# HW7_Soln

November 11, 2021

[2]:
```
import numpy as np
import matplotlib.pyplot as plt
```

## 0.1 Problem 1

Your company has two liquid streams available containing solutes that are not profitably marketable at the present time. One stream contains an aqueous solution of A. The second stream contains an aqueous solution of species B. Species A can react either with species B or with itself according to the following stoichiometric equations and rate expressions:

$$A + B \rightarrow V; r_V = k_1 C_A C_B (1)$$

$$2A \rightarrow W; r_W = \frac{k_2 C_A^2}{1 + k_3 C_V^{1/2}} (2)$$

### 0.1.1 Part (a)

You have two beakers containing samples of the two streams and desire to carry out a small-scale laboratory experiment in which you maximize the formation of species V. In what manner should you carry out this experiment; that is, in what order and at what rate would you add each beaker of the reactants to an empty container?

Reactant A should be slowly added to B, minimizing the amount of A in the vessel and favoring reaction 1.

### 0.1.2 Part (b)

If you desire to produce V in a flow reactor, what type of reactor and operating conditions do you recommend?

I would recommend a PFR, as this would allow an initial feed containing only B, and small amounts of A could be added along the length of the reactor. This would let us keep the rate of reaction 1 high relative to the undesirable reaction 2.

### 0.1.3 Part (c)

If the activation energies for the rate constants k1, k2, and k3 are 60, 40, and 50 kJ/mol, respectively, what additional statements can you make regarding the operating conditions recommended for maximizing production of species V?

$$\frac{r_V}{r_W} = \frac{A_1 e^{-60/RT} C_B}{A_2 e^{-40/RT} C_A}(1 + A_3 e^{-50/RT} C_V^{1/2})$$

since the activation energies associated with the valued reaction and with the denominator of the the unvalued reaction are both higher than the activation energy in the numerator of the unvalued reaction, a high temperature will improve the relative rate of the two reactions.

## 0.2 Problem 2

### 0.2.1 Part (a)

Consider the following network of competitive first-order reactions:

$$A \longleftrightarrow V$$

$$A \rightarrow W$$

in which species V is the desired product. If these reactions take place in a CSTR operating at steady state, derive the analytical relation between the space time that maximizes the effluent concentration of species V and the kinetic parameters of the system. You may assume that the feed consists of species A dissolved in a liquid to give a concentration A0.

Mass balances:

$$C_{A0} = C_A + \tau(k_f C_A - k_r C_V + k_2 C_A)$$
$$0 = -C_V + \tau(-k_r C_V + k_f C_A)$$

Solving for $C_V$ in terms of $C_{A0}$:

$$C_V = \frac{C_{A0} k_f \tau}{1 + k_f\tau + k_r\tau + k_2\tau(1 + k_r\tau)}$$

Then taking the derivative and solving for $\tau$

$$\tau = \frac{1}{\sqrt{k_2 k_r}}$$

### 0.2.2 Part (b)

If the reactor is operated at the flow rate corresponding to the optimum determined in part (a), determine the effluent concentrations of species A, V, and W when the temperature of the effluent is 60°C. At this temperature, kf = 0.50, kr = 0.125, and k2 = 0.08 (all in min1 ). The concentration of A in the feed stream is 2.0 M.

[43]:
```
k_f, k_r, k_2 = (0.5, 0.125, 0.08) #min^-1
CA0 = 2.0 #M

tau_1 = 1/np.sqrt(k_2*k_r)
print('tau_opt =', tau_1, 'min')

def C_func(k,tau):
```

```
    k_f,k_r,k_2=k
    CA = (CA0+tau*k_r*CA0)/(1+k_f*tau+k_r*tau+k_2*tau*(1+k_r*tau))
    CV = CA*k_f*tau/(1+k_r*tau)
    CW = k_2*CA*tau
    return CA,CV,CW

C_A, C_V, C_W = C_func((0.5, 0.125, 0.08),tau_1)

print('CA =', C_A, 'M')
print('CV =', C_V, 'M')
print('CW =', C_W, 'M')
```

```
tau_opt = 10.0 min
CA = 0.49723756906077343 M
CV = 1.1049723756906076 M
CW = 0.39779005524861877 M
```

### 0.2.3 Part (c)

For operation at the optimum space time determined in part (b), determine the rate at which thermal energy (heat) must be supplied to or removed from the reactor if the feed stream enters the reactor at 60°C. The standard enthalpy changes for the reversible and irreversible reactions are 50.0 and +30.0 kcal/mol, respectively. Be sure to indicate the direction of heat transfer. The volume of the reactor is 4.0m3 .

$$Q = V_{reac} \cdot (h_1 r_1 + h_2 r_2)$$

[41]:

```
h_1 = -50 #kcal/mol
h_2 = 30 #kcal/mol
V = 4*1000 #L

r_1 = k_f*C_A - k_r*C_V
r_2 = k_2*C_A
Q = V * (h_1*r_1 + h_2*r_2)

print('Q =', Q, 'kcal/min')
```

```
Q = -17325.966850828732 kcal/min
```

That is, we need to remove 17325 kcal/min

### 0.2.4 Part (d)

If the activation energies associated with kf , kr, and k2 are 20, 30, and 40 kcal/mol, does the maximum effluent concentration of species V increase, decrease, or stay the same when the operating temperature is increased by 10 K? First present a qualitative argument and then be as quantitative as possible.

$$\frac{k_f}{k_r} = \frac{A_f}{A_r} e^{E_{a,r}-E_{a,f}/RT} = \frac{A_f}{A_r} e^{10/RT} = K_{eq}$$

An increase in temperature will decrease $K_{eq}$, indicating a shift towards the reactant. In addition, the unfavorable reaction is irreversible, and will proceed faster.

[47]:

```
Ea_f = 20*4184 #J/mol
Ea_r = 30*4184 #J/mol
Ea_2 = 40*4184 #J/mol

T_1 = 273+60
T_2 = T_1 + 10

R = 8.314 #J/mol/K

#From given information, calculate Arrhenius prefactors, then new reaction␣
 ↪constants
A_f = k_f/np.exp(-Ea_f/R/T_1)
A_r = k_r/np.exp(-Ea_r/R/T_1)
A_2 = k_2/np.exp(-Ea_2/R/T_1)

k_f_2 = A_f * np.exp(-Ea_f/R/T_2)
k_r_2 = A_r * np.exp(-Ea_r/R/T_2)
k_2_2 = A_2 * np.exp(-Ea_2/R/T_2)
print(k_f_2)
print(k_r_2)
print(k_2_2)

tau_2 = 1/np.sqrt(k_2_2*k_r_2)
print(tau_2)

C_A, C_V, C_W = C_func((k_f_2,k_r_2,k_2_2),tau_2)
print('CA =', C_A, 'M')
print('CV =', C_V, 'M')
print('CW =', C_W, 'M')
```

```
1.2068943455385661
0.4687690016988761
0.4661100676137484
2.1393227796781358
CA = 0.6085885885195248 M
CV = 0.7845512842458366 M
CW = 0.6068601272346382 M
```

The new concentration of V is 0.785 M, lower than when the reactor is at 333 K.

### 0.3 Problem 3

A cascade of two identical CSTRs is being used to produce the intermediate V in the reaction sequence

$$A \longrightarrow V \longrightarrow W$$

In the presence of an appropriate catalyst, the first reaction is pseudo first-order:

$$r_1 = k_1 C_A$$

where the dependence of the rate on the catalyst concentration is incorporated in the rate constant. In the presence of the same catalyst, the second reaction in the sequence is pseudo zero-order in all species:

$$r_2 = k_2$$

If both reactors operate at the same temperature, derive an expression for the reactor space time that leads to the maximum concentration of species V in the effluent from the second reactor. Consider the general case in which both A and V are present in the feed stream at concentrations CA0 and CV0. Your expression need not be an explicit closed form expression for . The reaction takes place in the liquid phase. If one operates at the space time that maximizes the concentration of species V in the effluent from the second reactor, what fraction of the A fed to the cascade ends up as V when k1 = 8.33 ks1 , k2 = 0.5 kmol/(m3 ks), CA0 = 1.80 kmol/m3 , and CV0 = 0.18 kmol/m3 . Note that a trial-and-error solution will be required to arrive at a numerical answer.

$$C_{A1} = \frac{C_{A0}}{1+k_1\tau},\ and\ C_{A2} = \frac{C_{A0}}{(1+k_1\tau)^2}$$

$$\frac{dN_{V1}}{dt} = qC_{V0} - qC_{V1} + k_1C_{A1}V - k_2V = 0$$

$$C_{V1} = C_{V0} + (\frac{k_1C_{A0}}{1+k_1\tau} - k_2)\tau$$

$$\frac{dN_{V2}}{dt} = qC_{V1} - qC_{V2} + k_1C_{A2}V - k_2V = 0$$

$$C_{V2} = C_{V0} + \frac{k_1C_{A0}(2+k_1\tau)}{(1+k_1\tau)^2}\tau - 2k_2\tau$$

$$\frac{dC_{V2}}{d\tau} = \frac{2C_{A0}k_1}{(k_1\tau+1)^3} - 2k_2 = 0$$

[55]:
```
k1 = 8.33
k2 = 0.5
CA0 = 1.8
CV0 = 0.18

#Solving for tau
tau_opt = ((k1*CA0/k2)**(1/3) - 1)/k1
print('tau_opt =', tau, 'ks')

CV2 = CV0 + k1*CA0*tau_opt*(2*k1*tau_opt)/((1+k1*tau_opt)**2) - 2*k2*tau_opt
print('CV2 =', CV2, 'kmol/m^3')
```

```
print((CV2-CV0)/CA0)
```

```
tau_opt = 0.2529193461025727 ks
CV2 = 1.5825644571370299 kmol/m^3
0.7792024761872388
```

$$\frac{C_{V2} - C_{V0}}{C_{A0}} = 0.779$$

## 0.4 Problem 4

For autocatalytic reactions it is often appropriate to employ a reactor configuration in which a CSTR operating at the maximum rate is followed by a plug flow reactor. Another alternative would be to employ a recycle reactor in which a portion of the effluent from a PFR is recycled to the reactor inlet. Consider an irreversible autocatalytic reaction with the stoichiometry

$$A \longrightarrow B$$

and a rate expression

$$r = kC_AC_B$$

This reaction takes place in the liquid phase with k = 0.08 L/(molmin) at the temperature of interest. The recycle ratio R represents the ratio of the volumetric flow rate of the material recycled to the reactor inlet (i.e., at point 5) to the volumetric flow rate of the material leaving the composite system (i.e., at point 4). Consider a situation in which R = 1.5, the concentration of reactant A in the fresh feed (point 1) is 1.6 M, and the concentration of species B in the reactor effluent (point 3) is 1.2M. The reactor operates isothermally. The flow rate of the feedstock at point 1 is 2 L/min.

### 0.4.1 Part (a)

The volumetric flow rate at point 2.

$$F_1 = F_4 = 2\frac{L}{min}$$

$$R = \frac{F_5}{F_4} \Rightarrow F_5 = 3\frac{L}{min}$$

$$F_2 = F_1 + F_5 = 5\frac{L}{min}$$

### 0.4.2 Part (b)

The concentrations of species A and B at point 2

$$C_{A1} = 1.6M,\ F_1 = 2$$

$$C_{B5} = 1.2M,\ F_5 = 3$$

$$C_{A2} = \frac{F_1C_{A1} + F_5C_{A5}}{F_2}$$

$$C_{A3} = C_{A5} = C_{A1} - C_{B3} = 0.4M$$

$$C_{B2} = \frac{C_{B5} \cdot F_5}{F_2} = 0.72M$$

$$C_{A2} = 0.88M$$

### 0.4.3 Part (c)

The total length of the PFR necessary to accomplish this reaction if the inside diameter of the reactor is 10 cm.

$$V = F_{A0} \int_{X1}^{X2} \frac{dX}{-r_A} = F_{A2} \int_{X1}^{X2} \frac{dX}{kC_A C_B}$$

$$X1 = 0.45, \ X2 = 0.75$$

$$C_A = C_{A2}(1 - X), \ C_B = C_{A2}X + C_{B2}$$

$$V = 44.4L = 44400cm^3$$

Making the length of PFR = 566 cm

### 0.4.4 Part (d)

Maximizing the reaction rate means maximizing $C_A C_B$. Using the expressions from part (c) and taking the derivative gives $\Delta X = 0.09$

Solving the integral above again with an upper limit of 0.54 gives $V = 11.0L$, which corresponds to a reactor length of 140 cm.

## 0.5 Problem 5

For illustration 9.6, which value of fractional conversion gives the maximum rate of A reaction in a CSTR? ILLUSTRATION 9.6 Autocatalytic Decomposition of 5-Methyl-2-Oxazolidinone When heated above 200°C, pure 5-methyl-2-oxazolidinone decomposes into two products, CO2 gas and N-(2-hydroxypropyl) imidazolidinone. The stoichiometry is or

$$2A \to B + C$$

where C represents CO2. While we have taken some liberties with the numerical values that we will subsequently employ, the following set of mechanistic equations has been proposed in an effort to explain the observed autocatalytic kinetic behavior (13):

$$2A \to B + C$$

$$A + B \to AB$$

$$2AB \to 3B + C$$

where AB is an intermediate complex. Verify that this mechanism produces autocatalytic behavior. If the following values (in m3 /(kmol-Msec)) are assumed for the reaction rate constants: k1 = 1.02, k2 = 150, and k3 = 172, determine the fraction conversion of A that leads to the maximum rate at which B can be produced in an ideal CSTR with a fixed volume VR. No special constraint is to be placed on the volumetric feed rate or the initial concentration of species A.

$$
\begin{aligned}
-r_A &= 2k_1C_A^2 + k_2C_AC_B = 2k_1C_{A0}^2(1-X)^2 + k_2C_{A0}^2X(1-X) \\
\frac{d(-r_A)}{dX} &= -4k_1C_{A0}^2(1-X) + k_2C_{A0}^2(1-2X)
\end{aligned}
$$

Setting this to 0 and solving for X, gives a result of $X = 0.493$

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