# 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  $-r_A$  =  $10mol/(dm^3s)$ 
  - Solution  $\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c}$ Rate of disappearance of B =  $-r_B=\frac{10}{2}$  = 5  $mol/(dm^3s)$  Rate of production of C =  $r_C=\frac{10\times 3}{2}$  = 15  $mol/(dm^3s)$
- 2.  $NO_2$  is being formed at a rate of 4  $mol/(m^3s)$  in the reaction 2  $NO + O_2 \implies$  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  $mol/(m^3s)$  Rate of disappearance of O<sub>2</sub> =  $-r_{O_2}=\frac{4}{2}$  = 2  $mol/(m^3s)$ 

### 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  $A \longrightarrow B \text{ or } A + B \longrightarrow C.$ 

- 1. The units of the specific reaction rate are  $k = \begin{bmatrix} \frac{dm^3}{mol \ h} \end{bmatrix}$ . 2. The units of the specific reaction rate are  $k = \begin{bmatrix} \frac{mol}{kg-cat \ h \ (atm)^2} \end{bmatrix}$ .
- 3. The units of the specific reaction rate are  $k = \left[\frac{1}{h}\right]$ .
- 4. The units of a nonelementary reaction rate are  $k = \left[\frac{mol}{dm^3 h}\right]$ .

#### Solution

- 1. Second order reaction:  $-r_A = k C_A C_B$
- 2. Second order gas phase reaction  $-r_A^\prime = k P_A P_B$
- 3. First order reaction:  $-r_A = kC_A$
- 4. Second order non elementary reaction  $-r_A = kC_A^2$

### Rate law for reversible reaction

For the reaction

$$\mathsf{C}_{6}\mathsf{H}_{6} \xleftarrow[k_{-B}]{k_{-B}} \mathsf{C}_{6}\mathsf{H}_{4} + \mathsf{H}_{2}(\mathsf{B} \Longleftarrow \mathsf{D} + \mathsf{H}_{2})$$

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

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

💡 Solution

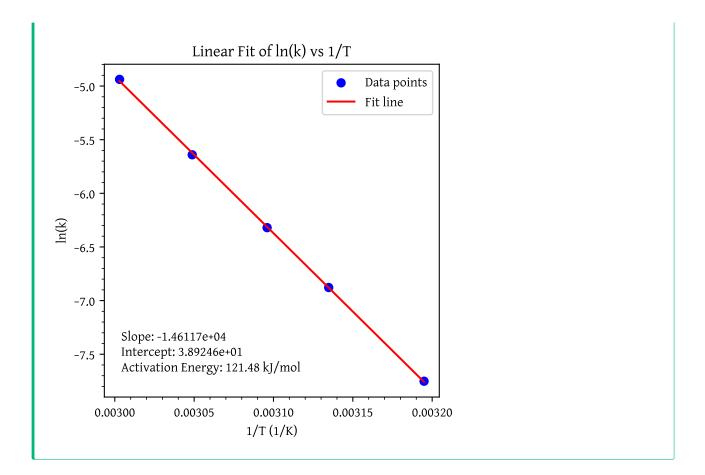
$$k = A e^{\frac{-E}{RT}}$$

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

```
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()
```



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

💡 Solution

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:

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

Setting up stoichiometric table

	Species	Initial	Change	Remaining
		$\begin{array}{c} N_{A0} \\ 0 \\ N_{T0} = N_{A0} \end{array}$	$+N_{A0}X/2$	$\begin{array}{l} N_A = N_{A0}(1-X) \\ N_B = N_{A0}X/2 \\ N_T = N_{A0} - N_{A0}X/2 \end{array}$
Constant Volu	ıme: V =	$V_0$		
		$C_A =$	$= \frac{N_A}{V} = C_{A0}($	1-X)
		$C_{E}$	$_{B} = \frac{N_{B}}{V} = \frac{C}{V}$	$\frac{A0}{2}X$
		$K_c = 1$	$\frac{C_{Be}}{C_{Ae}^2} = \frac{C_{Ae}}{C_{A0}^2}$	$\frac{40\frac{X_e}{2}}{1-X)^2}$
		2K	$C_c C_{A0} = \frac{\chi}{(1 - 1)^2}$	$\frac{T_e}{X)^2}$
	$2 \times 2$	$20 \times 0.2 = \frac{1}{(1)}$	$\frac{X_e}{-X)^2}; \qquad 8$	$3X_e^2 - 17X_e + 8 = 0$
Solving: Equilibrium c	onversion	: $X_e = 0.7$		

## 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 B	$F_{A0}$ 0		$\begin{split} F_A &= F_{A0}(1-X) \\ F_B &= F_{A0}X/2 \end{split}$

 $\begin{aligned} \text{Total} \qquad F_{T0} &= F_{A0} \qquad F_{T} = F_{A0} - F_{A0}X/2 \\ & C_{Ae} = \frac{C_{A0}(1-X_{e})}{(1+\epsilon X_{e})} \\ & C_{Be} = \frac{C_{A0}X_{e}}{2(1+\epsilon X_{e})} \\ & K_{C} = \frac{\frac{C_{A0}X_{e}}{2(1+\epsilon X_{e})}}{\left[\frac{C_{A0}(1-X_{e})}{(1+\epsilon X_{e})}\right]^{2}} &= \frac{X_{e}(1+\epsilon X_{e})}{2C_{A0}(1-X_{e})^{2}} \\ & K_{c} = \frac{C_{Be}}{C_{Ae}^{2}} = \frac{X_{e}(1+\epsilon X_{e})}{2C_{A0}(1-X_{e})^{2}} \\ & 2K_{c}C_{A0} = \frac{X_{e}+\epsilon X_{e}^{2}}{(1-2X_{e}+X_{e}^{2})} = 8 \\ & \epsilon = y_{A0}\delta = 1\left(\frac{1}{2}-1\right) = -\frac{1}{2} \\ & 8 = \frac{X_{e}+0.5X_{e}^{2}}{(1-2X_{e}+X_{e}^{2})} \end{aligned}$ 

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

### Saponification reaction

The saponification for the formation of soap is:

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

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  $3 \operatorname{NaOH} + (C_{17}H_{35}COO)_{3}C_{3}H_{5} \longrightarrow 3 C_{17}H_{35}COONa + C_{3}H_{5}(OH)_{3}$   $A + \frac{1}{3}B \longrightarrow C + \frac{1}{3}D$   $C_{A} = \frac{N_{A}}{V} = \frac{N_{A}}{V_{0}} = N_{A0}(1 - X) = C_{A0}(1 - X)$   $\Theta_{B} = \frac{C_{B0}}{C_{A0}}, \quad \Theta_{C} = \frac{C_{C0}}{C_{A0}}, \quad \Theta_{D} = \frac{C_{D0}}{C_{A0}}$ 

Species	Symbol	Initially	Change	Remaining	Concentration
NaOH $(C_{17}H_{35}CO)$ $C_{17}H_{35}CO$	, <b>0</b> 0 0	$\begin{array}{c} N_{A0} \\ N_{B0} \\ N_{C0} \end{array}$			$\begin{array}{c} C_{A0}(1-X) \\ C_{A0}\left(\Theta_B-\frac{X}{3}\right) \\ C_{A0}(\Theta_C+X) \end{array}$
$C_3H_5(OH)$ Water (inert)	) <sub>3</sub> D I	$\begin{array}{c} N_{D0} \\ N_{I0} \end{array}$	$\frac{\frac{1}{3}N_{A0}X}{-}$	- ( 0	$ \begin{array}{c} C_{A0} \left( \Theta_D + \frac{X}{3} \right) \\ C_{I0} \end{array} $
Totals		$N_{T0}$	0	$N_T = N_{T0}$	

# Determining $C_j = h_j(\boldsymbol{X})$ for a Gas-Phase Reaction

A mixture Of 28%  $\mathrm{SO}_2$  and 72% air is charged to a flow reactor in which  $\mathrm{SO}_2$  is oxidized.

$$2 \operatorname{SO}_2 + \operatorname{O}_2 \longrightarrow 2 \operatorname{SO}_3$$

- 1. First, set up a stoichiometric table using only the symbols (i.e.,  $\Theta_i, F_i$ ).
- 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

$$2 \operatorname{SO}_2 + \operatorname{O}_2 \longrightarrow 2 \operatorname{SO}_3$$

Take  $SO_2$  as basis of calculation

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$$

Stoichiometric table

Species	Symbol	Entering	Change	Leaving
$SO_2$	А	$F_{A0}$	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
$O_2$	В	$F_{B0} = \Theta_B F_{A0}$	$-\frac{F_{A0}X}{2}$	$F_B =$
<i>co</i>	2			$F_{A0}\left(\Theta_B - \frac{1}{2}X\right)$
$SO_3$	C	0	$+F_{A0}X$	$F_C = F_{A0}X$
$N_2$	1	$F_{I0} = \Theta_I F_{A0}$		$F_I = F_{I0} =$
-			F Y	$\Theta_I F_{A0}$
Totals		$F_{T0}$	$-\frac{F_{A0}X}{2}$	$F_T = F_{T0} - \frac{F_{A0}X}{2}$

Concentration:

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

volumetric flow rate:

$$\upsilon = \upsilon_0 (1 + \epsilon X) \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right)$$

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

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

$$C_A=\frac{F_{A0}(1-X)}{\upsilon_0(1+\epsilon X)}=C_{A0}\frac{1-X}{1+\epsilon X}$$

Similarly for B

$$\begin{split} C_B &= C_{A0} \frac{\left(\Theta_B - \frac{b}{a}X\right)}{1 + \epsilon X} = \frac{C_{A0}\left(\Theta_B - \frac{1}{2}X\right)}{1 + \epsilon X} \\ C_T &= C_{T0} = \frac{P_0}{RT_0} = \frac{1485}{8.314 \times 500} = 0.357 \frac{mol}{dm^3} \\ \epsilon &= y_{A0}\delta = 0.28 \times (1 - 1 - \frac{1}{2}) = -0.14 \end{split}$$

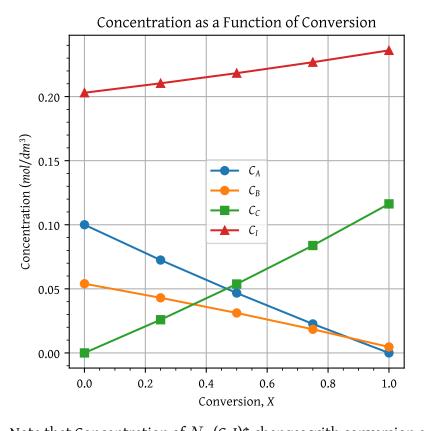
Initially, 72% of the total number of moles is air containing 21%  $\rm O_2$  and 79%  $\rm N_2$  , along with 28%  $\rm SO_2.$ 

$$\begin{split} F_{A0} &= (0.28)(F_{T0}) \\ F_{B0} &= (0.72)(0.21)(F_{T0}) \\ \Theta_B &= \frac{F_{B0}}{F_{A0}} = \frac{(0.72)(0.21)}{0.28} = 0.54 \\ \Theta_1 &= \frac{F_{I0}}{F_{A0}} = \frac{(0.72)(0.79)}{0.28} = 2.03 \end{split}$$

Substituting for  $C_{A0}$  and  $\epsilon$  in the species concentrations:

$$\begin{split} SO_2: \quad C_A &= C_{A0} \left( \frac{1-X}{1+\epsilon X} \right) = 0.1 \left( \frac{1-X}{1-0.14X} \right) \quad \text{mol/dm}^3 \\ O_2: \quad C_B &= C_{A0} \left( \frac{\Theta_B - \frac{1}{2}X}{1+\epsilon X} \right) = 0.1 \left( \frac{0.54 - 0.5X}{1-0.14X} \right) \quad \text{mol/dm}^3 \\ SO_3: \quad C_C &= \frac{C_{A0}X}{1+\epsilon X} = \frac{0.1X}{1-0.14X} \quad \text{mol/dm}^3 \\ N_2: \quad C_I &= \frac{C_{A0}\Theta_1}{1+\epsilon X} = \frac{(0.1)(2.03)}{1-0.14X} \quad \text{mol/dm}^3 \end{split}$$

```
import numpy as np
import matplotlib.pyplot as plt
# Constants
C AO = 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 \text{ values} = \text{np.arange}(0, 1.01, 0.25)
# Concentration calculations
def calculate_concentrations(X, C_AO, 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_AO, 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()
```



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  $188 \ ^{\circ}C$  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.

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

- (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  $188 \,^{\circ}C? r_A =$  \_\_\_\_\_
  - at 25 °C?  $-r_A$  = \_\_\_\_\_
  - at 288 °C?  $-r_A$  = \_\_\_\_\_

- (f) What is the rate of reaction when X = 0.90
  - at 188 °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 °*C*? V =\_\_\_\_
  - at 288 °*C*? V = \_\_\_\_\_

#### 💡 Solution

- $\mathsf{C}_6\mathsf{H}_4\mathsf{ClNO}_2 + 2\,\mathsf{NH}_3 \longrightarrow \mathsf{C}_6\mathsf{H}_6\mathsf{N}_2\mathsf{O}_2 + \mathsf{NH}_4\mathsf{Cl}$ 
  - $\mathbf{A} + \mathbf{2} \, \mathbf{B} \longrightarrow \mathbf{C} + \mathbf{D}; -r_A = k C_A C_B$

Table 6: Problem data

 $\begin{array}{ll} {\rm k} & {\rm 0.0017}\ m^3/kmolmin\ at\ 188^\circ C \\ {\rm E} & {\rm 11273\ cal/mol} \\ {\rm \$C\_A} & {\rm 1.8\ kmol/m^3} \\ {\rm \$C\_B} & {\rm 6.6\ kmol/m^3} \end{array}$ 

### a) Stoichiometric table for flow reactor

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

$$\Theta_B=\frac{6.6}{1.8}=3.67$$
 b)  $-r_A=kC_AC_B$  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

$$\begin{array}{l} -r_A = k C_A C_B \\ C_A = C_{A0} (1-X) \\ C_B = C_{A0} (\Theta_B - 2X) \\ -r_A = k C_{A0} (1-X) C_{A0} (\Theta_B - 2X) \\ -r_A = k C_{A0}^2 (1-X) (\Theta_B - 2X) \end{array}$$

e) Initial rates of reaction

k at different temperatures

$k = k_0 exp$	$p\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$
T (°C)	$\mathrm{k}\left(m^{3}/kmolmin\right)$
25 (298K)	$2.03\times 10^{-6}$
188 (461K)	0.0017
288 (561K)	0.152

1. At 188 °C

$$\begin{split} -r_A &= k C_{A0}^2 \Theta_B = 0.0017 \times (1.8)^2 \times 3.67 = 0.0202 \ kmol/m^3 min \\ \text{2. At 25 °C: } 2.41 \times 10^{-5} \ kmol/m^3 min \\ \text{3. At 288 °C: } 0.1806 \ kmol/m^3 min \\ \text{f) rates of reaction at } X &= 0.9 \\ -r_A &= k C_{A0}^2 (1 - X) (\Theta_B - 2X) \\ \text{1. At 188 °C: } 0.00103 \ kmol/m^3 min \\ \text{2. At 25 °C: } 1.23 \times 10^{-6} \ kmol/m^3 min \\ \text{3. At 288 °C: } 0.0092 \ kmol/m^3 min \\ \text{3. At 288 °C: } 0.0092 \ kmol/m^3 min \\ \text{g) CSTR Volume} \\ X &= 90 \\ F_{A0} &= C_{A0} v_0 = 3.6 mol/min \\ \text{1. V at 25 °C} \\ V &= \frac{F_{A0} X}{-r_A |_{exit}} \\ \text{V} &= 2634.1 \ m^3 \end{split}$$

2. V at 288 °C: 352  $m^3$