\,dt = 75.2$$

$$n = \frac{\tau^2}{\sigma^2} = 1.32$$

$$X = 1 - \frac{1}{(1 + \tau_i k)^n}$$

$$\tau_i = \frac{V}{v_0 n}$$

$$X = 52.4\%$$

(s) Using the dispersion model, find the Peclet number. What is the conversion of a first order reaction where

$k = 0.1\,\text{min}^{-1}$

For a Closed-Closed Vessel:

P14-13 cont'd

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}\left(1 - e^{-Pe_r}\right)$$

$Pe_r = 0.8875$

$$X = 1 - \frac{4q\exp\left[\frac{Pe_r}{2}\right]}{(1+q)^2\exp\left[\frac{Pe_r q}{2}\right] - (1-q)^2\exp\left[\frac{-Pe_r q}{2}\right]}$$

$Da = \tau k = 0.995$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = 2.34$$

$X = 52.75\%$

For an Open-Open Vessel:

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$$

$Pe_r = 4.861$

$Da = \tau k = 0.995$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = 1.35$$

Note: Conversion cannot be calculated using the previously found equation because the boundary conditions are not the same.

(t) For second order rxn:

$$Da = kC_{A0}\tau = 0.995$$

For closed system:

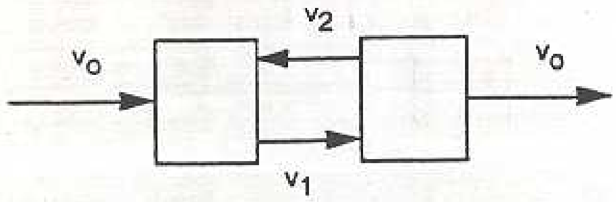
$$q = \sqrt{1 + \frac{4Da}{Pe_r}}, \qquad \text{Pe}_r = 0.8875$$

$= 2.34$

$x = 52.8\%$

P14-13 cont'd

(u) It is suspected that the reactor might be behaving as shown below. What is the "backflow" from the second to the first vessel as a multiple of v_0?



$$V\frac{dC_1}{dt}=(v_0C_0+v_2C_2)-v_1C_1$$

$$V\frac{dC_2}{dt}=v_1C_1-(v_0C_2+v_2C_2)$$

$$V\frac{dC_1}{dt}=\beta v_0C_2-(1+\beta)v_0C_1$$

$$V\frac{dC_2}{dt}=(1+\beta)v_0C_1-(v_0C_2+\beta v_0C_2)$$

$$V\frac{d^2C_2}{dt^2}=(1+\beta)v_0\left(\frac{dC_1}{dt}-\frac{dC_2}{dt}\right)$$

$$V\frac{d^2C_2}{dt^2}=(1+\beta)v_0\left(\frac{\beta v_0C_2-(1+\beta)v_0C_1}{V}-\frac{dC_2}{dt}\right)$$

$$V\frac{d^2C_2}{dt^2}=(1+\beta)v_0\left(\frac{\beta v_0C_2-(1+\beta)v_0\left(\dfrac{V_2\dfrac{dC_2}{dt}}{v_0(1+\beta)}+C_2\right)}{V}-\frac{dC_2}{dt}\right)$$

$$V\frac{d^2C_2}{dt^2}+2(1+\beta)v_0\frac{dC_2}{dt}+\frac{(1+\beta)v_0^2}{V}C_2=0$$

$$m_1,m_2=\frac{-2(1+\beta)v_0\pm\sqrt{(2(1+\beta)v_0)^2-4V\left(\dfrac{(1+\beta)v_0^2}{V}\right)}}{2V}$$

$$m_1,m_2=\frac{-(1+\beta)v_0\pm v_0\sqrt{\beta^2+\beta}}{V}$$

We will define m_1 as:

P14-13 cont'd

$$m_1 = \frac{-(1+\beta)v_0 + v_0\sqrt{\beta^2+\beta}}{V}$$

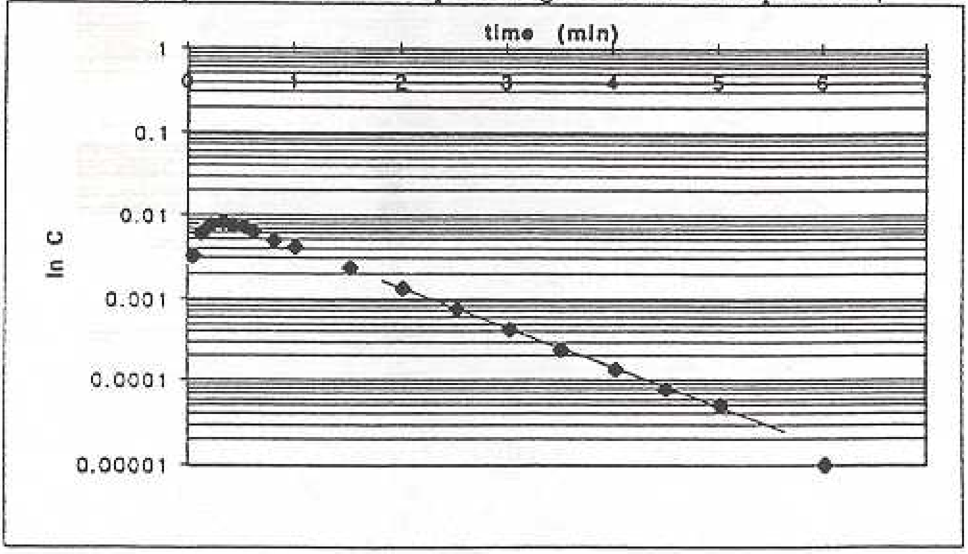
C_2 is defined as:

$$C_2 = Ae^{m_1 t} + Be^{m_2 t}$$

Because m_1 is smaller in magnitude than m_2, we know that m_1 will dominate at higher times. Therefore, at large time,

$$C_2 = Ae^{m_1 t}$$

When we graph lnC vs. t, the slope at large time will be equal to m_1.



The slope was found to be 0.1173.

Solving, we find that $\beta \cong 1.0$.

So backflow=v_o

(v)

Reactor 1: $C_{A0}v_0 + C_{A2}v_0 - 2C_{A1}v_0 - kC_{A1}^2 V = 0$

Reactor 2: $2C_{A1}v_0 - C_{A2}v_0 - C_{A2}v_0 - kC_{A2}^2 V = 0$

Solving for C_{A1} in Reactor 2 yields:

$$2C_{A1}v_0 = 2C_{A2}v_0 + kC_{A2}^2 V$$

P14-13 cont'd

Plugging into equation 1 and simplifying $\left(\tau = \frac{V}{v_0} = 0.995 * 5, C_{A0} = 1\right)$

We get

$$1 + C_{A2} - 2C_{A2} - 0.4975\left[C_{A2}^2 + \left(\frac{2C_{A2} + 0.4975C_{A2}^2}{2}\right)\right] = 0$$

Solving by trial and error:

$C_{A2} = 0{\cdot}545$

$X = 0{\cdot}455$

w)

Reactor Model	Conversion (%)
PFR	50.0
Laminar Flow	44.3
CSTR	38.2
Segregation	42.3
Maximum Mixedness	40.4
Tanks in Series	52.4
Dispersion (Closed-Closed)	52·8
Dispersion (Open-Open)	
"Backflow"	45·5