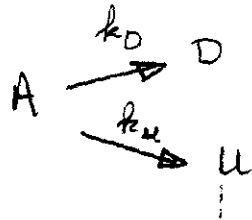
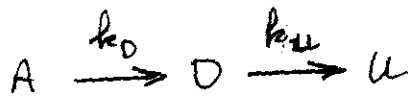


Multiple Reactions - Chapter 6

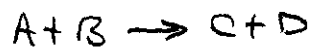
Parallel



Series



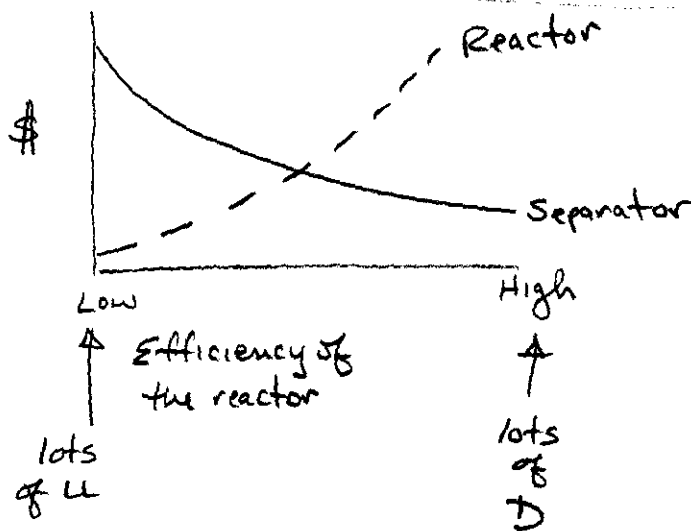
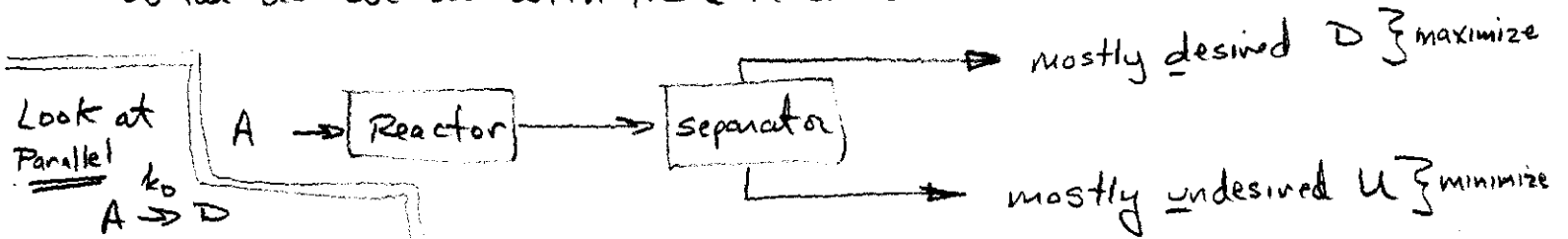
Combination of the above



Series in D

parallel in A

What do we do with these reactions?



$$A \begin{cases} \rightarrow D \\ \rightarrow U \end{cases} \quad \left. \begin{aligned} S &\equiv \frac{r_D}{r_U} \\ S &\equiv \frac{\text{moles D}}{\text{moles U}} \end{aligned} \right\} \text{selectivity}$$

$$Y \equiv \frac{\text{amount of a given product formed per mole of entering reactant}}{\text{amount of a given product formed per mole of entering reactant}}$$

$$Y \equiv \frac{r_D}{-r_A}$$

$$Y \equiv \frac{F_D}{F_{A_0} - F_A}$$

Assume

$$r_D = + k_D C_A^{\alpha_D}$$

$$r_u = + k_u C_A^{\alpha_u}$$

9-2

$$r_A = -r_D - r_u = -k_D C_A^{\alpha_D} - k_u C_A^{\alpha_u} \quad \leftarrow \text{net rate of reaction of A}$$

Rate Selectivity Parameter $S \equiv \frac{r_D}{r_u} = \frac{k_D C_A^{\alpha_D}}{k_u C_A^{\alpha_u}} = \frac{k_D}{k_u} C_A^{\alpha_D - \alpha_u}$

3 cases

CASE I

if $\alpha_D > \alpha_u$ $\alpha_D - \alpha_u > 0$

To achieve high concentrations of D :

High Concentrations of A
Basic Reactor
↳ PFR or Batch

CASE II $\alpha_D = \alpha_u$

$$S = \frac{k_D}{k_u} \rightarrow \text{maximize using temperature}$$

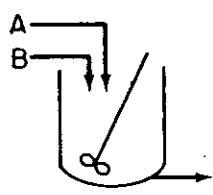
$$= \frac{A_D}{A_u} \exp\left[\frac{(E_u - E_D)}{RT}\right] \quad \text{if } E_u - E_D > 0 \quad T \downarrow$$

$$\text{if } E_u - E_D < 0 \quad T \uparrow$$

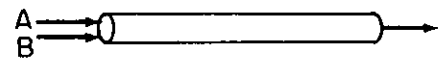
if $E_u = E_D$ tough!

Sec. 9.1 Conditions for Maximizing the Desired Product in Parallel Reactions

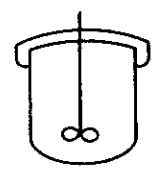
459
p 288
p 318
Figure 6.3



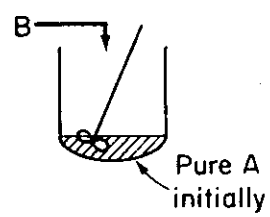
(a) CSTR



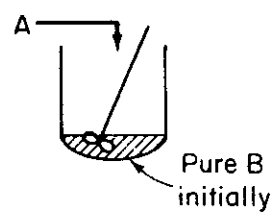
(b) Tubular reactor



(c) Batch

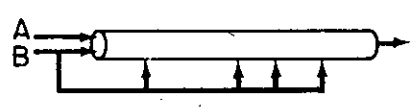


(d) Semibatch

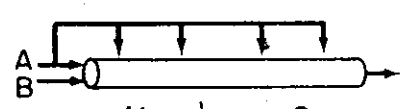


(e) Semibatch

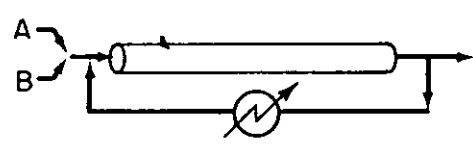
Choose from these or similar schemes to obtain the greatest amount of desired product and least amount of undesired product



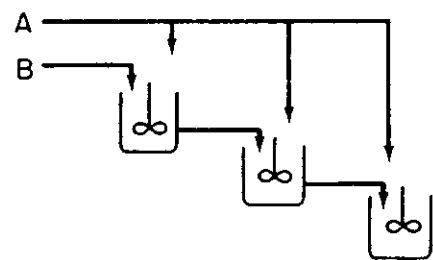
(f) Tubular reactor with side streams (Membrane reactor)



(g) Tubular reactor with side streams Membrane reactor



(h) Tubular reactor with recycle



(i) Series of small CSTRs

CSTR with recycle? (for highly exothermic)
membrane
reactive distillation equilibrium

6.3
Figure 9-4 Different reactors and schemes for minimizing the unwanted product.

To make S as large as possible we want to make the concentration of A high and the concentration of B low. To achieve this, use:

CA High
CB low

- A semibatch reactor in which B is fed slowly into a large amount of A (Fig. 9-4.d)
- A tubular reactor with side streams of B continually fed to the reactor (Fig. 9-4.f)
- A series of small CSTRs with A fed only to the first reactor and B fed to each reactor

CASE III

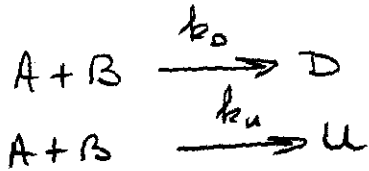
9-3

$$\alpha_D - \alpha_U < 0$$

Low Concentrations of A

Basic Reactor
CSTR - at high X_A

Parallel - Two Reactants



$$r_D = k_D C_A^{\alpha_D} C_B^{\beta_D}$$

$$r_U = k_U C_A^{\alpha_U} C_B^{\beta_U}$$

Same type of analysis

$$S \equiv \frac{k_D C_A^{\alpha_D} C_B^{\beta_D}}{k_U C_A^{\alpha_U} C_B^{\beta_U}} = \frac{k_D}{k_U} C_A^{\alpha_D - \alpha_U} C_B^{\beta_D - \beta_U}$$

CASE I

$\alpha_D - \alpha_U > 0$
 $\beta_D - \beta_U > 0$
High conc. of both A and B

CASE II

$\alpha_D - \alpha_U < 0$
 $\beta_D - \beta_U > 0$
Low C_A
High C_B


CASE III

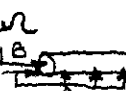
$\alpha_D - \alpha_U < 0$
 $\beta_D - \beta_U < 0$
Low C_A
Low C_B

CASE IV

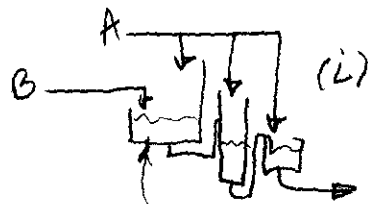
$\alpha_D - \alpha_U > 0$
 $\beta_D - \beta_U < 0$
(Reverse of CASE II)

Tubular Reactor
Batch

Semibatch (R) 

Tubular (g) 

CSTR in series



- 1) CSTR (a)
- 2) Tubular Reactor with recycle
- 3) Diluted feed
- 4) Low P

A is diluted

A is nearly all converted within the reactor.

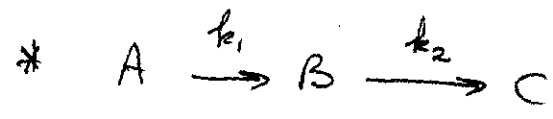
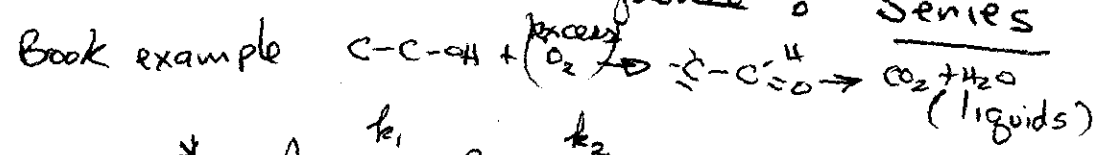
1) List the four basic types of multiple reactions

parallel
series
independent
complex

2) Determine the selectivity of a desired product over undesired byproducts

3) Select an appropriate reactor scheme that will maximize product selectivity

Simple Reaction Sequence Series



3 min: sketch the conc. of A, B & C
 as 1) function of t in a batch reactor
 2) function of L in a PFR

* $r_A = -k_1 C_A$

* $r_2 = -k_2 C_B$

mole balance on A PFR (keep in terms of concentration)

* $\frac{dF_A}{dV} = r_A$ $\phi \frac{dC_A}{dV} = -k_1 C_A$ $\frac{dC_A}{C_A} = -\frac{k_1 dV}{\phi}$
 $C_A = C_{A0}$ at $V=0$

$\ln C_A = -\frac{k_1 V}{\phi} \Rightarrow * \frac{C_A}{C_{A0}} = \exp\left[-\frac{k_1 V}{\phi}\right]$

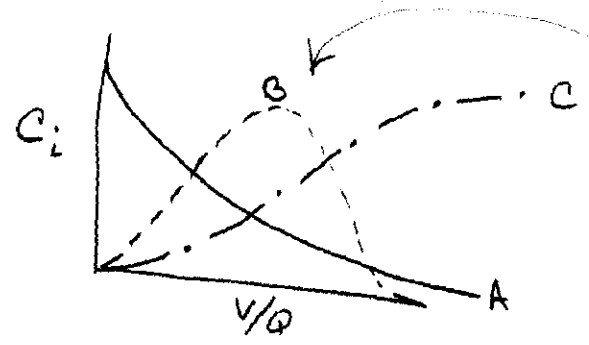
mole balance on B

* $\frac{dF_B}{dV} = r_B$ * $r_B = -r_1 + r_2 = k_1 C_A - k_2 C_B$

$\phi \frac{dC_B}{dV} = k_1 C_A - k_2 C_B = k_1 \exp\left[-\frac{k_1 V}{\phi}\right] - k_2 C_B$

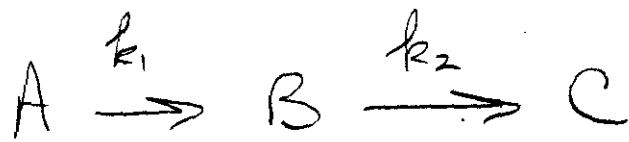
* $\frac{dC_B}{dV} + \frac{k_2 C_B}{\phi} = k_1 \exp\left[-\frac{k_1 V}{\phi}\right]$ $C_B = 0$ at $V=0$

using integrating factor method: $C_B = k_1 C_{A0} \left[\frac{e^{-k_1 V/\phi} - e^{-k_2 V/\phi}}{k_2 - k_1} \right]$



to maximize B find the maximum in the curve!

$\frac{dC_B}{d(V/\phi)} = \underline{\hspace{2cm}}$



$$r_1 = -k_1 C_A$$

$$r_2 = -k_2 C_B$$

} Assume ^{that} a liquid is the fluid
and

$$\left. \begin{array}{l} C_A = C_{A0} \\ C_B = 0 \\ C_C = 0 \end{array} \right\} \text{at } V=0$$

$T = T_0$ Isothermal

mole balance on A

$$\frac{dF_A}{dV} = v_A = -k_1 C_A$$

$$\phi \frac{dC_A}{dV} = -k_1 C_A \quad \int \frac{dC_A}{C_A} = -\frac{k_1}{\phi} \int dV$$

$$\ln C_A - \ln C_{A0} = -\left(\frac{k_1}{\phi}\right)V$$

$$\frac{C_A}{C_{A0}} = \exp\left(-\frac{k_1}{\phi}V\right) = \exp(-k_1 \tau) \quad \frac{V}{\phi} = \tau$$

mole balance on B

$$\frac{dF_B}{dV} = \phi \frac{dC_B}{dV} = k_1 C_A - k_2 C_B = k_1 C_{A0} \exp(-k_1 \tau) - k_2 C_B$$

$$\mu \left(\frac{dC_B}{d\tau} + k_2 C_B \right) = \left(k_1 C_{A0} \exp(-k_1 \tau) \right) \mu = d(\mu C_B) \frac{d\tau}{d\tau}$$

step ①

step ②

Step 1

2

$$\cancel{\mu} \frac{dc_B}{d\tau} + c_B \frac{d\mu}{d\tau} = \cancel{\mu} \frac{dc_B}{d\tau} + \mu k_2 c_B$$

$$\frac{d\mu}{d\tau} = \mu k_2 \quad \int \frac{d\mu}{\mu} = \int k_2 d\tau$$

$$\ln \mu = k_2 \tau$$

Step 2:

$$\frac{d(\exp(k_2 \tau) c_B)}{d\tau} = \exp(k_2 \tau) k_1 c_{A0} \exp(-k_1 \tau)$$

$$\exp(k_2 \tau) c_B = \text{const} + k_1 c_{A0} \int \exp[(-k_1 + k_2) \tau] d\tau$$

$$\exp(k_2 \tau) c_B = \text{const} + k_1 c_{A0} \frac{\exp[(k_2 - k_1) \tau]}{k_2 - k_1}$$

at $c_B = 0$ at $\tau = 0$

$$c_B = \text{const} \exp(-k_2 \tau) + \frac{k_1 c_{A0} \exp(-k_1 \tau)}{k_2 - k_1}$$

$$0 = \text{const} + \frac{k_1 c_{A0}}{k_2 - k_1} \quad (1)$$

$$c_B = + \frac{k_1 c_{A0}}{k_2 - k_1} \left[e^{-k_1 \tau} - e^{-k_2 \tau} \right]$$

$$\frac{dC_c}{d\tau} = k_2 C_B = \frac{k_2 k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 \tau} - e^{-k_2 \tau} \right]$$

$$C_c - C_{c0}^0 = \frac{k_1 k_2 C_{A0}}{k_2 - k_1} \int (e^{-k_1 \tau} - e^{-k_2 \tau}) d\tau$$

$$C_c = \frac{k_1 k_2 C_{A0}}{k_2 - k_1} \left[\frac{e^{-k_1 \tau}}{-k_1} - \frac{e^{-k_2 \tau}}{-k_2} \right]_{\tau=0}^{\tau}$$

$$C_c = \frac{k_1 k_2 C_{A0}}{k_2 - k_1} \left[\frac{k_1 e^{-k_2 \tau}}{k_1 k_2} - \frac{e^{-k_1 \tau}}{k_1 k_2} - \left(\frac{1}{-k_1 k_2} + \frac{1}{k_2 k_1} \right) \right]$$

mistake in plugging in limits made in section 2

$$C_c = \left[\frac{k_1 k_2 C_{A0}}{k_2 - k_1} \right] \left[\frac{k_1 e^{-k_2 \tau} - k_2 e^{-k_1 \tau} - k_1 + k_2}{k_1 k_2} \right]$$

$$C_c = \frac{C_{A0}}{k_2 - k_1} \left[k_2 (1 - e^{-k_1 \tau}) - k_1 (1 - e^{-k_2 \tau}) \right]$$

check limit as $\tau \rightarrow 0$ $C_c = 0$ ok!

$\tau \rightarrow \infty$ $C_c = C_{A0}$ ok!

in class $k_2 \gg k_1$ what happens to A, B and C

① A - does not change

② $C_B \approx \frac{k_1 C_{A0}}{k_2} \exp(-k_1 \tau) \rightarrow 0$

③ $C_c = \frac{C_{A0}}{k_2} \left[k_2 (1 - e^{-k_1 \tau}) - k_1 (1) \right] = C_{A0} (1 - e^{-k_1 \tau}) - \frac{k_1}{k_2} C_{A0}$

$C_c = C_{A0} - C_{A0} e^{-k_1 \tau}$ or $C_{A0} - C_A$ As if $A \xrightarrow{k_1} C$

6.3 Complex Reactions

Don't use X 's

Book
is for
Isothermal!
Be careful!

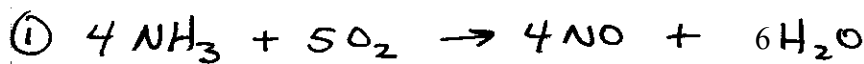
Algorithm for isothermal multiple reactions
page 298

- 1). Number each reaction
- 2). Mole Balance for each species ← this contains the net rate of rxn of that species
- 3). Find the rate law for each reaction and determine the units
- 4). Relate the reaction rate law for each reaction to the species involved in ~~that~~ ^{each} reaction.
- 5). Determine an expression for the net rate of reaction of each species
- 6). Add in all required support equations
$$v =$$
$$C_i = F_i/v$$
$$F_T = \sum F_i$$
etc.
- 7). Combine above and solve.

Book gives several examples

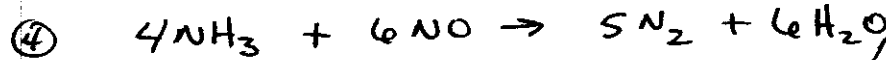
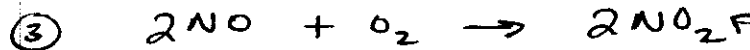
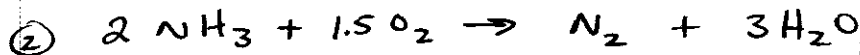
- 1) 6-4, to relate rates
- 2) 6-5 to combine rates from 6-4 into mole Bal.
- 3) Example 6-6 Hydrodealkylation of mesitylene in PFR
- 4) example 6-7 in CSTR
- 5) example 6-8 in PFR

Example 6-8 p 311



$$r_{\text{NH}_3} = -k_1 C_{\text{NH}_3} C_{\text{O}_2}^2$$

[=] $\frac{\text{mol NH}_3}{\text{L min}}$



$$r_{4 \text{NO}} = -k_4 C_{\text{NO}} C_{\text{NH}_3}^{2/3}$$

$$r_{2 \text{NH}_3} = -k_2 C_{\text{NH}_3} C_{\text{O}_2}$$

[=] $\frac{\text{mol NH}_3}{\text{L min}}$

$$r_{3 \text{O}_2} = -k_3 C_{\text{NO}}^2 C_{\text{O}_2}$$

[=] $\frac{\text{mol O}_2}{\text{L min}}$

$$v_0 = 10 \text{ L/min}$$

$$V = 10 \text{ L}$$

$$C_{\text{NH}_3 0} = C_{\text{O}_2 0} = 1 \text{ mol/L}$$

k 's given

gas phase reaction

1) Done

2)

$$\frac{dF_{\text{NH}_3}}{dV} = r_{\text{NH}_3}$$

$$\frac{dF_{\text{O}_2}}{dV} = r_{\text{O}_2}$$

$$\frac{dF_{\text{NO}}}{dV} = r_{\text{NO}}$$

$$\frac{dF_W}{dV} = r_W$$

$$\frac{dF_{\text{N}_2}}{dV} = r_{\text{N}_2}$$

$$\frac{dF_{\text{NO}_2}}{dV} = r_{\text{NO}_2}$$

3) Given rate laws. & units

4) reaction 1

$$r_{\text{NH}_3} = r_{\text{O}_2} \frac{4 \text{ mol NH}_3}{5 \text{ mol O}_2} = r_{\text{NO}} \left(\frac{-4 \text{ mol NH}_3}{4 \text{ mol NO}} \right)$$

$$= r_W \left(\frac{4 \text{ mol NH}_3}{6 \text{ mol H}_2\text{O}} \right)$$

reaction 2

$$r_{2 \text{NH}_3} = r_{2 \text{O}_2} \frac{2 \text{ mol NH}_3}{1.5 \text{ mol O}_2} = r_{2 \text{N}_2} \left(\frac{-2 \text{ mol NH}_3}{1 \text{ mol N}_2} \right)$$

$$= r_{2 \text{W}} \left(\frac{2 \text{ mol NH}_3}{-3 \text{ mol W}} \right)$$

reaction 3

$$r_{3O_2} = r_{3NO} \frac{1 \text{ mol } O_2}{2 \text{ mol } NO} = r_{3NO_2} \left(\frac{1 \text{ mol } O_2}{-2 \text{ mol } NO_2} \right)$$

reaction 4

$$r_{4NO} = r_{4NH_3} \frac{6 \text{ mol } NO}{4 \text{ mol } NH_3} = r_{4N_2} \frac{6 \text{ mol } NO}{-5 \text{ mol } N_2} = r_{4W} \left(\frac{6 \text{ mol } NO}{-6 \text{ mol } W} \right)$$

Net reaction rates

$$\rightarrow r_{NH_3} = r_{1NH_3} + r_{2NH_3} + r_{4NH_3}$$

$$= r_{1NH_3} + r_{2NH_3} + r_{4NH_3}$$

$$r_{NH_3} = r_{1NH_3} + r_{2NH_3} + r_{4NO} \frac{4 \text{ mol } NH_3}{6 \text{ mol } NO}$$

$$\rightarrow r_{O_2} = r_{1O_2} + r_{2O_2} + r_{3O_2}$$

$$= r_{1NH_3} \frac{5 \text{ mol } O_2}{4 \text{ mol } NH_3} + r_{2NH_3} \frac{1.5 \text{ mol } O_2}{2 \text{ mol } NH_3} + r_{3O_2}$$

$$\rightarrow r_{NO} = r_{1NO} + r_{3NO} + r_{4NO}$$

$$= r_{1NH_3} \left(\frac{-4 \text{ mol } NO}{4 \text{ mol } NH_3} \right) + r_{3O_2} \frac{2 \text{ mol } NO}{1 \text{ mol } O_2} + r_{4NO}$$

$$\rightarrow r_W = \left(r_{1NH_3} \frac{-6 \text{ mol } W}{4 \text{ mol } NH_3} \right) + r_{2NH_3} \frac{-3 \text{ mol } W}{2 \text{ mol } NH_3} + r_{4NO} \frac{-6 \text{ mol } W}{6 \text{ mol } NO}$$

$$\rightarrow r_{N_2} = r_{2NH_3} \frac{-1 \text{ mol } N_2}{2 \text{ mol } NH_3} + r_{4NO} \left(\frac{-5 \text{ mol } N_2}{6 \text{ mol } NO} \right)$$

$$\rightarrow r_{NO_2} = r_{3O_2} \left(\frac{-2 \text{ mol } NO_2}{1 \text{ mol } O_2} \right)$$

Gas phase reaction

$$\frac{P V}{P_0 V_0} = \frac{F_T R T}{F_{T_0} R T_0}$$

$$V = V_0 \frac{P_0 F_T T}{P F_{T_0} T_0}$$

Define concentrations in reaction rate expressions

$$C_{\text{NH}_3} = F_{\text{NH}_3} / V$$

$$C_{\text{O}_2} = F_{\text{O}_2} / V$$

$$C_{\text{NO}} = F_{\text{NO}} / V$$

$$F_T = \sum F_i$$

~~$$F_{T_0} = V_0$$~~

$$F_{\text{NH}_3} = \frac{\frac{\text{mol}}{\text{m}^3}}{\frac{\text{L}}{\text{min}}} = \frac{10 \text{ mol NH}_3}{\text{min}}$$

$$F_{\text{O}_2} = 10 \text{ mol O}_2 / \text{min}$$

Example 6-8 with allowances for a change in pressure or temperature

POLYMATH Results

Example 6-8 Calculating Concentrations for NH3 Oxidation in a PFR with varying T and/or P
Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	10	10
FNH3	10	1.5041315	10	1.5041315
FO2	10	2.4000442	10	2.4000442
FNO	0	0	1.6519764	0.6038323
FW	0	0	12.743803	12.743803
FN2	0	0	3.4829489	3.4829489
FNO2	0	0	0.9261383	0.9261383
Ft	20	20	21.660898	21.660898
Ft0	20	20	20	20
T0	500	500	500	500
P0	1	1	1	1
T	500	500	500	500
flow0	10	10	10	10
P	1	1	1	1
flow	10	10	10.830449	10.830449
CNH3	1	0.1388799	1	0.1388799
CO2	1	0.2216015	1	0.2216015
r1NH3	-5	-5	-0.0341	-0.0341
CNO	0	0	0.1578611	0.0557532
r4NO	0	-0.5619114	0	-0.0747595
r2NH3	-2	-2	-0.061552	-0.061552
rNH3	-7	-7	-0.1454917	-0.1454917
rw	10.5	0.2182375	10.5	0.2182375
rN2	1	0.0930755	1.0317586	0.0930755
r3O2	0	-0.1448595	0	-0.0068883
rO2	-7.75	-7.75	-0.0956774	-0.0956774
rNO	5	-0.2008305	5	-0.054436
rNO2	0	0	0.2897191	0.0137766

ODE Report (RKF45)

Differential equations as entered by the user

- [1] $d(\text{FNH3})/d(V) = r\text{NH3}$
- [2] $d(\text{FO2})/d(V) = r\text{O2}$
- [3] $d(\text{FNO})/d(V) = r\text{NO}$
- [4] $d(\text{FW})/d(V) = r\text{w}$
- [5] $d(\text{FN2})/d(V) = r\text{N2}$
- [6] $d(\text{FNO2})/d(V) = r\text{NO2}$

Explicit equations as entered by the user

- [1] $\text{Ft} = \text{FNH3} + \text{FO2} + \text{FNO} + \text{FW} + \text{FN2} + \text{FNO2}$
- [2] $\text{Ft0} = 20$
- [3] $\text{T0} = 500$
- [4] $\text{P0} = 1$
- [5] $\text{T} = 0 + \text{T0}$
- [6] $\text{flow0} = 10$
- [7] $\text{P} = 0 + \text{P0}$
- [8] $\text{flow} = \text{flow0} * \text{P0} * \text{Ft} * \text{T} / (\text{P} * \text{Ft0} * \text{T0})$
- [9] $\text{CNH3} = \text{FNH3} / \text{flow}$
- [10] $\text{CO2} = \text{FO2} / \text{flow}$
- [11] $r1\text{NH3} = -5 * \text{CNH3} * \text{CO2}^2$
- [12] $\text{CNO} = \text{FNO} / \text{flow}$
- [13] $r4\text{NO} = -5 * \text{CNO} * \text{CNH3}^{(2/3)}$

- [14] $r2\text{NH3} = -2 * \text{CNH3} * \text{CO2}$
- [15] $r\text{NH3} = r1\text{NH3} + r2\text{NH3} + 2 * r4\text{NO} / 3$
- [16] $r\text{w} = -1.5 * r1\text{NH3} - 1.5 * r2\text{NH3} - r4\text{NO}$
- [17] $r\text{N2} = -5 * r2\text{NH3} - 5 * r4\text{NO} / 6$
- [18] $r3\text{O2} = -10 * \text{CNO}^2 * \text{CO2}$
- [19] $r\text{O2} = 1.25 * r1\text{NH3} + 75 * r2\text{NH3} + r3\text{O2}$
- [20] $r\text{NO} = -r1\text{NH3} + 2 * r3\text{O2} + r4\text{NO}$
- [21] $r\text{NO2} = -2 * r3\text{O2}$

Comments

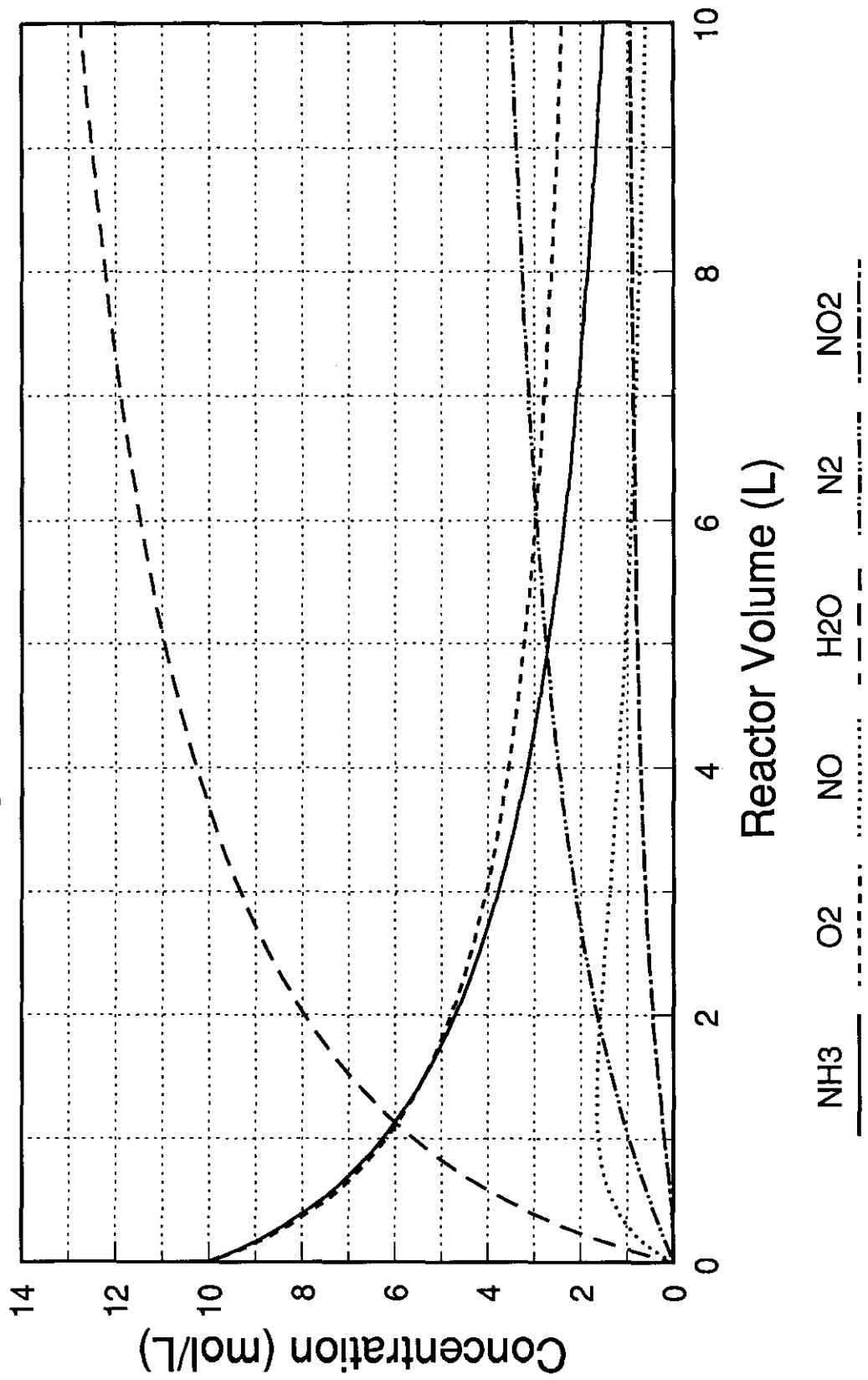
- [16] $\text{P} = 0 + \text{P0}$
replace with pressure drop
- [17] $\text{T} = 0 + \text{T0}$
replace with energy balance
- [24] $\text{flow0} = 10$
L/min
- [25] $\text{P0} = 1$
not used

Independent variable

variable name : V
 initial value : 0
 final value : 10

Concentration Profiles for PFR

Example Problem 9-8



definitions - other

Batch Reactor Selectivity

$$S = \frac{N_D}{N_u}$$

flow

$$S = \frac{F_D}{F_u}$$

instantaneous yield

$$Y_D = \frac{r_D}{r_A}$$

overall yield

$$Y_D = \frac{N_D}{N_{A_0} - N_A}$$

Batch

$$Y_D = \frac{F_D}{F_{A_0} - F_A}$$

flow

N are best for economics
\$

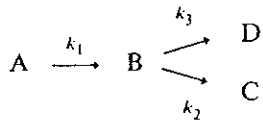
rate based are good for reactor selection

"Traditional" definitions

P9-12

F90

The reaction



(P9-6.1)

is carried out in a batch reactor in which there is pure A initially.

- (a) Derive an equation for the concentration of A as a function of time. If $k_1 = 0.01 \text{ s}^{-1}$, what is the ratio C_A/C_{A0} after 1.5 min?
- (b) Derive an equation that gives the concentration of B as a function of time. If $k_2 = 0.003 \text{ s}^{-1}$, $k_3 = 0.002 \text{ s}^{-1}$, and $C_{A0} = 0.2 \text{ g mol/dm}^3$, what is the concentration of B after 2 min?
- (c) What is the concentration of C after 1 min? 2 min?
- (d) Sketch the concentrations of A, B, and C as functions of time. At what time is the concentration of B at a maximum?
- (e) If the series reaction is carried out in a CSTR, determine the reactor volume that will maximize the production of B for a volumetric flow rate of $20 \text{ dm}^3/\text{min}$.

F90

P9-6

Pharmacokinetics concerns the ingestion, distribution, reaction, and elimination reaction of drugs in the body. Consider the application of pharmacokinetics to one of the major problems we have in the United States, drinking and driving. Here we shall model how long one must wait to drive after having a tall martini. In most states the legal intoxication limit is 1.0 g of ethanol per liter of body fluid. (In Sweden it is 0.5 g/liter, and in East Germany and the Soviet Union it is 0.0 g/liter.) The ingestion of ethanol into the bloodstream and subsequent elimination can be modeled as a series reaction. The rate of absorption from the gastrointestinal tract into the bloodstream and body is a first-order reaction with a specific reaction rate constant of 10 h^{-1} . The rate at which ethanol is broken down in the bloodstream is limited by regeneration of a coenzyme. Consequently, the process may be modeled as a zero-order reaction with a specific reaction rate of 0.192 g/h-liter of body fluid. How long would a person have to wait (a) In the United States; (b) In Sweden; and (c) In East Germany if they drank two tall martinis immediately after arriving at a party? How would your answer change if (d) the drinks were taken $1/2 \text{ h}$ apart; (e) the two drinks were consumed at a uniform rate during the first hour? (f) Suppose that one went to a party, had one and a half tall martinis right away, and then received a phone call saying an emergency had come up and they needed to drive home immediately. How many minutes would they have to reach home before they became legally intoxicated, assuming that the person had nothing further to drink? (g) How would your answers be different for a thin person? A heavy person? For each case make a plot of concentration as a function of time.

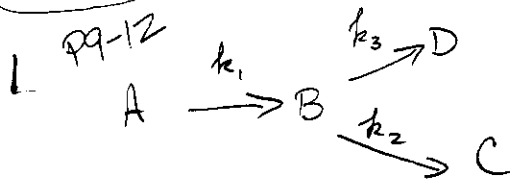
Additional data:

- Ethanol in a tall martini: 40 g
- Volume of body fluid: 40 liters

(SADD-MADD problem)

P9-6 35pt

(P9-6)-1



Batch reactor $t=0$ $C_A = C_{A0}$
 $C_B = C_C = C_D = 0$

No Volume change since 1 mole forms only 1 mole e.g. overall $A \rightarrow C$

a) Find A as a function of time

$$\frac{d(C_A V)}{dt} = r_A V$$

$$-C_{A0} \frac{dx}{dt} = r_A$$

$$x = \frac{C_{A0} - C_A}{C_{A0}} \quad C_{A0} dx = -dC_A$$

from the units of the reaction rate constant $k_1 = 0.015 s^{-1}$ the reaction is first order.

$$C_{A0} \frac{dx}{dt} = k_1 C_A = k_1 C_{A0} (1-x)$$

$$\int_{x_A=0}^{x_A} \frac{dx}{1-x} = \int_0^t k_1 dt$$

$$-\ln(1-x) \Big|_0^{x_A} = k_1 t$$

$$1-x_A = \exp(-k_1 t) \quad x_A = 1 - \exp(-k_1 t)$$

$$\frac{C_A}{C_{A0}} = (1-x) = \exp(-k_1 t) = \exp(-0.015^{-1} (1.5 \text{ min}) (60 \text{ s/min})) = 0.41$$

$$r_B = k_1 C_A - k_3 C_B - k_2 C_B = k_1 C_{A0} \exp(-k_1 t) - C_B (k_2 + k_3)$$

$$\frac{dC_B}{dt} = r_B = k_1 C_{A0} e^{-k_1 t} - C_B (k_2 + k_3)$$

$$\frac{dC_B}{dt} + C_B (k_2 + k_3) = k_1 C_{A0} e^{-k_1 t}$$

let $\mu = \exp((k_2 + k_3)t)$

$$\frac{d(\mu C_B)}{dt} = \mu \frac{dC_B}{dt} + \mu C_B (k_2 + k_3) = \mu k_1 C_{A0} e^{-k_1 t}$$

$$\mu \frac{dC_B}{dt} + C_B \frac{d\mu}{dt} = \mu \frac{dC_B}{dt} + \mu C_B (k_2 + k_3)$$

$$\ln \mu = (k_2 + k_3)t$$

$$\mu = \exp((k_2 + k_3)t)$$

	change	final
A	C_{A0}	
B	0	
C	0	
D	0	

$$\int d \exp[\underbrace{k_2+k_3}_\alpha t] C_B = \int \exp \alpha t k_1 C_{A_0} e^{-k_1 t} dt + k \quad (P9-6)-2$$

$$e^{\alpha t} C_B = \frac{k_1 C_{A_0} e^{[t(\alpha - k_1)]}}{\alpha - k_1} + k \quad \left[\begin{array}{l} \text{B.C.} \\ t=0 \quad C_B=0 \end{array} \right]$$

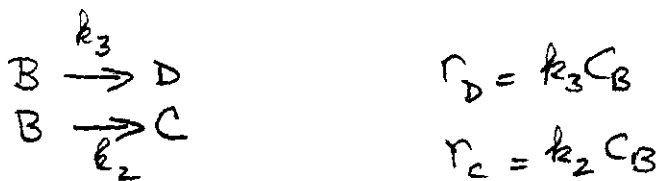
$$0 = \frac{k_1 C_{A_0}}{k_2+k_3-k_1} + k \quad k = \frac{k_1 C_{A_0}}{k_1 - k_2 - k_3}$$

$$C_B = \frac{k_1 C_{A_0}}{k_2+k_3-k_1} e^{-k_1 t} + \frac{k_1 C_{A_0}}{k_1 - k_2 - k_3} e^{-(k_2+k_3)t} = \frac{C_{A_0} k_1}{k_1 - k_2 - k_3} \left[-e^{-k_1 t} + e^{-(k_2+k_3)t} \right]$$

x5

$$C_B = \frac{0.01 (0.2 \text{ mol/L})}{-(0.003+0.002)+0.01} \left[e^{-(0.005)t} - e^{-0.01t} \right]$$

(b) at $t = 2 \text{ min}$ or 120 s $C_B = 0.4 \left[e^{-0.005(120)} - e^{-0.01(120)} \right] = 0.099 \text{ mol/dm}^3$



$$\frac{dC_D}{dt} = r_D = k_3 C_B \quad \frac{dC_C}{dt} = k_2 C_B$$

The solution of each equation will have the same form

$$\frac{dC_D}{dt} = 0.4 k_3 \left[e^{-0.005t} - e^{-0.01t} \right]$$

$$C_D = 0.4 k_3 \left[\frac{e^{-0.005t}}{-0.005} + \frac{e^{-0.01t}}{0.01} \right] + k$$

B.C. $C_D = 0$ at $t = 0$

$$0 = 0.4 k_3 \left[\frac{1}{0.01} - \frac{1}{0.005} \right] + k$$

$$k = 0.4 k_3 \left[\frac{1}{0.005} - \frac{1}{0.01} \right]$$

$$= k_3 (40) = 0.4 k_3 100$$

$$C_D = 0.4 k_3 \left[100 - 200 e^{-0.005t} + 100 e^{-0.01t} \right] \quad (P9-6)-3$$

$$C_C = 0.4 k_2 \left[100 - 200 e^{-0.005t} + 100 e^{-0.01t} \right] \quad \begin{matrix} k_3 = 0.002 \text{ s}^{-1} \\ k_2 = 0.003 \text{ s}^{-1} \end{matrix}$$

$\times 5$
(c) at 1 min (60 s) $C_D = 0.0054 \frac{\text{mol}}{\text{dm}^3}$ $C_C = 0.0081 \frac{\text{mol}}{\text{dm}^3}$

2 min (120 s) $C_D = 0.0163 \frac{\text{mol}}{\text{dm}^3}$ $C_C = 0.024 \frac{\text{mol}}{\text{dm}^3}$

$\times 10$
(d) See plot

$$\frac{dC_B}{dt} = 0.4 \left[-0.005 e^{-0.005t} + 0.01 e^{-0.01t} \right] = 0$$

$$0.005 e^{-0.005t} = 0.01 e^{-0.01t} \quad \frac{0.01}{0.005} = e^{+0.01t - 0.005t}$$

$$\ln(2) = t(0.01 - 0.005) \quad t = 139 \text{ s}$$

~~(e)~~ $\times 10$ CSTR

$$\frac{dC_L}{dt} = F_{i0} - F_i + r_i V$$

Goal: find maximum B and corresponding V_{CSTR}

for A $0 = Q(C_{A0} - C_A) - k_1 C_A V$

$$C_A = \frac{Q C_{A0}}{Q + k_1 V} \quad \tau = \frac{C_{A0}}{1 + k_1 \tau}$$

$$C_{A0} = 0.2 \frac{\text{g mol}}{\text{dm}^3}$$

$$Q = \frac{6}{20} \frac{\text{dm}^3}{\text{min}} \left(\frac{1 \text{ min}}{60 \text{ s}} \right)$$

$$Q = \frac{1}{3} \frac{\text{dm}^3}{\text{s}}$$

$$\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} = \frac{1}{3} \frac{1}{\text{s}}$$

for B, C and D $F_i = r_i V$ since $F_{i0} = 0$

$$C_B Q = r_B V = [k_1 C_A - k_3 C_B - k_2 C_B] V$$

$$C_B = k_1 C_A \tau - C_B \tau (k_3 + k_2) = \frac{k_1 \tau C_{A0}}{1 + k_1 \tau} - C_B \tau (k_3 + k_2)$$

$$C_B = \frac{(k_1 \tau C_{A0}) / (1 + k_1 \tau)}{1 + \tau(k_3 + k_2)}$$

(P9-6) - 4

$$C_B = \frac{k_1 \tau C_{A0}}{1 + k_1 \tau + \tau(k_3 + k_2) + k_1(k_2 + k_3) \tau^2}$$

$$0 = \frac{dC_B}{dt} = \frac{\left[1 + \tau(k_1 + k_2 + k_3) + k_1(k_2 + k_3) \tau^2 \right] k_1 C_{A0} - k_1 \tau C_{A0} \left[k_1 + k_2 + k_3 + 2k_1 \frac{(k_2 + k_3)}{\tau} \right]}{\left(\quad \right)^2}$$

$$0 = 1 + \tau(k_1 + k_2 + k_3) + k_1(k_2 + k_3) \tau^2 - (k_1 + k_2 + k_3) \tau - 2k_1(k_2 + k_3) \tau^2$$

$$0 = 1 + \tau[0.015] + 0.00005 \tau^2 - (0.015) \tau - \underbrace{2(0.01)(0.003 + 0.002)}_{0.0001 \tau^2} \tau^2$$

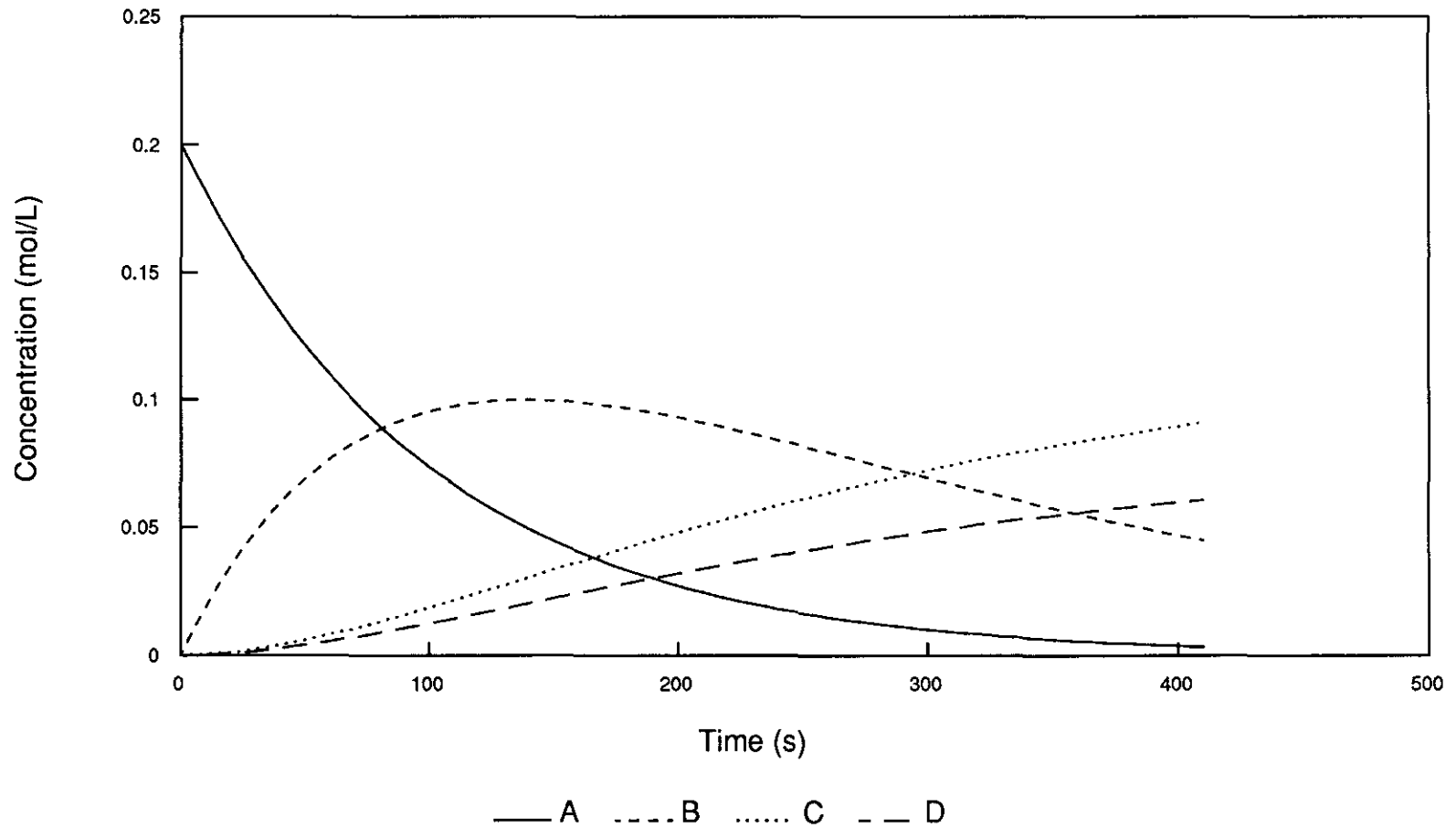
$$0 = \dots - 0.00005 \tau^2$$

$$\tau = \sqrt{\frac{1}{0.00005}} = 141.5$$

$$V = Q \tau = (141.5) \left(\frac{1}{3} \right) \text{ dm}^3/\text{s} = 47.1 \text{ dm}^3$$

ChE 4063 P9-6

Concentration Profiles for Batch Reactor

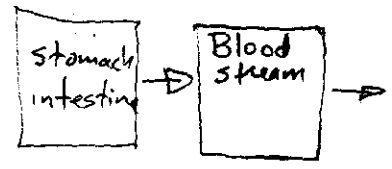


358x

U.S. $C_B = 1g/h(\text{body fluid})$
 Sweden = 0.5g/L
 E. Ger. A Soviet = 0g/L

Conc. of Ethanol
in bloodstream

(9-7)-1



$k_1 C_E$ = rate of absorption from the gastrointestinal tract into blood stream

$k_1 = 10h^{-1}$ $k_2 = 0.192 g/h(L \text{ body fluid})$

$-k_2$ = rate of ethanol breakdown in blood stream.

TREAT Ethanol in gastrointestinal and in blood as two different chemical compounds.

E - ethanol in gastrointestinal

B - ethanol in blood



$r_E = -k_1 C_E$

$r_B = k_1 C_E - k_2$

with $C_B > 0$ $k_2 = 0.192 g/h(L \text{ body fluid})$
 $C_B \leq 0$ $k_2 = 0$

Control volume is the body \rightarrow batch reactor well-mixed

Note this is a gross simplification of this process.

$\frac{dC_E}{dt} = r_E = -k_1 C_E$ $\frac{dC_E}{C_E} = -k_1 dt$ $\ln C_E = -k_1 t + C$ $t=0$
 $C_E = C_{Ei}$

$\ln(C_E/C_{Ei}) = -k_1 t$ or $C_E = C_{Ei} \exp(-k_1 t)$

$\frac{dC_B}{dt} = r_B = k_1 C_E - k_2 = k_1 C_{Ei} \exp(-k_1 t) - k_2$

$C_B = \frac{k_1 C_{Ei} \exp(-k_1 t)}{-k_1} - k_2 t + K$ $t=0$ $C_B = C_{Bi}$

$C_{Bi} = K + C_{Ei}$

$C_B = C_{Ei} (1 - \exp(-k_1 t)) - k_2 t + C_{Bi}$

parts a, b and c

(9-7)-2

$$t=0 \quad C_B = C_{B_i} = 0$$

$$C_{E_i} = \frac{2(40g)}{40L} = 2 g/L$$

$$C_E = (2 g/L) \exp(-10h^{-1}t) \quad C_B = (2 \frac{g}{L}) [1 - \exp(-10h^{-1}t)] - (0.192 \frac{g}{Lh})t$$

$$1 \frac{g}{L} = 2 \frac{g}{L} [1 - \exp(-10h^{-1}t)] - (0.192 \frac{g}{Lh})t$$

solve by trial & error, bisection, newton's method etc

a) U.S. $t = 5.2 \text{ hr}$

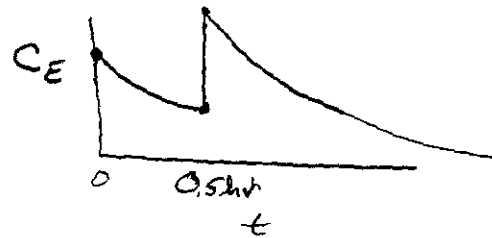
$$0.5 \frac{g}{L} = 2 [1 - e^{-10t}] - 0.192t$$

b) Sweden 7.8 hr

$$0 = 2 [1 - e^{-10t}] - 0.192t$$

c) E. Germany AND Soviet Union $t = 10.4 \text{ hr}$

d) Two drinks $\frac{1}{2}$ hr apart - the time would be come longer
 solve in two parts $t -$



$$C_B = \frac{1g}{L} [1 - \exp(-10t)] - 0.192t$$

at t just less than 0.5 hr $C_B = 0.897 \frac{g}{L}$

$$C_E = (1) \exp(-10t) = 0.0067$$

$$C_{E_i} = \frac{(0.00674g)(40L) + 40g}{40L} = 1.007 \frac{g}{L}$$

$$C_{B_i} = (0.897 \frac{g}{L})$$

$$C_B = 1.007 \left[1 - e^{-10t} \right] - 0.192t + 0.8979/L$$

(9-7)-3

total elapsed time

5.2

7.8

10.4

U.S	$t' = 4.7 \text{ hr}$	with $C_{B \text{ limit}} = 1 \text{ g/L}$
Sweden	$t' = 7.3 \text{ hr}$	$C_{B \text{ limit}} = 0.5 \text{ g/L}$
E. Ger AND USSR	$t' = 9.9$	$C_{B \text{ limit}} = 0 \text{ g/L}$

(e)
~~10~~ 10



$$\text{Intake} = \left(\frac{80 \text{ g}}{1 \text{ hr}} \right) t \quad \text{for } t \leq 1 \text{ hr}$$

$$= 0 \quad \text{for } t \geq 1 \text{ hr}$$

Derive new balance for first hour

$$V \frac{dC_E}{dt} = \text{Rate of Intake} + \text{gen} = 80 \text{ g/hr} + r_A V \quad V = 40 \text{ L}$$

$$\frac{dC_E}{dt} = \frac{2 \text{ g}}{\text{L hr}} - k_1 C_E \quad \frac{dC_E}{dt} + k_1 C_E = 2$$

$$\frac{d(\mu C_E)}{dt} = \mu \frac{dC_E}{dt} + \mu k_1 C_E = 2\mu \quad \frac{d\mu}{\mu} = +k_1 \quad \mu = e^{k_1 t}$$

$$d(e^{k_1 t} C_E) = \left(2e^{k_1 t} dt + k_1 e^{k_1 t} C_E dt \right) \quad e^{k_1 t} C_E = \frac{2}{k_1} e^{k_1 t} + k$$

$$t=0 \quad C_E = C_{Ei} \quad C_{Ei} = \frac{2}{k_1} + k \quad k = C_{Ei} - \frac{2}{k_1}$$

$$C_E = \frac{2}{k_1} + e^{-k_1 t} (C_{Ei} - \frac{2}{k_1}) = \frac{2}{k_1} [1 - e^{-k_1 t}] + e^{-k_1 t} C_{Ei}$$

for the case considered at $t=0 \quad C_E = 0 = C_{Ei}$

$$\frac{dC_B}{dt} = r_B = k_1 C_E - k_2 = \left(\frac{k_1}{k_1} \right) 2 [1 - e^{-k_1 t}] - k_2$$

$$C_B = 2 \left[t + \frac{e^{-k_1 t}}{k_1} \right] - k_2 t + k \quad (9-7)-4$$

$$t=0 \quad C_B = 0$$

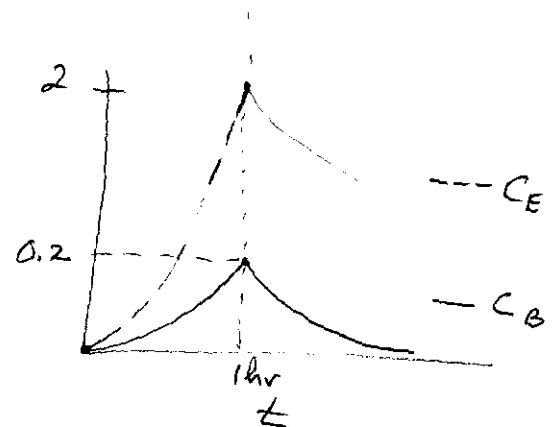
$$0 = 2 \left[0 + \frac{1}{k_1} \right] - 0 + k \quad k = -2/k_1$$

$$C_B = 2 \left[t + \frac{e^{-k_1 t}}{k_1} \right] - k_2 t - 2/k_1 = \frac{2}{k_1} \left[e^{-k_1 t} - 1 \right] + t(2 - k_2)$$

$$C_B = \left(\frac{2 \text{ hr}}{10} \right) \left[e^{-10t} - 1 \right] + t(2 - \underbrace{0.192}_{1.808})$$

$$\text{at } t=1 \text{ hr } C_B = 1.61 \text{ g/L}$$

$$C_E = 0.2 \text{ g/L}$$



at $t > 1 \text{ hr}$

$$C_{B_i} = 1.61 \quad C_{E_i} = 0.2 \text{ g/L}$$

$$C_B = 0.2(1 - e^{-10t}) - 0.192t + 1.61$$

	limit g/L	t'	(total elapsed)	t' is time from cessation of drinking
US	1	4.2	5.2	
Sweden	0.5	6.8	7.8	
E. Ger & USSR	0	9.4	10.4	

Note the rate limiting step was k_2 ! so all the answers are the same!

(f) on next page

+5 (g) Thin person vs. heavy person. }
+5

There is a difference in total fluid volume $V_{\text{Thin}} < V_{\text{heavy}}$. But there is also a

possible difference in the rate of metabolism of the ethanol in the blood stream, but I think this is minor.

A Heavy person will have a lower concentration of ethanol in the body than a thin person.

$$f) C_E = \frac{40+20}{40L} \text{ at } t=0$$

9-7-5

$$C_{E_i} = 1.59/L$$

from part a

$$C_B = C_{E_i} (1 - \exp(-k_1 t)) - k_2 t + 0$$

$$C_B \leq C_{B_{\text{limit}}} = 1.9/L$$

USA

{ In any other country you would ride the subway }

$$1.9/L \leq 1.59/L (1 - \exp(-10 \text{hr}^{-1} t)) - (0.192 \text{ g/hL}) t$$

$$t = 0.114 \text{ hr}$$

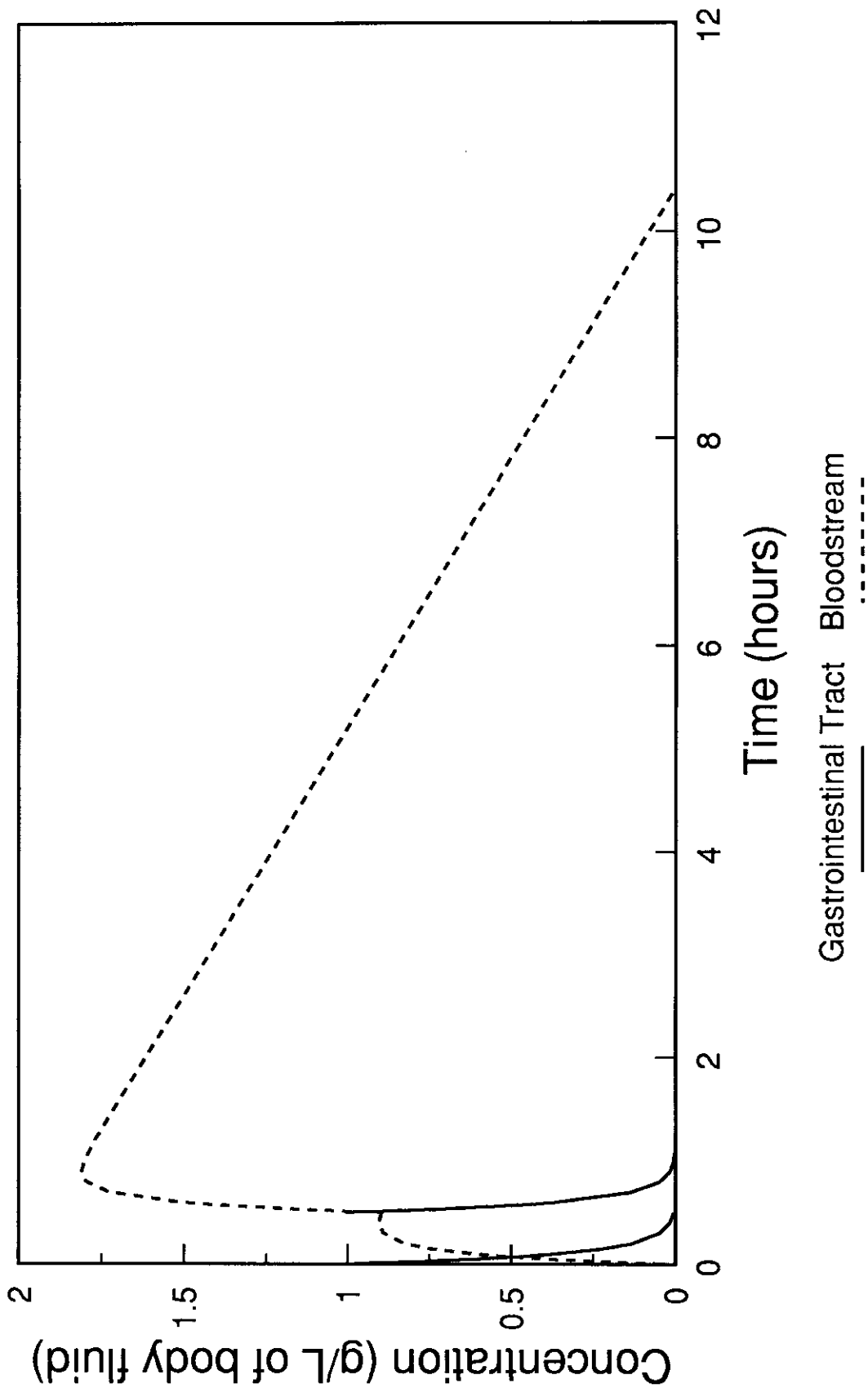
$$6.84 \text{ min}$$

$$t = 0.5 \text{ hr}$$

$$1.39$$

ChE 4063 P9-7 Alcohol Concentration Profiles

First tall martini at $t=0$; second tall martini at $t=0.5$ hr



ChE 4063 P9-7 Alcohol Concentration Profiles

Continuous tall martini intake rate of 80g/hr for 1 hour

