

Sheet 1

Q1 – The first order reaction $A \rightarrow B$ is carried out in a tubular reactor in which the Volumetric flowrate is constant.

1. Derive an equation relating the reactor volume to the entering and exiting concentrations of A, the rate constant k , and the volumetric flowrate v .
2. Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flowrate is 10 dm³/min (i.e., liters/min) and the specific reaction rate, k , is 0.23 min⁻¹

ANS: $V = \frac{v_0}{k} \ln \frac{C_{A0}}{C_A}$, 0.1 d³ (Fogler, example 1.1, page 51)

Q2- Calculate the time to reduce the number of moles of A to 1% of its initial value in a constant-volume batch reactor for the reaction and data in Q1.

ANS: 20 min (Fogler solution manual, P1-7)

Q3- What assumptions were made in the derivation of the design equation for:

- (a) the batch reactor?
- (b) the CSTR?
- (c) the plug-Row reactor (PRF) ?
- (d) the packed-bed reactor (PBR)?
- (e) State in words the meanings of $-r_A$, $-r_A'$. Is the reaction rate $-r_A$, an extensive quantity? Explain.

(Fogler solution manual, p1-8)

TABLE P1.13 COMPARISON OF REACTOR TYPES

Type of Reactor	Characteristics	Kinds of Phases Present	Use	Advantages	Disadvantages
Batch					
CSTR					
PFR					
PBR					

(Check Fogler solution manual , P1-13)

The reaction



is to be carried out isothermally in a continuous-flow reactor. Calculate both the CSTR and PFR reactor volumes necessary to consume 99% of A (i.e., $C_A = 0.01C_{A0}$) when the entering molar flow rate is 5 mol/h, assuming the reaction rate $-r_A$ is:

(a) $-r_A = k$ with $k = 0.05 \frac{\text{mol}}{\text{h} \cdot \text{dm}^3}$ (Ans.: $V = 99 \text{ dm}^3$)

(b) $-r_A = kC_A$ with $k = 0.0001 \text{ s}^{-1}$

(c) $-r_A = kC_A^2$ with $k = 3 \frac{\text{dm}^3}{\text{mol} \cdot \text{h}}$ (Ans.: $V_{\text{CSTR}} = 66,000 \text{ dm}^3$)

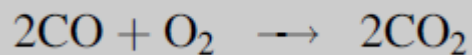
The entering volumetric flow rate is $10 \text{ dm}^3/\text{h}$. (Note: $F_A = C_A v$. For a constant volumetric flow rate $v = v_0$, then $F_A = C_A v_0$. Also, $C_{A0} = F_{A0}/v_0 = [5 \text{ mol/h}]/[10 \text{ dm}^3/\text{h}] = 0.5 \text{ mol/dm}^3$.)

(d) Repeat (a), (b), and (c) to calculate the time necessary to consume 99.9% of species A in a 1000 dm^3 constant volume batch reactor with $C_{A0} = 0.5 \text{ mol/dm}^3$.

(Fogler solution manual, P1-15)

$$\left(\begin{array}{c} \text{Excess} \\ \text{reactant} \\ B \end{array} \right) \equiv \frac{\text{Amount of } B \text{ fed} - \text{Stoichiometric amount of } B \text{ needed}}{\text{Stoichiometric amount of } B \text{ needed}}$$

$$\left| \frac{N_j(0)}{s_j} \right| \quad \text{or} \quad \left| \frac{F_{j\text{in}}}{s_j} \right| \quad j = A, B, \dots$$



Solution We select the given chemical reaction as the chemical formula, and the stoichiometric coefficients are

$$s_{\text{CO}} = -2 \quad s_{\text{O}_2} = -1 \quad s_{\text{CO}_2} = 2 \quad s_{\text{N}_2} = 0 \quad \Delta = -1$$

a. To identify the limiting reactant, apply Eq. 2.5.3 for each reactant:

$$\left| \frac{N_{\text{CO}}(0)}{s_{\text{CO}}} \right| = \left| \frac{1.5}{-2} \right| = 0.75 \quad \left| \frac{N_{\text{O}_2}(0)}{s_{\text{O}_2}} \right| = \left| \frac{1.0}{-1} \right| = 1.0 \quad (\text{a})$$

Hence, CO is the limiting reactant.

b. Now that the limiting reactant is identified, the stoichiometric amount of O₂ is readily determined using Eq. 2.5.2:

$$(N_{\text{O}_2})_{\text{stoich}} = \frac{s_{\text{O}_2}}{s_{\text{CO}}} N_{\text{CO}}(0) = \frac{-1}{-2} (1.5 \text{ kmol}) = 0.75 \text{ kmol} \quad (\text{b})$$

Using Eq. 2.5.4, the excess O₂ is

$$\left\{ \begin{array}{c} \text{Excess} \\ \text{O}_2 \end{array} \right\} \equiv \frac{(1 \text{ kmol}) - (0.75 \text{ kmol})}{0.75 \text{ kmol}} = 0.33 \quad (\text{c})$$

1.0 L/min of liquid containing **A** and **B** ($C_{AO}=0.10$ mol/L, $C_{BO}=0.01$ mol/L) flow into a mixed flow reactor of volume $V_R=1.0$ L. The materials in the reactor interact (react) in a complex manner for which the stoichiometry is unknown. The outlet stream from the reactor contains A, B and C at concentrations of $C_{Af} = 0.02$ mol/L, $C_{Bf}=0.03$ mol/L and $C_{Cf}=0.04$ mol/L.

Find the rate of reactions of A, B and C at conditions of the reactor.

Exercises:

Calculate the time to reduce the number of moles by of 10% from the initial moles in a constant volume batch reactor for the reaction $A \rightarrow B$. The reaction is first order and $K=0.046$ min⁻¹

Q1

2. Derive an equation relating V , v_0 , k , C_{A0} , and C_A .

For a tubular reactor, the mole balance on species A ($j = A$) was shown to be given by Equation (1-11). Then for species A ($j = A$) results

$$\frac{dF_A}{dV} = r_A \quad (1-11)$$

For a first-order reaction, the rate law (discussed in Chapter 3) is

$$-r_A = kC_A \quad (E1-1.1)$$

Because the volumetric flow rate, v , is constant ($v = v_0$), as it is for most liquid-phase reactions,

$$\frac{dF_A}{dV} = \frac{d(C_A v)}{dV} = \frac{d(C_A v_0)}{dV} = v_0 \frac{dC_A}{dV} = r_A \quad (E1-1.2)$$

Multiplying both sides of Equation (E1-1.2) by minus one and then substituting Equation (E1-1.1) yields

$$-\frac{v_0 dC_A}{dV} = -r_A = kC_A \quad (E1-1.3)$$

Rearranging gives

$$-\frac{v_0}{k} \left(\frac{dC_A}{C_A} \right) = dV$$

Using the conditions at the entrance of the reactor that when $V = 0$, then $C_A = C_{A0}$,

$$-\frac{v_0}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V dV \quad (E1-1.4)$$

Carrying out the integration of Equation (E1-1.4) gives

$$\boxed{V = \frac{v_0}{k} \ln \frac{C_{A0}}{C_A}} \quad (E1-1.5)$$

3. We want to find the volume, V_1 , at which $C_A = \frac{1}{10}C_{A0}$ for $k = 0.23 \text{ min}^{-1}$ and $v_0 = 10 \text{ dm}^3/\text{min}$.

Substituting C_{A0} , C_A , v_0 , and k in Equation (E1-1.5), we have

$$V = \frac{10 \text{ dm}^3/\text{min}}{0.23 \text{ min}^{-1}} \ln \frac{C_{A0}}{0.1 C_{A0}} = \frac{10 \text{ dm}^3}{0.23} \ln 10 = 100 \text{ dm}^3 \text{ (i.e., 100 L; } 0.1 \text{ m}^3\text{)}$$

We see that a reactor volume of 0.1 m^3 is necessary to convert 90% of species A entering into product B for the parameters given.

Q2 P1-7

$$t = \int_{N_{A0}}^{N_A} \frac{1}{-k \cdot N_A} dN_A$$

$$k = 0.23 \text{ min}^{-1}$$

From mole balance: $\frac{dN_A}{dt} = r_A \cdot V$

Rate law:

$$-r_A = k \cdot C_A$$

$$-r_A = k \cdot \frac{N_A}{V}$$

Combine:

$$\frac{dN_A}{dt} = -k \cdot N_A$$

$$\tau = 0 \int_0^t 1 dt = -\left(\frac{1}{k}\right) \cdot \int_{N_{A0}}^{N_A} \frac{1}{N_A} dN_A$$

at $\tau = 0$, $N_{A0} = 100 \text{ mol}$ and $\tau = \tau$, $N_A = (0.01)N_{A0}$

$$\rightarrow t = \frac{1}{k} \ln \left(\frac{N_{A0}}{N_A} \right)$$

$$= \frac{1}{0.23} \ln(100) \text{ min} \quad t = 20 \text{ min}$$

Q3

P1-8

- a) The assumptions made in deriving the design equation of a batch reactor are:
- Closed system: no streams carrying mass enter or leave the system.
 - Well mixed, no spatial variation in system properties
 - Constant Volume or constant pressure.
- b) The assumptions made in deriving the design equation of CSTR, are:
- Steady state.
 - No spatial variation in concentration, temperature, or reaction rate throughout the vessel.
- c) The assumptions made in deriving the design equation of PFR are:
- Steady state.
 - No radial variation in properties of the system.
- d) The assumptions made in deriving the design equation of PBR are:
- Steady state.
 - No radial variation in properties of the system.
- e) For a reaction,
 $A \rightarrow B$
 $-r_A$ is the number of moles of A reacting (disappearing) per unit time per unit volume [=] moles/
(dm³.s).

P1-13

Type	Characteristics	Phases	Usage	Advantage	Disadvantage
Batch	All the reactants fed into the reactor. During reaction nothing is added or removed. Easy heating or cooling.	1. Liquid phase 2. Gas phase 3. Liquid Solid	1. Small scale pdn. 2. Used for lab experimentation. 3. Pharmaceuticals 4. Fermentation	1. High Conversion per unit volume. 2. Flexibility of using for multiple reactions. 3. Easy to clean	1. High Operating cost. 2. Variable product quality.
CSTR	Continuous flow of reactants and products. Uniform composition throughout.	1. Liquid phase 2. Gas – liquid 3. Solid – liquid	1. Used when agitation required. 2. Series Configuration possible for different configuration streams	1. Continuous Operation. 2. Good Temperature Control 3. Two phase reactions possible. 4. Good Control 5. Simplicity of construction. 6. Low operating cost 7. Easy to clean	1. Lowest conversion per unit volume. 2. By passing possible with poor agitation. 3. High power Input reqd.
PFR	One long reactor or number of CSTR's in series. No radial variations. Conc. changes along the length.	1. Primarily gas Phase	1. Large Scale pdn. 2. Fast reactions 3. Homogenous reactions 4. Heterogeneous reactions 5. Continuous pdn.	1. High conversion per unit volume 2. Easy to maintain (No moving parts) 3. low operating cost 4. continuous operation	1. Undesired thermal gradient. 2. Poor temperature control 3. Shutdown and cleaning expensive.
PBR	Tubular reactor that is packed with solid catalyst particles.	1. Gas Phase (Solid Catalyst) 2. Gas – solid reactions.	1. Used primarily in the heterogeneous gas phase reaction with solid catalyst e.g Fischer tropesch synthesis.	1. High conversion per unit mass of catalyst 2. low operating cost 3. Continuous operation	1. Undesired thermal gradient. 2. Poor temperature control 3. Channeling 4. Cleaning expensive.

Q5

P1-15 (a)

$$-r_A = k \text{ with } k = 0.05 \text{ mol/h dm}^3$$

CSTR: The general equation is

$$V = \frac{F_{A0} - F_A}{-r_A}$$

Here $C_A = 0.01 C_{A0}$, $v_0 = 10 \text{ dm}^3/\text{min}$, $F_A = 5.0 \text{ mol/hr}$

Also we know that $F_A = C_A v_0$ and $F_{A0} = C_{A0} v_0$, $C_{A0} = F_{A0} / v_0 = 0.5 \text{ mol/dm}^3$

Substituting the values in the above equation we get,

$$V = \frac{C_{A0} v_0 - C_A v_0}{k} = \frac{(0.5)10 - 0.01(0.5)10}{0.05}$$
$$\rightarrow V = 99 \text{ dm}^3$$

PFR: The general equation is

$$\frac{dF_A}{dV} = r_A = k, \text{ Now } F_A = C_A v_0 \text{ and } F_{A0} = C_{A0} v_0 \Rightarrow \frac{dC_A v_0}{dV} = -k$$

Integrating the above equation we get

$$\frac{v_0}{k} \int_{C_{A0}}^{C_A} dC_A = \int_0^V dV \Rightarrow V = \frac{v_0}{k} (C_{A0} - C_A)$$

Hence $V = 99 \text{ dm}^3$

Volume of PFR is same as the volume for a CSTR since the rate is constant and independent of concentration.

P1-15 (b)

$$-r_A = kC_A \text{ with } k = 0.0001 \text{ s}^{-1}$$

CSTR:

We have already derived that

$$V = \frac{C_{A0}v_0 - C_A v_0}{-r_A} = \frac{v_0 C_{A0}(1 - 0.01)}{kC_A}$$

$$k = 0.0001 \text{ s}^{-1} = 0.0001 \times 3600 \text{ hr}^{-1} = 0.36 \text{ hr}^{-1}$$

$$\rightarrow V = \frac{(10 \text{ dm}^3 / \text{hr})(0.5 \text{ mol} / \text{dm}^3)(0.99)}{(0.36 \text{ hr}^{-1})(0.01 * 0.5 \text{ mol} / \text{dm}^3)} \Rightarrow V = 2750 \text{ dm}^3$$

PFR:

From above we already know that for a PFR

$$\frac{dC_A v_0}{dV} = r_A = kC_A$$

Integrating

$$\frac{v_0}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = - \int_0^V dV$$

$$\frac{v_0}{k} \ln \frac{C_{A0}}{C_A} = V$$

$$\text{Again } k = 0.0001 \text{ s}^{-1} = 0.0001 \times 3600 \text{ hr}^{-1} = 0.36 \text{ hr}^{-1}$$

Substituting the values in above equation we get

$$V = 127.9 \text{ dm}^3$$

P1-15 (d)

$$C_A = .001C_{A0}$$

$$t = \int_{N_A}^{N_{A0}} \frac{dN}{-r_A V}$$

Constant Volume $V=V_0$

$$t = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A}$$

Zero order:

$$t = \frac{1}{k} [C_{A0} - 0.001C_{A0}] = \frac{.999C_{A0}}{0.05} = 9.99 h$$

First order:

$$t = \frac{1}{k} \ln \left(\frac{C_{A0}}{C_A} \right) = \frac{1}{0.001} \ln \left(\frac{1}{.001} \right) = 6908 s$$

Second order:

$$t = \frac{1}{k} \left[\frac{1}{C_A} - \frac{1}{C_{A0}} \right] = \frac{1}{3} \left[\frac{1}{0.0005} - \frac{1}{0.5} \right] = 666 h$$