In class activity: Multiple reactions

Lecture notes for chemical reaction engineering

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Reactor selection and operating conditions

For each of the following sets of reactions, describe your reactor system and conditions to maximize the selectivity to D. Make sketches where necessary to support your choices. The rates are in $(mol/dm^3 \cdot s)$, and concentrations are in (mol/dm^3).

(a) (1) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{D}$ $\quad -r_{1A} = 10\exp(-8000K/T)C_A C_B$

(2) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{U}$ $\quad -r_{2A} = 100\exp(-1000K/T)C_A^{1/2} C_B^{3/2}$

(b) (1) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{D}$ $\quad -r_{1A} = 100\exp(-1000K/T)C_A C_B$

(2) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{U}$ $\quad -r_{2A} = 10^6\exp(-8000K/T)C_A C_B$

(c) (1) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{D}$ $\quad -r_{1A} = 10\exp(-1000K/T)C_A C_B$

(2) $\mathrm{B} + \mathrm{D} \longrightarrow \mathrm{U}$ $\quad -r_{2B} = 10^9\exp(-10000K/T)C_B C_D$

(d) (1) $\mathrm{A} \longrightarrow \mathrm{D}$ $\quad -r_{1A} = 4280\exp(-12000K/T)C_A$

(2) $\mathrm{D} \longrightarrow \mathrm{U}_1$ $\quad -r_{2D} = 10100\exp(-15000K/T)C_D$

(3) $\mathrm{A} \longrightarrow \mathrm{U}_2$ $\quad -r_{3A} = 26\exp(-18800K/T)C_A$

(e) (1) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{D}$ $\quad -r_{1A} = 10^9\exp(-10000K/T)C_A C_B$

(2) $\mathrm{D} \longrightarrow \mathrm{A} + \mathrm{B}$ $\quad -r_{2D} = 20\exp(-2000K/T)C_D$

(3) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{U}$ $\quad -r_{3A} = 10^3\exp(-3000K/T)C_A C_B$

(f) (1) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{D}$ $\quad -r_{1A} = 800\exp(-8000K/T)C_A^{0.5} C_B$

(2) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{U}_1$ $\quad -r_{2B} = 10\exp(-300K/T)C_A C_B$

(3) $\mathrm{D} + \mathrm{B} \longrightarrow \mathrm{U}_2$ $\quad -r_{3D} = 10^6\exp(-8000K/T)C_D C_B$

Solution

(a) (1) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{D}$ $\quad -r_{1A} = 10\exp(-8000K/T)C_A C_B$

(2) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{U}$ $\quad -r_{2A} = 100\exp(-1000K/T)C_A^{1/2} C_B^{3/2}$

(a) $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{D}$; $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{U}$

$$r_D = -r_{1A} = 10\exp(-8000K/T)C_AC_B$$

$$r_U = -r_{2A} = 100\exp(-1000K/T)C_A^{1/2}C_B^{3/2}$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{10\exp(-8000K/T)C_AC_B}{100\exp(-1000K/T)C_A^{1/2}C_B^{3/2}}$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{\exp(-8000K/T)C_A^{1/2}}{10\exp(-1000K/T)C_B^{1/2}}$$

To maximize $S_{D/U}$ operate at:

- High concentration of A
- Low concentration of B
- Reactors:
  - Semibatch: B is fed slowly into large amt of A
  - Tubular: Sidestream of B
  - Series of small CSTRs: A is fed to the first reactor, B is fed into all reactors

At 300 K: k_1 = 2.623e-11; k_2 = 3.567e+00; k_1/k_2 = 7.353e-12
At 1000 K: k_1 = 3.355e-03; k_2 = 3.679e+01 k_1/k_2 = 9.119e-05

- $E_D > E_U$: specific rate for D increases much more rapidly than U with temperature
- $S_{D/U}$ is very low ($E_D > E_U$): Operate at highest possible T
- Need to keep $(C_A/C_B)^{1/2} > 10^6$: Drop by drop addition of B

(b) (1) $A + B \longrightarrow D \qquad -r_{1A} = 100\exp(-1000K/T)C_AC_B$
(2) $A + B \longrightarrow U \qquad -r_{2A} = 10^6\exp(-8000K/T)C_AC_B$

(b) $A + B \longrightarrow D$; $A + B \longrightarrow U$

$$-r_{1A} = 100\exp(-1000K/T)C_AC_B$$

$$-r_{2A} = 10^6\exp(-8000K/T)C_AC_B$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{100\exp(-1000K/T)C_AC_B}{10^6\exp(-8000K/T)C_AC_B}$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{\exp(-1000K/T)}{10^4\exp(-8000K/T)}$$

$S_{D/U}$ does not depend on concentration.
At 300 K: k_1 = 3.567e+00; k_2 = 2.623e-06; $S_{D/U} = k_1/k_2$ = 1.360e+06
At 1000 K: k_1 = 3.679e+01; k_2 = 3.355e+02 $S_{D/U} = k_1/k_2$ = 1.097e-01

- $E_D < E_U$: specific rate for U increases much more rapidly than D with temperature
- Operate at as low temperature as possible

(c) (1) $A + B \longrightarrow D \qquad -r_{1A} = 10\exp(-1000K/T)C_A C_B$

(2) $B + D \longrightarrow U \qquad -r_{2B} = 10^9\exp(-10000K/T)C_B C_D$

(c) $A + B \longrightarrow D$; $B + D \longrightarrow U$

$$-r_{1A} = 10\exp(-1000K/T)C_A C_B$$

$$-r_{2B} = 10^9\exp(-10000K/T)C_B C_D$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{10\exp(-1000K/T)C_A C_B}{10^9\exp(-10000K/T)C_B C_D}$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{\exp(-1000K/T)C_A}{10^8\exp(-10000K/T)C_D}$$

$S_{D/U} \propto \frac{C_A}{C_D}$
To maximize $S_{D/U}$ operate at:

- High concentration of A
- Low concentration of D
- Reactors:
  - Membrane reactor: D is removed as it is formed
  - Reactive distillation.

At 300 K: k_1 = 3.567e-01; k_2 = 3.338e-06; k_1/k_2 = 1.069e+05
At 1000 K: k_1 = 3.679e+00; k_2 = 4.540e+04 k_1/k_2 = 8.103e-05

- $E_D < E_U$: specific rate for U increases much more rapidly than D with temperature
- Operate at as low temperature as possible

(d) (1) $A \longrightarrow D \qquad -r_{1A} = 4280\exp(-12000K/T)C_A$

(2) $D \longrightarrow U_1 \qquad -r_{2D} = 10100\exp(-15000K/T)C_D$

(3) $A \longrightarrow U_2 \qquad -r_{3A} = 26\exp(-18800K/T)C_A$

(d) $A \longrightarrow D$; $D \longrightarrow U_1$; $A \longrightarrow U_2$

$$-r_{1A} = 4280\exp(-12000K/T)C_A$$

$$-r_{2D} = 10100\exp(-15000K/T)C_D$$

$$-r_{3A} = 26\exp(-18800K/T)C_A$$

$$S_{D/U} = \frac{r_D}{r_{U_1} + r_{U_2}} = \frac{4280\,\text{exp}(-12000K/T)C_A - 10100\,\text{exp}(-15000K/T)C_D}{10100\,\text{exp}(-15000K/T)C_D + 26\,\text{exp}(-18800K/T)C_A}$$

At 300 K: k_1 = 1.818e-14; k_2 = 1.948e-18; k_3 = 1.582e-26.
$C_A \gg C_D$: $S_{D/U} = k_1/k_3$ = 1.149e+12
$C_A \sim C_D$: $S_{D/U} = (k_1 - k_2)/(k2 + k_3)$ = 9.333e+03
At 1000 K: k_1 = 2.630e-02; k_2 = 3.090e-03; k_3 = 1.779e-07.
$C_A \gg C_D$: $S_{D/U} = k_1/k_3$ = 1.478e+05
$C_A \sim C_D$: $S_{D/U} = (k_1 - k_2)/(k2 + k_3)$ = 7.511e+00

- High selectivity is achieved at low temperature and $C_A \gg C_D$
- Operate at as low as possible temperature
- Reactors:
  - Membrane : Remove D as it is formed
  - Reactive distillation

(e) (1) $\text{A} + \text{B} \longrightarrow \text{D}$ $\quad -r_{1A} = 10^9\,\text{exp}(-10000K/T)C_AC_B$
(2) $\text{D} \longrightarrow \text{A} + \text{B}$ $\quad -r_{2D} = 20\,\text{exp}(-2000K/T)C_D$
(3) $\text{A} + \text{B} \longrightarrow \text{U}$ $\quad -r_{3A} = 10^3\,\text{exp}(-3000K/T)C_AC_B$

(e) $\text{A} + \text{B} \longrightarrow \text{D}$; $\text{D} \longrightarrow \text{A} + \text{B}$; $\text{A} + \text{B} \longrightarrow \text{U}$

$$-r_{1A} = 10^9\,\text{exp}(-10000K/T)C_AC_B$$

$$-r_{2D} = 20\,\text{exp}(-2000K/T)C_D$$

$$-r_{3A} = 10^3\,\text{exp}(-3000K/T)C_AC_B$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{10^9\,\text{exp}(-10000K/T)C_AC_B - 20\,\text{exp}(-2000K/T)C_D}{10^3\,\text{exp}(-3000K/T)C_AC_B}$$

At 300 K: k_1 = 3.338e-06; k_2 = 2.545e-02; k_3 = 4.540e-02.
$C_AC_B \gg C_D$: $S_{D/U} = k_1/k_3$ = 7.353e-05
$C_AC_B \sim C_D$: $S_{D/U} = (k_1 - k_2)/(k_3)$ = -5.606e-01
At 1000 K: k_1 = 4.540e+04; k_2 = 2.707e+00; k_3 = 4.979e+01.
$C_AC_B \gg C_D$: $S_{D/U} = k_1/k_3$ = 9.119e+02
$C_AC_B \sim C_D$: $S_{D/U} = (k_1 - k_2)/(k_3)$ = 9.118e+02

- High selectivity is achieved at high temperature and $C_AC_B \gg C_D$
- Operate at as high as possible temperature
- Reactors:
  - Membrane : Remove D as it is formed
  - Reactive distillation

(f) (1) $A + B \longrightarrow D$ $\quad -r_{1A} = 800\exp(-8000K/T)C_A^{0.5}C_B$

(2) $A + B \longrightarrow U_1$ $\quad -r_{2B} = 10\exp(-300K/T)C_AC_B$

(3) $D + B \longrightarrow U_2$ $\quad -r_{3D} = 10^6\exp(-8000K/T)C_DC_B$

(f) $A + B \longrightarrow D$; $A + B \longrightarrow U_1$; $D + B \longrightarrow U_2$

$$-r_{1A} = 800\exp(-8000K/T)C_A^{0.5}C_B$$

$$-r_{2B} = 10\exp(-300K/T)C_AC_B$$

$$-r_{3D} = 10^6\exp(-8000K/T)C_DC_B$$

$$S_{D/U} = \frac{r_D}{r_{U_1} + r_{U_2}} = \frac{800\exp(-8000K/T)C_A^{0.5}C_B - 10^6\exp(-8000K/T)C_DC_B}{10\exp(-300K/T)C_AC_B + 10^6\exp(-8000K/T)C_DC_B}$$

$$S_{D/U} = \frac{r_D}{r_{U_1} + r_{U_2}} = \frac{800\exp(-8000K/T)C_A^{0.5} - 10^6\exp(-8000K/T)C_D}{10\exp(-300K/T)C_A + 10^6\exp(-8000K/T)C_D}$$

- Selectivity is independent of concentration of B.

At 300 K: k_1 = 2.098e-09; k_2 = 3.679e+00; k_3 = 2.623e-06.
$C_A^{0.5} \gg C_D$: $S_{D/U} = k_1/k_2$ = 5.704e-10
$C_A^{0.5} \sim C_D$: $S_{D/U} = (k_1 - k_3)/(k2 + k_3)$ = -7.125e-07
$\rightarrow$ Negative selectivity: $C_A^{0.5}/C_D$ must be maintained above 1.250e+03
At 1000 K: k_1 = 2.684e-01; k_2 = 7.408e+00; k_3 = 3.355e+02.
$C_A^{0.5} \gg C_D$: $S_{D/U} = k_1/k_2$ = 3.623e-02
$C_A^{0.5} \sim C_D$: $S_{D/U} = (k_1 - k_3)/(k2 + k_3)$ = -9.776e-01
$\rightarrow$ Negative selectivity: $C_A^{0.5}/C_D$ must be maintained above 1.250e+03

- At any condition, selectivity is very low.
- Desired product can be obtained at high temperature and $C_A \gg C_D$, $C_A^{0.5}/C_D >$ 1.250e+03
- Reactors:
  - Membrane : Remove D as it is formed
  - Reactive distillation

Series Reactions in a Batch Reactor

The elementary liquid-phase series reaction

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

is carried out in a batch reactor. The reaction is heated very rapidly to the reaction temperature, where it is held at this temperature until the time it is quenched.

(a) Plot and analyze the concentrations of species A, B, and C as a function of time.

(b) Calculate the time to quench the reaction when the concentration of B will be a maximum.

(c) What are the overall selectivity and yields at this quench time?

Additional Information:

$C_{A0} = 2M, k_1 = 0.5\, h^{-1}, k_2 = 0.2\, h^{-1}$

Solution

- Mole balance- constant volume batch reactor

$$\begin{aligned} \text{Component A:} \quad & \frac{dC_A}{dt} = r_A \\ \text{Component B:} \quad & \frac{dC_B}{dt} = r_B \\ \text{Component C:} \quad & \frac{dC_C}{dt} = r_C \end{aligned} \tag{1}$$

- Rate law

$$\begin{aligned} \mathrm{A} \xrightarrow{k_1} \mathrm{B} \qquad & -r_{1A} = k_1 C_A \\ \mathrm{B} \xrightarrow{k_2} \mathrm{C} \qquad & -r_{2B} = k_2 C_B \end{aligned}$$

$$\begin{aligned} r_A = & \quad r_{1A} = & -k_1 C_A \\ r_B = & \quad r_{1B} + r_{2B} = & k_1 C_A - k_2 C_B \\ r_C = & \quad r_{2B} = & k_2 C_B \end{aligned} \tag{2}$$

- combine

Solve system of equations comprising of Equation 1, and Equation 2.

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

def batch_reactor(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 = 0.5
k2 = 0.2

ca0 = 2

# initial conditions
y0 = [ca0, 0, 0]
args = (k1, k2)
t_final = 6

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

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

```python
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 (M)')

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

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

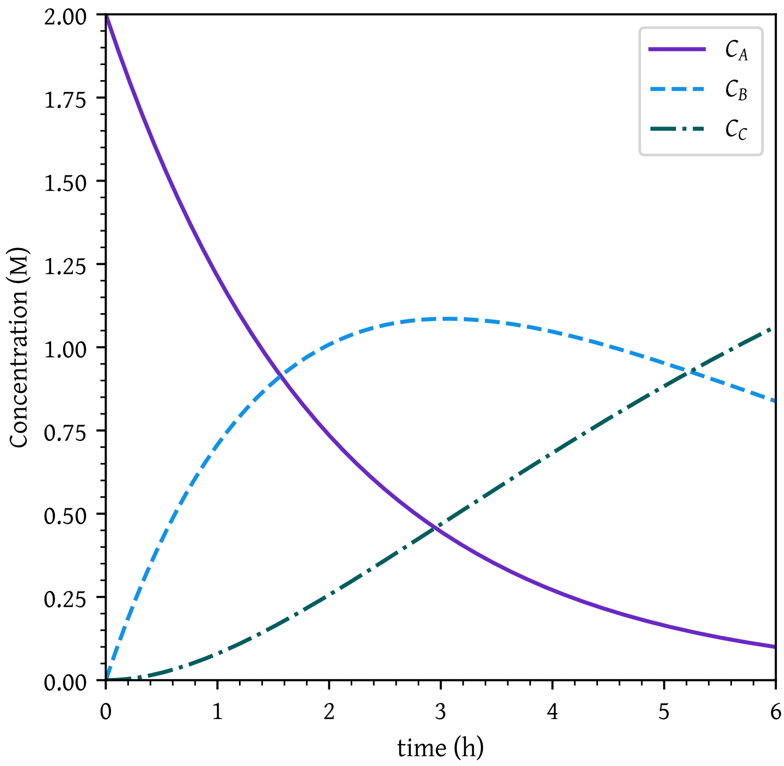

Figure 1: Concentration profile

```
cbmax_idx = np.argmax(cb)
tmax = t[cbmax_idx]

# selectivity and yield at quench time
# S = CB/CC
# Y = CB/(CA0 - CA)

caq = ca[cbmax_idx]
cbmax = cb[cbmax_idx]
ccq = cc[cbmax_idx]

sel = cbmax/ccq
yld = cbmax/(ca0 - caq)
```

- Quench time, t_{max} = 3.05 h
- Overall selectivity at t_{max}, S = 2.27
- Overall yield at t_{max}, Y = 0.69