In class activity: Rate law and stoichiometry

Lecture notes for chemical reaction engineering

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Relative rates

1. For the reaction $2\,A + B \longrightarrow 3\,C$, calculate rates of reaction of B and C if $-r_A = 10\,mol/(dm^3 s)$

> 💡 Solution
>
> $$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c}$$
>
> Rate of disappearance of B = $-r_B = \frac{10}{2}$ = 5 $mol/(dm^3 s)$
> Rate of production of C = $r_C = \frac{10 \times 3}{2}$ = 15 $mol/(dm^3 s)$

2. NO_2 is being formed at a rate of $4\,mol/(m^3 s)$ in the reaction $2\,NO + O_2 \rightleftharpoons 2\,NO_2$. Calculate the rate of consumption of NO, and O_2.

> 💡 Solution
>
> $$\frac{r_{NO}}{-2} = \frac{r_{O_2}}{-1} = \frac{r_{NO_2}}{2}$$
>
> Rate of disappearance of NO = $-r_{NO} = \frac{4 \times 2}{2}$ = 4 $mol/(m^3 s)$
> Rate of disappearance of O_2 = $-r_{O_2} = \frac{4}{2}$ = 2 $mol/(m^3 s)$

Rate law

Determine the rate law for the reaction described in each of the cases below involving species A, B, and C. The rate laws should be elementary as written for reactions that are either of the form $A \longrightarrow B$ or $A + B \longrightarrow C$.
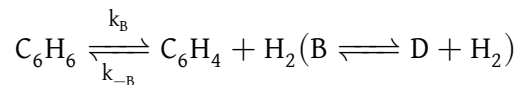
1. The units of the specific reaction rate are $k = \left[\frac{dm^3}{mol\ h}\right]$.
2. The units of the specific reaction rate are $k = \left[\frac{mol}{kg-cat\ h\ (atm)^2}\right]$.
3. The units of the specific reaction rate are $k = \left[\frac{1}{h}\right]$.
4. The units of a nonelementary reaction rate are $k = \left[\frac{mol}{dm^3\ h}\right]$.

Rate law for reversible reaction

For the reaction

$$C_6H_6 \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} C_6H_4 + H_2 \,(B \rightleftharpoons D + H_2)$$
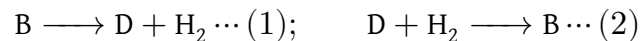
determine the rate expression for disappearance of benzene $(-r_B)$. Assume both the forward and reverse reactions are elementary.

> 💡 Solution
>
> We can write the reactions as two elementary reactions
>
> $$B \longrightarrow D + H_2 \cdots (1); \qquad D + H_2 \longrightarrow B \cdots (2)$$
>
> Net rate
>
> $$r_B = -r_{B,1} + r_{B,2}$$
>
> $$-r_B = k_B C_B - k_{-B} C_D C_{H_2}$$
>
> $$K = \frac{k_B}{k_{-B}}$$
>
> $$\therefore -r_B = k_B \left(C_B - \frac{C_D C_{H_2}}{K} \right)$$

Calculate the activation energy

The decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$
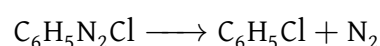
follows first order kinetics. The rate constant data at different temperatures is given in Table 1. Calculate the activation energy.

Table 1: Rate constant data

$k(s^{-1})$	0.00043	0.00103	0.00180	0.00355	0.00717
$T(K)$	313.0	319.0	323.0	328.0	333.0

💡 Solution

$$k = Ae^{\frac{-E}{RT}}$$

Linearize by taking log on both sides

$$\ln k = \ln A - \left(\frac{E}{R}\right)\left(\frac{1}{T}\right)$$

The plot of $\ln(k)$ vs. $1/T$ is linear with a slope of $-E/R$

```python
import numpy as np
import matplotlib.pyplot as plt
from scipy.stats import linregress

k = np.array([0.00043, 0.00103, 0.00180, 0.00355, 0.00717])
T = np.array([313.0, 319.0, 323.0, 328.0, 333.0])

R = 8.314 # J/mol K

ln_k = np.log(k)
inv_T = 1 / T

slope, intercept, r_value, p_value, std_err = linregress(inv_T, ln_k)
line = slope * inv_T + intercept

activation_energy = -slope*R/1000 # (kJ/mol)

# Plot
plt.scatter(inv_T, ln_k, color='blue', label='Data points')
plt.plot(inv_T, line, color='red', label='Fit line')

# Labels and title
plt.xlabel('1/T (1/K)')
plt.ylabel('ln(k)')
plt.title('Linear Fit of ln(k) vs 1/T')
plt.legend()

slope_text = f'Slope: {slope:.5e}'
intercept_text = f'Intercept: {intercept:.5e}'
e_text = f'Activation Energy: {activation_energy:.2f} kJ/mol'
plt.annotate(f'{slope_text}\n{intercept_text}\n{e_text}', xy=(0.05, 0.20), xycoords='a

# Show plot
plt.show()
```
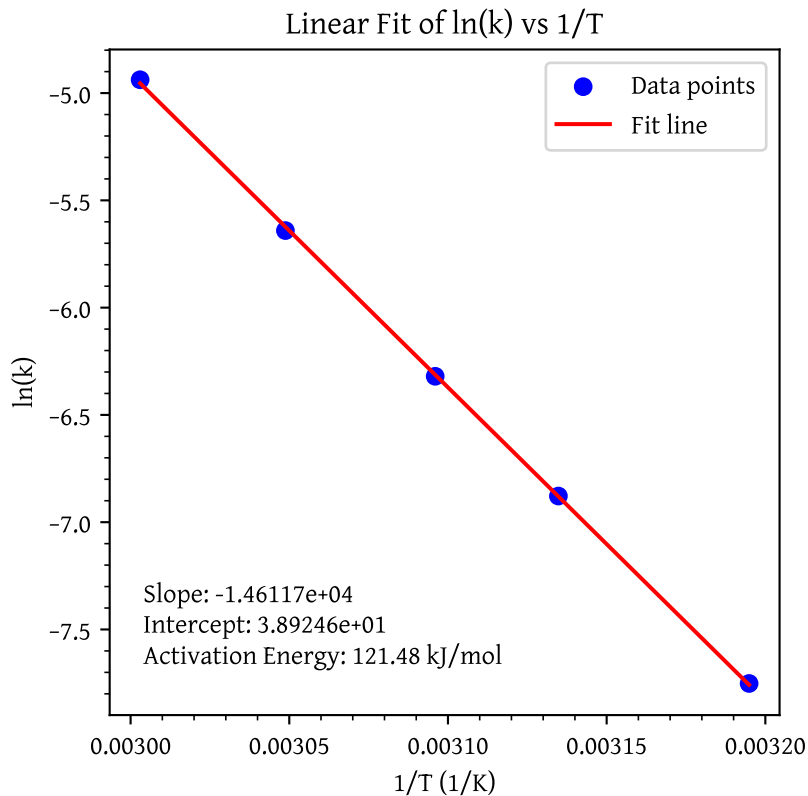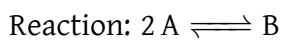
Linear Fit of ln(k) vs 1/T

Slope: -1.46117e+04
Intercept: 3.89246e+01
Activation Energy: 121.48 kJ/mol

Calculate the equilibrium conversion for gas phase reaction, X_e

Consider the following elementary reaction with $K_C = 20 \; dm^3/mol$ and $C_{A0} = 0.2 \; mol/dm^3$. Find X_e for both a batch reactor.

Reaction: $2\,A \rightleftharpoons B$

Rate law: $-r_A = k_A \left[C_A^2 - \dfrac{C_B}{K_C} \right]$

💡 **Solution**

Rate law: $-r_A = k_A \left[C_A^2 - \dfrac{C_B}{K_C} \right]$

At equilibrium

$$-r_A \equiv 0 \equiv k_A \left[C_A^2 - \frac{C_B}{K_C} \right]$$

$$K_c = \frac{C_{Be}}{C_{Ae}^2}$$

stoichiometry:

$$A \longrightarrow \frac{1}{2} B$$
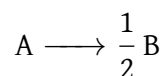
Setting up stoichiometric table

Species	Initial	Change	Remaining
A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
B	0	$+N_{A0}X/2$	$N_B = N_{A0}X/2$
Total	$N_{T0} = N_{A0}$		$N_T = N_{A0} - N_{A0}X/2$

Constant Volume: $V = V_0$

$$C_A = \frac{N_A}{V} = C_{A0}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{C_{A0}X}{2}$$

$$K_c = \frac{C_{Be}}{C_{Ae}^2} = \frac{C_{A0}\frac{X_e}{2}}{C_{A0}^2(1-X)^2}$$

$$2K_c C_{A0} = \frac{X_e}{(1-X)^2}$$

$$2 \times 20 \times 0.2 = \frac{X_e}{(1-X)^2}; \qquad 8X_e^2 - 17X_e + 8 = 0$$

Solving:
Equilibrium conversion: $X_e = 0.7$

Repeat the calculations above for a flow reactor

💡 Solution

With the flow reactor, we will need to consider changes in molar flow rate as this is a gas phase reaction.
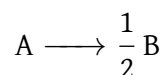Rate law: $-r_A = k_A \left[C_A^2 - \frac{C_B}{K_C} \right]$
At equilibrium

$$-r_A \equiv 0 \equiv k_A \left[C_A^2 - \frac{C_B}{K_C} \right]$$

$$K_c = \frac{C_{Be}}{C_{Ae}^2}$$

stoichiometry:

$$A \longrightarrow \frac{1}{2} B$$

Stoichiometric table is same as the batch system with moles replaced by molar flow rates.

Species	Entering	Change	Exiting
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	0	$+F_{A0}X/2$	$F_B = F_{A0}X/2$

$$\text{Total} \qquad F_{T0} = F_{A0} \qquad\qquad F_T = F_{A0} - F_{A0}X/2$$

$$C_{Ae} = \frac{C_{A0}(1 - X_e)}{(1 + \epsilon X_e)}$$

$$C_{Be} = \frac{C_{A0}X_e}{2(1 + \epsilon X_e)}$$

$$K_C = \frac{\frac{C_{A0}X_e}{2(1+\epsilon X_e)}}{\left[\frac{C_{A0}(1-X_e)}{(1+\epsilon X_e)}\right]^2} = \frac{X_e(1 + \epsilon X_e)}{2C_{A0}(1 - X_e)^2}$$

$$K_c = \frac{C_{Be}}{C_{Ae}^2} = \frac{X_e(1 + \epsilon X_e)}{2C_{A0}(1 - X_e)^2}$$

$$2K_c C_{A0} = \frac{X_e + \epsilon X_e^2)}{(1 - 2X_e + X_e^2)} = 8$$

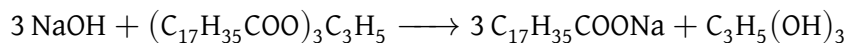$$\epsilon = y_{A0}\delta = 1\left(\frac{1}{2} - 1\right) = -\frac{1}{2}$$

$$8 = \frac{X_e + 0.5X_e^2)}{(1 - 2X_e + X_e^2)}$$

Solving for X_e:
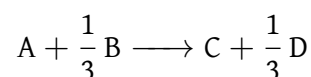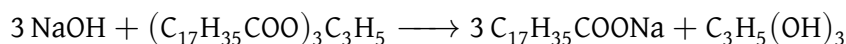Equilibrium conversion: $X_e = 0.757$

Saponification reaction

The saponification for the formation of soap is:

$$3\,\text{NaOH} + (\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5 \longrightarrow 3\,\text{C}_{17}\text{H}_{35}\text{COONa} + \text{C}_3\text{H}_5(\text{OH})_3$$

Letting X represent the conversion of NaOH set up a stoichiometric table expressing the concentration of each species in terms of the initial concentration of NaOH and the conversion of X.

💡 Solution

$$3\,\text{NaOH} + (\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5 \longrightarrow 3\,\text{C}_{17}\text{H}_{35}\text{COONa} + \text{C}_3\text{H}_5(\text{OH})_3$$

$$\text{A} + \frac{1}{3}\text{B} \longrightarrow \text{C} + \frac{1}{3}\text{D}$$

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0} = N_{A0}(1 - X) = C_{A0}(1 - X)$$

$$\Theta_B = \frac{C_{B0}}{C_{A0}}, \quad \Theta_C = \frac{C_{C0}}{C_{A0}}, \quad \Theta_D = \frac{C_{D0}}{C_{A0}}$$

| Species	Symbol	Initially	Change	Remaining	Concentration
NaOH	A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$	$C_{A0}(1-X)$
$(C_{17}H_{35}COO)_3C_3H_5$	B	N_{B0}	$-\frac{1}{3}N_{A0}X$	$N_{A0}\left(\Theta_B - \frac{X}{3}\right)$	$C_{A0}\left(\Theta_B - \frac{X}{3}\right)$
$C_{17}H_{35}COONa$	C	N_{C0}	$N_{A0}X$	$N_{A0}(\Theta_C + X)$	$C_{A0}(\Theta_C + X)$
$C_3H_5(OH)_3$	D	N_{D0}	$\frac{1}{3}N_{A0}X$	$N_{A0}\left(\Theta_D + \frac{X}{3}\right)$	$C_{A0}\left(\Theta_D + \frac{X}{3}\right)$
Water (inert)	I	N_{I0}	—	N_{I0}	C_{I0}
Totals		N_{T0}	0	$N_T = N_{T0}$	

Determining $C_j = h_j(X)$ for a Gas-Phase Reaction

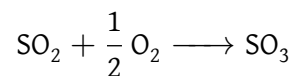A mixture Of 28% SO_2 and 72% air is charged to a flow reactor in which SO_2 is oxidized.

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$
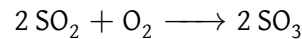
1. First, set up a stoichiometric table using only the symbols (i.e., Θ_i, F_i).

2. Next, prepare a second table evaluating the species concentrations as a function of conversion for the case when the total pressure is 1485 kPa (14.7 atm) and the temperature is constant at 227 °C.

3. Evaluate the parameters and make a plot of each of the concentrations SO_2, SO_3, N_2 as a function of conversion
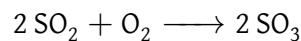
> 💡 **Solution**
>
> $$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$
>
> Take SO_2 as basis of calculation
>
> $$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$$
>
> Stoichiometric table
>
> | Species | Symbol | Entering | Change | Leaving |
> |---|---|---|---|---|
> | SO_2 | A | F_{A0} | $-F_{A0}X$ | $F_A = F_{A0}(1-X)$ |
> | O_2 | B | $F_{B0} = \Theta_B F_{A0}$ | $-\frac{F_{A0}X}{2}$ | $F_B = F_{A0}\left(\Theta_B - \frac{1}{2}X\right)$ |
> | SO_3 | C | 0 | $+F_{A0}X$ | $F_C = F_{A0}X$ |
> | N_2 | I | $F_{I0} = \Theta_I F_{A0}$ | — | $F_I = F_{I0} = \Theta_I F_{A0}$ |
> | Totals | | F_{T0} | $-\frac{F_{A0}X}{2}$ | $F_T = F_{T0} - \frac{F_{A0}X}{2}$ |

Concentration:

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1 - X)}{v}$$

volumetric flow rate:

$$v = v_0(1 + \epsilon X)\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)$$

Neglecting pressure drop in the reaction, and for isothermal reactions:

$$v = v_0(1 + \epsilon X)$$

$$C_A = \frac{F_{A0}(1 - X)}{v_0(1 + \epsilon X)} = C_{A0}\frac{1 - X}{1 + \epsilon X}$$

Similarly for B

$$C_B = C_{A0}\frac{\left(\Theta_B - \frac{b}{a}X\right)}{1 + \epsilon X} = \frac{C_{A0}\left(\Theta_B - \frac{1}{2}X\right)}{1 + \epsilon X}$$

$$C_T = C_{T0} = \frac{P_0}{RT_0} = \frac{1485}{8.314 \times 500} = 0.357\frac{mol}{dm^3}$$

$$\epsilon = y_{A0}\delta = 0.28 \times (1 - 1 - \frac{1}{2}) = -0.14$$

Initially, 72% of the total number of moles is air containing 21% O_2 and 79% N_2, along with 28% SO_2.

$$F_{A0} = (0.28)(F_{T0})$$

$$F_{B0} = (0.72)(0.21)(F_{T0})$$

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{(0.72)(0.21)}{0.28} = 0.54$$

$$\Theta_1 = \frac{F_{I0}}{F_{A0}} = \frac{(0.72)(0.79)}{0.28} = 2.03$$

Substituting for C_{A0} and ϵ in the species concentrations:

$$SO_2 : \quad C_A = C_{A0}\left(\frac{1 - X}{1 + \epsilon X}\right) = 0.1\left(\frac{1 - X}{1 - 0.14X}\right) \quad \text{mol/dm}^3$$

$$O_2 : \quad C_B = C_{A0}\left(\frac{\Theta_B - \frac{1}{2}X}{1 + \epsilon X}\right) = 0.1\left(\frac{0.54 - 0.5X}{1 - 0.14X}\right) \quad \text{mol/dm}^3$$

$$SO_3 : \quad C_C = \frac{C_{A0}X}{1 + \epsilon X} = \frac{0.1X}{1 - 0.14X} \quad \text{mol/dm}^3$$

$$N_2 : \quad C_I = \frac{C_{A0}\Theta_1}{1 + \epsilon X} = \frac{(0.1)(2.03)}{1 - 0.14X} \quad \text{mol/dm}^3$$

```python
import numpy as np
import matplotlib.pyplot as plt

# Constants
C_A0 = 0.1   # mol/dm^3
epsilon = -0.14   # unitless
Theta_B = 0.54   # unitless
Theta_I = 2.03   # unitless

# Conversion range from 0 to 1 with 0.25 interval
X_values = np.arange(0, 1.01, 0.25)

# Concentration calculations
def calculate_concentrations(X, C_A0, epsilon, Theta_B, Theta_I):
    C_A = C_A0 * ((1 - X)/(1 - epsilon * X))
    C_B = C_A0 * ((Theta_B - 0.5 * X) / (1 + epsilon * X))
    C_C = C_A0 * X / (1 + epsilon * X)
    C_I = C_A0 * Theta_I / (1 + epsilon * X)
    return C_A, C_B, C_C, C_I

# Calculate concentrations for each X value
C_A_values, C_B_values, C_C_values, C_I_values = [], [], [], []
for X in X_values:
    C_A, C_B, C_C, C_I = calculate_concentrations(X, C_A0, epsilon, Theta_B, Theta_I)
    C_A_values.append(C_A)
    C_B_values.append(C_B)
    C_C_values.append(C_C)
    C_I_values.append(C_I)

# Plotting the results
plt.plot(X_values, C_A_values, marker='o', label=r'$C_A$')
plt.plot(X_values, C_B_values, marker='o', label=r'$C_B$')
plt.plot(X_values, C_C_values, marker='s', label=r'$C_C$')
plt.plot(X_values, C_I_values, marker='^', label=r'$C_I$')

plt.xlabel('Conversion, $X$')
plt.ylabel('Concentration ($mol/dm^3$)')
plt.title('Concentration as a Function of Conversion')
plt.legend()
plt.grid(True)
plt.show()
```
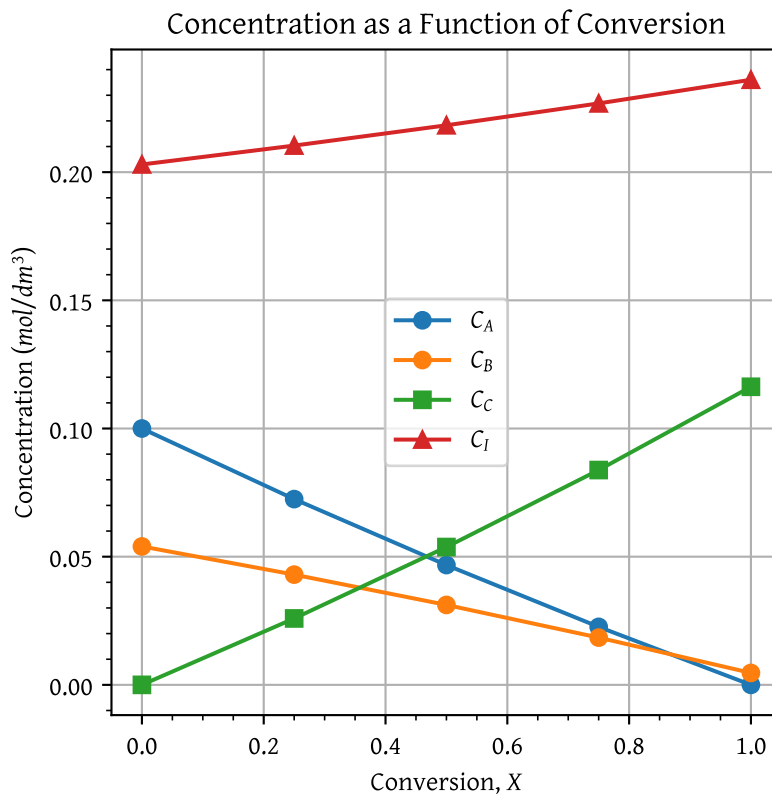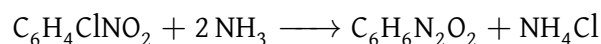
Concentration as a Function of Conversion

Note that Concentration of N_2 (C_I)$ changes with conversion even though nitrogen does not participate in the reaction.

Liquid phase first order reaction

Orthonitroanaline (an important intermediate in dyes—called *fast orange*) is formed from the reaction of *orthonitrochlorobenzene* (ONCB) and aqueous ammonia. The liquid-phase reaction is first order in both ONCB and ammonia with $k = 0.0017 \, m^3/kmol \cdot min$ at $188\,°C$ with $E = 11273 \, cal/mol$. The initial entering concentrations of ONCB and ammonia are $1.8 \, kmol/m^3$ and $6.6 \, kmol/m^3$, respectively.

$$C_6H_4ClNO_2 + 2\,NH_3 \longrightarrow C_6H_6N_2O_2 + NH_4Cl$$

(a) Set up a stoichiometric table for this reaction for a flow system.

(b) Write the rate law for the rate of disappearance of ONCB in terms of concentration.

(c) Explain how parts (a) and (b) would be different for a batch system.

(d) Write $-r_A$ solely as a function of conversion. $-r_A$ = _____

(e) What is the initial rate of reaction (X = 0)

at $188\,°C$? $-r_A$ = _____

at $25\,°C$? $-r_A$ = _____

at $288\,°C$? $-r_A$ = _____

(f) What is the rate of reaction when X = 0.90

at $188\,^\circ C$? $-r_A =$ _____

at $25\,^\circ C$? $-r_A =$ _____

at $288\,^\circ C$? $-r_A =$ _____

(g) What would be the corresponding CSTR reactor volume at $25\,^\circ C$ to achieve 90% conversion and at $288\,^\circ C$ for a feed rate of $2\,dm^3/min$

at $25\,^\circ C$? V = _____

at $288\,^\circ C$? V = _____
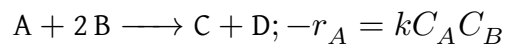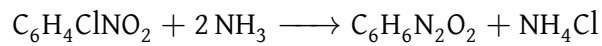
> 💡 Solution
>
> $$C_6H_4ClNO_2 + 2\,NH_3 \longrightarrow C_6H_6N_2O_2 + NH_4Cl$$
>
> $$A + 2\,B \longrightarrow C + D;\, -r_A = kC_AC_B$$
>
> Table 6: Problem data
>
> | | |
> |---|---|
> | k | $0.0017\,m^3/kmolmin\,at\,188^\circ C$ |
> | E | $11273\,cal/mol$ |
> | C_A | $1.8\,kmol/m^3$ |
> | C_B | $6.6\,kmol/m^3$ |

a) Stoichiometric table for flow reactor

Species	Entering	Change	Exiting
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1 - X)$
B	$F_{B0} = \Theta_B F_{A0}$	$-2F_{A0}X$	$F_B = F_{A0}(\Theta_B - 2X)$
C	0	$F_{A0}X$	$F_C = F_{A0}X$
D	0	$F_{A0}X$	$F_D = F_{A0}X$

$\Theta_B = \frac{6.6}{1.8} = 3.67$

b) $-r_A = kC_A C_B$

c) For batch system

$$C_A = \frac{N_A}{V}$$

The stoichiometric table needs to be set up in terms of N instead of F. The reaction rate expression would remain same.

d) $-r_A$ as a function of conversion

$-r_A = kC_A C_B$
$C_A = C_{A0}(1 - X)$
$C_B = C_{A0}(\Theta_B - 2X)$
$-r_A = kC_{A0}(1 - X)C_{A0}(\Theta_B - 2X)$
$-r_A = kC_{A0}^2(1 - X)(\Theta_B - 2X)$

e) Initial rates of reaction

k at different temperatures

$$k = k_0 exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

T (°C)	k $(m^3/kmolmin)$
25 (298K)	2.03×10^{-6}
188 (461K)	0.0017
288 (561K)	0.152

1. At 188 °C

$$-r_A = kC_{A0}^2 \Theta_B = 0.0017 \times (1.8)^2 \times 3.67 = 0.0202 \, kmol/m^3 min$$

2. At 25 °C: $2.41 \times 10^{-5} \, kmol/m^3 min$

3. At 288 °C: $0.1806 \, kmol/m^3 min$

f) rates of reaction at $X = 0.9$

$$-r_A = kC_{A0}^2 (1 - X)(\Theta_B - 2X)$$

1. At 188 °C: $0.00103 \, kmol/m^3 min$

2. At 25 °C: $1.23 \times 10^{-6} \, kmol/m^3 min$

3. At 288 °C: $0.0092 \, kmol/m^3 min$

g) CSTR Volume

$X = 90$
$F_{A0} = C_{A0} v_0 = 3.6 mol/min$

1. V at 25 °C

$$V = \frac{F_{A0} X}{-r_A|_{exit}}$$

V = 2634.1 m^3

2. V at 288 °C: 352 m^3