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Nomenclature

Roman

A  Arrhenius pre-exponential factor  $\text{varies}$  mol m$^{-3}$
C  Concentration  mol m$^{-3}$
$E_{\text{act}}$  Activation energy  J mol$^{-1}$
G  Generation  mol s$^{-1}$
K  Equilibrium constant  $\text{varies}$
k  Rate constant  $\text{varies}$
M  Ratio of $C_{B0}/C_{A0}$  mol
N  Moles  mol
n  Molar flow rate  mol m$^{-3}$ s$^{-1}$
P  Pressure  Pa
p  Partial pressure  Pa
R  8.314  J mol$^{-1}$ K$^{-1}$
r  Reaction rate  mol s$^{-1}$
S  Selectivity  $\frac{1}{2}$
T  Temperature  K
$t$  Time  s
$t_{1/2}$  Half-life  s
V  Volume  m$^3$
v  Volumetric flow rate  mol m$^{-3} s^{-1}$
X  Conversion  $\text{—}$
Y  Yield  $\text{—}$
y  Mole fraction  $\text{—}$

Greek

$\alpha$  Reaction order  $\text{—}$
$\beta$  Reaction order  $\text{—}$
$\delta$  Change in moles per mole of A  $\text{—}$
$\epsilon$  Change in mole fraction per mole of A  $\text{—}$
$\tau$  Residence time  s

Sub-/Super-scripts

0  Related to the start  $\text{—}$
e  Refers to the equilibrium  $\text{—}$
f  Related to the end  $\text{—}$
Chapter 1

Mole Balance for Reactors

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1.1 Introduction

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

1.1.1 Definitions of Reaction Rate

The reaction rate represents how fast a chemical component is converted into another by a chemical reaction. More specifically, the reaction rate, \( r_j \), is the moles of \( j \) formed (or appearing) per unit volume per unit time (mol m\(^{-3}\) s\(^{-1}\)). The reaction rate is negative when the moles of \( j \) 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 \( j \) increase 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.

1.1.2 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.

\[
A \rightarrow \text{products}
\]

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 \(-r_A = \frac{(k_1C_A)}{(1 + k_2C_A)}\).

For a given reaction, the concentration dependence of the rate must be determined from experimental observation. Typical examples of reaction rates are a first order reaction given by,

\[ -r_A = kC_A \]  \hspace{1cm} (1.1.1)

or a second order reaction,

\[ -r_A = kC_A^2 \]  \hspace{1cm} (1.1.2)

where \( k \) is called the rate constant, which varies with temperature. The order of the reaction with respect to a component \( j \) corresponds to the exponent of concentration \( j \) in the rate law. Note that the reaction rate, \( r \), corresponds to a rate for formation. For a reactant the rate of formation is going to be negative as the reactant is consumed by the reaction, hence the negative sign in Equations 1.1.1 and 1.1.2. Usually the order of
CHAPTER 1. MOLE BALANCE FOR REACTORS

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).

1.2 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. In this section we study three types of ideal reactors: the batch reactor, the continuously stirred tank reactor (CSTR), and the plug flow reactor (PFR). We show how to apply a mole balance to each of them, which forms the basis for the reactor design.

**[Reactor Mole Balance]**

The mole balance is used to determine either the time (for a batch reactor) or the reactor volume (for a flow reactor) required to convert a specified amount of reactants into products.

The mole balance can be written as:

\[
\begin{align*}
\text{In} & \quad - \quad \text{Out} \quad + \quad \text{Generation} \quad = \quad \text{Accumulation} \\
\begin{bmatrix}
\text{Rate of} \\
\text{flow of } j \text{ in} \\
\text{(moles/time)}
\end{bmatrix} & \quad - \quad \begin{bmatrix}
\text{Rate of} \\
\text{flow of } j \text{ out} \\
\text{(moles/time)}
\end{bmatrix} + \begin{bmatrix}
\text{Rate of} \\
\text{generation of} \\
\text{by chemical} \\
\text{reaction} \\
\text{(moles/time)}
\end{bmatrix} = \begin{bmatrix}
\text{Rate of} \\
\text{accumulation} \\
\text{of } j \\
\text{(moles/time)}
\end{bmatrix} \\
\quad n_{j0} & \quad - \quad n_j + G_j = \frac{d N_j}{dt} \\
\end{align*}
\]

(1.2.1)

where \( n_j \) is the molar flowrate of species \( j \) (with units of moles sec\(^{-1}\)) and \( N_j \) is number of moles of component \( j \) in the reactor. The above mole balance is performed about 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 \( G_j \) over a given volume element, \( V \), can be calculated from the rate of formation of \( j \), \( r_j \), by:

\[
G_j = r_j V
\]

(1.2.2)

Note that the production rate is negative when a reactant is being consumed.
1.2. MOLE BALANCE FOR REACTORS

1.2.1 Mole Balance Applied to Batch Reactors

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 1.2 is a schematic representation of a batch reactor in the form of mixing vessel.

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.

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. Because 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. There is no inflow or outflow in a batch
reactor, so \( n_{j0} = n_j = 0 \). Rearranging Equations 1.1.1 and 1.1.2 then gives us:

\[
 r_j V = \frac{dN_j}{dt}
\]  

(1.2.3)

Consider the reaction:

\[
 A \rightarrow B
\]

Rearranging Equation 1.2.3 for species A,

\[
 dt = \frac{dN_A}{r_A V}
\]  

(1.2.4)

Integrating with limits \( N_A = N_{A0} \) when \( t = 0 \) (i.e. the initial condition) and \( N_A = N_{Af} \) when \( t = t_1 \),

\[
 t_1 = \int_{N_{A0}}^{N_{Af}} \frac{dN_A}{r_A V}
\]  

(1.2.5)

Now we need to substitute in a rate law for the reaction, for example if the rate law is given by

\[
 -r_A = kC_A \quad \text{Rate equation for a 1st-order reaction}
\]

\[
 -r_A V = kC_A V = k \left( \frac{N_A}{V} \right) V = kN_A
\]  

(1.2.6)

then substituting into Equation 1.2.5 gives

\[
 t_1 = \int_{N_{A0}}^{N_{Af}} \frac{dN_A}{-kN_A} = \int_{N_{Af}}^{N_{A0}} \frac{dN_A}{kN_A}
\]  

(1.2.7)

The integration is performed to yield

\[
 t_1 = \frac{1}{k} \ln \frac{N_{A0}}{N_{Af}}
\]  

(1.2.8)

The mole-time trajectories for A and B as predicted by Equation 1.2.8 are illustrated in Figure 1.3.

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 1.2.3 and express the rate in terms of the changing concentration, \( C_j \):

\[
 r_j = \frac{1}{V} \frac{dN_j}{dt} = \frac{dN_j/V}{dt} = \frac{dC_j}{dt}
\]  

(1.2.9)

Equation 1.2.9 will appear throughout this set of lecture notes as constant volume batch reactors are often used for determining the parameters describing the kinetic rate laws. For a first order reaction, this equation can be integrated to obtain

\[
 t_1 = \frac{1}{k} \ln \frac{C_{A0}}{C_{Af}}
\]  

(1.2.10)

which is the same as Equation 1.2.8 above for a constant volume reactor.

**Question**

Substitute the second order rate equation \(-r_A = kC_A^2\) into Equation 1.2.5 and find the answer for \( t_1 \).
1.2. MOLE BALANCE FOR REACTORS

1.2.2 Mole Balance Applied to CSTR

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.

The first step in designing a CSTR is to determine the volume required to achieve a given conversion using a mole balance. In order to do this, we need to make the 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. Furthermore, under the well-mixed assumption, the exit stream is at the same composition and temperature as the contents inside the reactor. At steady state, the reactor contents do not change with time so that

\[
\frac{d N_j}{dt} = 0 \quad \text{(steady state)}
\]
Plugging Equation 1.2.11 into the mole balance gives

\[ n_{j0} - n_j + r_j V = 0 \]  

(1.2.12)

and solving for the volume of the reactor, we find

\[ V = \frac{n_{j0} - n_j}{-r_j} \]  

(1.2.13)

Equation 1.2.13 provides a relation to calculate the reactor volume in terms of the flow rates, \( n_{j0} \) and \( n_j \) when species \( j \) is disappearing at a rate, \(-r_j\).

According to the molar flow rate:

\[ n_j = C_j \times v \]  

(1.2.14)

where \( v \) is the volumetric flowrate (volume/time). Combining Equations 1.2.13 and 1.2.14 gives

\[ V = \frac{v_0 C_{j0} - vC_j}{-r_j} \]  

(1.2.15)

where the subscript 0 corresponds to an inlet flowrate. For a 1st-order reaction \( A \rightarrow B \) (\(-r_A = kC_A\) and \( n_A = C_Av \)):

\[ V = \frac{v_0 C_{A0} - vC_A}{kC_A} \]  

(1.2.16)

If \( v_0 = v \), i.e. the inlet and outlet flowrates are the same, then,

\[ V = \frac{v}{k} \left( \frac{C_{A0}}{C_A} - 1 \right) \]  

(1.2.17)

**Question**

Substitute the second order rate equation \(-r_A = kC_A^2\) into Equation 1.2.15 and find the answer for \( V \).

### 1.2.3 Mole Balance Applied to Plug Flow Reactor (PFR)

PFRs are mainly used for gas phase reactions and may be packed with catalyst. A schematic representation of a PFR is shown in Figure 1.5. 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.

In order to model a PFR, a few assumptions need to be made. In contrast to the CSTR or 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. $\Delta V$ in Figure 1.6 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.

Remember that the mole balance needs to be done over a volume element that has a uniform distribution of temperature and composition. This corresponds to the volume element shown in Figure 1.6. Consider the mole balance on $j$ in a differential segment of reactor volume $\Delta V$. Applying the mole balance,

$$\text{In} - \text{Out} + \text{Generation} = \text{Accumulation}$$

$$n_j|_{V+\Delta V} - n_j|_V + r_j\Delta V = 0$$

(1.2.18)

and dividing by $\Delta V$ gives

$$\frac{n_j|_{V+\Delta V} - n_j|_V}{\Delta V} = r_j$$

(1.2.19)

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

$$\frac{dn_j}{dV} = r_j$$

(1.2.20)

Consider the reaction $A \rightarrow B$ again. The reactor volume $V_1$ necessary to reduce $n_{A0}$ to $n_{Af}$ can be calculated from the differential in Equation 1.2.20:

$$dV = \frac{dn_A}{r_A}$$

(1.2.21)
Integrating with limits of $n_A = n_{A0}$ when $V = 0$ (the inlet) and $n_A = n_{Af}$ when $V = V_1$ (the outlet) gives,

$$V_1 = \int_{n_{A0}}^{n_{Af}} \frac{d n_A}{r_A} = \int_{n_{Af}}^{n_{A0}} \frac{d n_A}{-r_A}$$

(1.2.22)

For a 1st-order reaction ($-r_A = kC_A$ and $n_A = C_Av$),

$$V_1 = \int_{n_{Af}}^{n_{A0}} \frac{d n_A}{kC_A} = \frac{v}{k} \int_{n_{Af}}^{n_{A0}} \frac{d n_A}{n_A}$$

(1.2.23)

Therefore, upon integration, we find,

$$V_1 = \frac{v}{k} \ln \frac{n_{A0}}{n_{Af}} = \frac{v}{k} \ln \frac{C_{A0}}{C_{Af}}$$

(1.2.24)

In Figure 1.7 is shown a plot of the molar flowrates for A and B as a function of the reactor volume.

![Figure 1.7: Molar flowrate of component A and B as a function of volume in a PFR.](image)

Note that in deriving Equation 1.2.24, 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.
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.

**Question**

Substitute the second order rate equation $-r_A = kC_A^2$ into Equation 1.2.22 and find the answer for $V_1$.

Compare the PFR results with that of the batch reactor.

### 1.3 Summary

The key design equations have been derived for each type of ideal reactor 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.

**Reactor Design Equations**

**Batch:**

$$ t = \int_{N_{Af}}^{N_{Ao}} \frac{dN_A}{-r_AV} $$

**CSTR:**

$$ V = \frac{n_{j0} - n_j}{-r_j} $$

**PFR:**

$$ V = \int_{n_{Af}}^{n_{Ao}} \frac{dn_A}{-r_A} $$
1.4 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

\[ A \rightarrow B \]

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

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

\[ A \rightarrow B. \]

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$^{-1}$.

3. Calculate the volume of a CSTR for the conditions used in the above example. Which volume is larger, the PFR or CSTR? Explain why.

4. Calculate the time to reduce the number of moles of $A$ to 1% of its initial value in a constant volume batch reactor for the reaction and data in question 2.

5. 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 $5 \times 10^{-4} \text{ s}^{-1}$:

\[ A \rightarrow \text{products} \]

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?

\[ 0.0368 \text{ mol dm}^{-3} \]

6. 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.

\[ 5 \text{ s, 10 s} \]
# Chapter 2

## Conversion in Reactors

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2.1 Introduction

The concept of conversion is useful as it provides a direct measure of the extent of reaction. Furthermore, when only one reaction is occurring in the reactor, all molar flowrates can be expressed in terms of the conversion, which makes solving the design equation easier.

2.1.1 Definition of Conversion

Consider the reaction:

\[ aA + bB \rightarrow cC + dD \]

with lower-case letters the stoichiometric coefficients and upper-case letters the chemical species.

Take species A as the basis of calculation so divide through by the coefficient of A

\[ \frac{a}{a} A + \frac{b}{a} B \rightarrow \frac{c}{a} C + \frac{d}{a} D \]

Every quantity is now ‘per mole of A’

We can now ask,

- How can we quantify how far the reaction proceeds to the right?
- How many moles of C (or D) are formed for every mole of A consumed?

To answer these questions it is convenient to use a parameter, conversion. Conversion of A is defined as:

\[ X_A = \frac{\text{moles of A reacted}}{\text{moles of A fed}} \] \hspace{1cm} (2.1.1)

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 \( X_e \)

2.2 Conversion in Batch Reactors

We first need to write out all molar flowrates in terms of the conversion of A and the concentrations of components in the reactor before the reaction has started.

\[
\begin{bmatrix}
\text{moles of A reacted (consumed)}
\end{bmatrix}
= \begin{bmatrix}
\text{moles of A fed}
\end{bmatrix}
\times \begin{bmatrix}
\text{moles of A reacted}
\end{bmatrix}
= N_{A0} \times X
\] \hspace{1cm} (2.2.1)
The number of moles of A that remain in the reactor after time, \( t \), \( N_A \) is:

\[
\begin{bmatrix}
\text{moles of A in reactor at } t \\
\text{at } t
\end{bmatrix} = \begin{bmatrix}
\text{moles of A initially fed to reactor at } t = 0 \\
\text{N}_A \\
\end{bmatrix} - \begin{bmatrix}
\text{moles of A consumed by reactor} \\
\text{N}_A(1 - X)
\end{bmatrix}
\]

(2.2.2)

which can be rearranged to give

\[
X = \frac{N_{A_0} - N_A}{N_{A_0}}
\]

(2.2.3)

Taking an infinitesimally small change in \( N_A \) (i.e. \( N_{A_0} - N_A \to 0 \)), then we can say,

\[
dX = -\frac{dN_A}{N_{A_0}}
\]

(2.2.4)

When \( V \) is constant with time, we have:

\[
X = \frac{C_{A_0} - C_A}{C_{A_0}} \quad \text{so, } dX = -\frac{dC_A}{C_{A_0}}
\]

(2.2.5)

Equation 2.2.2 can be differentiated with respect to \( t \) to give,

\[
\frac{dN_A}{dt} = \frac{d}{dt} [N_{A_0} (1 - X)] = \frac{dN_{A_0}}{dt} - N_{A_0}\frac{dX}{dt} = -N_{A_0}\frac{dX}{dt}
\]

(2.2.6)

The design equation for a batch reactor is (Equation 1.2.3),

\[
\frac{dN_A}{dt} = r_AV
\]

(2.2.7)

Combining Equations 2.2.6 and 2.2.7 gives the design equation in terms of conversion:

\[
-N_{A_0}\frac{dX}{dt} = r_AV
\]

(2.2.8)

To determine the time to achieve a specified conversion, \( X \), we must separate the variables in Equation 2.2.8 and integrate with respect to conversion:

\[
t = N_{A_0} \int_0^X \frac{dX}{-r_AV}
\]

(2.2.9)

Equation 2.2.9 is the integral form of the design equation. In order to perform the integration, the rate of formation and the volume need to be expressed as a function of the conversion. As mentioned previously, often the volume is a constant for a batch reactor. Consider the case of a 1st-order rate law, where we showed that (Equation 1.2.6)

\[
-r_AV = kN_A
\]

(2.2.10)
which can be substituted into Equation 2.2.9 to give

\[ t = N_{A0} \int_0^X \frac{dX}{kN_A} \]  \hspace{1cm} (2.2.11)

By definition, \( N_A = N_{A0} (1 - X) \), so that Equation 2.2.11 becomes

\[ t = N_{A0} \int_0^X \frac{dX}{kN_{A0} (1 - X)} = \frac{1}{k} \int_0^X \frac{dX}{1 - X} \]  \hspace{1cm} (2.2.12)

Integrating Equation 2.2.12 gives,

\[ t = \frac{1}{k} \left[ -\ln (1 - X) \right]_0^X = -\frac{1}{k} \ln (1 - X) \]  \hspace{1cm} (2.2.13)

which provides a relationship between the time for the reaction needs to reach the specified conversion, \( X \). The only assumptions that have been used in deriving Equation 2.2.13 for the reaction of \( A \) to \( B \) is that the reactor is isothermal. If the reactor is not isothermal, then we would need to consider how \( k \) depends on \( T \). In this case, we would need to use an energy balance to derive a relationship between \( T \) and \( X \) and then express \( k \) as a function of \( T(X) \).

Question

Substitute the second order rate equation \(-r_A V = kN_A^2\) into Equation 2.2.9 and find the answer for \( t \).

### 2.3 Conversion in Flow Reactors

For a flow reactor, the total rate at which species \( A \) is reacting within the entire system is \( n_{A0}X \):

\[ n_{A0}X = \frac{\text{moles of } A \text{ fed}}{\text{time}} \times \frac{\text{moles of } A \text{ reacted}}{\text{moles of } A \text{ fed}} = \frac{\text{moles of } A \text{ reacted}}{\text{time}} \]  \hspace{1cm} (2.3.1)

Molar feed rate of \( A \) to the system minus the rate of reaction in the system equals molar flow rate leaving:

\[
\begin{bmatrix}
\text{molar flow rate} \\
\text{at which } A \text{ is fed} \\
\text{to the system} \\
\text{at which } A \text{ is} \\
\text{consumed} \\
\text{at which } A \text{ leaves}
\end{bmatrix}_n_{A0} - \begin{bmatrix}
\text{molar flow rate} \\
\text{at which } A \text{ is fed} \\
\text{to the system} \\
\text{at which } A \text{ is} \\
\text{consumed} \\
\text{at which } A \text{ leaves}
\end{bmatrix}_n_{A0} = \begin{bmatrix}
\text{molar flow rate} \\
\text{at which } A \text{ leaves} \\
\text{at which } A \text{ leaves}
\end{bmatrix}_n_A
\]  \hspace{1cm} (2.3.2)

Rearranging Equation 2.3.2 gives

\[ n_A = n_{A0} (1 - X) \]  \hspace{1cm} (2.3.3)
The rate of reaction is known in terms of concentration variables. The molar flowrates are converted to concentrations using the volumetric flowrates. The inlet flowrate is thus given by

\[ n_{A0} = C_{A0}v_0 \]  
(2.3.4)

For gases \( C_{A0} \) can be calculated from the entering temperature and pressure conditions using the ideal gas law:

\[ C_{A0} = \frac{p_{A0}}{RT_0} = \frac{y_{A0}P}{RT_0} \]  
(2.3.5)

where \( p_{A0} \) is the partial pressure of A in the inlet, \( P_0 \) is the inlet pressure, and \( y_{A0} \) is the inlet mole fraction.

### 2.3.1 CSTR Design Equations for Conversion

The design equation for CSTR is given by (see Equation 1.2.13)

\[ V = \frac{n_{A0} - n_A}{-r_A} \]  
(2.3.6)

After substitution of Equation 2.3.3 into Equation 2.3.6, we find

\[ V = \frac{n_{A0}X}{-r_A} \]  
(2.3.7)

Because the reactor is assumed to be perfectly mixed, the exit composition is the same as in the reactor so the rate of reaction is evaluated at the exit conditions. For a 1st-order reaction \( A \rightarrow B \) \((-r_A = kC_A\) and \( n_{A0} = C_{A0}v_0\)), we find

\[ V = \frac{n_{A0}X}{kC_A} = \frac{C_{A0}v_0X}{kC_A} \]  
(2.3.8)

Often the equation is written in terms of the mean residence time (Holding time or space time) defined by

\[ \tau = \frac{V}{v_0} \]  
(2.3.9)

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. Substitution of the space-time definition into Equation 2.3.9 gives

\[ \tau = \frac{C_{A0}X}{kC_A} \]  
(2.3.10)

If the volumetric flowrates of the inlet and outlet streams are equal, according to Equation 2.3.3, we have

\[ C_A = C_{A0}(1 - X) \]  
(2.3.11)

which can be substituted into Equation 2.3.10 to give an expression for the conversion in terms of the space time

\[ X = \frac{k\tau}{1 + k\tau} \]  
(2.3.12)
2.3. CONVERSION IN FLOW REACTORS

Equation 2.3.12 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.

**Question**

Substitute the second order rate equation $-r_A = kC_A^2$ into Equation 2.3.7 and find the relationship for $X$ in terms of the Dahmkohler number, $k\tau$.

2.3.2 PFR Design Equations for Conversion

Starting from the PFR design equation (see Equation 1.2.20):

$$\frac{dn_A}{dV} = r_A$$

The molar flowrate of $A$ at a given position in a PFR is given by $n_A = n_{A0} (1 - X)$ (Equation 2.3.3), where $X$ corresponds to the conversion as a function of position in the PFR. The latter relation can be derived by doing a mole balance about the entry to the PFR and any position in the PFR. Upon differentiation, we have $dn_A = -n_{A0} dX$. Substituting this result into the design equation gives

$$n_{A0} \frac{dX}{dV} = -r_A$$

The integral form of the design equation is obtained by separating variables and doing the volume integration from $0$ to $V$ in which case the conversion goes from $0$ to $X$:

$$V = n_{A0} \int_0^X \frac{dX}{-r_A}$$

For a first order reaction we use $-r_A = kC_A$ as before. Here, we solve the simplest case where the volumetric flowrate remains constant along the PFR, in which case, $C_A = C_{A0} (1 - X)$. Plugging this result into the rate law and Equation 2.3.14 gives

$$V = n_{A0} \int_0^X \frac{dX}{kC_{A0} (1 - X)}$$

Taking out the constant terms from the integral gives

$$V = \frac{n_{A0}}{kC_{A0}} \int_0^X \frac{dX}{1 - X}$$

Integrating and taking $n_{A0} = C_{A0}v_0$ gives

$$V = -\frac{v_0}{k} \ln (1 - X)$$

or from the definition of mean residence time

$$\tau = \frac{V}{v_0} = -\frac{1}{k} \ln (1 - X)$$
2.4 Application of the Design Equations for Flow Reactors

The aim of this section is to use the experimentally derived knowledge of the rate of reaction, \(-r_A\), as a function of conversion, \(X\), to size CSTRs and PFRs.

2.4.1 Design Equations for CSTR and PFR and the Levenspiel Plot

As discussed above, the design equations involving conversion for the CSTR and PFR for the reaction \(A \rightarrow B\) are:

\[
CSTR: \quad V = \frac{n_{A0}X}{-r_A} \quad \text{PFR:} \quad V = n_{A0} \int_0^X \frac{dX}{-r_A}
\]

It can be seen that the reactor volume varies as \(1/ -r_A\).

Table 2.1 shows some real data for an isothermal reaction with conditions of \(T = 500\) K, \(P = 8.2\) atm, and \(n_{A0} = 0.4\) mol s\(^{-1}\). In order to size a reactor from experimental rate data, we first need to plot \(n_{A0}/(-r_A)\) (m\(^3\)) as a function of \(X\) (this plot is called a Levenspiel plot). Figure 2.1 shows the Levenspiel plot for the data given in Table 2.1.

<table>
<thead>
<tr>
<th>(X)</th>
<th>(-r_A) (mol m(^{-3}) s(^{-1}))</th>
<th>(\frac{1}{-r_A}) (m(^3) s mol(^{-1}))</th>
<th>(\frac{n_{A0}}{-r_A}) (m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.45</td>
<td>2.22</td>
<td>0.89</td>
</tr>
<tr>
<td>0.1</td>
<td>0.37</td>
<td>2.7</td>
<td>1.08</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3</td>
<td>3.33</td>
<td>1.33</td>
</tr>
<tr>
<td>0.4</td>
<td>0.195</td>
<td>5.13</td>
<td>2.05</td>
</tr>
<tr>
<td>0.6</td>
<td>0.113</td>
<td>8.85</td>
<td>3.54</td>
</tr>
<tr>
<td>0.7</td>
<td>0.079</td>
<td>12.7</td>
<td>5.06</td>
</tr>
<tr>
<td>0.8</td>
<td>0.05</td>
<td>20</td>
<td>8</td>
</tr>
</tbody>
</table>

2.4.2 CSTR

How can we calculate the volume, \(V\), of a CSTR to give 80% conversion? From the data above when \(X = 0.8\), \(1/ -r_A = 20\) m\(^3\) s mol\(^{-1}\). If we substitute these values into the CSTR design equation then we can determine the volume:

\[
V = \frac{n_{A0}X}{-r_A} = \frac{n_{A0}}{-r_A} \times X = 8 \text{ (m}^3\text{)} \times 0.8 = 6.4 \text{ m}^3\text{ or 6400 dm}^3
\]
2.4. APPLICATION OF THE DESIGN EQUATIONS FOR FLOW REACTORS

The volume is equal to the area of a rectangle of height \((8 \text{ m}^3)\) and base \((X = 0.8)\) on the Levenspiel plot as shown in Figure 2.2(a) below.

\[
V = \int_{0}^{X} \frac{n_{A0} - r_A}{-r_A} \, dX
\]

2.4.3 PFR

The design equation for the PFR contains an integral. The required volume can therefore be determined from the area under the \(n_{A0} / -r_A\) curve as shown schematically in Figure 2.2(b).

\[
V = n_{A0} \int_{0}^{X} \frac{dX}{-r_A}
\]
The integration can be performed using the trapezium rule (or Simpson’s rule) with known data points. Alternatively one could count/estimate the area on graph paper. For this example the volume is \( V = 2.165 \text{ m}^3 = 2165 \text{ dm}^3 \).

### 2.4.4 PFR and CSTR Comparison

**PFR vs CSTR**

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

### 2.4.5 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 2.3.

![Schematic representation of multiple CSTR volumes and PFR volumes.](image)

Figure 2.3: Schematic representation of multiple (a) CSTR volumes and (b) PFR volumes.

### 2.5 Summary of Design Equations for Ideal Reactors

A summary of the comparison of the design equations among batch reactors, CSTRs and PFRs.
### Design Equations

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Differential</th>
<th>Algebraic</th>
<th>Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Batch</strong></td>
<td>[-\dfrac{d N_A}{d t} = -r_A V]</td>
<td>[N_{A_0} \dfrac{d X}{d t} = -r_A V]</td>
<td>[t = \int_{N_A}^{N_{A_0}} \dfrac{d N_A}{-r_A V}]</td>
</tr>
<tr>
<td><strong>CSTR</strong></td>
<td></td>
<td>[V = \frac{n_{A_0} - n_a}{-r_A}]</td>
<td>[V = \frac{n_{A_0} X}{-r_A}]</td>
</tr>
<tr>
<td><strong>PFR</strong></td>
<td>[-\dfrac{d n_A}{d V} = -r_A]</td>
<td>[n_{A_0} \dfrac{d X}{d V} = -r_A]</td>
<td>[V = \int_{n_A}^{n_{A_0}} \dfrac{d n_A}{-r_A}]</td>
</tr>
</tbody>
</table>
2.6 Problems

1. Draw up a summary table of differential and integral forms of design equations for each ideal reactor in terms of concentration and conversion.

2. 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 at 500 K. Calculate the entering concentration of A, $C_A^0$ and the entering molar flow rate, $n_{A0}$. ($R = 8.314$ dm$^3$/atm K$^{-1}$).

3. A 1st order irreversible reaction,

$$A \rightarrow B$$

with $k = 0.01$ 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 $10^{-3}$ m$^3$/s$^{-1}$?

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

4. 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

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

5. 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 $2 \times 10^6$ 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$^2$]

6. A reactor to be designed to have the conversion data as shown in Table 2.1. Also, the reactor conditions: 500 K, 8.2 atm $n_{A0} = 0.4$ mol 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$^{-1}$?
7. The exothermic reaction

\[ A \rightarrow B + C \]

was carried out adiabatically and the following data recorded:

<table>
<thead>
<tr>
<th>( X )</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.45</th>
<th>0.5</th>
<th>0.6</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-r_A) (mol dm(^{-3}) min(^{-1}))</td>
<td>1.0</td>
<td>1.67</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>1.25</td>
<td>0.91</td>
</tr>
</tbody>
</table>

The entering molar flow rate of A was 300 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 dm\(^3\) CSTR?
Chapter 3

Rate Laws and Stoichiometry

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3.1 Introduction

In the last Chapter, we have shown the calculation of reactor volume and the time to achieve a given conversion in batch systems. For CSTRs and PFRs, we calculated the volume required for the reactors to achieve a given conversion. However, it is not so often that we know the relationship between the reaction rate and conversion from experimental observation. More likely, designing the reactor requires using an equation for the reaction rate in terms of concentrations (in which case the rate constants are known as a function of temperature). In order to solve the design equations, each of the concentrations (and volumes or volumetric flowrates) needs to be expressed as a function of conversion. Here we show how this can be achieved using stoichiometric tables. A key step in writing the stoichiometric table is to understand how the rate of formation for any component is related to the rate of reaction. In addition, we provide an introduction to different rate laws and define the reaction order.

3.2 Relative Rates of Reaction

Consider the reaction:

\[ aA + bB \rightarrow cC + dD \]

or

\[ A + \frac{b}{a} B \rightarrow \frac{c}{a} C + \frac{d}{a} D \]

As discussed earlier, 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 \( \frac{c}{a} \) moles of C. Thus the rate of formation of C, \( r_C = \frac{c}{a} \times \) Rate of disappearance of A = \( \frac{c}{a} (-r_A) \). We can then write

\[ \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \]  \hspace{1cm} (3.2.1)

For instance, \( 2 \) NO + \( O_2 \rightarrow 2 \) 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 \( 4 \) mol dm\(^{-3}\) s\(^{-1}\), then the rate of formation of \( NO_2 \) is

\[ r_{NO} = \frac{-2}{2} r_{NO_2} = -4 \) mol dm\(^{-3}\) s\(^{-1}\)

The Rate of disappearance of NO is given by \( -r_{NO} = 4 \) and the rate of disappearance of \( O_2 \) is given by \( -r_{O_2} = (-1/ -2)r_{NO_2} = 2 \).
3.3 Stoichiometric tables for conversion

If we again consider:

\[ \frac{b}{a}A + \frac{c}{a}B \rightarrow \frac{d}{a}C + \frac{d}{a}D \]

We can express the number of remaining moles in a batch reaction vessel in terms of conversion \( X \) in a stoichiometric table given below (Table 3.1).

**Table 3.1: A stoichiometric table.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Initial Moles</th>
<th>Change in moles</th>
<th>Remaining moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( N_{A0} )</td>
<td>(- (N_{A0}X))</td>
<td>( N_A = N_{A0} - N_{A0}X )</td>
</tr>
<tr>
<td>B</td>
<td>( N_{B0} )</td>
<td>(- (b/a)(N_{A0}X))</td>
<td>( N_B = N_{B0} - (b/a) N_{A0}X )</td>
</tr>
<tr>
<td>C</td>
<td>( N_{C0} )</td>
<td>((c/a)(N_{A0}X))</td>
<td>( N_C = N_{C0} + (c/a) N_{A0}X )</td>
</tr>
<tr>
<td>D</td>
<td>( N_{D0} )</td>
<td>((d/a)(N_{A0}X))</td>
<td>( N_D = N_{D0} + (d/a) N_{A0}X )</td>
</tr>
<tr>
<td>I(inerts)</td>
<td>( N_{I0} )</td>
<td>(- )</td>
<td>( N_I = N_{I0} )</td>
</tr>
</tbody>
</table>

| Total   | \( N_{T0} \)  | \(- \)            | \( N_T = N_{T0} + (d/a + c/a - b/a - 1) N_{A0}X \) |

A similar table can be constructed for the molar flowrates in terms of conversion for a PFR or CSTR where we replace the \( N_i \) by \( n_i \). Note that the change in total number of moles (i.e. \( N_T - N_{T0} \) or \( n_T - n_{T0} \)) can be calculated in terms of the conversion and is equal to \( \delta_0X \), where \( \delta = (d/a + c/a - b/a - 1) \) is the change in moles per mole of A reacted. This quantity is especially important when working with gases in which case the change in total number of moles leads to a change in pressure with time in a batch reactor or in a PFR to a change in volumetric flowrate along the length of the reactor. The concentrations can be determined by dividing the items in the table by \( V \) for a batch reaction or by \( v \) for the case of a flowing system.

### 3.3.1 Change in pressure for a gas phase reaction in a constant volume batch reactor

For a gas phase reaction, we can use a gas law to relate the pressure to the volume of the reaction at any given instant in the batch reactor. 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

\[ PV = N_T RT \quad (3.3.1) \]

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

\[ P_0V = N_{T0} RT_0 \quad (3.3.2) \]

where we note that the volume of the reactor is not changing so that no subscript on \( V \) is used. The ratio of Equation 3.3.1 to 3.3.2 gives

\[ P = P_0 \frac{N_T}{N_{T0}} \frac{T}{T_0} \quad (3.3.3) \]
and plugging in the definition of $N_T$ from the stoichiometric Table 3.1 gives

\[ P = P_0 \left(1 + y_{A0} \delta X\right) \frac{T}{T_0} \]  

(3.3.4)

which provides the desired relationship between pressure in the reactor and the conversion. In this set of lecture notes we only consider isothermal reactors, nevertheless it is worthwhile to note that Equation 3.3.4 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 $X$.

### 3.3.2 Change in volumetric flowrate in a PFR

For a flowing vapour, we can use the ideal gas law to relate the volumetric flowrate to the total molar flowrate. 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

\[ P v = n_T RT \]  

(3.3.5)

Similarly at the inlet to the PFR we have

\[ P_0 v = n_{T0} RT_0 \]  

(3.3.6)

Taking the ratio of Equation 3.3.5 to 3.3.6 gives

\[ v = v_0 \frac{n_T}{n_{T0}} \frac{P_0}{P} \frac{T}{T_0} \]  

(3.3.7)

and using the stoichiometric table for replacing $n_T$ with an equation in terms of $X$ gives

\[ v = v_0 \left(1 + y_{A0} \delta X\right) \frac{P_0}{P} \frac{T}{T_0} \]  

(3.3.8)

As above, Equation 3.3.8 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. In this set of lecture notes we consider only isothermal reactors and in addition the pressure drop term is usually small. In that case, Equation 3.3.8 reduces to

\[ v = v_0 \left(1 + y_{A0} \delta X\right) = v_0 \left(1 + \varepsilon X\right) \]  

(3.3.9)

where we have defined $\varepsilon = y_{A0} \delta$. Equation 3.3.9 is especially significant because the concentrations of the components depend on the volumetric flowrate according to

\[ C_A = \frac{n_A}{v} \]  

(3.3.10)
Thus, if we plug in the equation for $n_A$ from the stoichiometric table, we find that

$$C_A = \frac{n_{A0} - n_{A0}X}{v_0 (1 + \varepsilon X)} = C_{A0} \frac{1 - X}{1 + \varepsilon X} \quad (3.3.11)$$

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. This effect is emphasized by considering the concentration of an inert as a function of conversion, which is given by

$$C_I = C_{I0} \frac{1}{1 + \varepsilon X} \quad (3.3.12)$$

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, you should be able to generate a stoichiometric table for concentrations, where for a reactant B

$$C_B = C_{A0} \frac{N_{B0} - b X}{N_{A0} + \frac{a}{1 + \varepsilon X}} \quad (3.3.13)$$

or for a product D

$$C_D = C_{A0} \frac{N_{D0} + d X}{N_{A0} + \frac{a}{1 + \varepsilon X}} \quad (3.3.14)$$

If a gas phase reaction is occurring, Equations 3.3.11 to 3.3.14 should to be used when solving the design equation for either a CSTR or a PFR.

**Question**

Carry out this analysis to find the equivalent relation as Equation 3.3.14 for $C_C$.

### 3.4 Reaction Rate Equation or Rate Law

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

$$-r_A = k(T) \times f(C_A, C_B, \cdots) \quad (3.4.1)$$

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:

$$-r_A = k_A C_A^\alpha C_B^\beta \quad (3.4.2)$$

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

$$2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$$
the rate law is given by

\[- r_{NO} = k_{NO} C_{NO}^2 C_{O_2} \]  

(3.4.3)

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 O₂. Note that the exponents \( \alpha, \beta \) are not always equal to the stoichiometric coefficients except for the case where the reaction is an elementary step as discussed below.

**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\(^{-1}\).

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

\[ H + Br_2 \rightarrow HBr + Br \]

occurs when one hydronium ion collides and reacts with one bromine molecule. In this case the rate of reaction is given by \( k [H] [Br_2] \). 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

\[ H_2 + Br_2 \rightarrow 2 HBr \]

the rate law is given by

\[- r_{HBr} = \frac{k_1 C_{H_2} C_{Br_2}^{3/2}}{C_{HBr} + k_2 C_{Br_2}} \]  

(3.4.4)

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

\[
\begin{align*}
Br_2 & \rightarrow 2 Br^* \\
Br^* + H_2 & \rightarrow HBr + H^* \\
H^* + Br_2 & \rightarrow HBr + Br^* \\
H^* + HBr & \rightarrow H_2 + Br^* \\
2 Br^* & \rightarrow Br_2
\end{align*}
\]

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.

In some cases, non-elementary reactions have stoichiometric coefficients identical to the orders, for example for the reaction of

\[ 2 NO + O_2 \rightarrow 2 NO_2 \]

the rate is equal to \( k_A C_{NO}^2 C_{O_2} \).
3.5 Problems

1. The reaction:

\[ 2 \text{A} + 3 \text{B} \rightarrow 5 \text{C} \]

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

(b) If \([A]\) had been \(5.0 \times 10^{-4} \text{ mol dm}^{-3}\) and \([B]\) had been \(2.0 \times 10^{-3} \text{ mol dm}^{-3}\) 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:

- \(\text{OH}^-\) reacting with protonated ester, \(\text{HE}^+\), and
- \(\text{OH}^-\) reacting with unprotonated ester, \(\text{E}\).

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

(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.

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]

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:

\[ 3 \text{NaOH}_{(aq)} + (\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5 \rightarrow 3 \text{C}_{17}\text{H}_{35}\text{COONa} + C_3\text{H}_5(\text{OH})_3 \]

Letting \(X\) represent the conversion of sodium hydroxide (the moles of sodium hydroxide 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 \(10 \text{ mol dm}^{-3}\) and of glyceryl stearate at a concentration of \(2 \text{ mol dm}^{-3}\), what is the concentration of glycerine when the conversion of NaOH is (a) 20% and (b) 90%?
Chapter 4

Experimental Determination of Rate Law Parameters

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4.1 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

\[ r_A = \frac{d C_A}{d t} \]  

(4.1.1)

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.

4.2 Experimental Determination of Rates

In some of the methods described below, we will need to obtain experimental measurements of the derivative \(-d C_A/d t\). 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 4.1 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 \(d C_A/d t\).

- 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:
CHAPTER 4. DETERMINATION OF RATE LAW PARAMETERS

\[ C_A = a_0 + a_1 t + a_2 t^2 + \cdots \]

Once the equation is known, it can be differentiated.

4.3 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 4.1 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 4.2, 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 4.3 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>
<thead>
<tr>
<th>( [C_A] )</th>
<th>1.0</th>
<th>2.0</th>
<th>4.0</th>
<th>12.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate</td>
<td>0.05</td>
<td>0.10</td>
<td>0.20</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table 4.1: First order reaction.

<table>
<thead>
<tr>
<th>( [C_A] )</th>
<th>4.0</th>
<th>8.0</th>
<th>16.0</th>
<th>32.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate</td>
<td>3.0</td>
<td>12.0</td>
<td>48.0</td>
<td>192.0</td>
</tr>
</tbody>
</table>

Table 4.2: Second order reaction.

<table>
<thead>
<tr>
<th>( [C_A] )</th>
<th>6.0</th>
<th>12.0</th>
<th>24.0</th>
<th>48.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate</td>
<td>5.0</td>
<td>4.9</td>
<td>5.1</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 4.3: Zero order reaction.

4.4 Differential Methods of Analysis

4.4.1 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 1.2.9) combined with the rate equation for an arbitrary order, \( \alpha \). (Remember that \( \alpha \) does not have to be an integer):

\[- r_A = - \frac{dC_A}{dt} = k_A C_A^{\alpha} \]  

(4.4.1)
Take the natural log of both sides:

$$\ln \left( -\frac{dC_A}{dt} \right) = \ln k_A + \alpha \ln C_A \quad (4.4.2)$$

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

![Log-Log plot of the differential rate for a constant volume batch reactor.](image)

Figure 4.2: Log-Log plot of the differential rate for a constant volume batch reactor.

### 4.4.2 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 $\alpha$ and $\beta$ respectively:

$$-r_A = kC_A^\alpha C_B^\beta \quad (4.4.3)$$

Using the differential method from above, we have:

$$\ln (-r_A) = \ln k + \alpha \ln C_A + \beta \ln C_B \quad (4.4.4)$$

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:

$$-\frac{dC_A}{dt} = -r_A = k'C_A^\alpha \quad (4.4.5)$$

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 $\alpha$. In this example it is called a
pseudo-first order reaction and \( k' \) is the pseudo 1st-order rate constant. The value of \( \beta \) can then be found by repeating with different values of \( C_B \), where

\[
\ln k' = \ln k + \beta \ln C_B
\]  

(4.4.6)

Thus a plot of \( \ln k' \) versus \( \ln C_B \) will yield values for \( k \) and \( \beta \). Alternatively, the same procedure can be done when using an excess of A, in which case \( C_A^0 \) is a constant. In this case

\[
-\frac{dC_A}{dt} = -r_A = k''C_B^\beta
\]  

(4.4.7)

where \( k'' = kC_A^\alpha \).

### 4.4.3 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, \( \alpha \).

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 \( \alpha \) and \( k \), Figure 4.3.

![Figure 4.3: Initial concentration vs rate curve.](image)

### 4.5 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.
4.5. INTEGRAL METHODS

4.5.1 Zeroth Order Reaction by Integral Method

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

$$\frac{dC_A}{dt} = -k$$  \hfill (4.5.1)

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

$$C_{A0} - C_A = C_{A0}X = kt$$  \hfill (4.5.2)

Thus a plot of concentration of A versus time will be linear with a slope of $-k$ as shown in Figure 4.4 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 4.4: Plot of $C_A$ vs time for a zeroth order irreversible reaction in a constant volume batch reactor.](image)

4.5.2 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 1.2.9)

$$-\frac{dC_A}{dt} = kC_A$$  \hfill (4.5.3)

We seek a relationship for the concentration of A in terms of time. This can be achieved by integrating Equation 4.5.3

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = -k \int_{0}^{t} dt$$  \hfill (4.5.4)

to give

$$-\ln \frac{C_A}{C_{A0}} = kt$$  \hfill (4.5.5)
CHAPTER 4. DETERMINATION OF RATE LAW PARAMETERS

Figure 4.5: Plot of $-\ln \left( \frac{C_A}{C_{A0}} \right)$ vs time for a first order reaction in a constant volume batch reactor.

Thus a plot of the left side of Equation 4.5.5 versus $t$ will yield a linear plot where the slope of the line gives the rate constant $k$ as shown in Figure 4.5 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 2.2.13,

$$t = -\frac{1}{k} \ln (1 - X) \tag{4.5.6}$$

Thus a plot of $-\ln (1 - X)$ versus time is linear where the line has a slope equal to $k$ as shown in Figure 4.6 below.

Figure 4.6: Plot of $-\ln (1 - X)$ vs time for a first order reaction in a constant volume batch reactor.

4.5.3 Second Order Reaction by Integral Method

Second order with A

For the following second order reaction:
A + A $\rightarrow$ products

The design equation for constant volume batch reactor is

$$- \frac{d C_A}{dt} = k C_A^2$$  \hspace{1cm} (4.5.7)

which can be rearranged and integrated to give

$$\int_{C_A_0}^{C_A} \frac{d C_A}{C_A^2} = -k \int_0^t d t$$

$$\frac{1}{C_A} - \frac{1}{C_{A_0}} = k t$$  \hspace{1cm} (4.5.8)

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 4.7.

![Figure 4.7: Plot of $1/C_A$ versus time for a second order reaction in a constant volume batch reactor.](image)

Equation 4.5.8 can be written in terms of conversion using the substitution that $C_A = C_{A_0} (1 - X)$ to give

$$C_{A_0} k t = \frac{X}{1 - X}$$  \hspace{1cm} (4.5.9)

**Second order reaction of** A + B $\rightarrow$ products

Next we consider the second order reaction of

A + B $\rightarrow$ 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. $C_{A_0} = C_{B_0}$, then $C_A = C_B$ for the entire reaction. In this case, Equations 4.5.8 and 4.5.9 apply.

For a second order reaction with $C_{A_0} \neq C_{B_0}$ we need to resolve the design equation for the constant volume batch reactor given by

$$- \frac{d C_A}{dt} = k C_A C_B$$  \hspace{1cm} (4.5.10)
According to the stoichiometric table, we have $C_A = C_{A0}(1 - X)$ and $C_B = C_{B0} - C_{A0}X$ and $dC_A = -C_{A0}dX$. Substituting these relations into the design equation we have

$$C_{A0} \frac{dX}{dt} = k(C_{A0} - C_{A0}X)(C_{B0} - C_{A0}X)$$ \hspace{1cm} (4.5.11)

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

$$\frac{dX}{dt} = kC_{A0}(1 - X)(M - X)$$ \hspace{1cm} (4.5.12)

which gives upon rearrangement

$$\int_0^X \frac{dX}{(1 - X)(M - X)} = kC_{A0} \int_0^t dt$$ \hspace{1cm} (4.5.13)

Below we provide the solution to the integration given by Equation 4.5.13 using the method of partial fractions. The integrand in Equation 4.5.13 needs to be expanded as the sum of two separate fractions\(^1\). Thus, we postulate that we can solve the integrand as

$$kC_{A0} \int_0^t dt = \int_0^X \frac{dX}{(1 - X)(M - X)}$$

$$= \int_0^X \left[ \left( \frac{1}{M - 1} \right) \left( \frac{1}{1 - X} \right) - \left( \frac{1}{M - 1} \right) \left( \frac{1}{M - X} \right) \right] dX$$

$$= \frac{1}{M - 1} \int_0^X \left[ \frac{1}{1 - X} - \frac{1}{M - X} \right] dX$$

$$= \frac{1}{M - 1} \left[ -\ln(1 - X) + \ln(M - X) \right]_0^X$$

$$= \frac{1}{M - 1} \left[ \ln \left( \frac{M - X}{1 - X} \right) \right]_0^X$$

$$kC_{A0} t = \frac{1}{M - 1} \ln \left( \frac{M - X}{X} \right)$$ \hspace{1cm} (4.5.14)

Note that Equation 4.5.14 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,

$$X^0 : 1 = PM + Q$$

$$X^1 : 0 = -P - Q$$

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

plot the left hand side of Equation 4.5.14 versus time. The slope of the line equal to \( kC_A \) 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 4.5.14, and then you should show that:

\[
\ln \frac{C_B C_{A0}}{C_{B0} C_A} = (C_{B0} - C_{A0}) \, kt
\] (4.5.15)

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 4.5.15 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 4.5.15 would be used for regressing the rate parameters. Alternatively, if only the conversion could be determined in terms of the concentration of A, Equation 4.5.14 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.

### 4.6 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:

\[
-\frac{dC_A}{dt} = -r_A = kC_A^\alpha
\] (4.6.1)

(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:

\[
t = \frac{1}{k(\alpha - 1)} \left( \frac{1}{C_A^{\alpha - 1}} - \frac{1}{C_{A0}^{\alpha - 1}} \right)
\] (4.6.2)

and factoring out a factor of \( C_{A0}^{\alpha - 1} \)

\[
t = \frac{1}{kC_{A0}^{\alpha - 1}(\alpha - 1)} \left[ \left( \frac{C_{A0}}{C_A} \right)^{\alpha - 1} - 1 \right]
\] (4.6.3)

We then use the definition of half-life, \( t = t_{1/2} \) when \( C_A = 1/2C_{A0} \). Substitution of this condition into Equation 4.6.3 gives

\[
t_{1/2} = \frac{2^{\alpha - 1} - 1}{k(\alpha - 1)C_{A0}^{\alpha - 1}}
\] (4.6.4)
Taking the natural log of both sides gives

\[
\ln t_{1/2} = \ln \left( \frac{2^{\alpha-1} - 1}{k (\alpha - 1)} \right) + (1 - \alpha) \ln C_{A0}
\]  
(4.6.5)

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

![Graph](image)

**Figure 4.8:** 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 \(C_{A0}\).
4.7 Problems

1. The half-life for the (first-order) radioactive decay of $^{14}$C is 5730 years. An archeological 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:

$$A \rightarrow \text{products}$$

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

<table>
<thead>
<tr>
<th>$t$/s</th>
<th>$0$</th>
<th>$100$</th>
<th>$500$</th>
<th>$1000$</th>
<th>$2000$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_A$/mol dm$^{-3}$</td>
<td>$0.100$</td>
<td>$0.0951$</td>
<td>$0.0779$</td>
<td>$0.0607$</td>
<td>$0.0368$</td>
</tr>
</tbody>
</table>

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

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

$$(C_6H_5)_3CCl + CH_3OH \rightarrow (C_6H_5)_3COCH_3 + HCl$$

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:

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>$0$</th>
<th>$50$</th>
<th>$100$</th>
<th>$150$</th>
<th>$200$</th>
<th>$250$</th>
<th>$300$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc of A (mol dm$^{-3} \times 10^3$)</td>
<td>$50$</td>
<td>$38$</td>
<td>$30.6$</td>
<td>$25.6$</td>
<td>$22.2$</td>
<td>$19.5$</td>
<td>$17.4$</td>
</tr>
</tbody>
</table>

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 $= -k'C_A^a$ with $k' = kC_{B0}^b$. Determine $\Delta C_A/\Delta t$ direct from the data.*

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

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

$$A \rightarrow R + S$$

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

<table>
<thead>
<tr>
<th>$t$/s</th>
<th>$0$</th>
<th>$30$</th>
<th>$90$</th>
<th>$120$</th>
<th>$180$</th>
<th>$240$</th>
<th>$360$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$/dm$^3$</td>
<td>$47$</td>
<td>$61$</td>
<td>$68$</td>
<td>$72$</td>
<td>$75$</td>
<td>$78.5$</td>
<td>$84$</td>
</tr>
</tbody>
</table>

This problem can be most conveniently solved on a spreadsheet.
Chapter 5

Temperature Dependence of Reaction Rates

Contents

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5.3 Example Calculation of the Arrhenius Parameters ........... 56
5.4 Problems .......................................................... 59
5.1 Introduction

In the last chapter, we have introduced some methods to determine the rate constant of the reaction equation. 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 dependent on 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. This is especially important when designing non-isothermal reactors. For instance, in a PFR, the temperature varies continuously along the length of the reactor. 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.

5.2 Arrhenius Equation

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

\[
\text{Arrhenius Equation} \quad k = A \exp \left( \frac{-E_{\text{act}}}{RT} \right) \quad (5.2.1)
\]

where \( A \) is a pre-exponential factor or frequency factor (same units as \( k \)), \( E_{\text{act}} \) is an activation energy (units of energy) for the reaction, \( R \) is the gas constant (i.e. equal to 8.314 J K\(^{-1}\) mol\(^{-1}\)), and \( T \) is temperature. \( A \) and \( E_{\text{act}} \) are termed the Arrhenius parameters. The experimental dependence of \( k \) on temperature is illustrated in Figure 5.1 below. The advantage of using Equation 5.2.1 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.

![Figure 5.1: Temperature dependence of the rate constant \( k \).](image)

Most reactions obey relation Equation 5.2.1 but very accurate measurements sometimes
show some curvature indicating a slight temperature dependence of $A$ and $E_{\text{act}}$.

Here we just briefly describe the meaning of the parameter $E_{\text{act}}$, which corresponds to an activation energy or an energetic barrier as illustrated in Figure 5.2. $E_{\text{act}}$ 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 $\exp \left(-\frac{E_{\text{act}}}{RT}\right)$ 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 5.2: Symbolic reaction showing the activation energy barrier.](image)

### 5.3 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 5.1. In order to determine the parameters, we take the natural log of both sides of Equation 5.2.1 to give

$$\ln k = \ln A - \frac{E_{\text{act}}}{RT} \hspace{1cm} (5.3.1)$$

<table>
<thead>
<tr>
<th>$k ; (\text{s}^{-1}) \times 10^{-8}$</th>
<th>4.53</th>
<th>59.3</th>
<th>197</th>
<th>613</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T ; (^\circ \text{C})$</td>
<td>90</td>
<td>110</td>
<td>120</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 5.1: Some real data of how $k$ depends on temperature

Thus the rate parameters can be determined from a plot of $\ln k$ against $1/T$ (data shown in Table 5.2 below). From Figure 5.3, the slope is calculated to be $-17.86 \times 10^{3} \; \text{K}$ which is $-E_{\text{act}}/R$, then $E_{\text{act}} = 8.314 \times 17.85 \times 10^{3} \; \text{J mol}^{-1} = 148 \; \text{kJ mol}^{-1}$. 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:

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

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

### Table 5.2: Data calculated from that in Table 5.1

<table>
<thead>
<tr>
<th>( k ) (s(^{-1})) \times 10^{-8}</th>
<th>4.53</th>
<th>59.3</th>
<th>197</th>
<th>613</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) (°C)</td>
<td>90</td>
<td>110</td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>( T ) (K)</td>
<td>363</td>
<td>383</td>
<td>393</td>
<td>403</td>
</tr>
<tr>
<td>( 1/T \times 10^{-3} )</td>
<td>2.754</td>
<td>2.610</td>
<td>2.544</td>
<td>2.480</td>
</tr>
</tbody>
</table>

### Figure 5.3: 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 \( T_1 \)

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

(5.3.2)
5.4 Problems

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

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. $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

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?
   
   \[53.6 \text{ kJ mol}^{-1}\]

4. The rate of the second-order decomposition of ethanal (CH$_3$CHO) was measured over the temperature range 700 to 1000 K and the rate constants are reported below:

<table>
<thead>
<tr>
<th>T/K</th>
<th>700</th>
<th>730</th>
<th>760</th>
<th>790</th>
<th>810</th>
<th>840</th>
<th>910</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>k/mol$^{-1} \text{ dm}^3 \text{s}^{-1}$</td>
<td>0.011</td>
<td>0.035</td>
<td>0.105</td>
<td>0.343</td>
<td>0.789</td>
<td>2.17</td>
<td>20.0</td>
<td>145</td>
</tr>
</tbody>
</table>

Find the activation energy and the pre-exponential factor.

\[184 \text{ kJ mol}^{-1}; 5.7 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{s}^{-1}\]
Chapter 6

Multiple Reactions

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6.1 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

\[ A \rightleftharpoons R \]

reactions that occur in series, such as

\[ A \rightarrow R \rightarrow S \]

and reactions that occur in parallel, such as

\[ A \rightarrow R \]
\[ A \rightarrow S \]

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.

6.2 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:

\[ S_{RS} = \frac{r_R}{r_S} \]  \hspace{1cm} (6.2.1)

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

\[ \bar{S}_{RS} = \frac{C_R}{C_S} \]  \hspace{1cm} (6.2.2)

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

\[ Y_R = \frac{r_R}{-r_A} \]  

(6.2.3)

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:

\[ \bar{Y}_R = \frac{N_R}{N_{A0} - N_A} \]  

(6.2.4)

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

\[ \bar{Y}_R = \frac{n_R}{n_{A0} - n_A} \]  

(6.2.5)

6.3 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:

\[ 2 \text{C}_6\text{H}_6 \xrightleftharpoons[k_2]{k_1} \text{C}_{12}\text{H}_{10} + \text{H}_2 \]

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

\[ \text{A} \xrightleftharpoons[k_2]{k_1} \text{R} \]

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

\[ -r_A = k_1 C_A - k_2 C_R \]  

(6.3.1)

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

\[ 0 = k_1 C_{A,e} - k_2 C_{R,e} \]  

(6.3.2)

where we use the subscript \( e \) to denote that the concentration is at equilibrium. Equation 6.3.2 can be rearranged to give

\[ \frac{C_{R,e}}{C_{A,e}} = \frac{k_1}{k_2} = K \]  

(6.3.3)

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:
6.3. REVERSIBLE REACTIONS

\[ \text{at } t = 1 \text{ concentration at } t \]
\[ A: \quad C_A = C_{A0} \quad C_A = C_{A0} - C_{A0}X \]
\[ R: \quad C_R = C_{R0} \quad C_R = C_{R0} + C_{A0}X \]

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

\[ -\frac{dC_A}{dt} = -r_A = C_{A0} \frac{dX}{dt} = \kappa_1 (C_{A0} - C_{A0}X) - \kappa_2 (C_{R0} + C_{A0}X) \]  \hspace{2cm} (6.3.4)

To simplify the equation, we make the substitution \( M = C_{R0}/C_{A0} \) and divide Equation 6.3.4 by \( C_{A0} \) to give

\[ \frac{dX}{dt} = \kappa_1 (1 - X) - \kappa_2 (M + X) \]  \hspace{2cm} (6.3.5)

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

\[ \frac{dC_A}{dt} = 0 \text{ and } \frac{dX}{dt} = 0 \]

Applying the equilibrium conditions to Equation 6.3.5 gives

\[ \frac{k_1}{k_2} = \frac{M + X_e}{1 - X_e} \]  \hspace{2cm} (6.3.6)

where \( X_e \) is the conversion at equilibrium. Equation 6.3.6 can be rearranged to give

\[ X_e = \frac{K - M}{K + 1} \]  \hspace{2cm} (6.3.7)

Equation 6.3.7 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 6.3.6) into Equation 6.3.5 and rearrange to give

\[ \frac{dX}{dt} = k_1 (1 - X) - k_1 \frac{1 - X_e}{M + X_e} (M + X) \]  \hspace{2cm} (6.3.8)

In order to integrate Equation 6.3.8, we can simplify the above equation to give,

\[ \frac{dX}{dt} = \frac{k_1}{M + X_e} [(1 - X) (M + X_e) - (1 - X_e) (M + X)] \]

\[ = \frac{k_1}{M + X_e} [X_e - MX - X + X_eM] \]

\[ = k_1 \frac{M + 1}{M + X_e} (X_e - X) \]  \hspace{2cm} (6.3.9)

Integrating Equation 6.3.9 gives

\[ \int_0^X \frac{dX}{X_e - X} = \int_0^t k_1 \frac{M + 1}{M + X_e} \, dt \]

\[ - \ln \left( \frac{1 - X}{X_e} \right) = k_1 \frac{M + 1}{M + X_e} t \]  \hspace{2cm} (6.3.10)
Figure 6.2 below shows a plot of the left hand side of Equation 6.3.10 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:

$$\frac{X_e - X}{X_e} = \frac{(C_{A0} - C_{A,e}) - (C_{A0} + C_A)}{(C_{A0} - C_{A,e})} = \frac{C_A - C_{A,e}}{C_{A0} - C_{A,e}}$$  \quad (6.3.11)$$

Thus Equation 6.3.10 can be changed to:

$$-\ln \left( \frac{C_A - C_{A,e}}{C_{A0} - C_{A,e}} \right) = k_1 \frac{M + 1}{M + X_e} t$$  \quad (6.3.12)$$

Figure 6.1: Plot of $\ln \left( 1 - \frac{X}{X_e} \right)$ 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.

### 6.4 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:

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

An example is the oxidation of ethylene to ethylene oxide.
6.4. PARALLEL REACTIONS

\[ \text{CH}_2=\text{CH}_2 \rightarrow (\text{O})\text{CH}_2=\text{CH}_2 \]
\[ \text{CH}_2=\text{CH}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

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

\[ -r_A = -\frac{dC_A}{dt} = k_1 C_A + k_2 C_A = (k_1 + k_2) C_A \] (6.4.1)

\[ r_R = \frac{dC_R}{dt} = k_1 C_A \] (6.4.2)

\[ r_S = \frac{dC_S}{dt} = k_2 C_A \] (6.4.3)

The rate of disappearance of A is the sum of the rates of formation of R and S. If we integrate Equation 6.4.1 we find that

\[ -\ln \left( \frac{C_A}{C_{A0}} \right) = (k_1 + k_2) t \] (6.4.4)

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 6.2.

\[ -\ln \left( \frac{C_A}{C_{A0}} \right) \]

\[ \text{Gradient} = k_1 + k_2 \]

Figure 6.2: Plot of \(-\ln \left( \frac{C_A}{C_{A0}} \right) \) 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 6.4.2 by Equation 6.4.3 to yield

\[ \frac{dC_R}{dC_S} = \frac{k_1}{k_2} \] (6.4.5)

which can be integrated to give

\[ \int_{C_{R0}}^{C_R} dC_R = \frac{k_1}{k_2} \int_{C_{S0}}^{C_S} dC_S \]

\[ C_R - C_{R0} = \frac{k_1}{k_2} (C_S - C_{S0}) \] (6.4.6)
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 6.3 below. Thus, the slopes from plots shown in Figure 6.2 and Figure 6.3 yield two linearly independent equations which can be used to solve for the values of $k_1$ and $k_2$.

![Figure 6.3: Concentration plot based on Equation 6.4.6 to determine $k_1/k_2$.](image)

We can also determine how the concentrations of R and S vary during the reaction. Combining Equations 6.4.2 and 6.4.4, we have:

$$\frac{dC_R}{dt} = k_1 C_A = k_1 C_{A0} \exp \left[ - (k_1 + k_2) t \right] \quad (6.4.7)$$

which can be integrated to obtain

$$\int_{C_{R0}}^{C_R} dC_R = \int_0^t k_1 C_{A0} \exp \left[ - (k_1 + k_2) t \right] dt$$

$$C_R - C_{R0} = \frac{k_1}{k_1 + k_2} C_{A0} \left[ 1 - \exp \left( - (k_1 + k_2) t \right) \right] \quad (6.4.8)$$

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

$$C_R = \frac{k_1}{k_1 + k_2} C_{A0} \left[ 1 - \exp \left( - (k_1 + k_2) t \right) \right] \quad (6.4.9)$$

A similar equation can be obtained for $C_S$ from integrating Equation 6.4.3.

$$C_S = \frac{k_2}{k_1 + k_2} C_{A0} \left[ 1 - \exp \left( - (k_1 + k_2) t \right) \right] \quad (6.4.10)$$

In the limit of $t \to \infty$ $C_R \to \frac{k_1}{k_1 + k_2} C_{A0}$ and $C_S \to \frac{k_2}{k_1 + k_2} C_{A0}$ and the ratio of concentrations is thus given $C_R/C_S = k_1/k_2$. In Figure 6.4 below are shown plots of the concentration profiles.

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

$$\bar{Y}_R = \frac{C_R}{C_{A0}} = \frac{k_1}{k_1 + k_2} \quad \text{As } t \to \infty$$
6.4. PARALLEL REACTIONS

Figure 6.4: 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

\[
\bar{Y}_S = \frac{C_S}{C_{A0}} = \frac{k_2}{k_1 + k_2} \quad \text{As } t \to \infty
\]

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

\[
\begin{align*}
    r_R &= k_R C_A^{\alpha_1} \\
    r_S &= k_S C_A^{\alpha_2}
\end{align*}
\]

then we need to optimize the selectivity given by

\[
S_{RS} = \frac{r_R}{r_S} = \frac{k_R}{k_S} C_A^{\alpha_1 - \alpha_2}
\]

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,\[
S_{RS} = \frac{k_R}{k_S} = \frac{A_R}{A_S} \exp \left( -\frac{E_S - E_R}{RT} \right)
\] (6.4.14)

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.

### 6.5 Series Reactions

Irreversible, series reactions are another example of multiple reactions:

\[ A \rightarrow R \rightarrow S \]

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.

\[
\begin{align*}
\text{NH}_3 + \text{(O)CH}_2\text{CH}_2 & \rightarrow \text{HOCH}_2\text{CH}_2\text{NH}_2 \\
+ \text{(O)CH}_2\text{CH}_2 & \rightarrow (\text{HOCH}_2\text{CH}_2)_{2}\text{NH} \\
+ \text{(O)CH}_2\text{CH}_2 & \rightarrow (\text{HOCH}_2\text{CH}_2)_{3}\text{N}
\end{align*}
\]

2. A chain reaction to produce \( \text{C}_6\text{Cl}_6 \).

\[
\text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{Cl}_2 \rightarrow \cdots \rightarrow \text{C}_6\text{Cl}_6
\]

First we consider \( A \xrightarrow{k_1} R \xrightarrow{k_2} S \) 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

\[
- \frac{dC_A}{dt} = -r_A = k_1C_A
\] (6.5.1)
6.5. SERIES REACTIONS

\[
\frac{dC_R}{dt} = r_R = k_1 C_A - k_2 C_R \tag{6.5.2}
\]

\[
\frac{dC_S}{dt} = r_S = k_2 C_R \tag{6.5.3}
\]

Initially, only molecules of A are in the reactor so that \(C_{R0} = C_{S0} = 0\). Integrating Equation 6.5.1 gives

\[-\ln \frac{C_A}{C_{A0}} = k_1 t \text{ or } C_A = C_{A0} \exp(-k_1 t) \tag{6.5.4}\]

Substituting Equation 6.5.4 into Equation 6.5.2 gives

\[
\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} \exp(-k_1 t) \tag{6.5.5}
\]

with the initial 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, \(^1\)

\[
C_R = \frac{k_1}{k_2 - k_1} C_{A0} \left[ \exp (-k_1 t) - \exp (-k_2 t) \right] \tag{6.5.6}
\]

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 6.5.4 and 6.5.6 is shown in Figure 6.5.

![Figure 6.5](image)

Figure 6.5: 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, \(C_{Rmax}\), we can differentiate Equation 6.5.6 with respect to time and set the derivative equal to 0, i.e. the maximum occurs at \(\frac{dC_R}{dt} = 0\). From this condition we find that

\[
t_{\text{max}} = \frac{\ln \left(\frac{k_2}{k_1}\right)}{k_2 - k_1} \tag{6.5.7}
\]

The following Figure 6.6 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.

---

\(^1\)You should be able to solve this differential equation as the integrating factor method is covered in the Maths notes.
Figure 6.6: Overall concentration profiles for series reactions with different rate constants.
Figure 6.7: Overall concentration profiles for parallel reactions with different rate constants.
6.6 Problems

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

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

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. A \begin{align*} \xrightarrow{k_1} & R \xrightarrow{k_2} S \end{align*}
2a. A \xrightarrow{k_1} R
2b. A \xrightarrow{k_2} 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.

\[ A \xrightarrow{k_1} R \]
\[ A \xrightarrow{k_2} S \]

(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 \( k_2 \).
Design structure for Isothermal Reactors

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7.1 Design structure for Isothermal 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 isothermal reactors. It is always the case that we first need to establish the mole balance.

**Design Structure**

1. The general mole balance equation:

   \[ n_{A0} - n_A + r_A = \frac{dN_A}{dt} \]

2. Apply the mole balance to specific reactor design equations:
   - **Batch:** \( N_{A0} \frac{dX}{dt} = -r_A V \)
   - **CSTR:** \( V = n_{A0}X \)
   - **PFR:** \( n_{A0} \frac{dX}{dV} = -r_A \)

3. Is \(-r_A = f (X)\) given?
   - **Yes** - Evaluate algebraic (CSTR) or integral (PFR) equations
   - **No** - go to 4

4. Determine the rate law in terms of the concentration of reacting species.
   e.g. \(-r_A = kC_A C_B\) or multiple reactions

5. Use stoichiometry to express concentration as a function of conversion:
   e.g. \( C_A = C_{A0} (1 - X) \)
   e.g. \( C_B = C_{A0} \left( \frac{N_{B0}}{N_{A0}} - \frac{b}{a} X \right) \)

6. Combine 2, 4 and 5 to determine rate law \(-r_A = f (X)\)

7. Evaluate mole balance/rate law/stoichiometry by one of the following:
   Analytically,
   Graphically, or
   Numerically
7.2 Problems

1. The elementary, liquid-phase, irreversible reaction

\[ A + B \rightarrow C \]

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, \( k = 0.07 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1} \)
\( E = 85000 \text{ J K}^{-1} \text{ mol}^{-1} \)
\( C_{AI} = C_{BI} = 2 \text{ mol dm}^{-3} \)
\( v_{AI} = v_{BI} = 0.5v_0 = 5 \text{ dm}^3 \text{ min}^{-1} \)

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 \( \text{H}_2\text{SO}_4 \). 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\(^\circ\)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:

\[ -r_A = kC_A \left( k = 0.1 \text{ min}^{-1} \right) \]

Calculate the time necessary to consume 99% of A.

(c) If the reaction is second order:

\[ -r_A = kC_A^2 \left( k = 0.7 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1} \right) \]

Calculate the time to consume 80% of A.