Assignment 4 - Solutions

1. For each of the following sets of reactions, describe reactor system and conditions to maximize the selectivity to D. The rates are in mol/(dm^3.s) and concentrations are in mol/dm^3. [6 Marks total]

(a) (1) A + B → D $-r_{1A} = 10 \exp(-8000\ ^oK/T)C_AC_B$

(2) A + B → U $-r_{2A} = 100 \exp(-1000\ ^oK/T)\ [C_A]^{1/2}\ [C_B]^{3/2}$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{10e^{-\frac{8000}{T}}C_AC_B}{100e^{-\frac{1000}{T}}C_A{}^{1/2}C_B{}^{3/2}} = \frac{0.1e^{-\frac{7000}{T}}C_A{}^{1/2}}{C_B{}^{1/2}}$$

[1 Mark] Reactor: Series of small CSTR with A flowing to the first CSTR and B added to each CSTR

PFR with A entering at the inlet, B as side streams

Semibatch reactor with A taken whole and B added slowly.

[1 Mark] Temperature: operate at high temperature

(b) (1) A + B → D $-r_{1A} = 100 \exp(-1000\ ^oK/T)C_AC_B$

(2) A + B → U $-r_{2A} = 10^6 \exp(-8000\ ^oK/T)\ C_AC_B$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{100e^{-\frac{1000}{T}}C_AC_B}{10^6e^{-\frac{8000}{T}}C_AC_B} = 10^{-4}e^{\frac{7000}{T}}$$

[1 Mark] Reactor: Any reactor type will do.

[1 Mark] Temperature: operate at low temperature

(c) (1) A + B → D $-r_{1A} = 10 \exp(-1000\ ^oK/T)C_AC_B$

(2) B + D → U $-r_{2A} = 10^9 \exp(-10000\ ^oK/T)\ C_BC_D$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{10e^{-\frac{1000}{T}}C_AC_B}{10^9e^{-\frac{10000}{T}}C_BC_D} = 10^{-4}e^{\frac{7000}{T}}\frac{C_A}{C_D}$$

[1 Mark] Reactor: PFR with high concentration of A (high pressure, no inert)

Remove D if possible; B can be introduced in any fashion.

Batch reactor with high concentration of A

Remove D if possible; B can be introduced in any fashion.

[1 Mark]Temperature: Operate at low temperature

2. Under certain conditions, A decomposes as follows

$$A \xrightarrow{k_1=0.1\ min^{-1}} R \xrightarrow{k_2=0.1\ min^{-1}} S$$

R is to be produced from 1000 liter/hr of feed in which C_{A0} = 1 mol/liter, C_{R0} = C_{S0} = 0.

(a) What size of plug flow reactor will maximize the concentration of R, and what is that concentration in the effluent stream from this reactor? [4 Marks total]

$$\tau_{max} = \frac{ln(k_2/k_1)}{k_2 - k_1}$$

For $k_2 = k_1$, $\tau_{max} = \frac{1}{k_1} = 10\ min.$ [2 Marks]

$$\frac{C_{R,max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}$$

For $k_2 = k_1$, $C_{R,max} = \frac{1}{e} = 0.368C_{A0}$ = 0.368 mol/liter. [2 Marks]

(b) What size of mixed flow reactor will maximize the concentration of R, and what is $C_{R,max}$ in the effluent stream from this reactor? [4 Marks total]

[2 Marks] $\tau_{max} = \frac{1}{\sqrt{k_1 k_2}} = 10\ min$

[2 Marks] $C_{R,max} = \frac{k_1 C_{A0}}{2\sqrt{k_1 k_2} + k_1 + k_2} = 0.25$ mol/lt

3. The following liquid-phase reactions were carried out in a CSTR at 325 K: [26 Marks total]

$3A \longrightarrow B + C$	$-r_{1A} = k_{1A}C_A$	k_{1A} = 7 min^{-1}
$2C + A \longrightarrow 3D$	$r_{2D} = k_{2D} C_A C_C^2$	k_{2D} = 3 $dm^6 mol^{-2} min^{-1}$
$4D + 3C \longrightarrow 3E$	$r_{3E} = k_{3E} C_D C_C$	k_{3E} = 2 $dm^3 mol^{-1} min^{-1}$

The concentrations measured inside the reactor were C_A = 0.1, C_B = 0.93, C_C = 0.51, and C_D = 0.049 all in mol/dm^3.

(a) What are the values of r_{1A}, r_{2A}, and r_{3A}?
$r_{1A} = - k_{1A}C_A = - 7*0.1 = - 0.7$ mol/(dm^3.min) [1 Mark]
$r_{2A} = - r_{2D} / 3 = - k_{2D}C_A C_C^2 = - 3*0.1*(0.51)^2 /3 = - 0.026$ mol/(dm^3.min) [1 Mark]
r_{2A} = 0[1 Mark]

(b) What are the values of r_{1B}, r_{2B}, and r_{3B}?
$r_{1B} = - r_{1A}/3 = 0.233$ mol/(dm^3.min) [1 Mark]
r_{2B} = 0[1 Mark]
r_{3B} = 0[1 Mark]

(c) What are the values of r_{1C}, r_{2C}, and r_{3C}?

r_{1C} = - $r_{1A}/3$ = 0.233 mol/(dm^3.min) [1 Mark]
r_{2C} = - 2/3r_{2D} = -0.052 mol/(dm^3.min) [1 Mark]
r_{3C} = - r_{3E} = $k_{3E} C_D C_C$ = -2*0.049*0.51 = -0.05 mol/(dm^3.min) [1 Mark]

(d) What are the values of r_{1D}, r_{2D}, and r_{3D}?
r_{1D} = 0[1 Mark]
r_{2D} = 0.078 mol/(dm^3.min) [1 Mark]
r_{3D} = -4/3 r_{3E} = - 4/3*2*0.049*0.51 = - 0.0667 mol/(dm^3.min) [1 Mark]

(e) What are the values of r_{1E}, r_{2E}, and r_{3E}?
r_{1E} = 0[1 Mark]
r_{2E} = 0[1 Mark]
r_{3E} = 0.05 mol/(dm^3.min) [1 Mark]

(f) What are the net rates of formation of species A, B, C, D and E?
r_A = -0.726 mol/(dm^3.min) [1 Mark]
r_B = 0.233 mol/(dm^3.min) [1 Mark]
r_C = 0.131 mol/(dm^3.min) [1 Mark]
r_D = 0.0113 mol/(dm^3.min) [1 Mark]
r_E = 0.05 mol/(dm^3.min) [1 Mark]

(g) The entering volumetric flow rate is 100 dm^3/min and the entering concentration of A is 3 mol/liter. What is the CSTR reactor volume?

$\frac{V}{v_0} = \frac{C_{A0}-C_A}{-r_A}$; $V = 400$ dm^3. [1 Mark]

(h) What are the exit molar flow rates from the CSTR of volume obtained in (*g*)?
$F_A = v_0 C_A$ = 10 mol/min[1 Mark]
$F_B = v_0 C_B$ = 93 mol/min[1 Mark]
$F_C = v_0 C_C$ = 51 mol/min[1 Mark]
$F_D = v_0 C_D$ = 4.9 mol/min[1 Mark]
C_E is not known. But we know that $\frac{V}{v_0} = \frac{C_{E0}-C_E}{-r_E} = 4$
Solving for C_E, $C_E = 0.2$ mol/dm^3
$F_E = v_0 C_E$ = 20 mol/min. [1 Mark]

4. The complex reactions involved in the oxidation of formaldehyde to formic acid over a Vanadium titanium oxide catalyst are shown below. Each reaction follows an elementary rate law:

HCHO + ½ O_2 $\xrightarrow{k_1}$ HCOOH $\xrightarrow{k_3}$ CO + H_2O

2HCHO $\xrightarrow{k_2}$ $HCOOCH_3$

$HCOOCH_3$ + H_2O $\xrightarrow{k_4}$ CH_3OH + HCOOH. [H_2O was missed in the problem sheet!]

Let A = HCHO, B = O_2, C = HCOOH, D = $HCOOCH_3$, E = CO, W = H_2O and G = CH_3OH.
The entering flow rates are F_{A0} = 10 mol/s and F_{B0} = 5 mol/s, and v_0 = 100 dm^3/s. At a total entering concentration C_{T0} = 0.147 mol/dm^3, the suggested reactor volume is 1000 dm^3.

Data available:
At 300 K,
k_1 = 0.014 (dm^3/mol)$^{1/2}$ s^{-1}.
k_2 = 0.007 dm^3/(mol.s)
k_3 = 0.014 s^{-1}
k_4 = 0.45 dm^3/(mol.s)

(a) Plot the molar flow rates of each species along the volume (length) of the reactor on the same figure.
(b) Plot and analyze $\tilde{Y}_C$, $\tilde{S}_{A/E}$, $\tilde{S}_{C/D}$ and $\tilde{S}_{D/G}$ along the length of the reactor. Find volume at which maximum occur, if any.

Solution: [10 marks]

$$A + \tfrac{1}{2} B \xrightarrow{k_1} C \xrightarrow{k_3} E + W$$

$$2A \xrightarrow{k_2} D$$

$$D + W \xrightarrow{k_4} G + C$$

$r_A = -k_1C_AC_B^{1/2} - k_2C_A^2$

$r_B = -\frac{1}{2}k_1C_AC_B^{1/2}$

$r_C = k_1C_AC_B^{1/2} - k_3C_C + k_4C_DC_W$

$r_D = \frac{1}{2}k_2C_A^2 - k_4C_DC_W$

$r_E = k_3C_C$

$r_G = k_4C_DC_W$

$r_W = k_3C_C - k_4C_DC_W$

$\frac{dF_i}{dV} = r_i$ and $C_i = C_{T0}\frac{F_i}{F_T}$ where $F_T = \sum F_i$

Solve the ODEs numerically in Matlab.