Chemical Reaction Engineering

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Contents

List of Figures

List of Tables

Nomenclature

Roman		
A	Arrhenius pre-exponential factor	*varies*
C	Concentration	$\mathrm{mol\,m^{-3}}$
E_{act}	Activation energy	$\mathrm{J\,mol^{-1}}$
G	Generation	$\mathrm{mol\,s^{-1}}$
K	Equilibrium constant	*varies*
k	Rate constant	*varies*
M	Ratio of C_{B0}/C_{A0}	–
N	Moles	mol
n	Molar flow rate	$\mathrm{mol\,m^{-3}\,s^{-1}}$
R	8.314	$\mathrm{J\,mol^{-1}\,K^{-1}}$
r	Reaction rate	$\mathrm{mol\,s^{-1}}$
S	Selectivity	–
T	Temperature	K
t	Time	s
$t_{1/2}$	Half-life	s
V	Volume	$\mathrm{m^3}$
v	Volumetric flow rate	$\mathrm{m^3\,s^{-1}}$
X	Conversion	–
Y	Yield	–
Greek		
α	Reaction order	–
β	Reaction order	–
δ	Change in moles per mole of A	–
ϵ	Change in mole fraction per mole of A	–
ν	Stoichiometric coefficient	–
0	Related to the start	
e	Refers to the equilibrium	
f	Related to the end	

Chapter 1

Reactions and Reactors

Contents

1.1 Introduction

Before describing particular chemical reactors, we need to first discuss how to provide mathematical expressions for the rate at which reactions occur using rate laws.

1.2 Reaction Rate

The reaction rate represents how fast a chemical component is converted into another by a chemical reaction. More specifically, the reaction rate, is the moles of a component formed (or appearing) per unit value per unit time. The reaction rate is negative when the moles of the component are being consumed by the reaction (as occurs for reactants before any product has been formed). The reaction rate is positive when the moles of the component increases with time due to the reaction (as occurs for products before any product has been formed).

Reaction Rate

The reaction rate can be positive or negative for any component of a reaction depending on the direction of the equilibrium from the initial compositions.

If we take the rate of reaction for the component i then we can base this on a number of key parameters of a reactor as,

Basis	Equation	Unit
Volume of reacting fluid	$r_i = \dfrac{1}{V}\dfrac{\mathrm{d}\,N_i}{\mathrm{d}\,t}$	$\mathrm{mol}_i\ \text{m-fluid}^{-3}\ \mathrm{s}^{-1}$
Mass of catalyst	$r_i' = \dfrac{1}{W}\dfrac{\mathrm{d}\,N_i}{\mathrm{d}\,t}$	$\mathrm{mol}_i\ \text{kg-cat}^{-1}\ \mathrm{s}^{-1}$
Surface area of catalyst	$r_i'' = \dfrac{1}{S}\dfrac{\mathrm{d}\,N_i}{\mathrm{d}\,t}$	$\mathrm{mol}_i\ \text{m-cat}^{-2}\ \mathrm{s}^{-1}$
Volume of catalyst	$r_i''' = \dfrac{1}{V_s}\dfrac{\mathrm{d}\,N_i}{\mathrm{d}\,t}$	$\mathrm{mol}_i\ \text{m-cat}^{-3}\ \mathrm{s}^{-1}$
Volume of reactor	$r_i'''' = \dfrac{1}{V_r}\dfrac{\mathrm{d}\,N_i}{\mathrm{d}\,t}$	$\mathrm{mol}_i\ \text{m-reactor}^{-3}\ \mathrm{s}^{-1}$

and thus,

$$V r_i = W r_i' = S r_i'' = V_s r_i''' = V_r r_i'''' \tag{1.2.1}$$

In homogeneous systems the volume of fluid in the reactor is often identical to the volume of the reactor, thus $V = V_r$. In heterogeneous systems all of the above definitions of the reaction rate are encountered, and the one used in any situation depends on convenience. In this course we will be focusing on homogeneous systems.

1.2.1 Reaction Equation or Rate Law

A reaction equation is an algebraic equation that is solely a function of the properties of the reacting materials and reaction conditions (e.g. species concentration, temperature, pressure, or type of catalyst) at any point in the system.

Rate Law

The rate equation is independent of the type of reactor (e.g. batch or continuous flow) in which the reaction is carried out.

$$A \longrightarrow \text{products}$$

The reaction rate may be a linear function of concentration, i.e. $-r_A = kC_A$ or may be some other algebraic function of concentration, such as $-r_A = kC_A^2$ or $-r_A = (k_1 C_A) / (1 + k_2 C_A)$.

$-r_A$ depends on concentration and temperature. This dependence can be written in general terms as

$$-r_A = k(T) \times f(C_A, C_B, \cdots) \tag{1.2.2}$$

where $k(T)$ (the rate constant) is a function of temperature. The rate law must be determined experimentally. The common form of the rate law is:

$$-r_A = kC_A^{\alpha} C_B^{\beta} \tag{1.2.3}$$

where α is defined as the reaction order with respect to A and β the reaction order with respect to B. The overall order of the reaction is given by the sum, $n = \alpha + \beta$.

Rate Constant Units

The units of k depend on the form of the rate law. We know that the rate must have units of moles/(volume-time) so that k has units of (concentration)$^{1-n}$/time. Thus when n is equal to 1, k has units of s^{-1}, for n equal to 2, k has units of $mol^{-1}\,dm^3\,s^{-1}$, and when n is equal to 3, k has units of $mol^{-2}\,dm^6\,s^{-1}$.

Typical examples of reaction rates are a first order reaction given by,

$$-r_A = kC_A \tag{1.2.4}$$

or a second order reaction,

$$-r_A = kC_A^2 \tag{1.2.5}$$

where k is called the rate constant,

Usually the order of the reaction provides some insight into the molecular mechanism for the reaction. A first order reaction corresponds to a uni-molecular process, whereas a second order reaction corresponds to reaction controlled by collisions between molecules. These rules are only strictly true when the reaction is an elementary step. Most reactions are combinations of elementary steps, which can lead to more complicated rate laws. In addition, the rate law can depend on the relative concentrations of the components. For instance, rate laws are independent of the concentrations of components, which occur at a large excess relative to another component (i.e. water).

For example, for the reaction of

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

the rate law is given by

$$-r_{\mathrm{NO}} = k_{\mathrm{NO}} C_{\mathrm{NO}}^2 C_{\mathrm{O}_2} \tag{1.2.6}$$

The overall order for the reaction is equal to 3, whereas the reaction is 2nd order with respect to NO and 1st order with respect to O_2. Note that the exponents α, β are not always equal to the stoichiometric coefficients except for the case where the reaction is an elementary step as discussed below.

An elementary reaction is one that involves only a single step. For instance:

$$\mathrm{H} + \mathrm{Br}_2 \longrightarrow \mathrm{HBr} + \mathrm{Br}$$

occurs when one hydronium ion collides and reacts with one bromine molecule. In this case the rate of reaction is given by $k\,[\mathrm{H}]\,[\mathrm{Br}_2]$. Because the step involves the collision of the two molecules, the rate is proportional to each of the concentrations. A general rule is thus that for an elementary reaction, *the reaction order follows from the stoichiometric coefficients*. However, many reactions are not elementary but instead have a complex, multistep reaction mechanism. In this case the rate of reaction does not often follow from the stoichiometric coefficients. For example, for the reaction of

$$\mathrm{H}_2 + \mathrm{Br}_2 \longrightarrow 2\,\mathrm{HBr}$$

the rate law is given by

$$-r_{\mathrm{HBr}} = \frac{k_1 C_{\mathrm{H}_2} C_{\mathrm{Br}_2}^{3/2}}{C_{\mathrm{HBr}} + k_2 C_{\mathrm{Br}_2}} \tag{1.2.7}$$

This reaction occurs due to a free radical mechanism, which actually corresponds to a series of elementary reaction steps as illustrated below.

$$\begin{aligned}
\mathrm{Br}_2 &\longrightarrow 2\,\mathrm{Br}^\bullet \\
\mathrm{Br}^\bullet + \mathrm{H}_2 &\longrightarrow \mathrm{HBr} + \mathrm{H}^\bullet \\
\mathrm{H}^\bullet + \mathrm{Br}_2 &\longrightarrow \mathrm{HBr} + \mathrm{Br}^\bullet \\
\mathrm{H}^\bullet + \mathrm{HBr} &\longrightarrow \mathrm{H}_2 + \mathrm{Br}^\bullet \\
2\,\mathrm{Br}^\bullet &\longrightarrow \mathrm{Br}_2
\end{aligned}$$

In this case, the rate law and reaction order must be determined experimentally. If a reaction has several steps then the slowest elementary reaction step often is the rate-limiting (or rate determining) step.

1.2.2 Relative Rates of Reaction

Consider the reaction:

$$(-\nu_A)\mathrm{A} + (-\nu_B)\mathrm{B} \longrightarrow \nu_C\mathrm{C} + \nu_D\mathrm{D}$$

where ν_A, ν_B, ν_C, and ν_D are called stoichiometric coefficients. Note that stoichiometric coefficients are negative for reactants and positive for products.

or sometimes written as,

$$\mathrm{A} + \frac{(-\nu_B)}{(-\nu_A)}\mathrm{B} \longrightarrow \frac{\nu_C}{(-\nu_A)}\mathrm{C} + \frac{\nu_D}{(-\nu_A)}\mathrm{D}$$

We usually express the reaction rate in terms one of the components, i.e. usually the rate of reaction is equal to the rate of formation of A in this case. Thus we need an expression for the rates of reaction for other components in terms of the rate of formation of A. For instance, every mole of A consumed gives $\nu_C/(-\nu_A)$ moles of C. Thus the rates are comparable as,

Relative Reaction Rates

$$\frac{r_A}{\nu_A} = \frac{r_B}{\nu_B} = \frac{r_C}{\nu_C} = \frac{r_D}{\nu_D} \tag{1.2.8}$$

For instance, $2\,NO + O_2 \longrightarrow 2\,NO_2$, the rates are:

$$\frac{r_{NO}}{-2} = \frac{r_{O_2}}{-1} = \frac{r_{NO_2}}{2}$$

If NO_2 is being formed at a rate of $4\,\mathrm{mol\,dm^{-3}\,s^{-1}}$, then the rate of formation of NO is

$$r_{NO} = \frac{\nu_{NO}}{\nu_{NO_2}} r_{NO_2} = \frac{-2}{2} r_{NO_2} = -4\,\mathrm{mol\,dm^{-3}\,s^{-1}}$$

i.e. the rate of disappearance of NO is $4\,\mathrm{mol\,dm^{-3}\,s^{-1}}$.

1.3 Extent of Reaction

Looking at reactions in terms of the concentration, or number of moles is not always the most convenient methos. Therefore we can introduce two other parameters that could be useful. These are the extent of reaction and the reaction conversion. When only one reaction is occurring in the reactor, all molar flowrates can be expressed in terms of these parameters, which makes solving the design equation easier.

For a general reaction, for each reactant the ratio of the change in the number of moles present, $\mathrm{d}\,N_i$, to the stoichiometric coefficient, ν_i, for the reactant is the same in each case, and this ratio is called the extent of reaction, ξ,

Extent of Reaction

$$\xi = \frac{\mathrm{d}\,N_i}{\nu_i} = \frac{N_i - N_{i,0}}{\nu_i} \tag{1.3.1}$$

The extent of reaction can be used in material balance calculations, if the number of moles of a species i present before the reaction is $N_{i,0}$, then the number of moles after the reaction can be found using,

$$N_i = N_{i,0} + \nu_i \xi \tag{1.3.2}$$

This can also be written in terms of a molar flow as,

$$\dot{n}_i = \dot{n}_{i,0} + \nu_i \xi \tag{1.3.3}$$

Consider the simple reaction A $\longrightarrow$ B, if this is first order, then the rate can be given by equation 1.2.4,

$$-r_i = kC_i$$

where C_i is the concentration of i and can be related to the number of moles, N_i, by,

$$N_i = C_i V \tag{1.3.4}$$

for a constant volume reactor, V, or, to the molar flow rate, $\dot{n}_i$, by

$$\dot{n}_i = C_i v \tag{1.3.5}$$

for a constant volumetric flow rate, v, reactor. This means that for a constant volumetric flow rate reactor with a first order reaction, we can write,

$$-r_i = \frac{k}{v}\dot{n}_i \tag{1.3.6}$$

From equation 1.3.3, we know that the number of moles in terms of the extent of reaction is,

$$\dot{n}_i = \dot{n}_{i,0} + \nu_i \xi$$

Substituting this into equation 1.3.6 gives,

$$-r_i = \frac{k}{v}\left(\dot{n}_{i,0} + \nu_i \xi\right) \tag{1.3.7}$$

This can also be carried out for other reaction rate functions.

1.4 Conversion

In many cases reactions will not proceed to completion, due to equilibrium limitatons or reaction kinetics. The conversion is often used as an indication of how far a reaction has proceeded. Conversion, X_i, is the fraction of a specified reactant which is consumed by the reaction,

Conversion

$$X_i = \frac{-\mathrm{d}\,N_i}{N_{i,0}} = \frac{N_{i,0} - N_i}{N_{i,0}} = -\frac{\xi \nu_i}{N_{i,0}} \tag{1.4.1}$$

Thus the conversion of A in our reaction is defined as,

$$X_A = \frac{\text{moles of A reacted}}{\text{moles of A fed}}$$

Usually we drop the subscript A so $X \equiv X_A$.

Conversion

- For irreversible reactions, at the start $X = 0$ and at the end $X = 1$, in cases where all of A is consumed (note that A will only be totally consumed if it is the limiting reactant in an irreversible reaction)
- For reversible reactions, the maximum conversion possible is controlled by the equilibrium constant; the maximum value is termed the equilibrium conversion X_e

The conversion can be used in material balance calculations as was the extent of reaction, if the number of moles of a species i present before the reaction is $N_{i,0}$, then the number of moles after the reaction can be found using,

$$N_i = N_{i,0}(1 - X_i) \tag{1.4.2}$$

This can also be written in terms of a molar flow as,

$$\dot{n}_i = \dot{n}_{i,0}(1 - X_i) \tag{1.4.3}$$

Again let us consider the simple reaction A $\longrightarrow$ B, with, for a constant volumetric flow rate, a first order reaction given by equation 1.3.6,

$$-r_i = \frac{k}{v}\dot{n}_i$$

From equation 1.4.3, we know the number of moles in terms of the conversion, thus giving us,

$$-r_i = \frac{k}{v}\dot{n}_{i,0}(1 - X_i) \tag{1.4.4}$$

1.5 General Mole Balance for Reactors

Ideal reactors normally refer to simplified models of reactors, in which various approximations are made. These approximations allow us to describe the behaviour of the reactor using simple mathematical expressions. We will study three types of ideal reactors: the batch reactor, the continuously stirred tank reactor (CSTR), and the plug flow reactor (PFR). To do this a general mole balance is needed for a general reactor as in Figure 1.1. The general mole balance can be written as,

$$\begin{array}{ccccccc}
\text{In} & - & \text{Out} & + & \text{Generation} & = & \text{Accumulation} \\
\begin{bmatrix}\text{Rate of} \\ \text{flow of } i \text{ in} \\ \text{(moles/time)}\end{bmatrix} & - & \begin{bmatrix}\text{Rate of} \\ \text{flow of } i \text{ out} \\ \text{(moles/time)}\end{bmatrix} & + & \begin{bmatrix}\text{Rate of} \\ \text{generation of} \\ i \text{ by chemical} \\ \text{reaction} \\ \text{(moles/time)}\end{bmatrix} & = & \begin{bmatrix}\text{Rate of} \\ \text{accumulation} \\ \text{of } i \\ \text{(moles/time)}\end{bmatrix} \\
n_i|_V & - & n_i|_{V+\delta V} & + & G_i & = & \frac{\mathrm{d}N_i}{\mathrm{d}t}
\end{array}$$

where n_i is the molar flowrate of species i (with units of moles sec^{-1}) and N_i is number of moles of component i in the reactor. The above mole balance is performed about

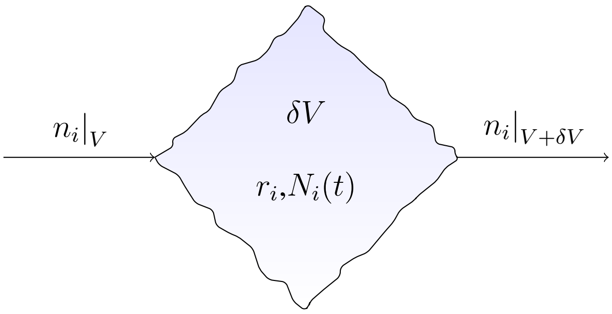


Figure 1.1: Schematic representation of the design of a reactor volume.

a volume element in the reactor over which all the system variables (e.g. temperature, concentration) are spatially uniform. In this case, the production rate in a reaction G_i over the given volume element, δV, can be calculated from the rate of formation of i, r_i, by,

$$G_i = r_i \times \delta V$$
$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{time} \times \text{volume}} \times \text{volume}$$

Thus the overall balance can be written as,

$$n_i|_V - n_i|_{V+\delta V} + r_i \delta V = \frac{\mathrm{d}\, N_i}{\mathrm{d}\, t} \tag{1.5.1}$$

1.6 Use of Extent of Reaction and Conversion

For example, lets think about a reactor with the following reaction taking place,

$$(-\nu_A)\mathrm{A} + (-\nu_B)\mathrm{B} \longrightarrow \nu_C\mathrm{C} + \nu_D\mathrm{D}$$

or sometimes written as,

$$\mathrm{A} + \frac{(-\nu_B)}{(-\nu_A)}\mathrm{B} \longrightarrow \frac{\nu_C}{(-\nu_A)}\mathrm{C} + \frac{\nu_D}{(-\nu_A)}\mathrm{D}$$

This can even be within the presence of an inert, I. We can express the total molar flowrates from the reactor effluent in terms of the extent of reaction or the conversion.

1.6.1 Extent of Reaction

If we assume a reactor operating at steady state, so the accumulation is zero, then we can use equation 1.5.1 and the extent of reaction, equation 1.3.1 to produce,

	Input +	Generation	= Output
	$n_i\|_V +$	$r_i \delta V$	$= n_i\|_{V+\delta V}$
A:	$n_{A,0} +$	$\xi \nu_{\mathrm{A}}$	$= n_A = n_{A,0} + \xi \nu_{\mathrm{A}}$
B:	$n_{B,0} = \frac{n_{B,0}}{n_{A,0}} n_{A,0} = \theta_B n_{A,0} +$	$\xi \nu_{\mathrm{B}}$	$= n_B = n_{A,0}\theta_B + \xi \nu_{\mathrm{B}}$
C:	$n_{C,0} = \frac{n_{C,0}}{n_{A,0}} n_{A,0} = \theta_C n_{A,0} +$	$\xi \nu_{\mathrm{C}}$	$= n_C = n_{A,0}\theta_C + \xi \nu_{\mathrm{C}}$
D:	$n_{D,0} = \frac{n_{D,0}}{n_{A,0}} n_{A,0} = \theta_D n_{A,0} +$	$\xi \nu_{\mathrm{D}}$	$= n_D = n_{A,0}\theta_D + \xi \nu_{\mathrm{D}}$
I:	$n_{I,0} = \frac{n_{I,0}}{n_{A,0}} n_{A,0} = \theta_I n_{A,0} +$	0	$= n_I = n_{A,0}\theta_I$
Total:	$n_{T,0} + \xi \left(\nu_A + \nu_B + \nu_c + \nu_D\right)$		$= n_{T,0} + \xi \left(\nu_A + \nu_B + \nu_c + \nu_D\right)$

Don't forget as ν_A and ν_B are negative we get a reduction in the amount of A and B, while ν_C and ν_D are positive so we get an increase in the amount of C and D.

Note that the change in total molar flowrates (i.e. $n_T - n_{T,0}$ can be calculated in terms of the extent of reaction as,

$$n_T = n_{T,0} + \xi \left(\nu_A + \nu_B + \nu_c + \nu_D\right) \tag{1.6.1}$$

1.6.2 Conversion

If we assume a reactor operating at steady state, so the accumulation is zero, then we can use equation 1.5.1 and the conversion, equation 1.4.1 to produce,

$$
\begin{array}{llcl}
 & \text{Input} + & \text{Generation} & = \text{Output} \\
 & n_i|_V + & r_i \delta V & = n_i|_{V+\delta V} \\
\hline
\text{A:} & n_{A,0} + & -n_{A,0}X & = n_A = n_{A,0}(1-X) \\
\text{B:}\ n_{B,0} = \frac{n_{B,0}}{n_{A,0}} n_{A,0} = & \theta_B n_{A,0} + & -\frac{\nu_\text{B}}{\nu_\text{A}} n_{A,0}X & = n_B = n_{A,0}\left(\theta_B - \frac{\nu_\text{B}}{\nu_\text{A}} n_{A,0}X\right) \\
\text{C:}\ n_{C,0} = \frac{n_{C,0}}{n_{A,0}} n_{A,0} = & \theta_C n_{A,0} + & -\frac{\nu_\text{C}}{\nu_\text{A}} n_{A,0}X & = n_C = n_{A,0}\left(\theta_C - \frac{\nu_\text{C}}{\nu_\text{A}} n_{A,0}X\right) \\
\text{D:}\ n_{D,0} = \frac{n_{D,0}}{n_{A,0}} n_{A,0} = & \theta_D n_{A,0} + & -\frac{\nu_\text{D}}{\nu_\text{A}} n_{A,0}X & = n_D = n_{A,0}\left(\theta_D - \frac{\nu_\text{D}}{\nu_\text{A}} n_{A,0}X\right) \\
\text{I:}\ n_{I,0} = \frac{n_{I,0}}{n_{A,0}} n_{A,0} = & \theta_I n_{A,0} + & 0 & = n_I = n_{A,0}\theta_I \\
\hline
\text{Total:} & n_{T,0} + & \delta n_{A,0}X & = n_T = n_{T,0} + \delta n_{A,0}X
\end{array}
$$

Don't forget as ν_A and ν_B are negative we get a reduction in the amount of A and B, while ν_C and ν_D are positive so we get an increase in the amount of C and D.

Note that the change in total molar flowrates (i.e. $n_T - n_{T,0}$) can be calculated in terms of the conversion and is equal to $\delta n_{A,0}X$ where,

$$
\begin{aligned}
\delta =& -1 - \frac{\nu_\text{B}}{\nu_\text{A}} - \frac{\nu_\text{C}}{\nu_\text{A}} - \frac{\nu_\text{D}}{\nu_\text{A}} \\
=& \frac{\nu_\text{D}}{-\nu_\text{A}} + \frac{\nu_\text{C}}{-\nu_\text{A}} - \frac{\nu_\text{B}}{\nu_\text{A}} - 1
\end{aligned}
\tag{1.6.2}
$$

is the change in moles per mole of A reacted. Thus in general for a single reaction,

$$
n_T = n_{T,0} + \delta n_{A,0}X = n_{T,0}(1 + \delta y_{A,0}X) = n_{T,0}(1 + \epsilon X) \tag{1.6.3}
$$

where $y_{A,0} = n_{A,0}/n_{T,0}$ as is the initial mole fraction of A.

[?]

1.7 References

1.8 Problems

1. The reaction:

$$2\,A + 3\,B \longrightarrow 5\,C$$

is carried out in a reactor. If at a particular point, the rate of disappearance of A is $10\,\mathrm{mol\,dm^{-3}\,s^{-1}}$, What are the rates of B and C?

2. (a) The reaction between A + B is first order in A and second order in B. Give the rate expression, and then find the units of k (assume time in minutes)

   (b) A reaction between P and Q is 3/2 order in P and order -1 in Q. Give the rate expression and find the units of k (assume time in minutes).

3. (a) If $k = 5.7 \times 10^{-4}\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ calculate the rate of reaction which is first order in both A and B when [A] = $5.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ and [B] = $2.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$.

   (b) If [A] had been $5.0 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ and [B] had been $2.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ what would the rate have been?

   (c) What conclusion can you draw from this?

4. Base hydrolyses of amino-acid esters have two contributing reactions:

   - OH^- reacting with protonated ester, HE^+, and
   - OH^- reacting with unprotonated ester, E.

   At 25°C the rate constant for the protonated ester is $1550\,\mathrm{mol^{-1}\,dm^3\,min^{-1}}$ and the rate constant for the unprotonated ester is $42\,\mathrm{mol^{-1}\,dm^3\,min^{-1}}$. At pH = 9.30, $[OH^-]$ = $2.0 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, and if the total [ester] = $2 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, then $[HE^+]$ = $5 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, and [E] = $195 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$.

   (a) Calculate the contributions to the overall rate from the two reactions.

   (b) What conclusions can be drawn?

5. Construct a stoichiometric table for the following batch reaction and derive expressions relating the concentrations of the reactants to the conversion.

$$N_2 + 3\,H_2 \longleftrightarrow 2\,NH_3$$

6. Soap consists of the sodium and potassium salts of various fatty acids such as oleic, stearic, palmitic, lauric, and myristic acids. The saponification for the formation of soap from aqueous caustic soda and glyceryl stearate is:

$$3\,NaOH_{(aq)} + (C_{17}H_{35}COO)_3C_3H_5 \longrightarrow 3\,C_{17}H_{35}COONa + C_3H_5(OH)_3$$

   Letting X represent the conversion of sodium hydroxide (the moles of sodium hydoxide reacted per mole of sodium hydroxide initially present), set up a stoichiometric table expressing the concentration of each species in terms of its initial concentration and the conversion X.

7. Using the information from question 6, if the initial mixture consists solely of NaOH at a concentration of $10\,\mathrm{mol\,dm^{-3}}$ and of glyceryl stearate at a concentration of $2\,\mathrm{mol\,dm^{-3}}$, what is the concentration of glycerine when the conversion of NaOH is (a) 20% and (b) 90%?

Chapter 2

Batch Reactors

Contents

2.1 Introduction

A batch reactor is a reactor in which reactants are mixed together and the reaction is allowed to proceed for a given time in a closed vessel with no inlet or outlet flows. Provision for mixing, heating or cooling of the reactants may be required. Figure 2.1 is a schematic representation of a batch reactor in the form of mixing vessel.

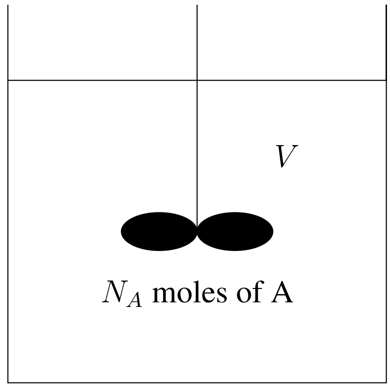


Figure 2.1: Schematic representation of a batch reactor.

Batch reactors are normally used for small-scale operation, testing new processes, the manufacture of expensive products, and processes difficult to convert to continuous. The advantage is that high conversions can be achieved due to leaving the reactants in reactor. The disadvantages are high labour costs, variability of products (batch to batch), and they are difficult to operate/automate for large-scale production.

2.2 Mole Balance Applied to Batch Reactors

In order to model a batch reactor, we need to make the assumption that at any given time the reactor is well-mixed so that the composition, temperature, and pressure are the same everywhere in the reactor. When the reaction takes place in a liquid (or sometimes solids), very often the reacting component occurs at a much lower concentration then the principal component of the liquid (i.e. the solvent). In this case, a good approximation is that the volume of the liquid and pressure in the reactor remain constant with time as there is only a small change in the density of the liquid during the reaction.

For gas-phase reactions, the entire volume of the reactor is filled by the gas, so that the reaction volume is equal to the reactor volume (whereas for a liquid, the reaction volume is the volume of the liquid which is less than the reactor volume). Thus for a gas-phase reaction, if the reaction either consumes or generates moles, the net effect will be a change to the pressure in the reactor, because the volume remains constant. If the reaction generates moles, the pressure in the reactor will increase, whereas if moles are consumed, the pressure in the reactor will decrease. We will examine this affect later.

Taking that mole balance from equation 1.5.1,

$$n_i|_V - n_i|_{V+\delta V} + r_i \delta V = \frac{\mathrm{d}\, N_i}{\mathrm{d}\, t}$$

As we assume that the batch reactor is well mixed (remember the mole balance must be made over a volume element which is spatially uniform with respect to composition and temperature) we can apply the mole balance over the entire volume of the reactor, so that $\delta V = V$. There also is no inflow or outflow in a batch reactor, so $n_i|_V = n_i|_{V+\delta V} = 0$. Therefore we can say,

$$r_i V = \frac{\mathrm{d}\,N_i}{\mathrm{d}\,t} \tag{2.2.1}$$

This equation can now be rearranged and integrated with limits $N_i = N_{i,0}$ when $t = 0$ (i.e. the initial condition) and $N_i = N_{i,f}$ when $t = t$,

$$\mathrm{d}\,t = \frac{\mathrm{d}\,N_i}{r_i V}$$

$$t = \int_{N_{i,0}}^{N_{i,f}} \frac{\mathrm{d}\,N_i}{r_i V} \tag{2.2.2}$$

To solve the right hand integral we now need a particular rate law, which of course depends on the reaction we are interested in. Let us consider the simple reaction,

$$\mathrm{A} \longrightarrow \mathrm{B}$$

as a simple first order rate law,

$$\begin{aligned} -r_A &= kC_A \\ r_A V &= -kC_A V = -k\left(\frac{N_A}{V}\right)V = -kN_A \end{aligned} \tag{2.2.3}$$

then substituting into equation 2.2.2 where $i = A$ and integrating gives,

$$\begin{aligned} t &= \int_{N_{A,0}}^{N_{A,f}} \frac{\mathrm{d}\,N_A}{-kN_A} \\ &= \frac{1}{k}\int_{N_{A,f}}^{N_{A,0}} \frac{\mathrm{d}\,N_A}{N_A} \\ &= \frac{1}{k}\left[\ln N_A\right]_{N_{A,f}}^{N_{A,0}} \\ &= \frac{1}{k}\left[\ln N_{A,0} - \ln N_{A,f}\right] \\ &= \frac{1}{k}\ln\left(\frac{N_{A,0}}{N_{A,f}}\right) \end{aligned} \tag{2.2.4}$$

The mole-time trajectories for A and B as predicted by Equation 2.2.4 are illustrated in Figure 2.2.

Very often we need to consider a constant volume batch reactor. In this case, we can take V to the right hand side of Equation 2.2.1 and express the rate in terms of the changing concentration, C_i, as,

$$r_i = \frac{1}{V}\frac{\mathrm{d}\,N_i}{\mathrm{d}\,t} = \frac{\mathrm{d}\,N_i/V}{\mathrm{d}\,t} = \frac{\mathrm{d}\,C_i}{\mathrm{d}\,t} \tag{2.2.5}$$

Equation 2.2.5 will appear often as constant volume batch reactors are often used for determining the parameters describing the kinetic rate laws (see Chapter 5). For a first

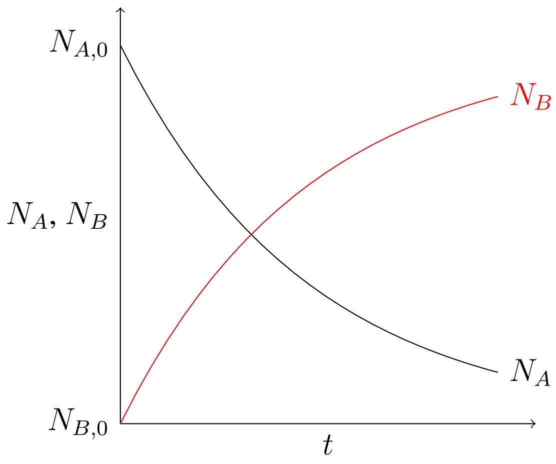


Figure 2.2: Mole-time trajectories for component A and B.

order reaction (equation 2.2.3), this equation can be integrated to obtain,

$$\begin{aligned} t &= \int_{C_{A,0}}^{C_{A,f}} \frac{\mathrm{d}\, C_A}{-kC_A} \\ &= \frac{1}{k} \int_{C_{A,f}}^{C_{A,0}} \frac{\mathrm{d}\, C_A}{C_A} \\ &= \frac{1}{k} [\ln C_A]_{C_{A,f}}^{C_{A,0}} \\ &= \frac{1}{k} [\ln C_{A,0} - \ln C_{A,f}] \\ &= \frac{1}{k} \ln \left(\frac{C_{A,0}}{C_{A,f}} \right) \end{aligned} \tag{2.2.6}$$

which is the same as Equation 2.2.4 above for a constant volume reactor.

2.3 Extent of Reaction in Batch Reactors

As with the reaction rates, it is also useful to think about the balance for a batch reactor in terms of the extent of reaction. From equation 1.3.1 we can see that,

$$\frac{\mathrm{d}\, N_i}{\mathrm{d}\, \xi} = \nu_i \tag{2.3.1}$$

Thus substituting into equation 2.2.1 gives and integrating with limits $\xi = 0$ when $t = 0$ (i.e. the initial condition) and $\xi = \xi$ when $t = t$ (i.e. the reaction time),

$$\begin{aligned} r_i V &= \frac{\mathrm{d}\, N_i}{\mathrm{d}\, t} \\ &= \nu_i \frac{\mathrm{d}\, \xi}{\mathrm{d}\, t} \\ t &= \int_0^{\xi} \frac{\nu_i}{r_i V} \mathrm{d}\, \xi \end{aligned} \tag{2.3.2}$$

Now if we take an example first order reaction in terms of the extent of reaction, equation 1.3.7,

$$-\,r_iV = k\left(N_{i,0} + \nu_i\xi\right)$$

then it can be substituted into equation 2.3.2,

$$\begin{aligned} t =& -\frac{\nu_i}{k}\int_0^\xi \frac{1}{\left(N_{i,0} + \nu_i\xi\right)}\mathrm{d}\,\xi \\ =& -\frac{\nu_i}{k}\left[\frac{1}{\nu_i}\ln\left(N_{i,0} + \nu_i\xi\right)\right]_0^\xi \\ =& -\frac{1}{k}\ln\left(\frac{N_{i,0} + \nu_i\xi}{N_{i,0}}\right) \\ =& -\frac{1}{k}\ln\left(1 + \frac{\nu_i\xi}{N_{i,0}}\right) \end{aligned} \tag{2.3.3}$$

2.4 Conversion in Batch Reactors

As with the reaction rates, it is also useful to think about the balance for a batch reactor in terms of the conversion. From equation 1.4.1 we can see that,

$$\frac{\mathrm{d}\,N_i}{\mathrm{d}\,X} = -N_{i,0} \tag{2.4.1}$$

Thus substituting into equation 2.2.1 gives and integrating with limits $X = 0$ when $t = 0$ (i.e. the initial condition) and $X = X$ when $t = t$ (i.e. the reaction time),

$$\begin{aligned} r_iV =& \frac{\mathrm{d}\,N_i}{\mathrm{d}\,t} \\ =& -\,N_{i,0}\frac{\mathrm{d}\,X}{\mathrm{d}\,t} \\ t =& \int_0^X \frac{N_{i,0}}{-r_iV}\mathrm{d}\,X \end{aligned} \tag{2.4.2}$$

Now if we take an example first order reaction in terms of the conversion, equation 1.4.4,

$$-\,r_iV = kN_{i,0}\left(1 - X\right)$$

then it can be substituted into equation 2.4.2,

$$\begin{aligned} t =& \int_0^X \frac{N_{i,0}}{kN_{i,0}\left(1 - X\right)}\mathrm{d}\,X \\ =& \frac{1}{k}\int_0^X \frac{1}{\left(1 - X\right)}\mathrm{d}\,X \\ =& \frac{1}{k}\left[-\ln\left(1 - X\right)\right]_0^X \\ =& \frac{1}{k}\left(-\ln\left(1 - X\right) + \ln(1)\right) \\ =& -\frac{1}{k}\left(\ln\left(1 - X\right) - \ln(1)\right) \\ =& -\frac{1}{k}\ln\left(1 - X\right) \end{aligned} \tag{2.4.3}$$

2.5 Summary

The key design equations have been derived for ideal batch reactors using the assumptions involved in the ideal reactor definitions. Additionally, the expressions have been derived to determine the time or volume required to achieve a reactant concentration for 1st-order reactions.

Batch Reactor Design Equations

Basis	Differential	Integral
Moles	$\frac{\mathrm{d}\,N_i}{\mathrm{d}\,t} = r_i V$	$t = \int_{N_{i,0}}^{N_{i,f}} \frac{\mathrm{d}\,N_i}{r_i V}$
Concentration	$\frac{\mathrm{d}\,C_i}{\mathrm{d}\,t} = r_i$	$t = \int_{C_{i,0}}^{C_{i,f}} \frac{\mathrm{d}\,C_i}{r_i}$
Extent of Reaction	$\frac{\mathrm{d}\,\xi}{\mathrm{d}\,t} = \frac{r_i V}{\nu_i}$	$t = \nu_i \int_0^{\xi} \frac{\mathrm{d}\,\xi}{r_i V}$
Conversion	$\frac{\mathrm{d}\,X}{\mathrm{d}\,t} = -\frac{r_i V}{N_{i,0}}$	$t = -N_{i,0} \int_0^{X} \frac{\mathrm{d}\,X}{r_i V}$

[?]

2.6 References

2.7 Problems

1. Calculate the time to reduce the number of moles by a factor of 10 ($N_A = N_{A0}/10$) in a batch reactor for the reaction

$$\text{A} \longrightarrow \text{B}$$

   with $-r_A = kC_A$, when $k = 0.046\,\text{min}^{-1}$.

2. 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 question 1 with $k = 0.23\,\text{min}^{-1}$.

3. Liquid A decomposes by first-order kinetics. In a batch reactor 50% of A is converted in 5 s. How much longer would it take to reach 75% conversion? Repeat this problem for the case when the decomposition follows second-order kinetics.

   [5 s, 10 s]

Chapter 3

Plug Flow Reactors (PFR)

Contents

3.1 Introduction

PFRs are mainly used for gas phase reactions and may be packed with catalyst. A schematic representation of a PFR is shown in Figure 3.1. The reactants are continuously fed into a cylindrical tube, while the products are continuously withdrawn. The reaction occurs as the stream flows through the reactor; the amount reacted increases with the distance down the cylindrical tube. The length needs to be chosen such that the desired conversion can be achieved. The PFR is similar to the CSTR in that it is operated under steady-state conditions except for the start-up and shut down of the reactor. The analysis below is only given for the steady state condition, which is used for sizing the reactor.

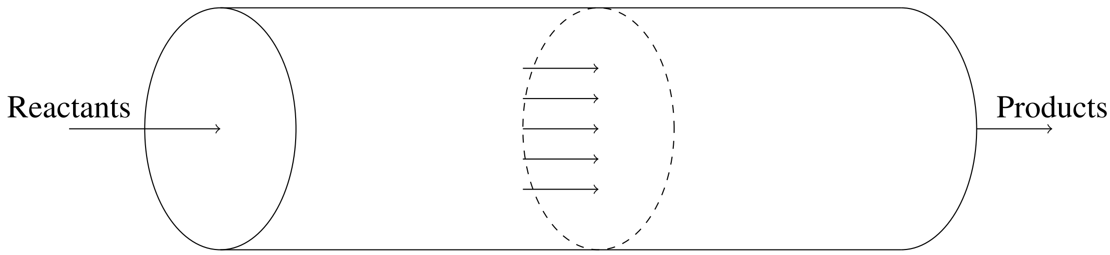


Figure 3.1: Schematic representation of a PFR.

3.2 Mole Balance Applied to PFR

In order to model a PFR, a few assumptions need to be made. In contrast to the batch reactor, the PFR is not well-mixed as the conversion increases with the distance down the tube. However, the well-mixed assumption is applied, but only in the radial direction, that is, we assume that there are no gradients of composition or temperature in the radial direction. Thus a slice of the reactor (i.e. δV in Figure 3.2 below) contains a homogeneous distribution of temperature and composition. Having no radial variation also requires that the velocity distribution in the PFR is flat, which is better approximated under turbulent flowing conditions. Lastly, we also assume that there is no axial mixing, this allows us to omit terms due to diffusion or dispersion in the mole balance.

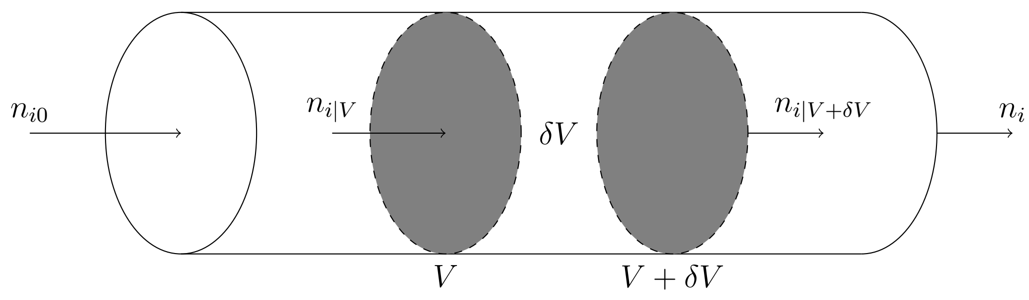


Figure 3.2: Mole balance of component i in a differential segment of δV.

Taking that mole balance from equation 1.5.1,

$$n_i|_V - n_i|_{V+\delta V} + r_i \delta V = \frac{\mathrm{d}\, N_i}{\mathrm{d}\, t}$$

As we assume that the PFR is at steady state, i.e. there is no change in the composition at a given position, then $\mathrm{d}\,N_i/\mathrm{d}\,t = 0$ as there is no accumulation. Therefore we can say,

$$\begin{aligned} n_i|_V - n_i|_{V+\delta V} + r_i\delta V &= 0 \\ n_i|_{V+\delta V} - n_i|_V &= r_i\delta V \\ \frac{n_i|_{V+\delta V} - n_i|_V}{\delta V} &= r_i \end{aligned} \tag{3.2.1}$$

Now if we take the limit as $\delta V \to 0$, then

$$\frac{\mathrm{d}\,n_i}{\mathrm{d}\,V} = r_i \tag{3.2.2}$$

This equation can now be rearranged and integrated with limits $n_i = n_{i,0}$ when $V = 0$ (i.e. the initial condition) and $n_i = n_{i,f}$ when $V = V$ (i.e. the outlet condition),

$$\begin{aligned} \mathrm{d}\,V &= \frac{\mathrm{d}\,n_i}{r_i} \\ V &= \int_{n_{i,0}}^{n_{i,f}} \frac{\mathrm{d}\,n_i}{r_i} \end{aligned} \tag{3.2.3}$$

To solve the right hand integral we now need a particular rate law, which of course depends on the reaction we are interested in. Let us consider the simple reaction,

$$\mathrm{A} \longrightarrow \mathrm{B}$$

as a simple first order rate law,

$$\begin{aligned} -r_A &= kC_A \\ r_A &= -kC_A\frac{v}{v} = -\frac{k}{v}\left(\frac{n_A}{v}\right)v = -\frac{k}{v}n_A \end{aligned} \tag{3.2.4}$$

then substituting into equation 3.3.1 where $i = A$ and integrating gives,

$$\begin{aligned} V &= \int_{n_{A,0}}^{n_{A,f}} \frac{v\mathrm{d}\,n_A}{-kn_A} \\ &= \frac{v}{k}\int_{n_{A,f}}^{n_{A,0}} \frac{\mathrm{d}\,n_A}{n_A} \\ &= \frac{v}{k}\left[\ln n_A\right]_{n_{A,f}}^{n_{A,0}} \\ &= \frac{v}{k}\left[\ln n_{A,0} - \ln n_{A,f}\right] \\ &= \frac{v}{k}\ln\left(\frac{n_{A,0}}{n_{A,f}}\right) \end{aligned} \tag{3.2.5}$$

For a plug flow reactor, it is also common to define a mean residence time as,

$$\tau = \frac{V}{v} = \frac{1}{k}\ln\left(\frac{n_{A,0}}{n_{A,f}}\right) \tag{3.2.6}$$

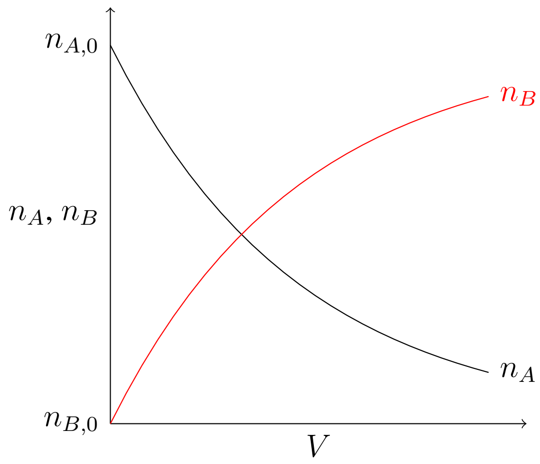


Figure 3.3: Molar flowrate of component A and B as a function of volume in a PFR.

In Figure 3.3 is shown a plot of the molar flowrates for A and B as a function of the reactor volume.

Note that in deriving Equation 3.2.5, we have assumed that the volumetric flowrate v of the gas is independent of the position in the PFR. The conditions when v is a constant can be deduced from considering the ideal gas law $v = n_t RT/P$ (assuming that a gas is being reacted in the PFR), where n_t is the total molar flowrate. Thus, the temperature, pressure, and total molar flowrate must be constants for v to be a constant. In the reaction of A going to B, for each mole of A consumed, one mole of B is formed so that indeed the total molar flowrate is a constant. However, if the number of moles reacted does not equal the moles consumed, we would need to account for the change in v as a function of the change in mole number along the reactor. In addition, if the reactor is not isothermal, we would also have to consider how v depends on T. How T depends on position in reactor would be determined from a differential energy balance. This behaviour should be contrasted to what happens in a gas phase reaction in a batch reactor. In this case, the volume of the reactor is a constant so that the pressure changes when the reaction either generates or consumes moles. This will be discussed more in Chapter 5.

The pressure profile in a PFR is not related to the gas law (the gas law controls the volumetric flowrate), but instead the pressure profile in a PFR is determined from the momentum balance (i.e. fluid flow). The Ergun Equation is often used to calculate the pressure drop in a PFR containing catalyst particles in terms of the diameter of the cylinder, the size of catalyst particles, the viscosity of the medium and the velocity of the gas.

As we have assumed above the volumetric flow rate of the reactor is constant then we can multiply left side of equation 3.2.2 and express the rate in terms of the changing concentration, C_i, as,

$$r_i = \frac{v}{v}\frac{\mathrm{d}\,n_i}{\mathrm{d}\,V} = v\frac{\mathrm{d}\,C_i}{\mathrm{d}\,V} \qquad (3.2.7)$$

For a first order reaction (equation 3.2.4), this equation can be integrated to obtain,

$$
\begin{aligned}
V &= \int_{C_{A,0}}^{C_{A,f}} v \frac{\mathrm{d}\, C_A}{-kC_A} \\
&= \frac{v}{k} \int_{C_{A,f}}^{C_{A,0}} \frac{\mathrm{d}\, C_A}{C_A} \\
&= \frac{v}{k} \left[\ln C_A\right]_{C_{A,f}}^{C_{A,0}} \\
&= \frac{v}{k} \left[\ln C_{A,0} - \ln C_{A,f}\right] \\
&= \frac{v}{k} \ln\left(\frac{C_{A,0}}{C_{A,f}}\right) \qquad (3.2.8)
\end{aligned}
$$

3.3 Extent of Reaction in PFR

As with the reaction rates, it is also useful to think about the balance for a plug flow reactor in terms of the extent of reaction. Thus substituting equation 2.3.1 into into equation 3.2.2 and integrating with limits $\xi = 0$ when $V = 0$ (i.e. the initial condition) and $\xi = \xi$ when $V = V$ (i.e. the reactor volume),

$$
\begin{aligned}
r_i &= \frac{\mathrm{d}\, n_i}{\mathrm{d}\, V} \\
&= \nu_i \frac{\mathrm{d}\, \xi}{\mathrm{d}\, V} \\
V &= \int_0^{\xi} \frac{\nu_i}{r_i} \mathrm{d}\, \xi \qquad (3.3.1)
\end{aligned}
$$

Now if we take an example first order reaction in terms of the extent of reaction, equation 1.3.7,

$$
-\, r_i = \frac{k}{v}\left(n_{i,0} + \nu_i \xi\right)
$$

then it can be substituted into equation 3.3.1,

$$
\begin{aligned}
V &= -\,\frac{\nu_i v}{k} \int_0^{\xi} \frac{1}{\left(n_{i,0} + \nu_i \xi\right)} \mathrm{d}\, \xi \\
&= -\,\frac{\nu_i v}{k} \left[\frac{1}{\nu_i} \ln\left(n_{i,0} + \nu_i \xi\right)\right]_0^{\xi} \\
&= -\,\frac{v}{k} \ln\left(\frac{n_{i,0} + \nu_i \xi}{n_{i,0}}\right) \\
&= -\,\frac{v}{k} \ln\left(1 + \frac{\nu_i \xi}{n_{i,0}}\right) \qquad (3.3.2)
\end{aligned}
$$

3.4 Conversion in PFR

As with the reaction rates, it is also useful to think about the balance for a plug flow reactor in terms of the conversion. Thus substituting equation 2.4.1 into into equation 3.2.2 and integrating with limits $X = 0$ when $V = 0$ (i.e. the initial condition) and $X = X$ when $V = V$ (i.e. the reactor volume),

$$\begin{aligned} r_i &= \frac{\mathrm{d}\, n_i}{\mathrm{d}\, V} \\ &= -\, n_{i,0} \frac{\mathrm{d}\, X}{\mathrm{d}\, V} \\ V &= \int_0^X \frac{n_{i,0}}{-r_i} \mathrm{d}\, X \end{aligned} \tag{3.4.1}$$

Now if we take an example first order reaction in terms of the conversionn, equation 1.4.4,

$$-\, r_i = \frac{k}{v} n_{i,0} \left(1 - X\right)$$

then it can be substituted into equation 3.4.1,

$$\begin{aligned} V &= \int_0^X \frac{v n_{i,0}}{k n_{i,0} \left(1 - X\right)} \mathrm{d}\, X \\ &= \frac{v}{k} \int_0^X \frac{1}{\left(1 - X\right)} \mathrm{d}\, X \\ &= \frac{v}{k} \left[-\ln\left(1 - X\right)\right]_0^X \\ &= \frac{v}{k} \left(-\ln\left(1 - X\right) + \ln(1)\right) \\ &= -\, \frac{v}{k} \left(\ln\left(1 - X\right) - \ln(1)\right) \\ &= -\, \frac{v}{k} \ln\left(1 - X\right) \end{aligned} \tag{3.4.2}$$

3.5 Summary

The key design equations have been derived for ideal plug flow reactors using the assumptions involved in the ideal reactor definitions. Additionally, the expressions have been derived to determine the volume required to achieve a reactant concentration for 1st-order reactions.

Plug Flow Reactor Design Equations

Basis	Differential	Integral
Moles	$\frac{\mathrm{d}\, N_i}{\mathrm{d}\, V} = r_i$	$V = \int_{n_{i,0}}^{n_{i,f}} \frac{\mathrm{d}\, n_i}{r_i}$
Concentration	$\frac{\mathrm{d}\, C_i}{\mathrm{d}\, V} = \frac{r_i}{v}$	$V = v \int_{C_{i,0}}^{C_{i,f}} \frac{\mathrm{d}\, C_i}{r_i}$
Extent of Reaction	$\frac{\mathrm{d}\, \xi}{\mathrm{d}\, V} = \frac{r_i}{\nu_i}$	$V = \nu_i \int_0^{\xi} \frac{\mathrm{d}\, \xi}{r_i}$
Conversion	$\frac{\mathrm{d}\, X}{\mathrm{d}\, V} = -\frac{r_i}{n_{i,0}}$	$V = -n_{i,0} \int_0^X \frac{\mathrm{d}\, X}{r_i}$

[?]

3.6 References

3.7 Problems

1. Consider the liquid phase cis-trans isomerisation of 2-butene which can be written symbolically as

   $$\text{A} \longrightarrow \text{B}.$$

   The first order ($-r_A = kC_A$) reaction is carried out in a tubular reactor in which the volumetric flow rate, v, is constant, i.e. $v = v_0$.

   (a) Sketch the concentration profile.

   (b) Derive an equation relating the reactor volume to the entering and exiting concentrations of A, the rate constant k, and the volumetric flow rate, v.

   (c) Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is 10 dm^3 min^{-1} and the specific reaction rate constant k, is 0.23 min^{-1}.

2. Consider a plug flow reactor operating steady-state and constant temperature. The following (first-order) reaction (for which there is no volume change) takes place and the rate constant is 5×10^{-4} s^{-1}:

   $$\text{A} \longrightarrow \text{products}$$

   If the inlet concentration is 0.1 mol dm^{-3}, the reactor volume 0.6 m^3 and the volumetric flow 0.3 dm^3 s^{-1}, what is the outlet concentration?

   [0.0368 mol dm^{-3}]

3. A gas of pure A at 830 kPa (8.2 atm) enters a reactor with a volumetric flow rate, v_0, of 2 dm^3 s^{-1} at 500 K. Calculate the entering concentration of A, C_{A0} and the entering molar flow rate, n_{A0}. ($R = 8.314$ dm^3 kPa mol^{-1} K^{-1}).

Chapter 4

Continously Stirred Tank Reactors (CSTR)

Contents

4.1 Introduction

In a CSTR reactor there is a constant inflow of reactants in the feed stream and a constant outflow of products in the exit stream. Except for the start-up and shut-down, the reactor is operated at a steady state in which the reactor contents do not change with time.

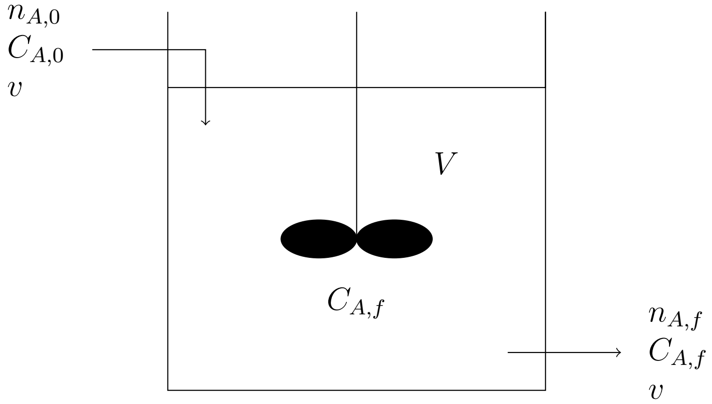


Figure 4.1: A typical CSTR showing the flow of the reacting material A. Here v is the volumetric flowrate and the subscript 0 denotes a property of the feed stream (this contrasts with the batch reactor where subscript 0 corresponds to a property at time equal to 0).

4.2 Mole Balance Applied to CSTR

The first step in designing a CSTR is to determine the volume required to achieve a given change in moles using a mole balance. Taking that mole balance from equation 1.5.1,

$$n_i|_V - n_i|_{V+\delta V} + r_i \delta V = \frac{\mathrm{d}\, N_i}{\mathrm{d}\, t}$$

As this is an ideal CSTR, we can make the same well-mixed assumption used for the batch reactor. Thus we assume that the composition and temperature in the reactor are uniformly distributed and we can then apply the mole balance about the entire reactor volume, $\delta V = V$. Furthermore, under the well-mixed assumption, the exit stream is at the same composition and temperature as the contents inside the reactor, thus $n_i = n_{i,f}$ and the reaction rate proceeds based on this concentration. At steady state, the reactor contents do not change with time so that $\mathrm{d}\, N_i / \mathrm{d}\, t = 0$. Therefore we can say,

$$n_{i,0} - n_{i,f} + r_{i,f} V = 0 \tag{4.2.1}$$

This equation can now be directly rearranged for the reactor volume as,

$$V = \frac{n_{i,0} - n_{i,f}}{-r_{i,f}} \tag{4.2.2}$$

To solve the right hand side we now need a particular rate law, which of course depends on the reaction we are interested in. Let us consider the simple reaction,

$$\text{A} \longrightarrow \text{B}$$

as a simple first order rate law,

$$\begin{aligned} -r_A &= kC_A \\ -r_A &= kC_A \frac{v}{v} = \frac{k}{v}\left(\frac{n_A}{v}\right) v = \frac{k}{v} n_A \end{aligned} \tag{4.2.3}$$

then substituting into equation 4.2.2 where $i = A$ and integrating gives,

$$\begin{aligned} V &= \frac{v\left(n_{A,0} - n_{A,f}\right)}{kn_{A,f}} \\ &= \frac{v}{k}\left(\frac{n_{A,0}}{n_{A,f}} - 1\right) \end{aligned} \tag{4.2.4}$$

For a CSTR at steady state with no change in the density or the total number of moles in the reaction, the inlet and the outlet volumetic flow rates must be equal otherwise the volume of the reactor contents would change (or the pressure would change if a gas reaction). For a CSTR in this case, it is also common to define a mean residence time as,

$$\tau = \frac{V}{v} = \frac{1}{k}\left(\frac{n_{A,0}}{n_{A,f}} - 1\right) \tag{4.2.5}$$

As we have assumed above the volumetric flow rate of the reactor is constant then we can multiply left side of equation 4.2.2 and express the rate in terms of the changing concentration, C_i, as,

$$V = \frac{v}{v}\frac{n_{i,0} - n_{i,f}}{-r_{i,f}} = \frac{v\left(C_{i,0} - C_{i,f}\right)}{-r_{i,f}} \tag{4.2.6}$$

For a first order reaction (equation 4.2.3), this equation can be combined to obtain,

$$\begin{aligned} V &= \frac{v\left(C_{A,0} - C_{A,f}\right)}{kC_{A,f}} \\ &= \frac{v}{k}\left(\frac{C_{A,0}}{C_{A,f}} - 1\right) \end{aligned} \tag{4.2.7}$$

4.3 Extent of Reaction in CSTR

As with the reaction rates, it is also useful to think about the balance for a continuously stirred tank reactor in terms of the extent of reaction. Thus substituting equation 1.3.1,

$$n_{i,0} - n_{i,f} = -\xi\nu_i \tag{4.3.1}$$

into into equation 4.2.2, gives,

$$\begin{aligned} V &= \frac{n_{i,0} - n_{i,f}}{-r_{i,f}} \\ &= \frac{\xi\nu_i}{r_{i,f}} \end{aligned} \tag{4.3.2}$$

Now if we take an example first order reaction in terms of the extent of reaction, equation 1.3.7,

$$r_i = -\frac{k}{v}\left(n_{i,0} + \nu_i \xi\right)$$

then it can be substituted into equation 4.3.2,

$$\begin{aligned} V &= \frac{v \xi \nu_i}{-k\left(n_{i,0} + \nu_i \xi\right)} \\ &= -\frac{v}{k}\frac{\left(\frac{\nu_i \xi}{n_{i,0}}\right)}{\left(1 + \frac{\nu_i \xi}{n_{i,0}}\right)} \end{aligned} \tag{4.3.3}$$

4.4 Conversion in CSTR

As with the reaction rates, it is also useful to think about the balance for a continuously stirred tank reactor in terms of the conversion. Thus substituting equation 1.4.1,

$$n_{i,0} - n_{i,f} = n_{i,0} X \tag{4.4.1}$$

into into equation 4.2.2, gives,

$$\begin{aligned} V &= \frac{n_{i,0} - n_{i,f}}{-r_{i,f}} \\ &= \frac{n_{i,0} X}{-r_{i,f}} \end{aligned} \tag{4.4.2}$$

Now if we take an example first order reaction in terms of the conversionn, equation 1.4.4,

$$-r_i = \frac{k}{v} n_{i,0}\left(1 - X\right)$$

then it can be substituted into equation 4.4.2,

$$\begin{aligned} V &= \frac{v n_{i,0} X}{k n_{i,0}\left(1 - X\right)} \\ &= \frac{v}{k}\frac{X}{1 - X} \end{aligned} \tag{4.4.3}$$

Often for the conversion of the CSTR the mean residence time is used, which is the time necessary to process one volume of reactor fluid at the entrance conditions. The mean residence time provides a measure of how long the fluid is in the reactor, which controls the conversion, the larger the residence time, the greater the conversion, thus,

$$\begin{aligned} \tau &= \frac{V}{v} = \frac{1}{k}\frac{X}{1 - X} \\ X &= \frac{k\tau}{1 + k\tau} \end{aligned} \tag{4.4.4}$$

Equation 4.4.4 provides a rapid way for estimating the conversion in terms of the product $k\tau$, which is known as the reaction Dahmkohler number. Values of the Damkohler number equal to 0.1 give conversions of about 10 percent, whereas values equal to 10 give conversions of close to 90 percent.

4.5 Levenspiel Plots

The design equations involving conversion for the CSTR (equation 4.4.2) and PFR (equation 3.4.1) are,

$$\text{CSTR:} \qquad V = \frac{n_{A,0}X}{-r_{A,f}} \qquad \text{PFR:} \qquad V = n_{A,0}\int_0^X \frac{\mathrm{d}\,X}{-r_A}$$

Therefore it can be seen that the reactor volume varies with $n_{A,0}/-r_A$, but one as a multiplication and one as an integral.

Figure 4.2 shows some real data for an isothermal reaction with conditions of $T = 500\,\mathrm{K}$, $P = 8.2\,\mathrm{atm}$, and $n_{A0} = 0.4\,\mathrm{mol\,s^{-1}}$. In order to size a reactor from experimental rate data, we first need to plot $n_{A,0}/-r_A$ (m^3) as a function of X (this plot is called a Levenspiel plot).

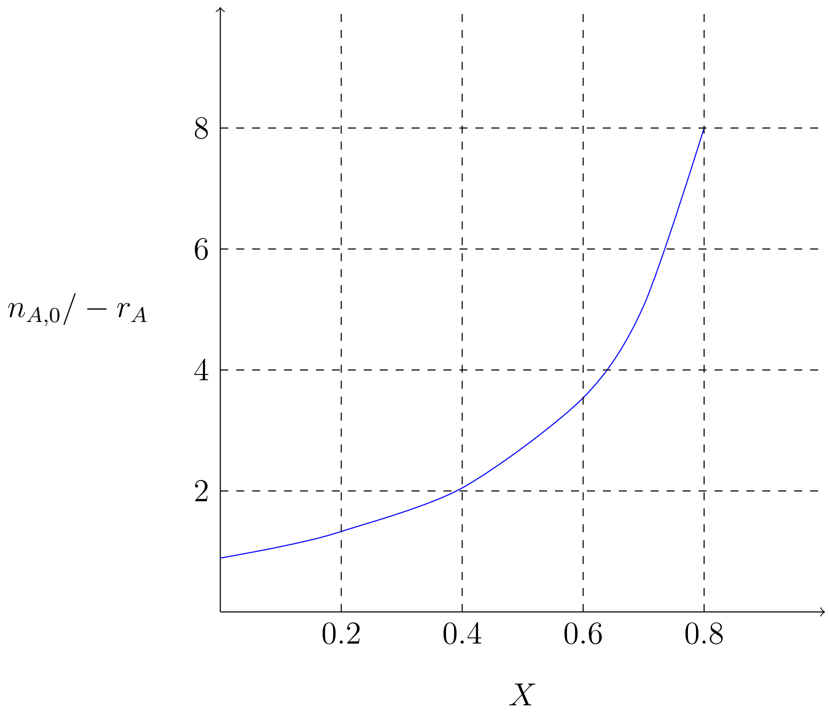


Figure 4.2: Levenspiel plot of example reaction data with conditions of $T = 500\,\mathrm{K}, P = 8.2\,\mathrm{atm}$, and $n_{A0} = 0.4\,\mathrm{mol\,s^{-1}}$.

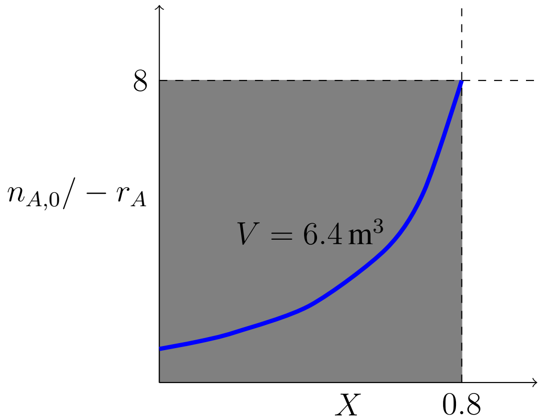
4.5.1 CSTR

From our CSTR equation we develop,

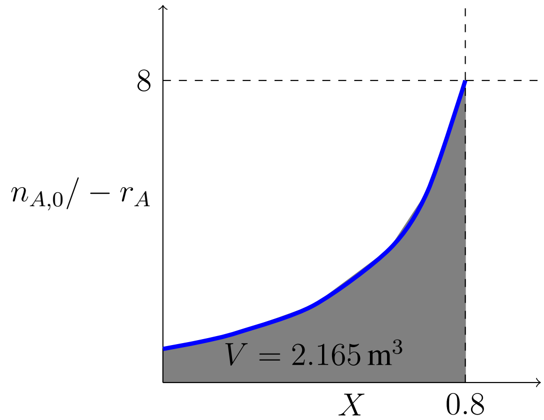
$$V = \left(\frac{n_{A,0}}{-r_{A,f}}\right) \times X \tag{4.5.1}$$

The volume is therefore equal to the area of a rectangle of height $n_{A,0}/-r_{A,f}$ and base X on the Levenspiel plot as shown in Figure 4.3(a) below for the example of $X = 0.8$,

$$V = \left(\frac{n_{A,0}}{-r_A}\right) \times X = 8\left(\mathrm{m}^3\right) \times 0.8 = 6.4\,\mathrm{m}^3$$



(a) CSTR



(b) PFR

Figure 4.3: Schematic representation of a (a) CSTR volume and (b) PFR volume calculation.

4.5.2 PFR

From our PFR equation we develop,

$$V = \int_0^X \left(\frac{n_{A,0}}{-r_A}\right) \mathrm{d}\,X \tag{4.5.2}$$

The volume is therefore equal to the area under the curve of $n_{A,0}/-r_{A,f}$ against X on the Levenspiel plot as shown in Figure 4.3(b) below for the example of $X = 0.8$.

The integration can be performed using the trapezium rule (or Simpson's rule) with known data points (taken from the curve). Alternatively one could count/estimate the area on graph paper. For this example the volume is,

$$V = 2.165\,\mathrm{m}^3$$

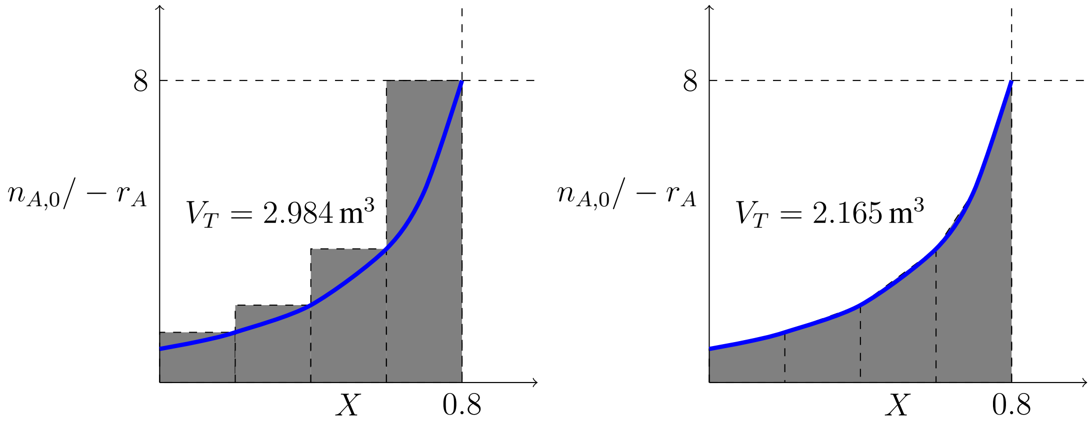
PFR vs CSTR

The CSTR volume required is greater than the PFR volume for the same conversion and reaction conditions.

The concentration in the CSTR everywhere is equal to the exit concentration, so that the reaction rate is proportional to the exit concentration over the entire volume of the CSTR. In a PFR, the concentration of the reactant A gradually decreases along the reactor until it reaches a minimum value given by the exit concentration. As a consequence, the concentration of A in the PFR is always greater than that in the CSTR when the same exit conversion is achieved. Because the rate is proportional to the concentration of A, the rate is also greater everywhere in the PFR versus in the CSTR.

4.5.3 Reactors in Series

Putting CSTRs in series reduces the volume required. An infinite number in series is equivalent to a PFR. Putting PFRs in series is equivalent of a longer PFR, Figure 4.4.



(a) CSTR (b) PFR

Figure 4.4: Schematic representation of multiple (a) CSTR volumes and (b) PFR volumes.

4.6 Summary

The key design equations have been derived for ideal continuously stirred tank reactors using the assumptions involved in the ideal reactor definitions. Additionally the expressions have been derived to determine the volume required to achieve a reactant concentration for 1st-order reactions.

Continuously Stirred Tank Reactor Design Equations

Basis	Algebraic
Moles	$V = \dfrac{n_{i,0} - n_{i,f}}{-r_{i,f}}$
Concentration	$V = \dfrac{v\left(C_{i,0} - C_{i,f}\right)}{-r_{i,f}}$
Extent of Reaction	$V = \dfrac{\xi \nu_i}{r_{i,f}}$
Conversion	$V = \dfrac{n_{i,0} X}{-r_{i,f}}$

[?]

4.7 References

4.8 Problems

1. A 1st order irreversible reaction,

$$\text{A} \longrightarrow \text{B}$$

with $k = 0.01\,\text{s}^{-1}$ is required to reach 30% conversion. (Assume constant volume)

   (a) How long will it take in a batch reactor?

   (b) What CSTR reactor volume and residence time would be required given a volumetric flow rate of $10^{-3}\,\text{m}^3\text{s}^{-1}$?

   (c) What PFR reactor volume and residence time would be required given a volumetric flow rate of $10^{-3}\,\text{m}^3\text{s}^{-1}$?

2. Show that for a CSTR,

$$n_A = n_{A0}\,(1 - X) \text{ where } n_A \text{ is the molar flow rate of A}$$

Show also that

$$V = n_{A0}X/\,(-r_A)_{\text{exit}}$$

3. Aerated lagoons can be thought of as CSTR's with bacteria inside that consume the substrates in wastewater. The evaluation of the lagoon involves the definition of the mass balance and application of the rate law to determine the lagoon volume required to reduce TOC (Total Organic Carbon) concentration to an acceptable level. In many cases, the decomposition of TOC can be approximated through 1st order kinetics:

$$r = -kC_s$$

Knowing that the common depth of the aerated lagoon is 4 m, determine the area of land needed to reduce the 2×10^6 litres/day of wastewater with a substrate concentration of 300 mg/litre to 50 mg/litre operating at steady state. Assume $k = 1.5\,\text{day}^{-1}$.

[1667 m^2]

4. A reactor to be designed to have the conversion data as shown in Figure 4.3. Also, the reactor conditions: 500 K, 8.2 atm $n_{A0} = 0.4\,\text{mol}\,\text{s}^{-1}$ and the initial charge was pure A.

   (a) Calculate the volume necessary to achieve 80% conversion in

      i. a CSTR reactor and

      ii. a PFR reactor under these conditions

   (b) How would your answers change if the flow rate, n_{A0}, were reduced to 0.2 mol s^{-1}?

   (c) How would your answers change if the flow rate, n_{A0}, were reduced to 0.8 mol s^{-1}?

5. The exothermic reaction

$$\text{A} \longrightarrow \text{B + C}$$

was carried out adiabatically and the following data recorded:

X	0	0.2	0.4	0.45	0.5	0.6	0.8	0.9
$-r_A$ (mol dm^{-3} min^{-1})	1.0	1.67	5.0	5.0	5.0	5.0	1.25	0.91

The entering molar flow rate of A was $300\,\mathrm{mol\,min^{-1}}$.

(a) What are the PFR and CSTR volumes necessary to achieve 40% conversion?

(b) Over what range of conversions would the CSTR and PFR reactor volumes be identical?

(c) What is the maximum conversion that can be achieved in a $105\,\mathrm{dm^3}$ CSTR?

Chapter 5

Experimental Determination of Rate Law Parameters

Contents

5.1 Introduction

As discussed in the previous chapters, it is essential to determine the reaction rate equation experimentally. This chapter looks at several approaches to experimentally evaluate rate data using the differential method, the method of initial rates, integral methods, and by the method of half-lives. The differential and integral methods only require one reactor run to determine the rate constants, whereas the methods of initial rates and of half-lives require multiple runs to determine the rate constants. In each of these methods, data from batch reactors are analysed. As mentioned earlier, batch reactors usually occur as constant volume processes in which case the design equation reduces to the form

$$r_A = \frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} \tag{5.1.1}$$

so that the constants in the rate law can be evaluated from experimental data of how concentration or reactants (or products) varies with time in batch reactors.

5.2 Experimental Determination of Rates

In some of the methods described below, we will need to obtain experimental measurements of the derivative $-\mathrm{d}\,C_A/\mathrm{d}\,t$. There are several ways to do this. In either approach, first concentration data for A must be measured as a function of time in the batch reactor. Once this function is known, the following approaches can be used

- Graphical of direct methods $-\Delta\,C_A/\Delta\,t$

  From a plot of concentration against time, the gradient at any time can be determined as shown in Figure 5.1 below. At set intervals along the plot, the tangent to the plot needs to be determined graphically. The tangent line provides the estimate for the value of $\mathrm{d}\,C_A/\mathrm{d}\,t$.

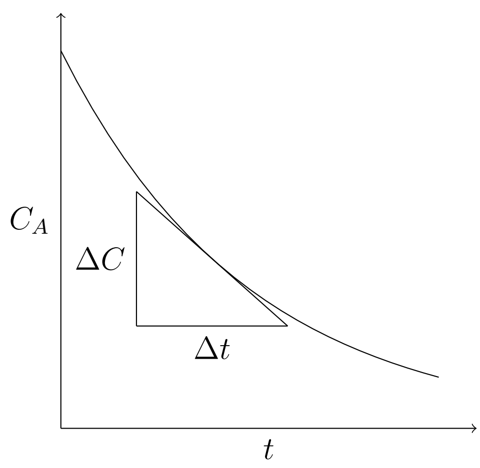


Figure 5.1: Concentration vs time curve.

- Fit a polynomial to the curve of C against t

  In the second approach, a polynomial can be fit to the experimental curve of C_A versus t. This can be done using for instance Excel to obtain:

$$C_A = a_0 + a_1 t + a_2 t^2 + \cdots$$

Once the equation is known, it can be differentiated.

5.3 Determination of Reaction Orders by Inspection

In some cases the reaction order can be determined by inspection, for instance consider the experimental data given in Table 5.1 below. In this case the rate doubles when concentration doubles. This means that the rate is proportional to concentration thus the rate equals $k\,[C_A]^1$. k can be determined from any one of the data points once the reaction order is known. In Table 5.2, experimental data is given for the case when concentration doubles, the rate increases by a factor of 4. In this case, the rate is given by a second order law equal to $k\,[C_A]^2$. In Table 5.3 below, when the concentration changes, the rate stays the same. This corresponds to a zeroth order reaction in A, where rate is equal to $k\,[C_A]^0$.

Table 5.1: First order reaction.

$[C_A]$	1.0	2.0	4.0	12.0
rate	0.05	0.10	0.20	0.60

Table 5.2: Second order reaction.

$[C_A]$	4.0	8.0	16.0	32.0
rate	3.0	12.0	48.0	192.0

Table 5.3: Zero order reaction.

$[C_A]$	6.0	12.0	24.0	48.0
rate	5.0	4.9	5.1	5.0

5.4 Differential Methods of Analysis

5.4.1 For Rates Dependent on the Concentration of Only One Species

The differential method starts with the design equation for a batch reactor at constant volume (Equation 2.2.5) combined with the rate equation for an arbitrary order, α. (Remember that α does not have to be an integer):

$$-r_A = -\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = k_A C_A^{\alpha} \tag{5.4.1}$$

Take the natural log of both sides:

$$\ln\left(-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t}\right) = \ln k_A + \alpha \ln C_A \tag{5.4.2}$$

Plotting the left hand side against $\ln C_A$ should enable the reaction order to be determined from the gradient.

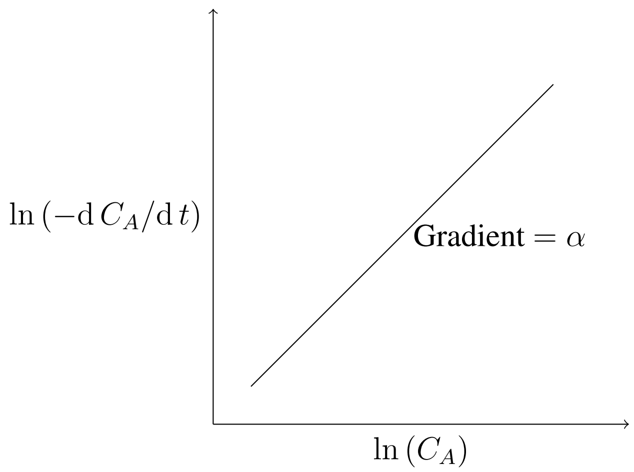


Figure 5.2: Log-Log plot of the differential rate for a constant volume batch reactor.

5.4.2 For More Complex Reactions (Dependence on C_A and C_B)

In these cases it may be necessary to simplify the system in order to determine the reaction orders. We can use the approach of pseudo-order reactions or method of excess. If we take the general rate equation for two species, A and B reacting with orders α and β respectively:

$$-r_A = kC_A^{\alpha}C_B^{\beta} \tag{5.4.3}$$

Using the differential method from above, we have:

$$\ln(-r_A) = \ln k + \alpha \ln C_A + \beta \ln C_B \tag{5.4.4}$$

Now there are too many unknowns and so a simple log-log plot is not possible. One approach to overcoming this difficulty is to keep one of the reactants in large excess so then its concentration is effectively constant. In this example if B is in large excess then:

$$C_B^{\beta} = \text{constant}$$

The rate equation then becomes:

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = -r_A = k'C_A^{\alpha} \tag{5.4.5}$$

where $k' = kC_B^{\beta}$This now looks like a simple first-order reaction rate equation and can be solved in the same way as above to determine k' and α. In this example it is called a pseudo- 1st order reaction and k' is the pseudo 1st-order rate constant. The value of β can then be found by repeating with different values of C_B, where

$$\ln k' = \ln k + \beta \ln C_B \tag{5.4.6}$$

Thus a plot of $\ln k'$ versus $\ln C_B$ will yield values for k and β. Alternatively, the same procedure can be done when using an excess of A, in which case C_A^α is a constant. In this case

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = -r_A = k''C_B^\beta \tag{5.4.7}$$

where $k'' = kC_A^\alpha$.

5.4.3 Method of Initial Rates

For more complex reactions e.g. reversible reactions, the above methods may not work because reverse reactions can be significant. An alternative approach is then to use the method of initial rates. A series of experiments is carried out at different *initial* concentrations C_{A0} and the initial rate, $-r_{A0}$ can be determined for each for each of the initial concentrations. The initial concentration of A is known; therefore, if the initial reaction rate is measured, the only unknown in the rate law are the rate constant, k, and the reaction order, α.

If the rate law is, $-r_A = kC_A^\alpha$ then a plot of $\ln(-r_{A0})$ against $\ln C_{A0}$ enables the determination of α and k, Figure 5.3.

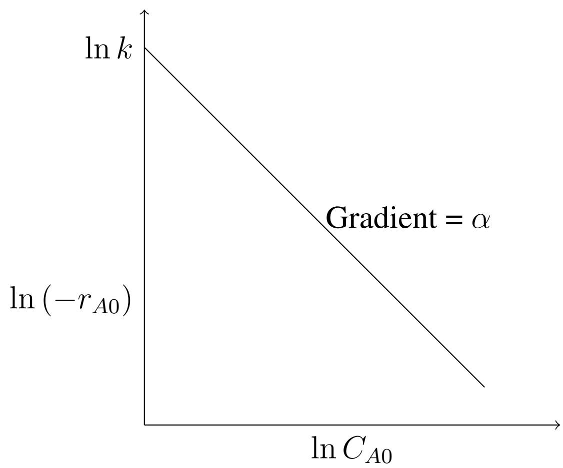


Figure 5.3: Initial concentration vs rate curve.

5.5 Integral Methods

Determining rates from C vs t data can be inaccurate and tedious so once the order is known, or can be speculated then we can use the integrated rate equations. This method is used for accurate k determination e.g. when k is required at different temperatures. The aim is to generate *linear* plots for C_A versus t. The method for linearizing the plot depends on the order of the reaction. Below we describe the approach for a zeroth, first and second order reactions.

5.5.1 Zeroth Order Reaction by Integral Method

For a zeroth order constant volume batch reactor, the design equation is given by

$$\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = -k \tag{5.5.1}$$

Integrating with $C_A = C_{A0}$ at $t = 0$, we obtain:

$$C_{A0} - C_A = C_{A0}X = kt \tag{5.5.2}$$

Thus a plot of concentration of A versus time will be linear with a slope of $-k$ as shown in Figure 5.4 below. Reactions are only zero order in certain concentration ranges — usually higher concentrations and often determined by some other factor e.g. intensity of radiation for photochemical reactions or catalyst surface area.

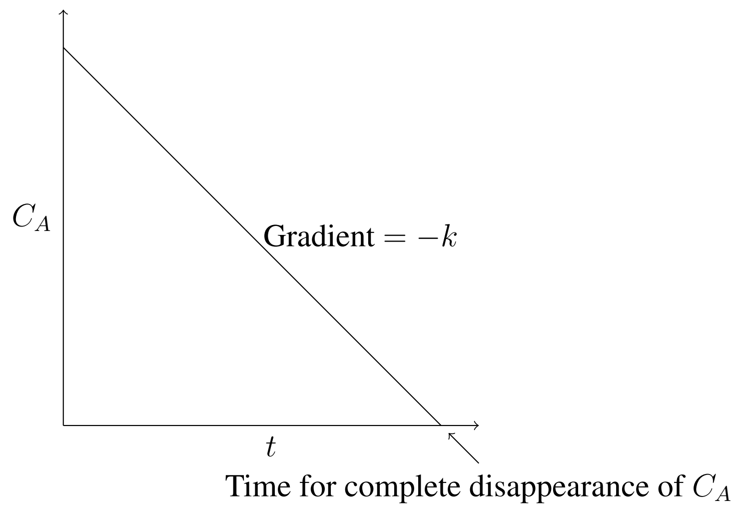


Figure 5.4: Plot of C_A vs time for a zeroth order irreversible reaction in a constant volume batch reactor.

5.5.2 First Order Irreversible Reaction by Integral Method

For a first order irreversible reaction the rate is given by $-r_A = kC_A$ so that the design equation for a constant volume batch reactor is (see Equation 2.2.5)

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = kC_A \tag{5.5.3}$$

We seek a relationship for the concentration of A in terms of time. This can be achieved by integrating Equation 5.5.3

$$\int_{C_{A0}}^{C_A} \frac{\mathrm{d}\,C_A}{C_A} = -k\int_0^t \mathrm{d}\,t \tag{5.5.4}$$

to give

$$-\ln\frac{C_A}{C_{A0}} = kt \tag{5.5.5}$$

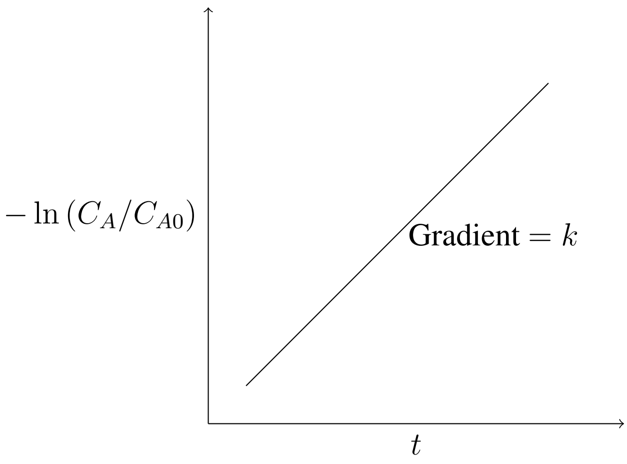


Figure 5.5: Plot of $-\ln(C_A/C_{A0})$ vs time for a first order reaction in a constant volume batch reactor.

Thus a plot of the left side of Equation 5.5.5 versus t will yield a linear plot where the slope of the line gives the rate constant k as shown in Figure 5.5 below.

The above approach only works for a constant volume reactor. A more general approach is achievable if we derive an equation in terms of conversion instead of concentration. This was done in Chapter 2 and the result is given by Equation **??**,

$$t = -\frac{1}{k}\ln(1-X) \tag{5.5.6}$$

Thus a plot of $-\ln(1-X)$ versus time is linear where the line has a slope equal to k as shown in Figure 5.6 below.

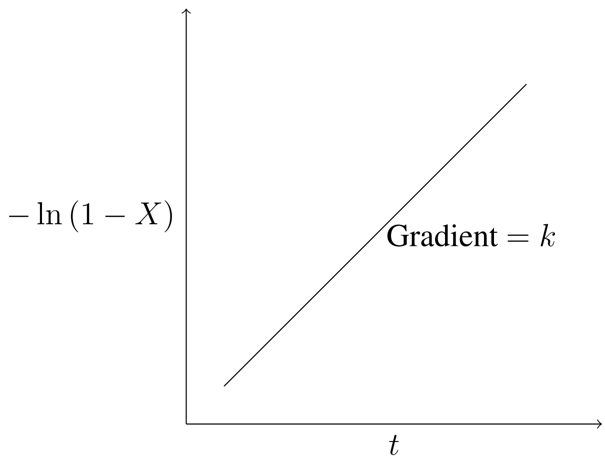


Figure 5.6: Plot of $-\ln(1-X)$ vs time for a first order reaction in a constant volume batch reactor.

5.5.3 Second Order Reaction by Integral Method

Second order with A

For the following second order reaction:

$$A + A \longrightarrow \text{products}$$

The design equation for constant volume batch reactor is

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = kC_A^2 \tag{5.5.7}$$

which can be rearranged and integrated to give

$$\int_{C_{A0}}^{C_A} \frac{\mathrm{d}\,C_A}{C_A^2} = -k\int_0^t \mathrm{d}\,t$$
$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \tag{5.5.8}$$

Thus a plot of the inverse of concentration of A versus time gives a line with slope equal to k and y-intercept equal to the inverse of initial concentration of A, Figure 5.7.

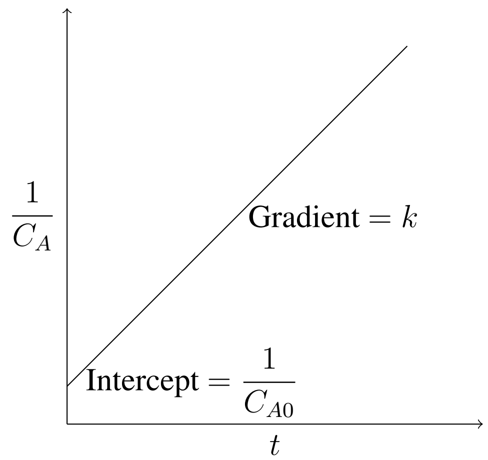


Figure 5.7: Plot of $1/C_A$ versus time for a second order reaction in a constant volume batch reactor.

Equation 5.5.8 can be written in terms of conversion using the substitution that $C_A = C_{A0}(1 - X)$ to give

$$C_{A0}kt = \frac{X}{1 - X} \tag{5.5.9}$$

Second order reaction of A + B $\longrightarrow$ products

Next we consider the second order reaction of

$$A + B \longrightarrow \text{products}$$

Here, two different cases occur with different solutions. Because the stoichiometric coefficients of A and B are equal, the change in moles of A equals the change in moles of B. Thus, when the initial number of moles of A and B are equal, i.e. $C_{A0} = C_{B0}$, then $C_A = C_B$ for the entire reaction. In this case, Equations 5.5.8 and 5.5.9 apply.

For a second order reaction with $C_{A0} \neq C_{B0}$ we need to resolve the design equation for the constant volume batch reactor given by

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = kC_AC_B \tag{5.5.10}$$

According to the stoichiometric table, we have $C_A = C_{A0}(1-X)$ and $C_B = C_{B0} - C_{A0}X$ and $\mathrm{d}C_A = -C_{A0}\mathrm{d}X$. Substituting these relations into the design equation we have

$$C_{A0}\frac{\mathrm{d}X}{\mathrm{d}t} = k(C_{A0} - C_{A0}X)(C_{B0} - C_{A0}X) \tag{5.5.11}$$

In order to simplify the equation we make the substitution $M = C_{B0}/C_{A0}$, then

$$\frac{\mathrm{d}X}{\mathrm{d}t} = kC_{A0}(1-X)(M-X) \tag{5.5.12}$$

which gives upon rearrangement

$$\int_0^{X_A} \frac{\mathrm{d}X}{(1-X)(M-X)} = kC_{A0}\int_0^t \mathrm{d}t \tag{5.5.13}$$

Below we provide the solution to the integration given by Equation 5.5.13 using the method of partial fractions. The integrand in Equation 5.5.13 needs to be expanded as the sum of two separate fractions[1]. Thus, we postulate that we can solve the integrand as

$$\begin{aligned}
kC_{A0}\int_0^t \mathrm{d}t &= \int_0^{X_A} \frac{\mathrm{d}X}{(1-X)(M-X)} \\
&= \int_0^{X_A} \left[\left(\frac{1}{M-1}\right)\left(\frac{1}{1-X}\right) - \left(\frac{1}{M-1}\right)\left(\frac{1}{M-X}\right)\right]\mathrm{d}X \\
&= \frac{1}{M-1}\int_0^{X_A}\left[\frac{1}{1-X} - \frac{1}{M-X}\right]\mathrm{d}X \\
&= \frac{1}{M-1}\left[-\ln(1-X) + \ln(M-X)\right]_0^{X_A} \\
&= \frac{1}{M-1}\left[\ln\left(\frac{M-X_A}{1-X_A}\right) - \ln M\right] \\
kC_{A0}t &= \frac{1}{M-1}\ln\left(\frac{M-X_A}{M(1-X_A)}\right)
\end{aligned} \tag{5.5.14}$$

Note that Equation 5.5.14 diverges when $M = 1$, which corresponds to the case when $C_{A0} = C_{B0}$, which we considered earlier.

Thus, in order to determine k by the integral method we would need to measure the conversion X as a function of time for given values of C_{A0} and C_{B0}. We could then

[1] Solving partial fractions,

$$\frac{1}{(1-X)(M-X)} = \frac{P}{1-X} + \frac{Q}{M-X} = \frac{P(M-X) + Q(1-X)}{(1-X)(M-X)}$$

Therefore,

$$1 = P(M-X) + Q(1-X)$$

Thus,

$$\begin{aligned}
X^0 &: 1 = PM + Q \\
X^1 &: 0 = -P - Q
\end{aligned}$$

Simultaneously solving for P and Q gives $P = 1/(M-1)$ and $Q = -1/(M-1)$.

plot the left hand side of Equation 5.5.14 versus time. The slope of the line equal to kC_{A0} can be used to determine k. Alternatively, we could construct the plot in terms of concentrations of A and B. In this case, we first back substitute $M = C_{B0}/C_{A0}$ into Equation 5.5.14, and then you should show that:

$$\ln \frac{C_B C_{A0}}{C_{B0} C_A} = \left(C_{B0} - C_{A0}\right) kt \tag{5.5.15}$$

In this case, in order to determine k, one would measure C_A and C_B as a function of time and then plot the left hand side of Equation 5.5.15 versus t.

A key point is that the method to use depends on what is easiest to measure. If concentrations of A and B are experimentally accessible, Equation 5.5.15 would be used for regressing the rate parameters. Alternatively, if only the conversion could be determined in terms of the concentration of A, Equation 5.5.14 would be used. For gas phase reactions in batch reactors, the pressure in the batch reactor is the experimentally accessible variable. In this case, the design equation would need to be rewritten in terms of pressure instead of conversion and then any of the methods illustrated above could be used for determining the rate parameters. This is left as an important exercise for you to do. For further details see Fogler, Chapter 5.

5.6 Method of Half-Lives

In some cases, an experimentally measured property is the half-life, $t_{1/2}$, which is defined as the time for the concentration of the reactant to fall to half its initial value. Knowledge of the half life can also be used for calculating the rate parameters. Consider the design equation for the constant volume batch reactor:

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = -r_A = kC_A^{\alpha} \tag{5.6.1}$$

(Note for 2 or more reactants, the method of pseudo-order reactions can be used using the same approach as outlined below). Integrating the design equation with $C_A = C_{A0}$ when $t = 0$ yields:

$$t = \frac{1}{k\left(\alpha - 1\right)} \left(\frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}}\right) \tag{5.6.2}$$

and factoring out a factor of C_{A0}

$$t = \frac{1}{kC_{A0}^{\alpha-1}\left(\alpha - 1\right)} \left[\left(\frac{C_{A0}}{C_A}\right)^{\alpha-1} - 1\right] \tag{5.6.3}$$

We then use the definition of half-life, $t = t_{1/2}$ when $C_A = 1/2C_{A0}$. Substitution of this condition into Equation 5.6.3 gives

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k\left(\alpha - 1\right)} \frac{1}{C_{A0}^{\alpha-1}} \tag{5.6.4}$$

Taking the natural log of both sides gives

$$\ln t_{1/2} = \ln \frac{2^{\alpha-1} - 1}{k\,(\alpha - 1)} + (1 - \alpha) \ln C_{A0} \tag{5.6.5}$$

As illustrated in Plotting $\ln t_{1/2}$ against $\ln C_{A0}$ gives a line with a slope equal to $(1 - \alpha)$ where α is the reaction order.

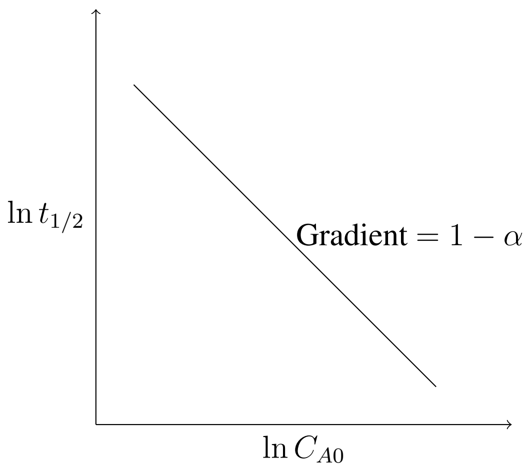


Figure 5.8: Plot of $\ln t_{1/2}$ vs $\ln C_{A0}$ for data taken from a constant volume batch reactor.

Note, for 1st-order reactions the half-life is independent of C_{A0}.

[**?**]

5.7 References

5.8 Problems

1. The half-life for the (first-order) radioactive decay of ^{14}C is 5730 years. An archaeological sample contained wood that had only 72% of the ^{14}C found in the living trees. What is its age?

   [2720 years]

2. The following reaction is irreversible and first-order and can be described by the relation:

$$A \longrightarrow \text{products}$$

   From the following concentration/time data, determine the rate constant. What is the half-life of the reaction?

t/s	0	100	500	1000	2000
C_A/mol dm^{-3}	0.100	0.0951	0.0779	0.0607	0.0368

   [$5 \times 10^{-4}\,\mathrm{s}^{-1}$; 1386 s]

3. The reaction of triphenyl methyl chloride (trityl) (A) and methanol (B)

$$(C_6H_5)_3CCl + CH_3OH \longrightarrow (C_6H_5)_3COCH_3 + HCl \quad A + B \longrightarrow C + D$$

   was carried out in a solution of benzene and pyridine at 25 °C. Pyridine reacts with HCl that then precipitates as pyridine hydrochloride thereby making the reaction irreversible. The concentration – time data was obtained in a batch reactor:

Time (mins)	0	50	100	150	200	250	300
Conc of A (mol dm$^3 \times 10^3$)	50	38	30.6	25.6	22.2	19.5	17.4

   The initial concentration of methanol was 0.5 mol dm^3.

   (a) Determine the reaction order with respect to triphenyl methyl chloride.

   (b) In a separate set of experiments, the reaction order with respect to methanol was found to be first order. Determine the specific reaction rate constant.

   (c) Use the integral method to confirm the order of reaction

   Hint:

   The initial concentration of B is 10 times that of A so apply pseudo-order kinetics i.e. the concentration of B is constant. $C_B = C_{B0}$ *and rate* $= -k'C_A^{\alpha}$ *with* $k' = kC_{B0}^{\beta}$. *Determine* $\Delta C_A/\Delta t$ *direct from the data.*

   [2nd order, $k = 0.244(\mathrm{dm^3\,mol^{-1}})^2\,\mathrm{min}^{-1})$]

4. The following gas phase reaction takes place at constant pressure and temperature:

$$A \longrightarrow R + S$$

   From the volumetric data given below, determine the reaction order.

t/s	0	30	90	120	180	240	360
V/dm^3	47	61	68	72	75	78.5	84

   This problem can be most conveniently solved on a spreadsheet.

Chapter 6

Temperature and Pressure Dependance of Reactions

Contents

6.1 Introduction

So far we have examined some methods to determine the rate constant of the reaction equation at constant temperature and pressue. We call k a rate *constant* because it does not depend on the concentrations of any species. However, this does not mean k is a constant; k depends on whether or not a catalyst is present, is highly dependant temperature, and may also be a function of the total pressure of the reaction system. In this section, we discuss the temperature dependence of the rate constant, which is given by the Arrhenius equation. We show how to determine the Arrhenius parameters (activation energy and pre-exponential factor) from experimental data. Once these parameters are known, the rate constant can be determined at any temperature.

We will also examine the effect of pressure and volumetric flow rate changes on reactions due to changes in the number of moles by non-equimolar reactions. These affects are especially important when designing non-ideal reactors. For instance, in a PFR, the temperature may vary continuously along the length of the reactor, the volumetic flow rate can change due to the reaction, and there can be a pressure drop due to the flow. As a consequence, designing a PFR requires knowledge of the rate constant as a function of temperature for the entire range of temperatures that occur within the reactor, and understanding a stoichiometric balance for the reaction.

6.2 Arrhenius Equation

The dependence of the rate constant on temperature is described to a good approximation by the Arrhenius equation given by

Arrhenius Equation

$$k = A \exp\left(-\frac{E_{\text{act}}}{RT}\right) \tag{6.2.1}$$

where A is a pre-exponential factor or frequency factor (same units as k), E_{act} is an activation energy (units of energy) for the reaction, R is the gas constant (i.e. equal to $8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$), and T is temperature. A and E_{act} are termed the Arrhenius parameters. The experimental dependence of k on temperature is illustrated in Figure 6.1 below. The advantage of using Equation 6.2.1 is that once the Arrhenius parameters are known, then the rate constant can be determined at any temperature because the Arrhenius parameters do not depend on temperature.

Most reactions obey relation Equation 6.2.1 but very accurate measurements sometimes show some curvature indicating a slight temperature dependence of A and E_{act}.

Here we just briefly describe the meaning of the parameter E_{act}, which corresponds to an activation energy or an energetic barrier as illustrated in Figure 6.2. E_{act} can be thought of as an energy barrier that the reactants need to overcome in order for the reaction to take place. This energy barrier occurs because the reactants must rearrange themselves into a high-energy configuration before the products can be formed. Thus in order for the reaction to proceed, when the reactants collide with each other, the kinetic energy from the collision must be of a similar magnitude to the energy barrier. The term $\exp\left(-E_{\text{act}}/RT\right)$

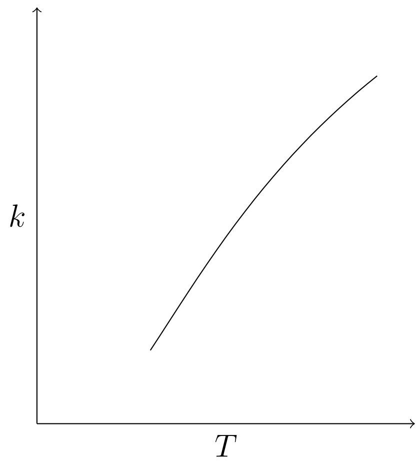


Figure 6.1: Temperature dependence of the rate constant k.

corresponds to the fraction of collisions that have a kinetic energy greater than the activation barrier. As temperature increases, the molecules have a greater amount of kinetic energy, so that the fraction of collisions with energy greater than the activation barrier increases.

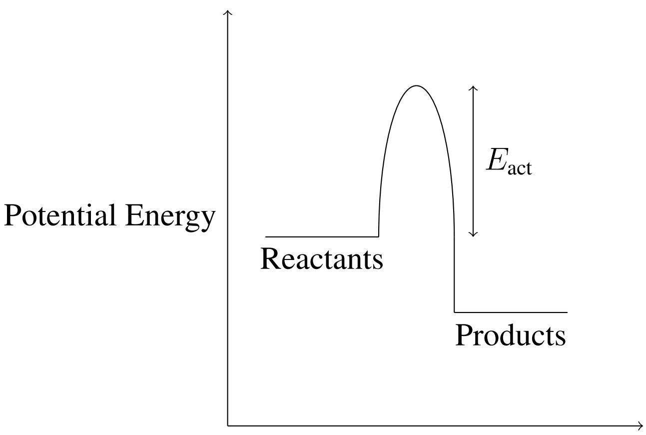


Figure 6.2: Symbolic reaction showing the activation energy barrier.

6.2.1 Example Calculation of the Arrhenius Parameters

Thus, in designing non-isothermal reactors, the Arrhenius parameters need to be determined from experimental rate data as a function of temperature. An example of experimental data is given in Table 6.1. In order to determine the parameters, we take the natural log of both sides of Equation 6.2.1 to give

$$\ln k = \ln A - \frac{E_{\text{act}}}{RT} \tag{6.2.2}$$

Table 6.1: Some real data of how k depends on temperature

k (s^{-1}) $\times 10^{-8}$	4.53	59.3	197	613
T (°C)	90	110	120	130

Thus the rate parameters can be determined from a plot of $\ln k$ against $1/T$ (data shown in Table 6.2 below). From Figure 6.3, the slope is calculated to be -17.86×10^3 K which is $-E_{\text{act}}/R$, then $E_{\text{act}} = 8.314 \times 17.85 \times 10^3\,\text{J mol}^{-1}$ = 148 kJ mol^{-1}. The value of A must be found by calculation not by extrapolation. For instance, we have $k = 4.53 \times 10^{-8}\,\text{s}^{-1}$ at $T = 363\,\text{K}$. Then A can be found from the Arrhenius Equation by substitution:

$$4.53^{-8}(\text{s}^{-1}) = A\exp(-148 \times 10^3(\text{J mol}^{-1})/8.314 \times 363(\text{K}))$$

which gives $A = 8.8 \times 10^{13}\,\text{s}^{-1}$.

Table 6.2: Data calculated from that in Table 6.1

k (s^{-1}) $\times 10^{-8}$	4.53	59.3	197	613
T (°C)	90	110	120	130
$\ln k$	-16.910	-14.338	-13.137	-12.002
T (K)	363	383	393	403
$1/T \times 10^{-3}$	2.754	2.610	2.544	2.480

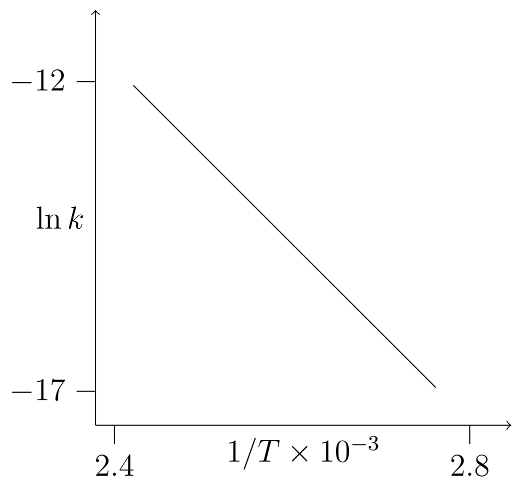


Figure 6.3: Plot of $\ln k$ vs $1/T$.

Note that we do not necessarily have to determine A if we know the rate constant at one temperature (T_1) and we know the activation energy. In this case, we could calculate the rate constant at a second temperature (T_2) by subtracting the Arrhenius equation evaluated at T_2 minus that evaluated at T_1

$$\ln\frac{k_2}{k_1} = -\frac{E_{\text{act}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{6.2.3}$$

6.3 Reactors with a Change in Pressure at Constant Volume

For a gas phase reaction in a batch reactor, we can use a gas law to relate the pressure to the volume of the reaction at any given instant. Remember that a vapour will take up the entire volume of the reactor so that the reaction volume equals the reactor volume, which is usually fixed. Under most conditions of gas phase reactions (i.e. high temperature), the ideal gas law provides a good approximation to the thermodynamic behaviour of the gas. The ideal gas law is

$$PV = N_T RT \tag{6.3.1}$$

where R is the ideal gas constant. We can write a similar equation, which applies at the start of the reaction

$$P_0 V = N_{T,0} RT_0 \tag{6.3.2}$$

where we note that the volume of the reactor is not changing so that no subscript on V is used. The ratio of Equation 6.3.1 to 6.3.2 gives

$$P = P_0 \frac{N_T}{N_{T,0}} \frac{T}{T_0} \tag{6.3.3}$$

Assuming a reaction of,

$$(-\nu_A)\mathrm{A} + (-\nu_B)\mathrm{B} \longrightarrow \nu_C\mathrm{C} + \nu_D\mathrm{D}$$

then using equation 1.6.3 for the change in the total molar flowrate in terms of X gives,

$$P = P_0 (1 + \epsilon X) \frac{T}{T_0} \tag{6.3.4}$$

which provides the desired relationship between pressure in the reactor and the conversion. Equation 6.3.4 could also be used for calculating how changes in temperature will alter the pressure in the reactor. For instance an energy balance would be used to derive a relationship between T and X in a similar manner that we used the stoichiometric table to arrive at a relationship between N_T and X.

6.4 Reactors with a Change in Volumetric Flowrate

For a flowing vapour in a PFR or a CSTR, we can use the ideal gas law to relate the volumetric flowrate, v, to the total molar flowrate, n_T (assuming we can make the assumption the system is approximately ideal). In this case, we take the time derivative of the ideal gas law to give the relationship between the volumetric and total molar flowrates at a given distance along the PFR in terms of the pressure and temperature at the same location,

$$Pv = n_T RT \tag{6.4.1}$$

Similarly at the inlet to the PFR we have,

$$P_0 v = n_{T,0} RT_0 \tag{6.4.2}$$

Taking the ratio of Equation 6.4.1 to 6.4.2 gives

$$v = v_0 \frac{n_T}{n_{T,0}} \frac{P_0}{P} \frac{T}{T_0} \tag{6.4.3}$$

Assuming a reaction of,

$$(-\nu_A)\mathrm{A} + (-\nu_B)\mathrm{B} \longrightarrow \nu_C\mathrm{C} + \nu_D\mathrm{D}$$

then using equation 1.6.3 for the change in the total molar flowrate in terms of X gives,

$$v = v_0 (1 + \epsilon X) \frac{P_0}{P} \frac{T}{T_0} \tag{6.4.4}$$

As above, Equation 6.4.4 could be used for calculating the volumetric flowrate in terms of temperature and pressure. In a PFR, the change in pressure would need to be calculated from a momentum balance and the temperature could be calculated in terms of conversion using an energy balance. Equation 6.4.4 is especially significant because the concentrations of the components depend on the volumetric flowrate according to,

$$C_A = \frac{n_A}{v} \tag{6.4.5}$$

Thus, if we plug in equation 1.4.3 as $n_A = n_{A,0} (1 - X)$, we find that,

$$C_A = C_{A0} \frac{1 - X}{1 + \varepsilon X} \frac{P_0}{P} \frac{T}{T_0} \tag{6.4.6}$$

Thus, the change in concentration of A with increasing conversion is not only due to losing moles to the reaction, but also occurs due to changes in volumetric flowrate, which, in turn, are due to changes in the total molar flowrate.

For the balance shown in Section 1.6.2, then we can consider the concentration of an inert as a function of conversion, which is given by,

$$C_I = C_{I0} \frac{1}{1 + \varepsilon X} = C_{A0} \frac{\theta_I}{1 + \varepsilon X} \tag{6.4.7}$$

Thus the concentration of an inert will be reduced with increasing conversion if the reaction generates moles, and the concentration of the inert will increase if the reaction consumes moles. Similarly, for a reactant B,

$$C_B = C_{A0} \frac{\theta_B - \frac{\nu_B}{\nu_A} X}{1 + \varepsilon X} \tag{6.4.8}$$

or for a product D,

$$C_D = C_{A0} \frac{\theta_D + \frac{\nu_D}{-\nu_A} X}{1 + \varepsilon X} \tag{6.4.9}$$

If a gas phase reaction is occurring, Equations 6.4.6 to 6.4.9 should to be used when solving the design equation for either a CSTR or a PFR.

[?]

6.5 References

6.6 Problems

1. The rate constant for a particular reaction is 2.80×10^{-3} mol^{-1} dm^3 s^{-1} at 30 °C and 1.38^{-2} mol^{-1} dm^3 s^{-1} at 50 °C. Evaluate the Arrhenius parameters for this reaction. What is the order of reaction? $R = 8.314$ J K^{-1} mol^{-1}.

2. Milk is pasteurised if it is heated to 63 °C for 30 minutes, but if it is heated to 74 °C it only needs 15 seconds for the same result. Find the activation energy of this sterilisation process. $R = 8.314$ J K^{-1} mol^{-1}.

3. A 'rule of thumb' in chemical kinetics is that the rate of reaction doubles if the temperature increases by 10 K. At around 300 K, what value for the activation energy does this imply?

   [53.6 kJ mol^{-1}]

4. The rate of the second-order decomposition of ethanal (CH_3CHO) was measured over the temperature range 700 to 1000 K and the rate constants are reported below:

T/K	700	730	760	790	810	840	910	1000
k/mol^{-1} dm^3 s^{-1}	0.011	0.035	0.105	0.343	0.789	2.17	20.0	145

   Find the activation energy and the pre-exponential factor.

   [184 kJ mol^{-1}; 5.7×10^{11} mol^{-1} dm^3 s^{-1}]

Chapter 7

Multiple Reactions

Contents

7.1 Introduction

In chemical reactors, it is mostly inevitable that multiple reactions will occur, some desired and some not. One of the key tasks of chemical engineers is to design and operate the reactor such that the unwanted side reactions are minimised in order to achieve a maximum economic success. The discussion in this chapter is concerned with optimizing *reversible* reactions such as

$$\mathrm{A} \rightleftharpoons \mathrm{R}$$

reactions that occur in *series*, such as

$$\mathrm{A} \longrightarrow \mathrm{R} \longrightarrow \mathrm{S}$$

and reactions that occur in *parallel*, such as

$$\mathrm{A} \longrightarrow \mathrm{R}$$
$$\mathrm{A} \longrightarrow \mathrm{S}$$

For each of these reaction sequences, we first show how to calculate the conversion as a function of time in a constant volume batch reactor from the design equation. After this, we show how to optimize the reactions for the production of a specific product in flowing reactors by introducing the concepts of yield and selectivity.

7.2 Yield and Selectivity

Yield and selectivity are parameters used to characterize the extent of a desired reaction over any unwanted side reactions. The selectivity is defined as the ratio of the rate of formation of the desired product R over the rate of formation of the undesired product S:

Selectivity

$$S_{RS} = \frac{r_R}{r_S} \tag{7.2.1}$$

Note that in the literature, another definition of selectivity can be found in terms of mole numbers or molar flowrates. For a batch reactor, the selectivity is sometimes defined as the ratio of moles of desired product to moles of undesired product remaining at the end of the reaction. For a flowing system, the selectivity is defined as the ratio of molar flowrates of desired to undesired product exiting the reactor. In both cases, the definition of selectivity reduces to

$$\bar{S}_{RS} = \frac{C_R}{C_S} \tag{7.2.2}$$

Here we use the overline to designate that the selectivity is taken with respect to mole numbers. No matter what definition is used, the selectivity should be maximized. The *yield* of a product R also has two definitions. The first definition is the rate of formation of a product R divided by the rate of consumption of the key reactant A

Yield

$$Y_R = \frac{r_R}{-r_A} \tag{7.2.3}$$

Alternatively, the yield can be defined in terms of mole numbers. For a batch reactor, the yield is the number of moles of product formed per mole of key reactant consumed:

$$\bar{Y}_R = \frac{N_R}{N_{A0} - N_A} \tag{7.2.4}$$

or for a flowing system, the yield is defined in terms of molar flowrates

$$\bar{Y}_R = \frac{n_R}{n_{A0} - n_A} \tag{7.2.5}$$

7.3 Reversible Reactions

As an example of a reversible reaction consider the combination of two benzene molecules to form one molecule of hydrogen and one of diphenyl:

$$2\,C_6H_6 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_{12}H_{10} + H_2$$

In reversible reactions, complete conversion cannot be achieved. All rate laws for reversible reactions must reduce to the thermodynamic relationship relating the reacting species concentrations at equilibrium. At equilibrium the reaction rate is zero for all species. Consider the simple reversible reaction of

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$$

The rate equation (assuming an elementary reaction) can be written as:

$$-r_A = k_1 C_A - k_2 C_R \tag{7.3.1}$$

At equilibrium, the net rate of the reaction is equal to zero, which means the forward rate is equal to the reverse rate

$$0 = k_1 C_{A,e} - k_2 C_{R,e} \tag{7.3.2}$$

where we use the subscript e to denote that the concentration is at equilibrium. Equation 7.3.2 can be rearranged to give

$$\frac{C_{R,e}}{C_{A,e}} = \frac{k_1}{k_2} = K \tag{7.3.3}$$

where K is the equilibrium constant.

Equilibrium Constant

The equilibrium constant K is related to the Gibbs free energy change for the reaction and is dependant on the temperature.

We can set up the stoichiometric table for this reaction for a constant volume batch reactor:

	at $t = 1$	concentration at t
A	$C_A = C_{A0}$	$C_A = C_{A0} - C_{A0}X$
R	$C_R = C_{R0}$	$C_R = C_{R0} + C_{A0}X$

where X is conversion with respect to A. These concentrations can be substituted into the design equation for the batch reactor rate

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = -r_A = C_{A0}\frac{\mathrm{d}\,X}{\mathrm{d}\,t} = k_1\left(C_{A0} - C_{A0}X\right) - k_2\left(C_{R0} + C_{A0}X\right) \tag{7.3.4}$$

To simpify the equation, we make the substitution $M = C_{R0}/C_{A0}$ and divide Equation 7.3.4 by C_{A0} to give

$$\frac{\mathrm{d}\,X}{\mathrm{d}\,t} = k_1\left(1 - X\right) - k_2\left(M + X\right) \tag{7.3.5}$$

At equilibrium we have a steady-state, so that we have the following conditions

$$\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = 0 \text{ and } \frac{\mathrm{d}\,X}{\mathrm{d}\,t} = 0$$

Applying the equilibrium conditions to Equation 7.3.5 gives

$$\frac{k_1}{k_2} = \frac{M + X_e}{1 - X_e} \tag{7.3.6}$$

where X_e is the conversion at equilibrium. Equation 7.3.6 can be rearranged to give

$$X_e = \frac{K - M}{K + 1} \tag{7.3.7}$$

Equation 7.3.7 allows us to calculate the maximum conversion achievable in the reversible reaction, this is the conversion that occurs at equilibrium. Next we rewrite the design equation in terms of the equilibrium conversion by substituting $k_2 = k_1(1-X_e)/(M+X_e)$ (from Equation 7.3.6) into Equation 7.3.5 and rearrange to give

$$\frac{\mathrm{d}\,X}{\mathrm{d}\,t} = k_1\left(1 - X\right) - k_1\frac{1 - X_e}{M + X_e}\left(M + X\right) \tag{7.3.8}$$

In order to integrate Equation 7.3.8, we can simplify the above equation to give,

$$\begin{aligned}
\frac{\mathrm{d}\,X}{\mathrm{d}\,t} &= \frac{k_1}{M + X_e}\left[\left(1 - X\right)\left(M + X_e\right) - \left(1 - X_e\right)\left(M + X\right)\right] \\
&= \frac{k_1}{M + X_e}\left[X_e - MX - X + X_eM\right] \\
&= k_1\frac{M + 1}{M + X_e}\left(X_e - X\right) \qquad (7.3.9)
\end{aligned}$$

Integrating Equation 7.3.9 gives

$$\begin{aligned}
\int_0^X \frac{\mathrm{d}\,X}{X_e - X} &= \int_0^t k_1\frac{M + 1}{M + X_e}\mathrm{d}\,t \\
-\ln\left(1 - \frac{X}{X_e}\right) &= k_1\frac{M + 1}{M + X_e}t \qquad (7.3.10)
\end{aligned}$$

Figure 7.2 below shows a plot of the left hand side of Equation 7.3.10 versus time which can be used for determining the rate constants according to the integral method. The expression can also be considered in terms of concentration (for a constant volume reactor) as:

$$\frac{X_e - X}{X_e} = \frac{(C_{A0} - C_{A,e}) - (C_{A0} + C_A)}{(C_{A0} - C_{A,e})} = \frac{C_A - C_{A,e}}{C_{A0} - C_{A,e}} \tag{7.3.11}$$

Thus Equation 7.3.10 can be changed to:

$$-\ln\left(\frac{C_A - C_{A,e}}{C_{A0} - C_{A,e}}\right) = k_1 \frac{M+1}{M+X_e} t \tag{7.3.12}$$

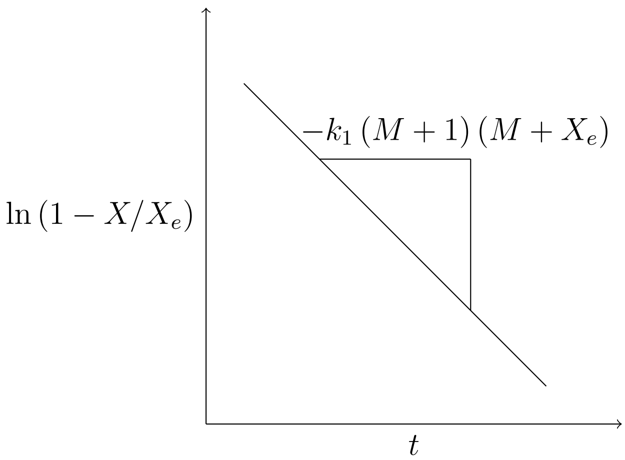


Figure 7.1: Plot of $\ln(1 - X/X_e)$ vs t to determine $-k_1 (M+1) / (M+X_e)$.

Note, an irreversible reaction is simply a special case of a reversible reaction with $C_{A,e} = 0$ or $X_e = 1$ or $K = \infty$, i.e.

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = -\ln(1 - X) = k_1 t$$

Therefore, in summary, from an experiment we would first determine the equilibrium concentration, $C_{A,e}$, equilibrium constant ($K = C_{R,e}/C_{A,e}$), and the equilibrium conversion, X_e. We could then determine the kinetic parameters k_1 (and hence k_2) from the integral method.

7.4 Parallel Reactions

Parallel reactions are also called 'competing reactions'. The reactant is consumed by two different reactions to give two different products. Product R may be the desired product whereas product S is an undesired product:

$$\mathrm{A} \xrightarrow{\mathrm{k_1}} \mathrm{R}$$
$$\mathrm{A} \xrightarrow{\mathrm{k_2}} \mathrm{S}$$

An example is the oxidation of ethylene to ethylene oxide

$$CH_2{=}CH_2 \longrightarrow (O)CH_2{-}CH_2$$
$$CH_2{=}CH_2 \longrightarrow CO_2 + 2\,H_2O$$

The second reaction, leading to combustion products is the unwanted reaction. We can write down the rate equations for the two reactions by assuming that they are both 1st order. Here we will also consider the case where the reactions occur in a batch reactor at constant volume, so that the combined rate law and design equation gives

$$-\,r_A = -\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = k_1 C_A + k_2 C_A = (k_1 + k_2)\,C_A \qquad (7.4.1)$$

$$r_R = \frac{\mathrm{d}\,C_R}{\mathrm{d}\,t} = k_1 C_A \qquad (7.4.2)$$

$$r_S = \frac{\mathrm{d}\,C_S}{\mathrm{d}\,t} = k_2 C_A \qquad (7.4.3)$$

The rate of disappearance of A is the sum of the rates of formation of R and S. If we integrate Equation 7.4.1 we find that

$$-\ln\frac{C_A}{C_{A0}} = (k_1 + k_2)\,t \qquad (7.4.4)$$

The disappearance of A is determined by the sum of 1st order rate constants. $k_1 + k_2$ can be determined from the slope of the plot shown in Figure 7.2.

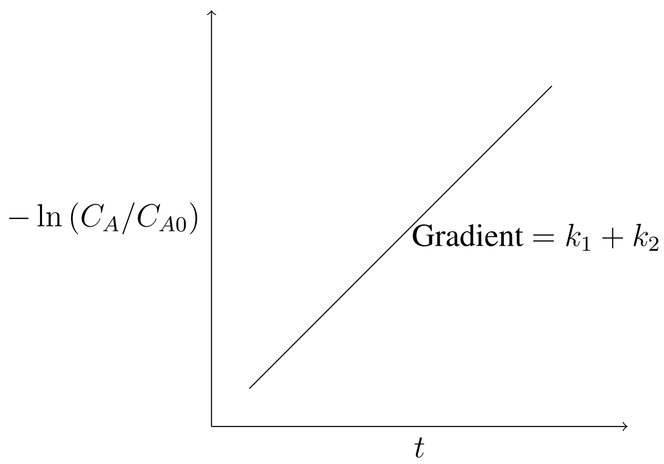


Figure 7.2: Plot of $-\ln(C_A/C_{A0})$ vs t to determine $(k_1 + k_2)$ for a batch reactor at constant volume.

In order to obtain values for k_1 and k_2 we need an additional equation. This can be obtained by dividing Equation 7.4.2 by Equation 7.4.3 to yield

$$\frac{\mathrm{d}\,C_R}{\mathrm{d}\,C_S} = \frac{k_1}{k_2} \qquad (7.4.5)$$

which can be integrated to give

$$\int_{C_{R0}}^{C_R} \mathrm{d}\,C_R = \frac{k_1}{k_2}\int_{C_{S0}}^{C_S} \mathrm{d}\,C_S$$
$$C_R - C_{R0} = \frac{k_1}{k_2}\,(C_S - C_{S0}) \qquad (7.4.6)$$

Thus a plot of C_R versus C_S can be used to determine the ratio of k_1/k_2 as shown by Figure 7.3 below. Thus, the slopes from plots shown in Figure 7.2 and Figure 7.3 yield two linearly independent equations which can be used to solve for the values of k_1 and k_2.

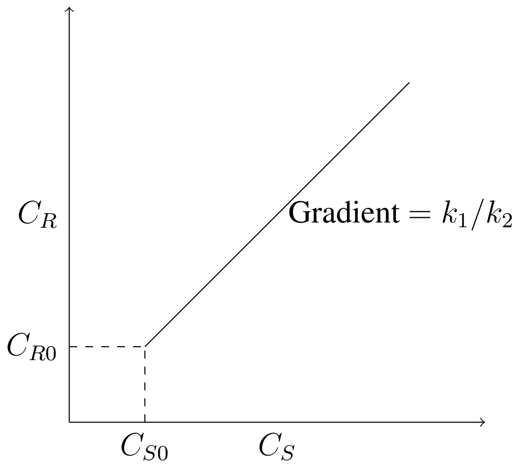


Figure 7.3: Concentration plot based on Equation 7.4.6 to determine k_1/k_2.

We can also determine how the concentrations of R and S vary during the reaction. Combining Equations 7.4.2 and 7.4.4, we have:

$$\frac{\mathrm{d}\,C_R}{\mathrm{d}\,t} = k_1 C_A = k_1 C_{A0} \exp\left[-\left(k_1 + k_2\right) t\right] \tag{7.4.7}$$

which can be intergrated to obtain

$$\int_{C_{R0}}^{C_R} \mathrm{d}\,C_R = \int_0^t k_1 C_{A0} \exp\left[-\left(k_1 + k_2\right) t\right] \mathrm{d}\,t$$
$$C_R - C_{R0} = \frac{k_1}{k_1 + k_2} C_{A0} \left[1 - \exp\left(-\left(k_1 + k_2\right) t\right)\right] \tag{7.4.8}$$

As $C_{R0} = 0$, we have

$$C_R = \frac{k_1}{k_1 + k_2} C_{A0} \left[1 - \exp\left(-\left(k_1 + k_2\right) t\right)\right] \tag{7.4.9}$$

A similar equation can be obtained for C_S from integrating Equation 7.4.3.

$$C_S = \frac{k_2}{k_1 + k_2} C_{A0} \left[1 - \exp\left(-\left(k_1 + k_2\right) t\right)\right] \tag{7.4.10}$$

In the limit of $t \rightarrow \infty$ $C_R \rightarrow \frac{k_1}{k_1+k_2} C_{A0}$ and $C_s \rightarrow \frac{k_2}{k_1+k_2} C_{A0}$ and the ratio of concentrations is thus given $C_R/C_S = k_1/k_2$. In Figure 7.4 below are shown plots of the concentration profiles.

The yields of the main and side products in parallel reactions are given by

$$\bar{Y}_R = \frac{C_R}{C_{A0}} = \frac{k_1}{k_1 + k_2} \qquad \text{As } t \rightarrow \infty$$

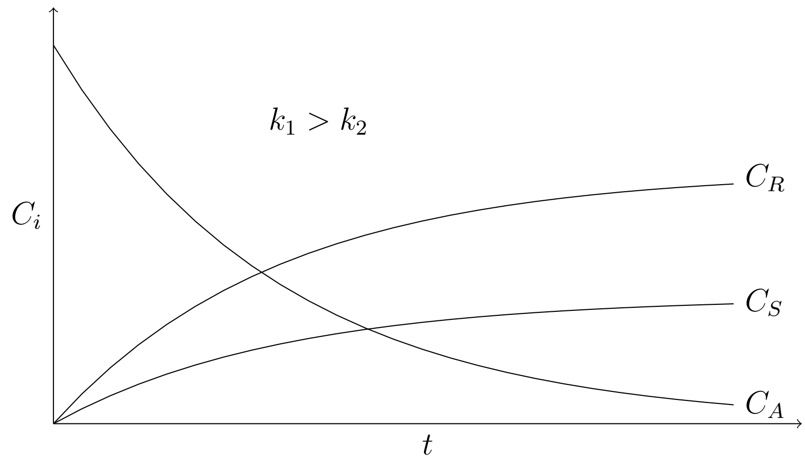


Figure 7.4: Overall concentration plot for the reactant A and two parallel products R and S in the case of $k_1 > k_2$ for a constant volume batch reactor.

and

$$\bar{Y}_S = \frac{C_S}{C_{A0}} = \frac{k_2}{k_1 + k_2} \qquad \text{As } t \to \infty$$

Also note that in this case, the yield defined in terms of the rate of the reaction is equal to the yield defined in terms of mole numbers, i.e. $Y_R = \bar{Y}_R$ .The selectivity is determined by the ratio of k_1 to k_2:

$$S_{RS} = \frac{r_R}{r_S} = \frac{k_1}{k_2}$$

As with the yield, the selectivity is independent of its definition, i.e. $S_{RS} = \bar{S}_{RS}$, for this case.

The example used above corresponds to the simplest case of first order reactions without any volume change in an isothermal batch reactor. For more complicated reactions, it is not always possible to solve the design equations analytically to obtain the concentration profiles. In these more complicated cases, it is still possible to generate rules of thumb for finding the optimal condition for running the reaction by just considering the definition of the selectivity (note that calculating the selectivity only requires evaluating the rate laws). For instance, if the rate laws for the formation of R and S are not linear, but instead are given by

$$r_R = k_R C_A^{\alpha_1} \tag{7.4.11}$$
$$r_S = k_S C_A^{\alpha_2} \tag{7.4.12}$$

then we need to optimize the selectivity given by

$$S_{RS} = \frac{r_R}{r_S} = \frac{k_R}{k_S} C_A^{\alpha_1 - \alpha_2} \tag{7.4.13}$$

If the reaction order of the desired product R is greater than the reaction order of the undesired product S (i.e. $\alpha_1 > \alpha_2$) then

- the reaction must be carried out with the concentration of A as high as possible.
- If the reaction takes place in the gas phase, the reactor should be run without inerts and at high pressure.

- For a liquid phase reaction, diluents should be kept to a minimum.
- In addition, a PFR reactor should be used instead of a CSTR, because the concentration of the reactant A is on average higher in a PFR than in a CSTR. In a PFR, the concentration of A is everywhere greater than in a CSTR (except in the exit stream) if the same conversion of A is to be achieved.

If the order of the desired product R is less than that of the undesired product S (i.e. $\alpha_2 > \alpha_1$) then

- having a low concentration of A is desirable.
- In this case using a CSTR over a PFR is preferred.
- In addition, the reaction should be run with inerts and at low pressure (for a gas phase reaction) or with diluents in a liquid phase reaction.

We can also optimize the selectivity by manipulating the temperature. In this case, we need to consider how the selectivity depends on temperature by explicitly accounting for the temperature dependence of the rate parameters by using the Arrhenius Equation. Thus,

$$S_{RS} = \frac{k_R}{k_S} = \frac{A_R}{A_S} \exp\left(-\frac{E_S - E_R}{RT}\right) \tag{7.4.14}$$

where A_j is the pre-exponential factor (or frequency factor) for component j and E_j is the activation energy for component j. In the case, where $E_R > E_S$, k_R increases more rapidly with temperature than k_S. Thus, the selectivity can be maximised by running at high temperature. Conversely, for $E_R < E_S$, the reaction should be carried out at low temperature to maximise selectivity, but not too low that the desired reaction does not proceed.

7.5 Series Reactions

Irreversible, series reactions are another example of multiple reactions:

$$\mathrm{A} \longrightarrow \mathrm{R} \longrightarrow \mathrm{S}$$

There are many examples of this type of reaction chain such as:

1. Reaction of ethylene oxide (EO) with ammonia to form mono-, di- and triethanolamine.

$$\begin{aligned} NH_3 &+ (O)CH_2{-}CH_2 \longrightarrow HOCH_2CH_2NH_2 \\ &+ (O)CH_2{-}CH_2 \longrightarrow (HOCH_2CH_2)_2NH \\ &+ (O)CH_2{-}CH_2 \longrightarrow (HOCH_2CH_2)_3N \end{aligned}$$

2. A chain reaction to produce C_6Cl_6.

First we consider $\mathrm{A} \xrightarrow{k_1} \mathrm{R} \xrightarrow{k_2} \mathrm{S}$ and the case where each of the reactions is first order. As before we also consider a constant volume batch reactor in which case we can write the combined rate law and design equations as

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = -r_A = k_1 C_A \tag{7.5.1}$$

$$\frac{\mathrm{d}\,C_R}{\mathrm{d}\,t} = r_R = k_1 C_A - k_2 C_R \tag{7.5.2}$$

$$\frac{\mathrm{d}\,C_S}{\mathrm{d}\,t} = r_S = k_2 C_R \tag{7.5.3}$$

Initially, only molecules of A are in the reactor so that $C_{R0} = C_{S0} = 0$. Integrating Equation 7.5.1 gives

$$-\ln \frac{C_A}{C_{A0}} = k_1 t \text{ or } C_A = C_{A0} \exp\left(-k_1 t\right) \tag{7.5.4}$$

Substituting Equation 7.5.4 into Equation 7.5.2 gives

$$\frac{\mathrm{d}\,C_R}{\mathrm{d}\,t} + k_2 C_R = k_1 C_{A0} \exp\left(-k_1 t\right) \tag{7.5.5}$$

with the intial conditions: $t = 0$, $C_{R0} = 0$. This equation is a linear (first-order) ordinary differential equation, which can be solved using the integrating factor method. The solution to the differential equation is given by, [1]

$$C_R = \frac{k_1}{k_2 - k_1} C_{A0} \left[\exp\left(-k_1 t\right) - \exp\left(-k_2 t\right)\right] \tag{7.5.6}$$

According to the stoichiometry, we also know that $C_{A0} = C_A + C_R + C_S$, then $C_S = C_{A0} - C_A - C_R$. A concentration plot based on Equations 7.5.4 and 7.5.6 is shown in Figure 7.5.

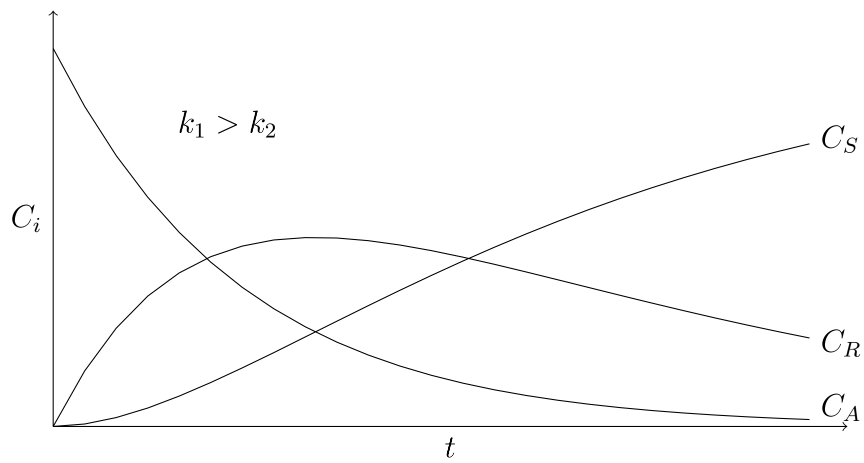
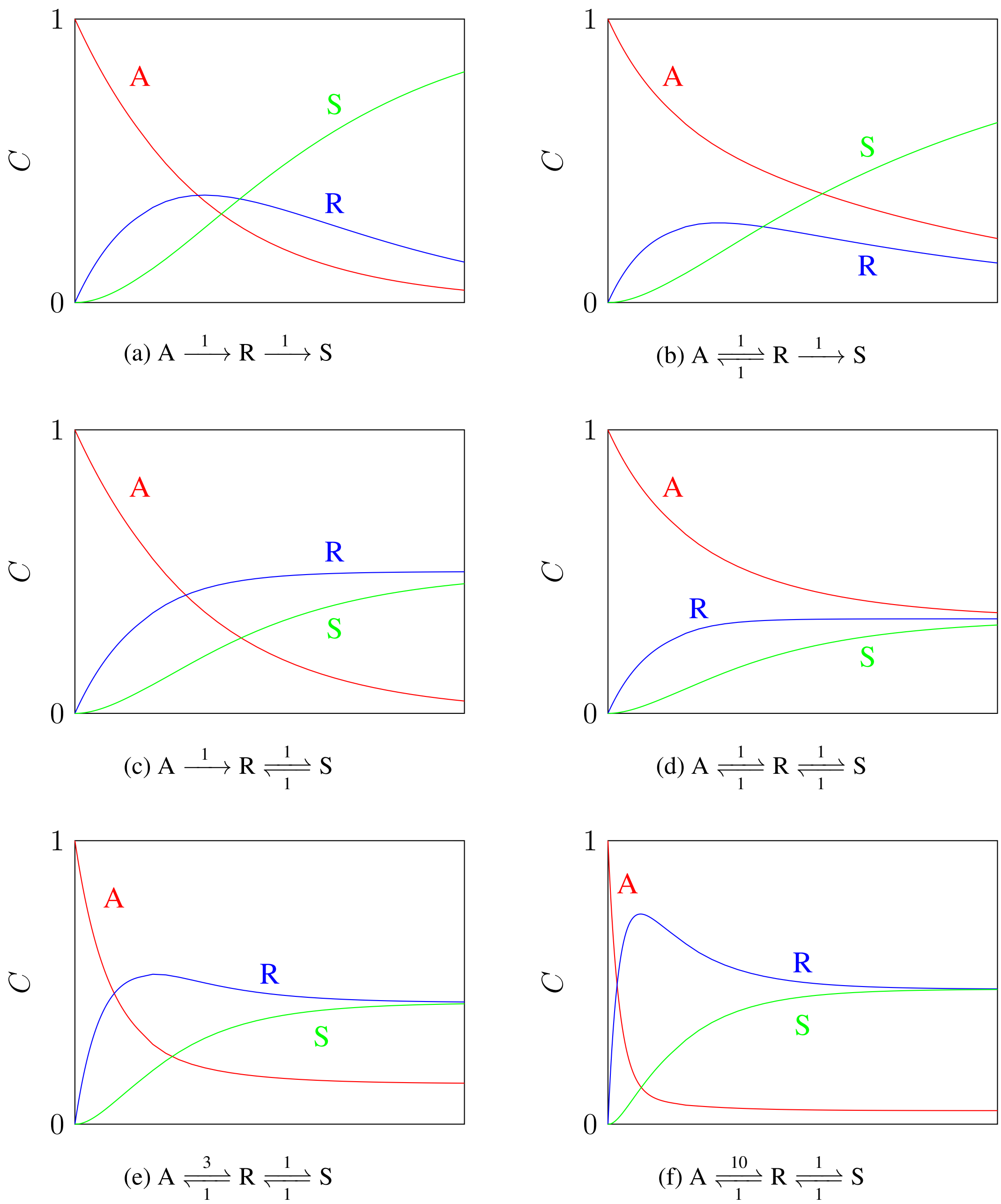


Figure 7.5: Overall concentration plot for the reactant A and two products R and S in a chain reaction based on a first order rate law in a constant volume batch reactor.

To find the maximum concentration of R, $C_{R\text{max}}$, we can differentiate Equation 7.5.6 with respect to time and set the derivative equal to 0, i.e. the maximum occurs at $\frac{\mathrm{d}\,C_R}{\mathrm{d}\,t} = 0$. From this condition we find that

$$t_{\text{max}} = \frac{\ln\left(k_2/k_1\right)}{k_2 - k_1} \tag{7.5.7}$$

The following Figure 7.6 shows the change of the concentrations of A, R, and S in chain reactions at different rate constants. In Figure the change of the concentrations of A, R, and S in parallel reactions in different rate constants is given.



(a) A $\xrightarrow{1}$ R $\xrightarrow{1}$ S

(b) A $\underset{1}{\overset{1}{\rightleftharpoons}}$ R $\xrightarrow{1}$ S

(c) A $\xrightarrow{1}$ R $\underset{1}{\overset{1}{\rightleftharpoons}}$ S

(d) A $\underset{1}{\overset{1}{\rightleftharpoons}}$ R $\underset{1}{\overset{1}{\rightleftharpoons}}$ S

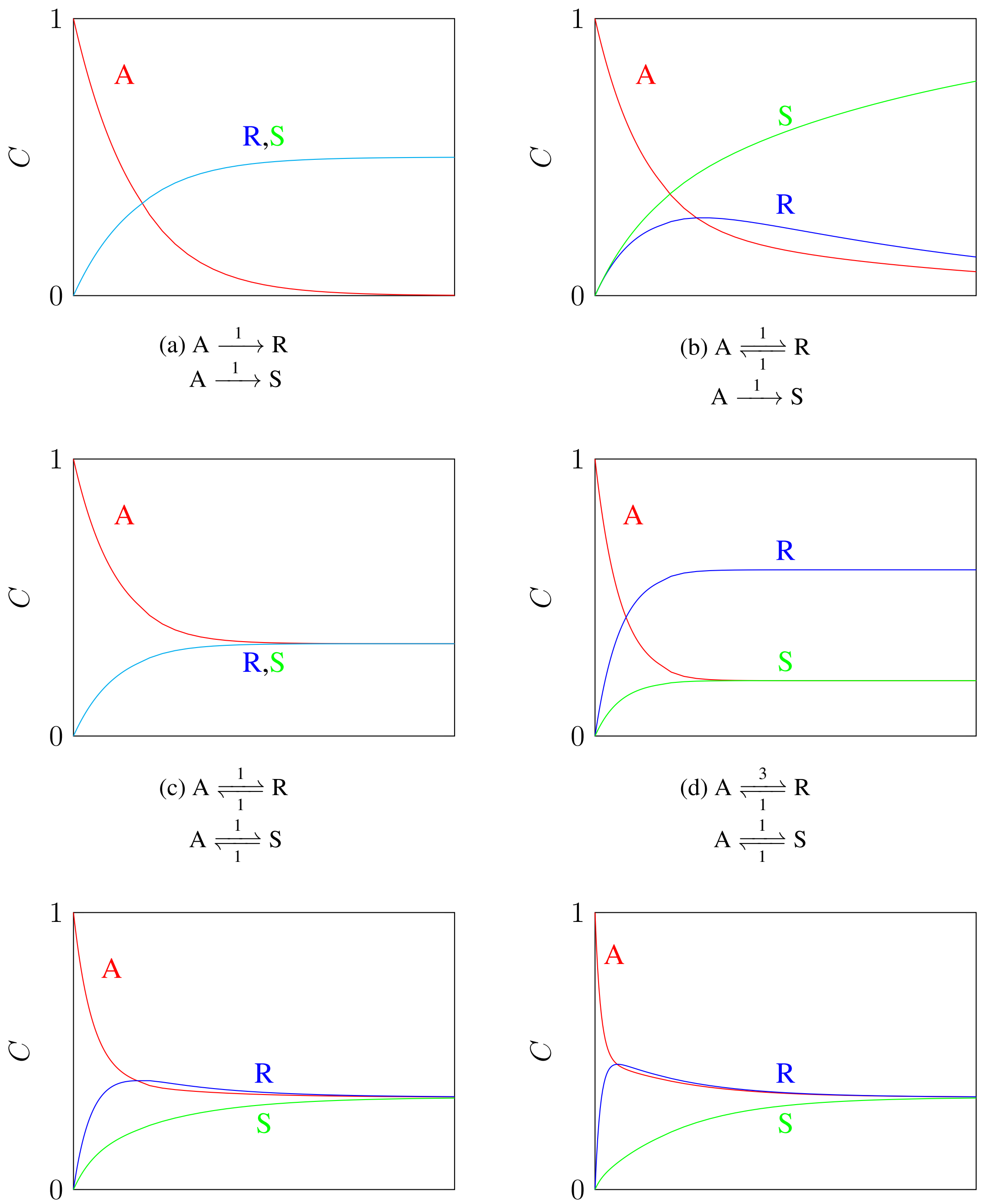
(e) A $\underset{1}{\overset{3}{\rightleftharpoons}}$ R $\underset{1}{\overset{1}{\rightleftharpoons}}$ S

(f) A $\underset{1}{\overset{10}{\rightleftharpoons}}$ R $\underset{1}{\overset{1}{\rightleftharpoons}}$ S

Figure 7.6: Overall concentration profiles for series reactions withdifferent rate constants.

[?]

[1] You should be able to solve this differential equation as the integrating factor method is covered in the Maths notes



(a) $A \xrightarrow{1} R$
$A \xrightarrow{1} S$

(b) $A \underset{1}{\overset{1}{\rightleftharpoons}} R$
$A \xrightarrow{1} S$

(c) $A \underset{1}{\overset{1}{\rightleftharpoons}} R$
$A \underset{1}{\overset{1}{\rightleftharpoons}} S$

(d) $A \underset{1}{\overset{3}{\rightleftharpoons}} R$
$A \underset{1}{\overset{1}{\rightleftharpoons}} S$

(e) $A \underset{3}{\overset{3}{\rightleftharpoons}} R$
$A \underset{1}{\overset{1}{\rightleftharpoons}} S$

(f) $A \underset{10}{\overset{10}{\rightleftharpoons}} R$
$A \underset{1}{\overset{1}{\rightleftharpoons}} S$

Figure 7.7: Overall concentration profiles for parallel reactions with different rate constants.

7.6 References

7.7 Problems

1. The following first-order reversible reaction takes place in the liquid phase in a batch reactor:

$$\text{A} \rightleftharpoons \text{R},\ C_{A0} = 0.5\,\text{mol}\,\text{dm}^{-3},\ C_{R0} = 0$$

After 8 min, the conversion is $1/3$ and the equilibrium conversion is $2/3$. Determine the rate constants for the forward and reverse reactions.

2. Consider the following reaction sequences. These take place at constant volume and temperature in batch reactors. Each step is elementary.

$$1.\ \text{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{R} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{S}$$
$$2a.\ \text{A} \xrightarrow{k_1} \text{R}$$
$$2b.\ \text{A} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \text{S}$$

Formulate rate equations describing the change in concentration of A, R and S as a function of time. If the initial concentrations of A, R and S are 1, 0 and 0 mol dm^{-3}, respectively, what are their values after infinite time? Assume $k_1 = k_2 = k_3 = k_4$.

3. (a) Formulate rate equations describing the change in concentration of A, R and S as a function of time for the following elementary first-order irreversible parallel reactions.

$$\text{A} \xrightarrow{k_1} \text{R}$$
$$\text{A} \xrightarrow{k_2} \text{S}$$

   (b) Derive expressions for the integrated forms of these equations and thus show how the rate constants k_1 and k_2 can be determined by graphical means.

   (c) For the reactions shown in part (a), sketch how the concentrations of A, R and S vary with time for the following two cases (assume the initial concentrations of R and S are 0):

      i. $k_1 = k_2$

      ii. $k_1 > k_2$

   The initial concentrations of A, R and S in the parallel reaction of part (a) are 1.0, 0.1 and 0.2 mol dm^{-3}, respectively. After 1000 s in a batch reactor the concentrations of A, R and S are 0.4, 0.3 and 0.6 mol dm^{-3}, respectively. Calculate the rate constants k_1 and k_2.

Chapter 8

Design Structure for Reactors

Contents

8.1 Design Structure for Reactors

In the previous chapters, we have discussed various aspects for the design of ideal reactors: batch reactors, CSTRs, and PFRs, particularly in the respects of mole balances, design equations, rate constants and concentration profiles. In this section, we introduce some structure (procedures) for the design of reactors.

1. Recall the general mole balance for any reactor, equation 1.5.1,

$$n_i|_V - n_i|_{V+\delta V} + r_i \delta V = \frac{\mathrm{d}\,N_i}{\mathrm{d}\,t}$$

2. Apply the relevant assumptions to our reactor, e.g. well mixed for a batch reactor or CSTR, or no axial mixing and negligible diffusion for a PFR, to produce the specific reactor design equations in terms of the required parameter, in this case conversion,

$$\begin{aligned} \text{Batch:} \quad \frac{\mathrm{d}\,X}{\mathrm{d}\,t} &= \frac{-r_A V}{N_{A,0}} \\ \text{CSTR:} \quad V &= \frac{n_{A0} X}{-r_A} \\ \text{PFR:} \quad \frac{\mathrm{d}\,X}{\mathrm{d}\,V} &= \frac{-r_A}{n_{A,0}} \end{aligned}$$

3. Determine the rate law in terms of the concentration of reacting species. This can be a single reaction or multiple reactions.

4. Make sure your rate of reaction is converted to be based on volume of the reactor, as in Section1.2 (for the homogeneous systems used here the fulid volume and reactor volume are the same).

5. Write all species in terms of the chosen paremeter, e.g. $C_B = f(X)$.

6. Examine the reactions to see if the system can be assumed to be isothermal, if not then determine the relevant balance of the temperature, e.g. $\mathrm{d}\,T/\mathrm{d}\,dV$, from an energy balance and relevant heat transfer.

7. Examine the reactor to see if the system can be assumed to be isobaric, if not then determine the relevant balance of the pressure, e.g. $\mathrm{d}\,P/\mathrm{d}\,dV$, from a momentum balance.

8. Evaluate the design equations for the reactor by one of the following,

   Analytically,

   Graphically, or

   Numerically

8.1.1 Example

Ammonia reacts with methanol to form mono-methylamine. However, this product can react further with methanol to produce di-methylamine, and methanol can also react with itself to form dimethylether[1]. These reactions are,

[1] This is in fact a simplified set for this example.

Reaction			Reaction rate	Conversion
$CH_3OH + NH_3$	$\rightleftharpoons$	$CH_3NH_2 + H_2O$	$-r_{1,A} = k_1 C_A C_B - k_{-1} C_C C_D$	X
$CH_3OH + CH_3NH_2$	$\rightleftharpoons$	$(CH_3)_2NH + H_2O$	$-r_{2,A} = k_2 C_A C_C - k_{-2} C_E C_D$	Y
CH_3OH	$\rightleftharpoons$	$\frac{1}{2}CH_3OCH_3 + \frac{1}{2}H_2O$	$-r_{3,A} = k_3 C_A - k_{-3} C_F^{0.5} C_D^{0.5}$	Z

where A is CH_3OH, B is NH_3, C is CH_3NH_2, D is H_2O, E is $(CH_3)_2NH$, and F is CH_3OCH_3.

In this case we will use a PFR, as we have 3 reactions we have 3 reactor equations,

$$\begin{aligned}\frac{\mathrm{d}\,X}{\mathrm{d}\,V} &= \frac{-r_{1,A}}{n_{A,0}}\\ \frac{\mathrm{d}\,Y}{\mathrm{d}\,V} &= \frac{-r_{2,A}}{n_{A,0}}\\ \frac{\mathrm{d}\,Z}{\mathrm{d}\,V} &= \frac{-r_{3,A}}{n_{A,0}}\end{aligned} \tag{8.1.1}$$

These equations will end up being coupled as each reaction involves some of the same components. This means that the simplest was to solve the equations will be numerically, which we will examine later. In this case, we have a homogeneous reaction, so the volume of the fluid is equal to the reactor volume.

Our rate of reactions are as above,

$$\begin{aligned}-r_{1,A} &= k_1 C_A C_B - k_{-1} C_C C_D\\ -r_{2,A} &= k_2 C_A C_C - k_{-2} C_E C_D\\ -r_{3,A} &= k_3 C_A - k_{-3} C_F^{0.5} C_D^{0.5}\end{aligned} \tag{8.1.2}$$

The mole balance for the reactor can be calculated in terms of the conversion of each of the reactions, as in Section 1.6.2,

Chemical	In moles	Generation	Out moles
A	$n_{A,0}$	$-n_{A,0}X - n_{A,0}Y - n_{A,0}Z$	$n_{A,0}\left(1 - X - Y - Z\right)$
B	$\theta_B n_{A,0}$	$-n_{A,0}X$	$n_{A,0}\left(\theta_B - X\right)$
C	$\theta_C n_{A,0}$	$n_{A,0}X - n_{A,0}Y$	$n_{A,0}\left(\theta_C + X - Y\right)$
D	$\theta_D n_{A,0}$	$n_{A,0}X + n_{A,0}Y + 0.5n_{A,0}Z$	$n_{A,0}\left(\theta_D + X + Y + 0.5Z\right)$
E	$\theta_E n_{A,0}$	$n_{A,0}Y$	$n_{A,0}\left(\theta_E + Y\right)$
F	$\theta_F n_{A,0}$	$0.5n_{A,0}Z$	$n_{A,0}\left(\theta_F + 0.5Z\right)$
Total	$n_{T,0}$	0	$n_T = n_{T,0}$

The volumetric flowrate in the reactor can be given by equation 6.4.3,

$$v = v_0 \frac{n_T}{n_{T,0}} \frac{P_0}{P} \frac{T}{T_0}$$

In this case the number of moles doesn't change, $n_T = n_{T,0}$, so,

$$v = v_0 \frac{P_0}{P} \frac{T}{T_0}$$

Slight out of order, but to help simplify the equation steps at this stage, we can assume isothermal (heat transfer into the reactor is good) and we can assume isobaric (the pressure drop is very small), but this means,

$$v = v_0$$

The concentration of each component can therefore be calculated as,

$$\begin{aligned}
C_A &= \frac{n_A}{v} = \frac{n_{A,0}}{v_0}(1-X-Y-Z) &&= C_{A,0}(1-X-Y-Z)\\
C_B &= \frac{n_B}{v} = \frac{n_{A,0}}{v_0}(\theta_B-X) &&= C_{A,0}(\theta_B-X)\\
C_C &= \frac{n_C}{v} = \frac{n_{A,0}}{v_0}(\theta_C+X-Y) &&= C_{A,0}(\theta_C+X-Y)\\
C_D &= \frac{n_D}{v} = \frac{n_{A,0}}{v_0}(\theta_D+X+Y+0.5Z) &&= C_{A,0}(\theta_D+X+Y+0.5Z)\\
C_E &= \frac{n_E}{v} = \frac{n_{A,0}}{v_0}(\theta_E+Y) &&= C_{A,0}(\theta_E+Y)\\
C_F &= \frac{n_F}{v} = \frac{n_{A,0}}{v_0}(\theta_F+0.5Z) &&= C_{A,0}(\theta_F+0.5Z)
\end{aligned} \tag{8.1.3}$$

So now we have our design equations, equation 8.1.1, our reaction rates, equation 8.1.2, and our concentrations in terms of the inlet conditions and the conversion of the three reactors, equation 8.1.3.

As we have multiple reactions we need a numerical solution, Euler's method for numerical integration is fine, but any numerical integration method would work,

$$\begin{aligned}
X_{n+1} &= X_n + \frac{-r_{1,A}}{n_{A,0}}\Delta V\\
Y_{n+1} &= Y_n + \frac{-r_{2,A}}{n_{A,0}}\Delta V\\
Z_{n+1} &= Z_n + \frac{-r_{3,A}}{n_{A,0}}\Delta V && (8.1.4)\\
& && (8.1.5)
\end{aligned}$$

where ΔV is a small step in the reactor volume.

At the entrance to the reactor the conversion is zero, $X = Y = Z = 0$. This allows the concentrations to be calculated from equation 8.1.3 and in turn the reaction rates from equation 8.1.2. The conversions, X, Y, and Z are then updated for the next step by equation 8.1.4, i.e. at volume $V_{n+1} = V_n + \Delta V$. This process is then repeated until the desired conversion is reached, which then gives the total reactor volume.

[**?**]

8.2 References

8.3 Problems

1. The elementary, liquid-phase, irreversible reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}$$

is to be carried out in a flow reactor. Two reactors are available, an 800 dm^3 PFR that can only be operated at 300 K and a 200 dm^3 CSTR that can be operated at 350 K. The two feed streams to the reactor mix to form a single feed stream that is equimolar in A and B, with a total volumetric flowrate of 10 dm^3 min^{-1}. Which of the two reactors will give the highest conversion?
Additional information:
At 300 K, $k = 0.07\,\mathrm{dm^3\,mol^{-1}\,min^{-1}}$
$E = 85000\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$C_{AI} = C_{BI} = 2\,\mathrm{mol\,dm^{-3}}$
$v_{AI} = v_{BI} = 0.5v_0 = 5\,\mathrm{dm^3\,min^{-1}}$

2. It is desired to produce 20 million kg per year of ethylene glycol (EG). The reactor is to be operated isothermally. A 3.5 mol dm^{-3} solution of ethylene oxide (EO) in water is fed to the reactor together with an equal volumetric solution of water containing 0.9 wt% of the catalyst H_2SO_4. The specific reaction rate constant is 0.311 min^{-1} (1st order in EO). If 80% conversion is to be achieved, determine the necessary CSTR volume.

3. A 200 dm^3 constant volume batch reactor is pressurised to 20 atm with a mixture of 75% A and 25% inert. The gas phase reaction is carried out isothermally at 227°C.

   (a) Assuming that the ideal gas law is valid, how many moles of A are in the reactor initially? What is the initial concentration of A?

   (b) If the reaction is first order:

   $$-r_A = kC_A \left(k = 0.1\,\mathrm{min^{-1}}\right)$$

   Calculate the time necessary to consume 99% of A.

   (c) If the reaction is second order:

   $$-r_A = kC_A^2 \left(k = 0.7\,\mathrm{dm^3\,mol^{-1}\,min^{-1}}\right)$$

   Calculate the time to consume 80% of A.