Solutions to workshop 06: Multiple reactions

Lecture notes for chemical reaction engineering

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Try following problems from Fogler 5e (Fogler 2016). P 8-3, P 8-4, P 8-7, P 8-9

We will go through some of these problems in the workshop.

P 8-3

The following reactions

$$\mathrm{A} \underset{}{\overset{k_1}{\rightleftharpoons}} \mathrm{D} \qquad -r_{1A} = k_1\left[C_A - C_D/K_{1A}\right]$$

$$\mathrm{A} \underset{}{\overset{k_2}{\rightleftharpoons}} \mathrm{U} \qquad -r_{2A} = k_2\left[C_A - C_U/K_{2A}\right]$$

take place in a batch reactor.

Additional information:

k_1 = 1.0 min^{-1}; K_{1A}= 10

k_2 = 100 min^{-1}; K_{2A} = 1.5

C_{A0} = 1 mol/dm^3

(a) Plot and analyze conversion and the concentrations of A, D, and U as a function of time. When would you stop the reaction to maximize the concentration of D? Describe what you find.

(b) When does the maximum concentration of U occur? (Ans.: t = 0.04 min)

(c) What are the equilibrium concentrations of A, D, and U?

(d) What would be the exit concentrations from a CSTR with a space time of 1.0 min? Of 10.0 min? Of 100 min?

Solution

Hand written solution

```python
import numpy as np
from scipy.integrate import solve_ivp
from scipy.optimize import fsolve
import matplotlib.pyplot as plt
from IPython.display import display, Markdown

def batch_reactor(t, y, *args):
  ca, cd, cu = y
  k1, k2, k1A, k2A = args

  r1a = k1 * (ca - cd/k1A)
  r2a = k2 * (ca - cu/k2A)

  dcadt = -r1a -r2a
  dcddt = r1a
  dcudt = r2a

  return [dcadt, dcddt, dcudt]

k1 = 1.0 # 1/min
k2 = 100 # 1/min
k1A = 10.0
k2A = 1.5

ca0 = 1.0

# initial conditions
y0 = [ca0, 0, 0]
args = (k1, k2, k1A, k2A)
t_final = 12

sol = solve_ivp(batch_reactor, [0, t_final], y0, args=args, dense_output=True)

t = np.linspace(0,t_final, 1000)
ca, cd, cu = sol.sol(t)
```

```python
plt.plot(t, ca, label='$C_A$')
plt.plot(t, cd, label='$C_D$')
plt.plot(t, cu, label='$C_U$')

plt.xlabel('time (min)')
plt.ylabel('Concentration ($mol/dm^3$)')

# Setting x and y axis limits
plt.xlim(0, t_final)
plt.ylim(0, ca0)

plt.legend()
plt.show()
```

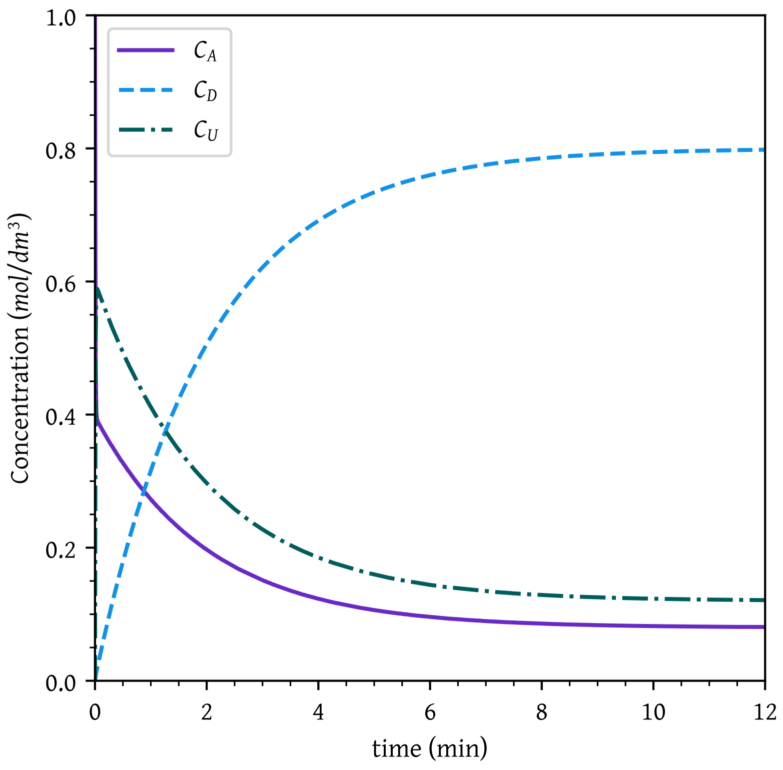


Figure 1: Concentration profile

```
cumax_idx = np.argmax(cu)
tumax = t[cumax_idx]
cumax = cu[cumax_idx]
```

- Maximum concentration of U, C_U = C_{Umax} = 0.59 mol/dm^3 occurs at t_{Umax} = 0.04 min
- As C_D keeps on increasing with time until the equilibrium is reached, To maximize C_D, stop the reaction after equilibrium is reached.

```
cae = ca[-1]
cde = cd[-1]
cue = cu[-1]
```

- Equilibrium concentrations

  C_{Ae} = 0.08 mol/dm^3

  C_{De} = 0.80 mol/dm^3

  C_{Ue} = 0.12 mol/dm^3

```
def cstr(vars, *args):
  ca, cd, cu = vars
  t, k1, k2, k1A, k2A = args

  r1a = k1 * (ca - cd/k1A)
  r2a = k2 * (ca - cu/k2A)

  eq1 = ca0 - ca - t * (r1a + r2a)
  eq2 = -cd + t * r1a
  eq3 = -cu + t * r2a

  return [eq1, eq2, eq3]


initial_guess = [ca0, 0, 0]
times = [1, 10, 100]

md = ""

for tau in times:
  args = (tau, k1, k2, k1A, k2A)
  ca, cd, cu = fsolve(cstr, initial_guess, args=args)

  md += (
    f"At $\\tau$ = {tau:.2f} min.:\n"
    f"$C_A$ = {ca:.2f} $mol/dm^3$,\n"
    f"$C_D$ = {cd:.2f} $mol/dm^3$,\n"
    f"$C_U$ = {cu:.2f} $mol/dm^3$ \n\n"
  )

display(Markdown(md))
```

At τ = 1.00 min.: C_A = 0.30 mol/dm^3, C_D = 0.27 mol/dm^3, C_U = 0.44 mol/dm^3
At τ = 10.00 min.: C_A = 0.13 mol/dm^3, C_D = 0.67 mol/dm^3, C_U = 0.20 mol/dm^3
At τ = 100.00 min.: C_A = 0.09 mol/dm^3, C_D = 0.78 mol/dm^3, C_U = 0.13 mol/dm^3

P 8-4

Consider the following system of gas-phase reactions:

$$\begin{array}{lll} \mathrm{A} \longrightarrow \mathrm{X} & r_X = k_1 C_A^{1/2} & k_1 = 0.004\ (mol/dm^3)^{1/2} \cdot min^{-1} \\ \mathrm{A} \longrightarrow \mathrm{B} & r_B = k_2 C_A & k_2 = 0.3\, min^{-1} \\ \mathrm{A} \longrightarrow \mathrm{Y} & r_Y = k_3 C_A^2 & k_3 = 0.25\, dm^3/mol \cdot min^{-1} \end{array}$$

B is the desired product, and X and Y are foul pollutants that are expensive to get rid of. The specific reaction rates are at 27 °C. The reaction system is to be operated at 27 °C and 4 atm. Pure A enters the system at a volumetric flow rate of 10 dm^3/min.

(a) Sketch the instantaneous selectivities ($S_{B/X}$, $S_{B/Y}$, and $S_{B/XY} = r_B/(r_X + r_Y)$) as a function of the concentration of $C_A$.

(b) Consider a series of reactors. What should be the volume of the first reactor?

(c) What are the effluent concentrations of A, B, X, and Y from the first reactor?

(d) What is the conversion of A in the first reactor?

(e) If 99% conversion of A is desired, what reaction scheme and reactor sizes should you use to maximize $S_{B/XY}$?

(f) Suppose that E_1 = 20,000 cal/mol, E_2=10,000 cal/mol, and E_3=30,000 cal/mol. What temperature would you recommend for a single CSTR with a space time of 10 min and an entering concentration of A of 0.1 mol/dm^3 ?

Solution

Hand written solution

```
import numpy as np
from scipy.integrate import solve_ivp
from scipy.optimize import fsolve
from scipy.optimize import minimize_scalar
from scipy.integrate import quad
import matplotlib.pyplot as plt
from IPython.display import display, Markdown


rx = lambda ca: 0.004 * ca**0.5
rb = lambda ca: 0.3 * ca
ry = lambda ca: 0.25 * ca**2

sbx = lambda ca: rb(ca)/rx(ca)
sby = lambda ca: rb(ca)/ry(ca)
sbxy = lambda ca: rb(ca)/(rx(ca) + ry(ca))

ca = np.linspace(1e-4,1,100)
```

```
plt.plot(ca,sbx(ca))

plt.xlabel('$C_A$ ($mol/dm^3$)')
plt.ylabel('$S_{B/X}$')

# Setting x and y axis limits
plt.xlim(0, ca[-1])
plt.ylim(0, np.ceil(sbx(ca[-1])))

plt.show()
```

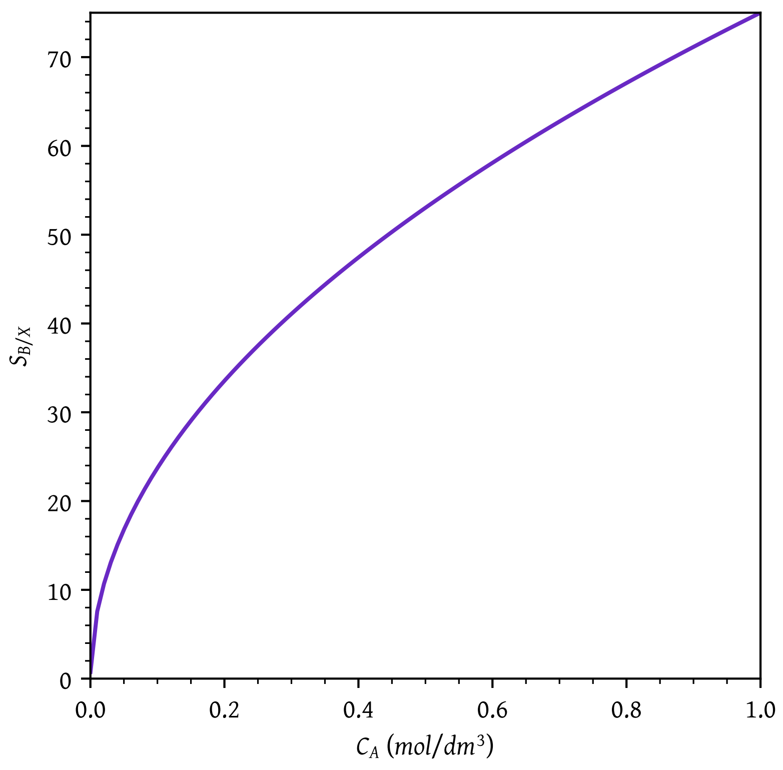


Figure 2: $S_{B/X}$

```
plt.plot(ca,sby(ca))

plt.xlabel('$C_A$ ($mol/dm^3$)')
plt.ylabel('$S_{B/Y}$')

# Setting x and y axis limits
plt.xlim(0, ca[-1])
plt.ylim(0, 20)

plt.show()
```

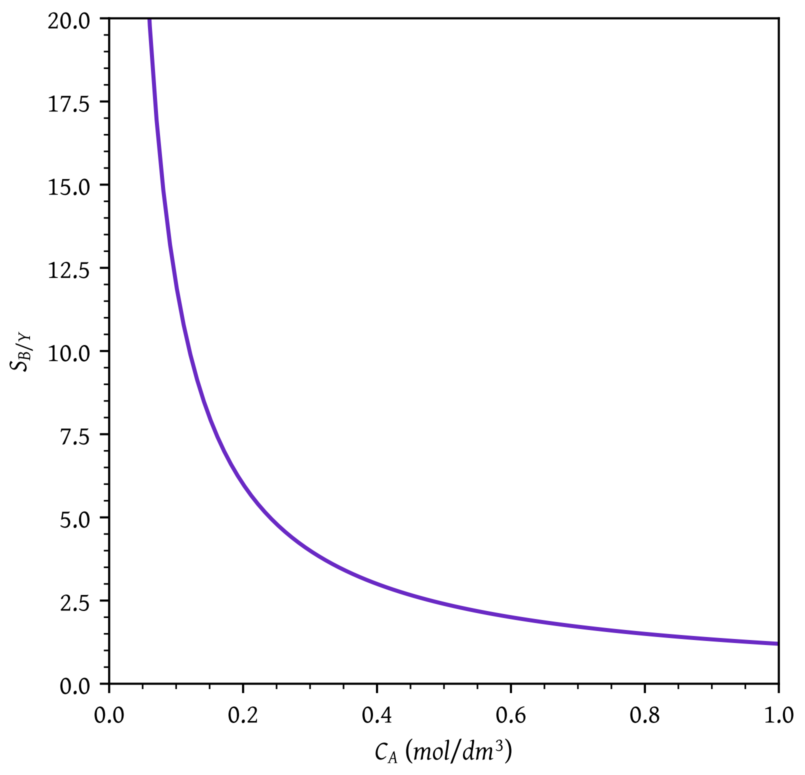


Figure 3: $S_{B/Y}$

```
plt.plot(ca,sbxy(ca))

plt.xlabel('$C_A$ ($mol/dm^3$)')
plt.ylabel('$S_{B/XY}$')

# Setting x and y axis limits
plt.xlim(0, ca[-1])
plt.ylim(0, 12)

plt.show()
```

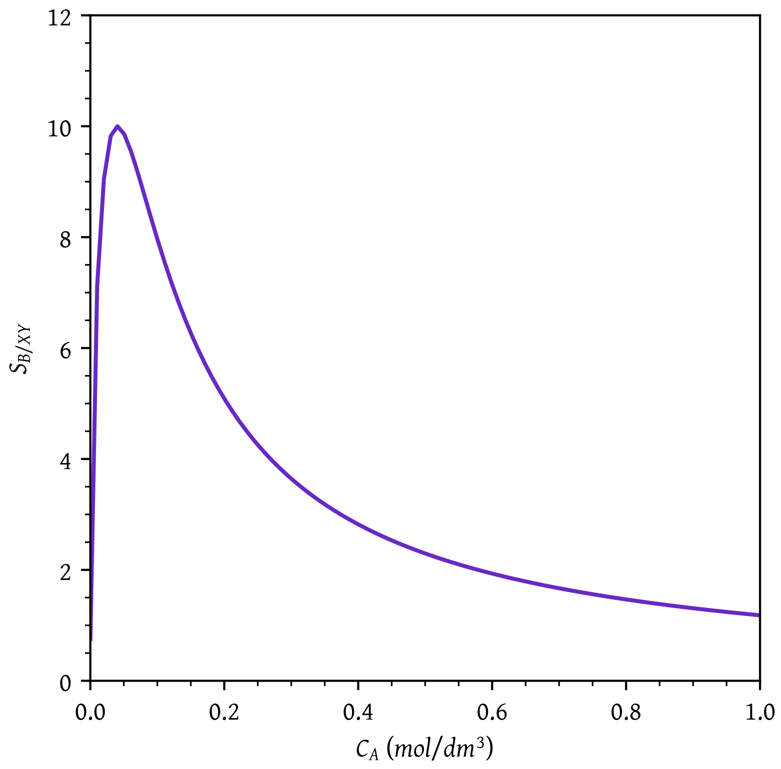


Figure 4: $S_{B/XY}$

```python
# Maximize S_B/XY
bounds=(1e-4, 1)
# Maximize the selectivity by minimizing the negative of the selectivity function
result = minimize_scalar(lambda ca: -sbxy(ca), method='bounded', bounds=bounds)

camax = result.x
sbxy_max = sbxy(camax)
```

- Maximum concentration of A, C_{Amax} = 0.04 mol/dm^3

  Maximum selectivity = 10.00

- The CSTR operates at exit concentration of 0.04 mol/dm^3

```python
T = 27 + 273.15 # K
v0 = 10 # dm^3/min
P = 4 # atm
ya0 = 1 # pure A
R = 0.082

ca0 = ya0 * P /(R * T)

rate = rx(camax) + rb(camax) + ry(camax)
v_cstr = v0 * (ca0 - camax)/ rate
```

- C_{A0} = 0.163 mol/dm^3

- V_{CSTR} = 92.81 dm^3

```
tau_cstr = v_cstr/v0

cb_cstr = tau_cstr* rb(camax)
cx_cstr = tau_cstr* rx(camax)
cy_cstr = tau_cstr* ry(camax)
```

Exit concentration of CSTR

- C_B = 1.114e-01 mol/dm^3
- C_X = 7.425e-03 mol/dm^3
- C_Y = 3.713e-03 mol/dm^3

```
x_cstr = (ca0 - camax)/ca0
```

Conversion in first reactor = 0.75

```
fa0 = ca0*v0
fa0_by_ra = fa0/(rb(ca) + rx(ca) + ry(ca))
x = (ca0 - ca)/ca0
plt.plot(x,fa0_by_ra)

plt.xlabel('$X$')
plt.ylabel('$F_{A0}/-r_A$')

# Setting x and y axis limits
plt.xlim(0, 1)
# plt.ylim(0, 10000)

plt.show()
```

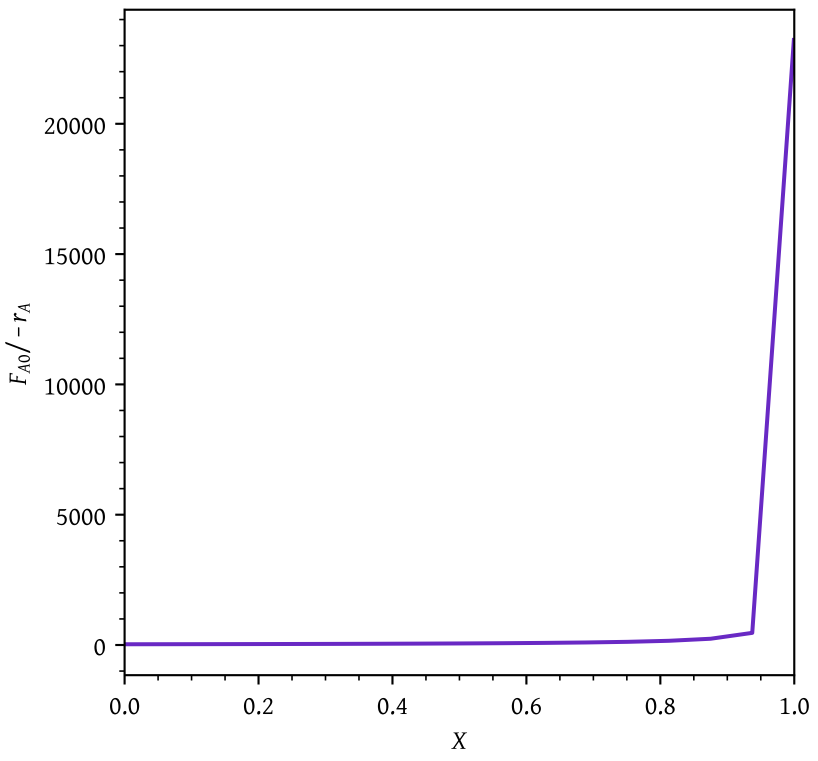


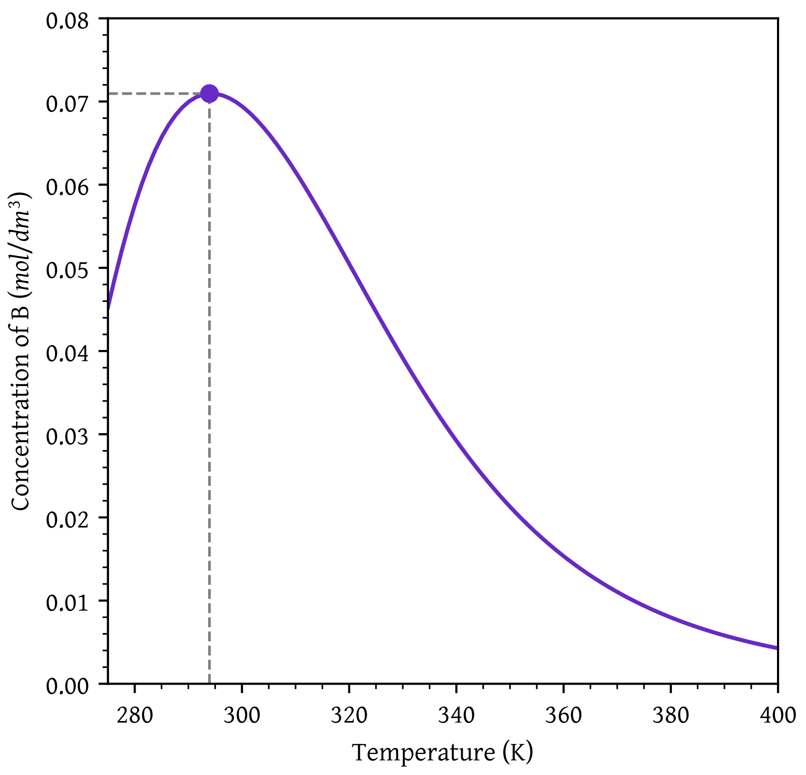
Figure 5: Levenspiel plot

```
def pfr(x, *args):
  fa0 = args[0]

  ca = ca0 * (1 - x)
  return fa0/(rb(ca) + rx(ca) + ry(ca))

x_start = x_cstr
x_end = 0.99

v_pfr, _ = quad(pfr, x_start, x_end, args=(fa0))
```

Figure 6

PFR volume required to achieve final conversion of 0.99 = 91.18 dm^3

```
e1 = 20000
e2 = 10000
e3 = 30000

k1 = lambda T: 0.004 * np.exp((e1/1.98) * ((1/T) - (1/300)))
k2 = lambda T: 0.3   * np.exp((e2/1.98) * ((1/T) - (1/300)))
k3 = lambda T: 0.25  * np.exp((e3/1.98) * ((1/T) - (1/300)))

rxt = lambda ca,T: k1(T) * ca**0.5
rbt = lambda ca,T: k2(T) * ca
ryt = lambda ca,T: k3(T) * ca**2

sbxt = lambda ca,T: rbt(ca,T)/rxt(ca,T)
sbyt = lambda ca,T: rbt(ca,T)/ryt(ca,T)
sbxyt = lambda ca,T: rbt(ca,T)/(rxt(ca,T) + ryt(ca,T))

tau = 10
ca0 = 0.1

initial_guess = [ca0, 0, 0, 0]

def cstr_btx(vars, *args):
  ca, cx, cb, cy = vars
  tau, T = args

  r1 = rxt(ca,T)
  r2 = rbt(ca,T)
  r3 = ryt(ca,T)

  eq1 = ca0 - ca - tau * (r1 + r2 + r3)
  eq2 = -cx + tau * r1
  eq3 = -cb + tau * r2
  eq4 = -cy + tau * r3

  return [eq1, eq2, eq3, eq4]

# Function to solve the CSTR equations for a given temperature
def maximize_cb(T):
    args = (tau, T)
    ca, cx, cb, cy = fsolve(cstr_btx, initial_guess, args=args)
    return -cb

result = minimize_scalar(maximize_cb, bounds=(275, 400), method='bounded')

optimal_temp = result.x
max_cb = -result.fun


temps = np.linspace(275,400,100)
cb_values = []

for temp in temps:
  args = (tau, temp)
  ca, cx, cb, cy = fsolve(cstr_btx, initial_guess, args=args)
```



- Optimal temperature for maximizing C_B = 294.26 K. Maximum C_B= 0.07

P 8-9

The elementary liquid-phase series reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

is carried out in a 500-dm^3 batch reactor. The initial concentration of A is 1.6 mol/dm^3. The desired product is B, and separation of the undesired product C is very difficult and costly. Because the reaction is carried out at a relatively high temperature, the reaction is easily quenched.

(a) Plot and analyze the concentrations of A, B, and C as a function of time. Assume that each reaction is irreversible, with $k_1 = 0.4\,h^{-1}$ and $k_2 = 0.01\,h^{-1}$.

(b) Plot and analyze the concentrations of A, B, and C as a function of time when the first reaction is reversible, with $k_{-1} = 0.3\,h^{-1}$.

(c) Plot and analyze the concentrations of A, B, and C as a function of time for the case where both reactions are reversible, with $k_{-2} = 0.005\,h^{-1}$.

(d) Compare (a), (b), and (c) and describe what you find.

(e) Vary k_1, k_2, k_{-1}, and k_{-2}. Explain the consequence of $k_1 > 100$ and $k_2 < 0.1$ and with $k_{-1} = k_{-2} = 0$ and with $k_{-2} = 1, k_{-1} = 0$, and $k_{-2} = 0.25$.

Solution

Hand written solution

```
import numpy as np
from scipy.integrate import solve_ivp
import matplotlib.pyplot as plt

def batch_reactor_a(t, y, *args):
  ca, cb, cc = y
  k1, k2 = args

  r1a = k1 * ca
  r2b = k2 * cb

  dcadt = - r1a
  dcbdt = r1a - r2b
  dccdt = r2b

  return [dcadt, dcbdt, dccdt]

k1 = 0.4 # 1/h
k2 = 0.01

ca0 = 1.6

# initial conditions
y0 = [ca0, 0, 0]
args = (k1, k2)
t_final = 50

sol = solve_ivp(batch_reactor_a, [0, t_final], y0, args=args, dense_output=True)

t = np.linspace(0,t_final, 1000)
ca, cb, cc = sol.sol(t)
```

```
plt.plot(t, ca, label='$C_A$')
plt.plot(t, cb, label='$C_B$')
plt.plot(t, cc, label='$C_C$')

plt.xlabel('time (h)')
plt.ylabel('Concentration ($mol/dm^3$)')

# Setting x and y axis limits
plt.xlim(0, t_final)
plt.ylim(0, ca0)

plt.legend()
plt.show()
```

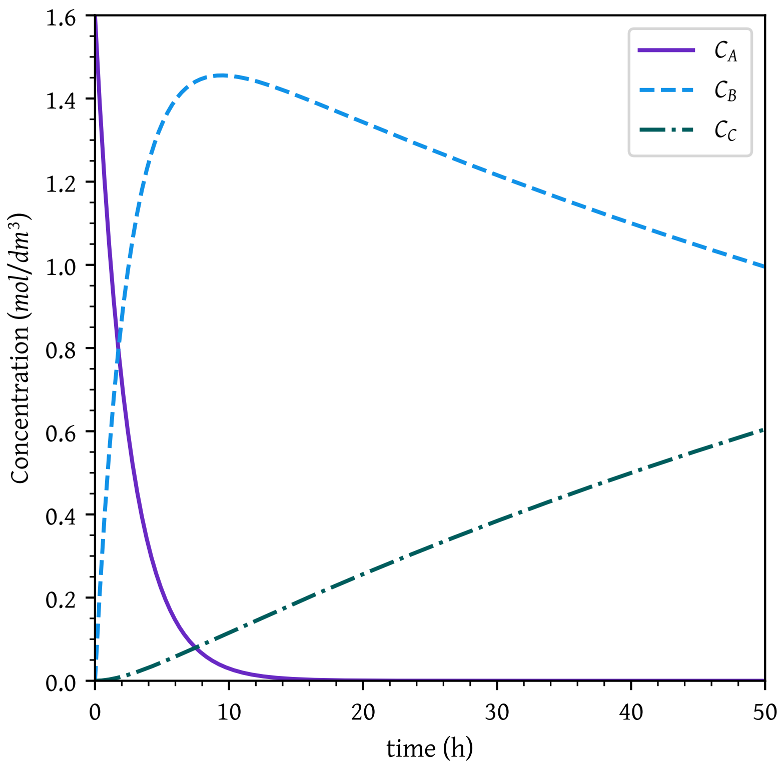


Figure 7: Concentration profile case A

```
def batch_reactor_b(t, y, *args):
  ca, cb, cc = y
  k1, k2, km1 = args

  r1a = k1 * ca
  r1b = km1 * cb
  r2b = k2 * cb

  dcadt = - r1a + r1b
  dcbdt = r1a -r1b - r2b
  dccdt = r2b

  return [dcadt, dcbdt, dccdt]

km1 = 0.3

# initial conditions
y0 = [ca0, 0, 0]
args = (k1, k2, km1)
t_final = 50

sol = solve_ivp(batch_reactor_b, [0, t_final], y0, args=args, dense_output=True)

t = np.linspace(0,t_final, 1000)
ca, cb, cc = sol.sol(t)
```

```
plt.plot(t, ca, label='$C_A$')
plt.plot(t, cb, label='$C_B$')
plt.plot(t, cc, label='$C_C$')

plt.xlabel('time (h)')
plt.ylabel('Concentration ($mol/dm^3$)')

# Setting x and y axis limits
plt.xlim(0, t_final)
plt.ylim(0, ca0)

plt.legend()
plt.show()
```

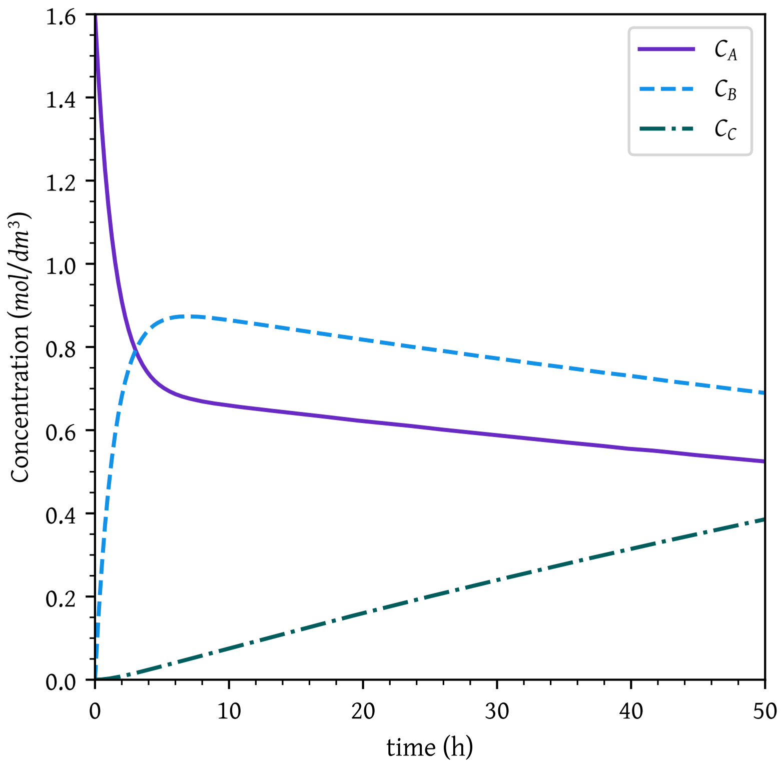


Figure 8: Concentration profile case B

```
def batch_reactor_c(t, y, *args):
  ca, cb, cc = y
  k1, k2, km1, km2 = args

  r1a = k1 * ca
  r1b = km1 * cb
  r2b = k2 * cb
  r2c = km2 * cc

  dcadt = - r1a + r1b
  dcbdt = r1a -r1b - r2b + r2c
  dccdt = r2b - r2c

  return [dcadt, dcbdt, dccdt]

km1 = 0.3
km2 = 0.005

# initial conditions
y0 = [ca0, 0, 0]
args = (k1, k2, km1, km2)
t_final = 50

sol = solve_ivp(batch_reactor_c, [0, t_final], y0, args=args, dense_output=True)

t = np.linspace(0,t_final, 1000)
ca, cb, cc = sol.sol(t)
```

```
plt.plot(t, ca, label='$C_A$')
plt.plot(t, cb, label='$C_B$')
plt.plot(t, cc, label='$C_C$')

plt.xlabel('time (h)')
plt.ylabel('Concentration ($mol/dm^3$)')

# Setting x and y axis limits
plt.xlim(0, t_final)
plt.ylim(0, ca0)

plt.legend()
plt.show()
```

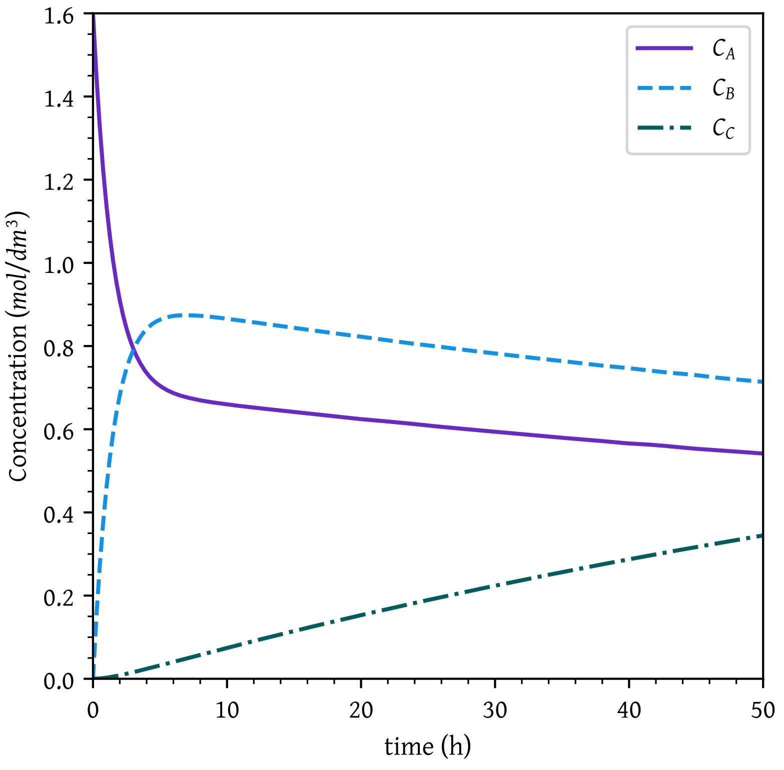


Figure 9: Concentration profile case C

```
k1 = 100
k2 = 1
km1 = 0
km2 = 0

# initial conditions
y0 = [ca0, 0, 0]
args = (k1, k2, km1, km2)
t_final = 10

sol = solve_ivp(batch_reactor_c, [0, t_final], y0, args=args, dense_output=True)

t = np.linspace(0,t_final, 1000)
ca, cb, cc = sol.sol(t)

plt.plot(t, ca, label='$C_A$')
plt.plot(t, cb, label='$C_B$')
plt.plot(t, cc, label='$C_C$')

plt.xlabel('time (h)')
plt.ylabel('Concentration ($mol/dm^3$)')

# Setting x and y axis limits
plt.xlim(0, t_final)
plt.ylim(0, ca0)

plt.legend()
plt.show()
```

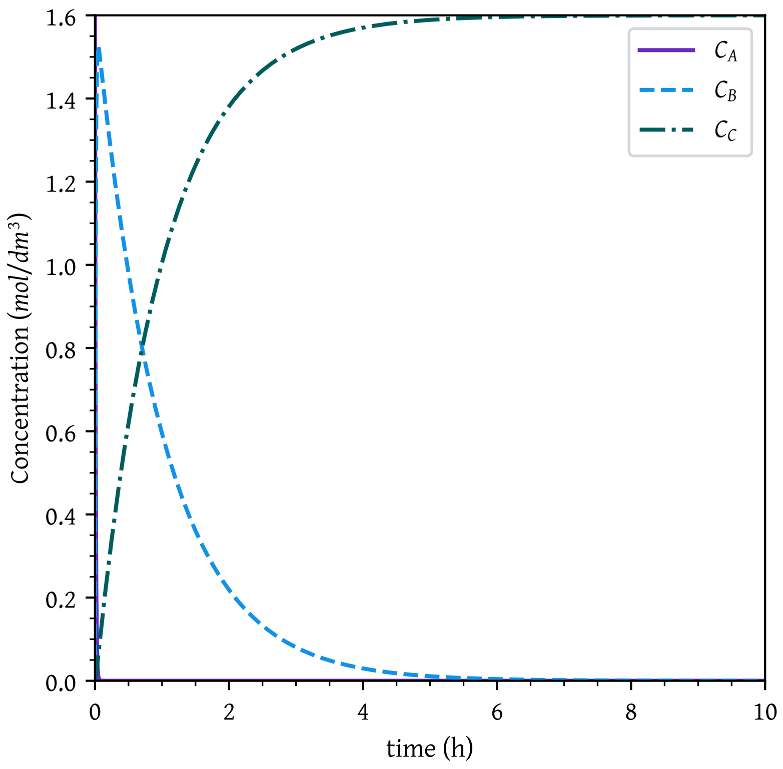


Figure 10: Concentration profile case C, k_1 = 100, k_2 = 1, k_{-1}= 0, k_{-2} = 0

When k_1 > 100, the first reaction is very fast. Therefore, all A is immediately converted to B and the concentration of B immediately reaches close to C_{A0}.
As k_2 < 0.1, the second reaction is much slower. Since both the reactions are irreversible (k_{-1}, and k_{-2} both are zero), B gets slowly converted to C. Given sufficient time, all B is converted to C.

```python
k1 = 100
k2 = 1
km1 = 0
km2 = 1

# initial conditions
y0 = [ca0, 0, 0]
args = (k1, k2, km1, km2)
t_final = 10

sol = solve_ivp(batch_reactor_c, [0, t_final], y0, args=args, dense_output=True)

t = np.linspace(0,t_final, 1000)
ca, cb, cc = sol.sol(t)

plt.plot(t, ca, label='$C_A$')
plt.plot(t, cb, label='$C_B$')
plt.plot(t, cc, label='$C_C$')

plt.xlabel('time (h)')
plt.ylabel('Concentration ($mol/dm^3$)')

# Setting x and y axis limits
plt.xlim(0, t_final)
plt.ylim(0, ca0)

plt.legend()
plt.show()
```

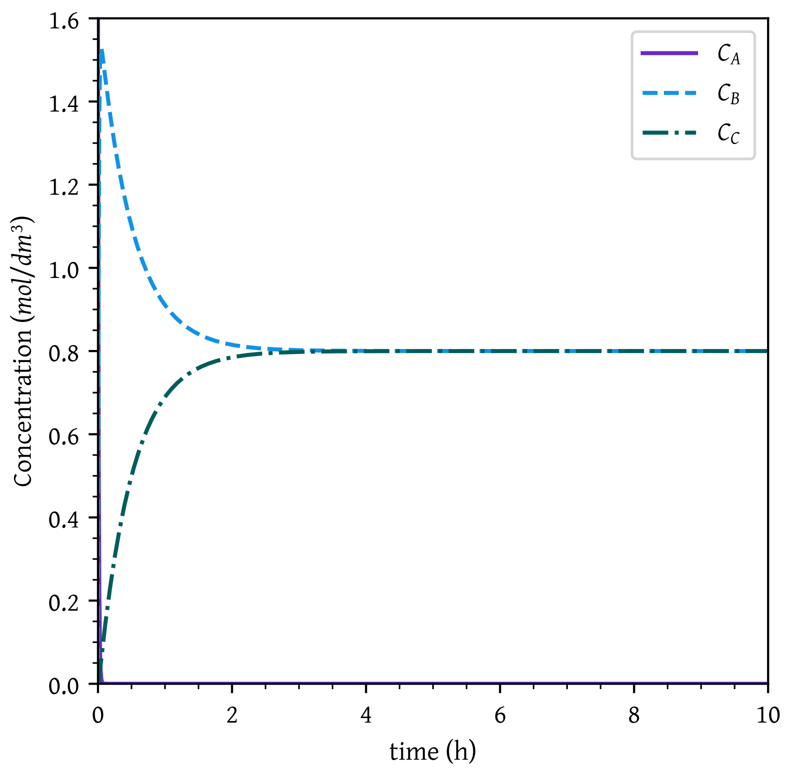


Figure 11: Concentration profile case C, k_1 = 100, k_2 = 1, k_{-1}= 0, k_{-2} = 1

Since second reaction is reversible and $K_{eq,2} = k_2/k_{-2} = 1$, a steady state (equilibrium) is achieved where $C_B = C_C$

```python
k1 = 100
k2 = 1
km1 = 0
km2 = 0.25

# initial conditions
y0 = [ca0, 0, 0]
args = (k1, k2, km1, km2)
t_final = 10

sol = solve_ivp(batch_reactor_c, [0, t_final], y0, args=args, dense_output=True)

t = np.linspace(0,t_final, 1000)
ca, cb, cc = sol.sol(t)

plt.plot(t, ca, label='$C_A$')
plt.plot(t, cb, label='$C_B$')
plt.plot(t, cc, label='$C_C$')

plt.xlabel('time (h)')
plt.ylabel('Concentration ($mol/dm^3$)')

# Setting x and y axis limits
plt.xlim(0, t_final)
plt.ylim(0, ca0)

plt.legend()
plt.show()
```

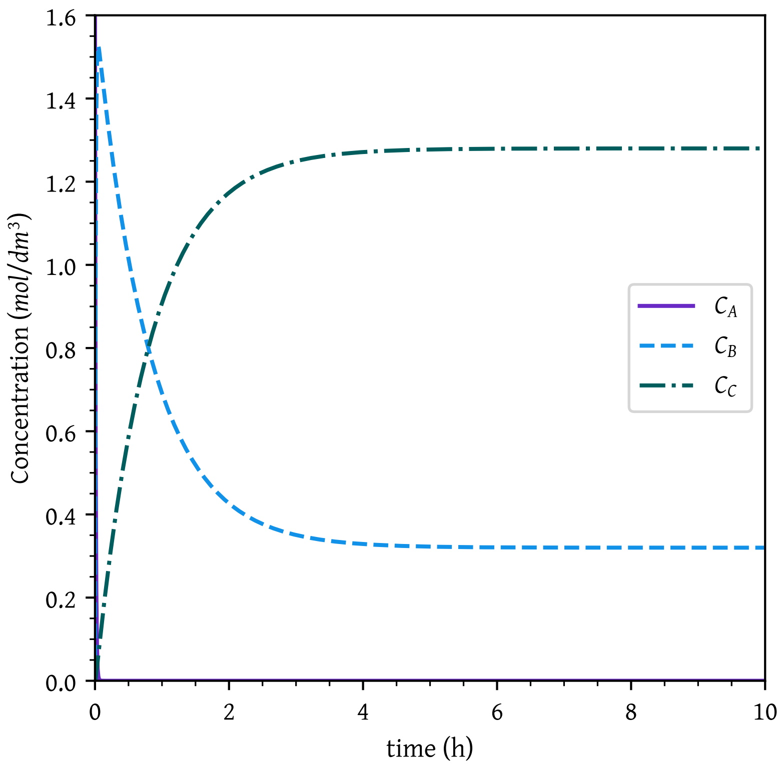


Figure 12: Concentration profile case C, k_1 = 100, k_2 = 1, k_{-1}= 0, k_{-2} = 0.25

$K_{eq} = k_2/k_{-2} = 1/0.25 = 4$, Therefore at equilibrium is achieved where $C_C = 4C_B$
At equilibrium C_B = 0.32 mol/dm^3, C_C = 1.28 mol/dm^3

References

Fogler, H. Scott. 2016. *Elements of Chemical Reaction Engineering*. Fifth edition. Boston: Prentice Hall.