Reaction Kinetics and Reactor Design in Food Production

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Main Texts:


Additional Recommended Texts:

CLASS CONDUCTS

- 2 hours lecture
- 1 hour tutorial
- Assignments
- Quiz
- Final Exam
OVERVIEW OF SYLLIBUS

- Topic 1: Introduction to Reaction Kinetics in Food Processing
- Topic 2: Determination of Kinetics Parameter
- Topic 3: Effect of Concentration
- Topic 4: Effect of Temperature
- Topic 5: Combining Effect of Temperature and Time
- Topic 6: Case Study: Canning and Shelf Life of Food
- Topic 7: Kinetics of Enzymatic Reaction
- Topic 8: Application of Reaction Kinetics on Novel Food Processing Technology
- Topic 8: Design of Mix Flow Reactor
- Topic 10: Design of Plug Flow Reactor
INTRODUCTION TO REACTION KINETICS IN FOOD PROCESSING
Agricultural and marine products

Processing leads to:

- More attractive food
- Safer
- Easier to eat
- Preserved from deterioration
Process Includes:

- Building up desirable constituents
- Removing undesirable constituents
- Encourage enzyme to develop flavour and texture
- Removing enzymes
- Growing microorganisms to create flavour and texture
- Destroys microorganisms to prevent harm to consumers
Changes in food materials during processing

<table>
<thead>
<tr>
<th>Category</th>
<th>Changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Hydrolysis, oxidation, polymerisation, denaturation, de-amination, browning, hydrogenation, esterification, destruction of toxic substances</td>
</tr>
<tr>
<td>Physical</td>
<td>Gelation, hardening, softening, toughening, emulsifying, colour loss/gain</td>
</tr>
<tr>
<td>Biological</td>
<td>Growth and death of microorganisms, glycolysis, physiological changes in ripening</td>
</tr>
<tr>
<td>Nutritional</td>
<td>Constituent availability, protein changes, loss of vitamins, amino acids loss, destruction of anti-nutritional substances</td>
</tr>
<tr>
<td>Sensory</td>
<td>Aroma and flavour loss, aroma and flavour changes, texture changes, colour bleaching and darkening</td>
</tr>
</tbody>
</table>
EXAMPLES OF REACTIONS IN FOOD PROCESSING

- Browning of sugar and protein resulting in darkening and bitter flavors (Maillard reaction)
- Starch gelatinization
- Sucrose hydrolysis to glucose and fructose
- Color formation during meat processing
- Microbial growth during food processing
- Nutrient degradation during thermal processing
- Fermentation process - yoghurt, baking
- Protein denature
- Hydrogenation of cooking oil
- Acid base reaction in baking – baking soda + lemon juice
Examples of reaction in food: hydrolysis
Examples of reaction in food: protein denature
Examples of reaction in food: Maillard reaction/browning
Examples of reaction in food: Hyodrogenation of oil

$$\text{C} = \text{C} \quad + \quad \text{H}_2 \quad \rightarrow \quad \text{C} - \text{C}$$

General Hydrogenation Process:
- Hydrogen gas is added under pressure in the form of tiny bubbles at the base of the agitator.
- Nickel catalyst is added in an oil slurry.
Some reactions in jam making

Reactions

- Sucrose hydrolysis catalysed by acid
- Sucrose hydrolysis catalysed by enzymes
- Caramelisation/burning of sugars
- Browning sugar/protein (Maillard) reactions
- Colour bleaching
- Pectin polymerisation
- Pectin breakdown catalysed by enzymes
- Enzyme activation/inactivation

Products

- Glucose + Fructose
- Glucose + Fructose
- Darkening and caramel/burnt flavours
- Darkening, bitter flavours
- Colourless compounds
- Gelation
- Simpler carbohydrates
- Increase or stopping of reactions
Consumer expectations

- Appearance
  - Colour
  - Aroma

- Price/value
- Nutritional value
- Safety
- Packaging, brand

- Sensory Properties
  - Attractiveness
  - Convenience
  - Versatility
  - Ease of storage

- Nutritional value
  - Pleasant after-taste
  - Digestibility
  - Stomach filling

- Safety
- Packaging, brand

- Functional product
  - Physical: size, shape, hardness, softness, colour
  - Nutritional: calories, fats, proteins, vitamins, minerals, amino acids, fatty acids: saturation
  - Microbiological: pathogens, bacteria, yeasts, moulds
  - Sensory: Colour, aroma, flavour, texture
  - Chemical: Composition, flavour compounds, fatty acids: hydrolysis, oxidation, browning compounds
Progress of changes can be measured during processing

- Chemical analysis of composition changes
- Physical measurements
- Counts of microorganisms
- Colour assessment
- Texture assessment
- Flavour assessment
Knowledge of raw material attributes

**Raw materials**
- Nature
- Composition
- Concentrations
- Attributes

**Reactions**
- Chemical changes
- Attribute changes

**Production specifications**

**Control of process conditions**

Rate of change in food attributes in all stages of food processing

- Temperature
- Time
- pH
- Moisture
- Catalysts
- Enzymes
- Atmosphere

Levels of product attributes in final product

**Product specifications**
Changes of product attributes with time

The changes in product attributes are mainly due to physical or chemical reactions within the food products.
What is Reaction Kinetics

The study of how reaction progress:

- Rate of reaction
- Development mathematical model to quantify rate of reaction
- Factors that affect reaction rate
- Mechanism of reactions
Examples of Application of Reaction Kinetics in Food Processing

- Assessing sensitivity of products attributes (i.e. time, catalyst, temperature, moisture) to the processing conditions
- Control of processing conditions (i.e. time, pH, temperature) to attain specific product attributes
  - Processing of juice
  - Pasteurization milk
  - Canning
- Design of New products
- Product Shelf life
- Food Process Design
Pasteurisation of milk

Alternative process:
- Higher temperature
- Shorter time

Unwanted reactions
- Browning
- Caramelization
- Vitamin losses

Pasteurised milk
Faster production
Rate can be quantified and the sensitivity to time and temperature of each product attributes can be measured.

- Optimum process condition can be found – give superior product.
- Wanted reaction can be maximized.
- Unwanted reaction can be minimized.
Design of New Products

- Milk protein products
  - Whey was produced in huge quantities in the dairy industry as the byproduct of the manufacture of butter and cheese
  - Major waste problem
  - Utilization of whey
    - Whey is heated to denature the different protein and the different protein precipitate out from the whey
    - Rates of precipitation different with different protein – different time and temperature
    - Systematic separation from of different protein from milk – new products
Design of New Products

- Pasteurized egg in shells
  - Vegetative pathogens in eggs can be destroyed by heat treatment
  - But this also denature the protein
  - However rate of denaturation and pathogen destruction varies significantly with time and temperature
  - At longer processing time and lower temperature, destruction of pathogen is faster than protein denaturation
  - Can lead to pasteurization of eggs in their shell
Shelf life study

- Shelf life of frozen foods can be predicted at different storage temperature based on kinetics study of products attribute

- Deterioration of quality at different storage temperature can be predicted
Definition of Rate of Reaction

Rate or Reaction

\[ \frac{\text{Change in Amount of Reactant/Product}}{\text{Time Taken for the Change}} \]

\[ r_i = \frac{dN_i}{V \, dt} = \frac{\text{moles } i \text{ formed}}{\text{(volume of fluid) (time)}} \]
Factors that effect the rate of reaction

- Concentration of Reactants
- Pressure (Gas only)
- Nature of Reactants
- Catalyst
- Temperature
- Surface Area
Nature of Reactants

- Acid-base reactions, formation of salts, and exchange of ions are fast reactions.
- Reactions in which large molecules are formed or break apart are usually slow.
- Reactions breaking strong covalent bonds are also slow.
Concentration

- Usually, the higher the concentration the higher the rate.
- The more molecules available per unit volume, the higher the probability of collision.
- The dependence on concentration can be modeled by a rate law equation.

Here we have a few molecules. There are few collisions. The rate of reaction is low.

Here we have many molecules. There are more collisions. The rate of reaction is greater.
Temperature

- Usually, the higher the temperature, the faster the reaction.
- The higher the temperature, molecules move faster and stronger collisions happen between molecules.
- Collision has higher energy to pass the activation energy barrier. Higher probability for reaction to occur.
**Catalyst**

- **Catalysts**: substances used to facilitate reactions without changing forms and being consumed in the reaction
- Catalyst provides a different path for reaction to occur
- It reduce the activation energy barrier
- Reaction can occur faster
Surface Area

- For heterogeneous reaction, the higher the surface area, the more sites for reaction to occur, the faster the reaction.
Think Break

- What is the discipline that studies chemical reactions with respect to reaction rates, effect of various variables, re-arrangement of atoms, formation of intermediates etc?

- Which one of the following reactions reacts the most rapidly at room temperature.
  a. $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$
  b. $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ (neutralization)
  c. $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sugar) $\rightarrow 12 \text{C} + 11 \text{H}_2\text{O}$
  d. $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ (radical reaction)

- Which one of the following burns easily and why?
  a. a bar of steel
  b. steel wool
  c. steel sheet
  d. steel pipe

- Which one takes the least period of time to cook a potato of 10 cm in diameter?
  a. boil in a pressure cooker
  b. boil on top of a 6000-m mountain
  c. bath in a steam
TOPIC 2 :

DETERMINATION OF KINETICS PARAMETERS
Chapter 2 Kinetics of Homogenous Reaction

Suppose a reaction:

- \( aA + bB \rightarrow rR + sS \)
- \( A + \frac{b}{a} B \rightarrow \frac{r}{a} R + \frac{s}{a} S \)

The rates of reaction of all materials are related by:

\[
\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}
\]
Rate Equation

\[-r_A = f[T,c]\]

as an example

\[k c_A^a = k_0 e^{-\frac{E}{RT}} c_A^a\]

Specific reaction rate

activation energy

reaction order

temperature dependent term
The Reaction Order and Rate Law

- Example rate law:
  
  \[-r_A = k_A C_A^\alpha C_B^\beta\]
  
  Reaction is \(\alpha\) order with respect to A and \(\beta\) order with respect to B

  Overall reaction order \(n = \alpha + \beta\)

- Rate law is determined from experimental observation
Zero order reaction

For zero order when \( n=0 \), then

\[-r = \frac{dC_A}{dt} = kC_A^0 = k\]

Integrate this equation

\[dC_A = kdt\]

\[C_A - C_{A0} = -kt\]

*where* \( C_{A0} \) *is the concentration of A at time 0*
Example 1: ascorbic acid loss on multivitamin storage

In a classical investigation of loss of ascorbic acid in a multivitamin mix on storage at different temperatures, the concentrations of ascorbic acid at different times when stored at 50 °C were:

<table>
<thead>
<tr>
<th>TIME (days)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid (mg/ml)</td>
<td>21</td>
<td>19</td>
<td>16</td>
<td>14</td>
<td>12</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

Determine the rate law for ascorbic acid degradation and the kinetics constant

**SOLUTION**

Try zero order reaction: Plot concentration versus time.

The graph clearly shows the linear relationship with time, independent of concentration.

so this is a zero order reaction: 

\[-r = k\]

the rate k can be determined by taking:

\[
\text{rate} = \frac{\text{change in concentration}}{\text{time taken}} = \frac{21 - 8}{70 - 10} = \frac{13}{60} = 0.22 \text{ mg/ml/day}.
\]
Example 1
First Order Reaction

First order \( n = 1 \)

\[ -r = -\frac{dC}{dt} = kC \]

\[ \frac{dC}{C} = -k \, dt \]

\[ \ln \frac{C}{C_0} = -k \, (t-t_0) \]

if \( C=C_0 \) when \( t=t_0 = 0 \)

\[ - \ln \frac{C}{C_0} = kt \]
First Order Reaction

Plot $-\ln C_A/C_{A0}$ versus time
EXAMPLE 2: First order reaction - Hydrolysis of sucrose

The times needed for hydrolysis of sucrose in HCl at 80°C, are given at 50% after 9.1 min, 90% after 30.3 min and 99.9% after 90 min. Find the rate law and the kinetics constant.

Test first order rate law: Plot $\ln \left( \frac{C}{C_0} \right)$ versus $t$. 

Example 2:
Second Order Reaction

\[ n = 2 \]

\[-r = -\frac{dC}{dt} = kC^2\]
\[ dC/C^2 = -k \, dt \]

\[ \frac{1}{C_A} - \frac{1}{C_{A0}} = kt \]

if \( C = C_0 \) when \( t = t_0 = 0 \)

Plot \( \frac{1}{C_A} - \frac{1}{C_{A0}} \) versus \( t \) with slope \( k \)
Plot experimental data using X axis and Y axis to produce a straight line for different orders: 

<table>
<thead>
<tr>
<th>Order</th>
<th>X axis</th>
<th>Y axis</th>
<th>Slope Y/X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 order</td>
<td>time</td>
<td>$C$, $-\ln \frac{C}{C_0}$</td>
<td>$-k$</td>
</tr>
<tr>
<td>1 order</td>
<td>time</td>
<td>$C$, $\left(\frac{1}{C} - \frac{1}{C_0}\right)$</td>
<td>$k$</td>
</tr>
<tr>
<td>2 order</td>
<td>time</td>
<td></td>
<td>$k$</td>
</tr>
</tbody>
</table>

Where ‘$C$’ is typically concentration, but may be some other convenient, consistent measure, and $k$ is the reaction rate constant.
The reaction of chlorophyll degradation can be represented by the equation

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

occurred in a constant volume batch reactor at 50°C. The initial concentration of chlorophyll (A) is 0.1 mg/l. The progress of the reaction was monitored by measuring the concentration of chlorophyll (A) as follows:

<table>
<thead>
<tr>
<th>$t$(min)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_A$(mg/L)</td>
<td>0.33</td>
<td>0.23</td>
<td>0.146</td>
<td>0.096</td>
<td>0.063</td>
</tr>
</tbody>
</table>

- Determine whether the reaction is zero, first or second order and calculate the reaction rate constant, $k$, and its unit.
Solution : tutorial 1

n = 0

\[ y = 0.2084x - 0.0235 \]
\[ R^2 = 0.9991 \]

n = 1

\[ y = 0.2084x - 0.0235 \]
\[ R^2 = 0.9991 \]

n = 2

\[ R^2 = 0.9153 \]
Reactions in parallel

Irreversible reaction in parallel

\[ A \rightarrow R, \quad A \rightarrow S \]

The rate of equations are

\[ -r_A = -\frac{dc_A}{dt} = k_1 c_A + k_2 c_A \]

\[ r_R = \frac{dc_R}{dt} = k_1 c_A, \quad r_S = \frac{dc_S}{dt} = k_2 c_A \]

After integration, it gives

\[ -\ln \frac{c_A}{c_{A0}} = (k_1 + k_2)t \]

and

\[ \frac{r_R}{r_S} = \frac{dc_R}{dc_S} = \frac{c_R - c_{R0}}{c_S - c_{S0}} = \frac{k_1}{k_2} \]
Reversible first order reaction

**First-order reversible reactions**

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

The rate of equations are

\[ -r_A = -\frac{dC_A}{dt} = k_1C_A - k_2C_R \]

At equilibrium, \( \frac{dC_A}{dt} = 0 \), it becomes

\[ K_C = \frac{k_1}{k_2} = \frac{(C_{A0} - C_{Ae})}{(C_{Ae})} \]

Equilibrium Constant

\[ C_{R0} = 0 \]

\[ C_{A0} = \frac{(C_{Ae} - C_{A0})}{(C_{A0} - C_{Ae})} \times k \cdot t \]
Reactions of shifting order

$A \rightarrow R$

With the rate equation

$$-r_A = -\frac{dc_A}{dt} = \frac{k_1c_A}{1+k_2c_A}$$

After integration and linearization, it gives

$$\ln\left(\frac{c_{A0}}{c_A}\right) = -k_2 + \frac{k_1t}{c_{A0} - c_A}$$
The reversible reaction was performed in a batch reactor using pure A ($C_{R_0} = 0$). The following data were obtained from the laboratory experiment. If the equilibrium constant is 9, determine whether the rate can be represented by $-r_A = k_1 C_A - k_2 C_R$ and find $k_1$ and $k_2$. You may use the graph paper to plot the data if needed.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$C_A$ (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>1.27</td>
</tr>
<tr>
<td>40</td>
<td>0.83</td>
</tr>
<tr>
<td>60</td>
<td>0.57</td>
</tr>
<tr>
<td>80</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Solution: tutorial 2

\[ -\ln \left( \frac{C_A - C_{Ae}}{C_{Ao} - C_{Ae}} \right) = \frac{0.0266}{t} \]

\[ R^2 = 0.9997 \]
3.15. At room temperature sucrose is hydrolyzed by the catalytic action of the enzyme sucrase as follows:

\[
sucrose \xrightarrow{\text{sucrase}} \text{products}
\]

Starting with a sucrose concentration \( C_{A0} = 1.0 \text{ millimol/liter} \) and an enzyme concentration \( C_{E0} = 0.01 \text{ millimol/liter} \), the following kinetic data are obtained in a batch reactor (concentrations calculated from optical rotation measurements):

<table>
<thead>
<tr>
<th>( t ), hr</th>
<th>0.84</th>
<th>0.68</th>
<th>0.53</th>
<th>0.38</th>
<th>0.27</th>
<th>0.16</th>
<th>0.09</th>
<th>0.04</th>
<th>0.018</th>
<th>0.006</th>
<th>0.0025</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_A ), millimol/liter</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
</tr>
</tbody>
</table>

Determine whether these data can be reasonably fitted by a kinetic equation

\[
-r_A = -\frac{dc_A}{dt} = \frac{k_1c_A}{1 + k_2c_A}
\]

Find \( k_1 \) and \( k_2 \)
## Solution

<table>
<thead>
<tr>
<th>t</th>
<th>CA</th>
<th>ln(CA_0/CA_0-CA)</th>
<th>t/C_0-CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.84</td>
<td>1.09</td>
<td>6.25</td>
</tr>
<tr>
<td>2</td>
<td>0.68</td>
<td>1.2</td>
<td>6.75</td>
</tr>
<tr>
<td>3</td>
<td>0.53</td>
<td>1.35</td>
<td>6.39</td>
</tr>
<tr>
<td>4</td>
<td>0.38</td>
<td>1.56</td>
<td>6.45</td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
<td>1.80</td>
<td>6.85</td>
</tr>
<tr>
<td>6</td>
<td>0.16</td>
<td>2.18</td>
<td>7.15</td>
</tr>
<tr>
<td>7</td>
<td>0.09</td>
<td>2.65</td>
<td>7.7</td>
</tr>
<tr>
<td>8</td>
<td>0.04</td>
<td>3.36</td>
<td>8.34</td>
</tr>
<tr>
<td>9</td>
<td>0.018</td>
<td>4.08</td>
<td>9.17</td>
</tr>
<tr>
<td>10</td>
<td>0.006</td>
<td>5.15</td>
<td>10.1</td>
</tr>
<tr>
<td>11</td>
<td>0.0025</td>
<td>6.01</td>
<td>11.0</td>
</tr>
</tbody>
</table>

![Graph showing the relationship between ln(CA_0/CA_0-CA) and t/C_0-CA]
Topic 3:

Effect of Concentration on Rate
Time for reaction

- Zero order reaction
  \[ t = \frac{(C_A - C_{A0})}{-k} \]

- First order reaction
  \[ t = \frac{(-\ln C_A/C_{A0})}{k} \]

- Second order reaction
  \[ t = \frac{(1/C_A - 1/C_{A0})}{k} \]
Processing times and rates of reactions
Assume zero order and \( C_{A_0} = 1 \)

<table>
<thead>
<tr>
<th>Rate ((\text{min}^{-1}))</th>
<th>Time ((\text{min}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^2)</td>
<td>0.01 ((0.6\text{s}))</td>
</tr>
<tr>
<td>(10^1)</td>
<td>0.10 ((6\text{s}))</td>
</tr>
<tr>
<td>(10^0)</td>
<td>1.0</td>
</tr>
<tr>
<td>(10^{-1})</td>
<td>10</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>100 ((1.7\text{h}))</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>1000 ((17\text{h}))</td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>10,000 ((7\text{days}))</td>
</tr>
<tr>
<td>(10^{-5})</td>
<td>100,000 ((70\text{days}))</td>
</tr>
</tbody>
</table>
Some practical examples are

- Seconds to 1 min: very short-time flow heat sterilisations, rates $10^1$ to $10^0$ min
- 10 min to 1 hour: heating, cooking, canning, baking, rates $10^{-1}$ to $1.6 \times 10^{-2}$ min$^{-1}$
- 2 hours to a day: curing meat, rates $8.3 \times 10^{-3}$ to $6.9 \times 10^{-4}$ min$^{-1}$
- 10 days to 2 years: ambient, chilled and frozen storage, maturation, rates $7 \times 10^{-5}$ to $1 \times 10^{-6}$ min$^{-1}$
Half life of Reaction for first order reaction

- Time for the concentration to reduce by half \( t_{0.5} \)

First order reaction

\[ \frac{CA}{CA_0} = 0.5 \]

\[ t_{0.5} = \left(-\ln 0.5\right)/k \]

If \( t = 9.1 \text{ min} \)

In 9.1 min the concentration reduce by half and in another 9.1 min it will half again.
Example: sucrose hydrolysis: calculations of concentration with time

To see how concentration change is calculated, consider again the sucrose hydrolysis. It is known that its half-life at a particular temperature is 20 min. This means that starting at a concentration of 0.5 kg sucrose/litre

After 20 min it will have fallen to \((0.50/2) = 0.25\) kg/l, and

After a further 40 min to \((0.25/2^2) = (0.25/4) = 0.063\) kg/l

This can be extended to take into account any desired time by returning to the fundamental first-order equation.

\[
\ln \left\{ \frac{C_0}{C} \right\} = k \cdot t \]

And finding \(k\) from the fundamental first-order constant/half-life relationship of

\[
k = \frac{0.693}{t_{0.5}}\]
Example (contd)

In this case, for a half-life of 20 min, \( k = \frac{0.693}{20} = 0.035 \text{min}^{-1} \)

If the time to reach 0.20kg/l is required, then:

\[
\ln \left( \frac{0.5}{0.20} \right) = \ln (2.50) = 0.92
\]

\[
= k \cdot t
\]

\[
= 0.035 \cdot t
\]

\[
t = \frac{0.92}{0.035}, \text{ so that the required time is 26.3 min}
\]

Or, if the sucrose concentration is wanted after 20 min,

\[
\ln \left( \frac{0.5}{C} \right) = (0.035)(20) = 0.70 \text{ and so}
\]

\[
C = 0.5/\exp(0.70) = (0.5)/2 = 0.25 \text{kg/l}
\]
Effect of reaction order on rate

Relative changes in concentrations with relative times for different values of reaction orders ($n$): 0, 0.25, 0.5, 0.75, 1, 1.5, 2.0, reference curves.
Using the information from the previous sucrose example:
- Work out intermediate sucrose concentration at times: 10, 15, 50, 70 min.
- Work out times for the concentrations to reduce to 60, 70, 80, 90%
TUTORIAL 2:

• Using a hand calculator, arbitrarily select a value for the reaction rate constant (perhaps 1 min^{-1}) and an initial food constituent concentration (perhaps 300 g/l), and, assuming a first order reaction, calculate progressive concentration/time values until the concentration reduces to 1% of its initial value

• Plot the concentrations linearly and logarithmically, against time
Topic 4

Effect of Temperature
Temperature-dependent term of a rate equation

- Elementary reactions rate can be written as:
  \[ r_A = f_1(\text{temperature}) \cdot f_2(\text{composition}) = k \cdot f_2(\text{composition}) \]

- Reaction rate constant can be represented by the Arrhenius’ Law:
  \[ k = k_0 e^{-E/RT}, \text{ E is activation energy} \]

- For n-order reaction, the reaction rate can be simplified as:
  \[ r_A = k_0 e^{-E/RT} \cdot c_A^n \]
Activation Energy

Reaction path

$E_a \rightarrow XY$

$E_a \rightarrow YX$

$\Delta H$

$X$

$Y$
Temperature-dependent term of a rate equation

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

\[ \ln k \quad \text{slope} = - \frac{E}{R} \]

\[ \frac{1}{T} \]

For two different temperature, Arrhenius’ Law indicates as:

\[ \ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]
Temperature Dependency of Reaction

How does temperature affect reaction with high $E$ compared to low $E$?
Activation energies for selected food reactions:  
(Handbook of Food Eng., Heldman & Lund)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation energy (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enzyme reactions</td>
<td>0 - 8</td>
</tr>
<tr>
<td>Chlorophyll degradation</td>
<td>5 - 27</td>
</tr>
<tr>
<td>Ascobic acid</td>
<td>5 - 40</td>
</tr>
<tr>
<td>Anthocyanins</td>
<td>7 - 30</td>
</tr>
<tr>
<td>Alpha-tocopherol</td>
<td>9 - 13</td>
</tr>
<tr>
<td>Trans-retinol</td>
<td>9 - 29</td>
</tr>
<tr>
<td>Hydrolysis of disaccharides</td>
<td>10 - 15</td>
</tr>
<tr>
<td>Carotenoid oxidation</td>
<td>10 - 22</td>
</tr>
<tr>
<td>Lipid oxidation</td>
<td>10 - 25</td>
</tr>
<tr>
<td>Vegetable cell destruction</td>
<td>50 - 150</td>
</tr>
<tr>
<td>Protein denaturation</td>
<td>80 - 120</td>
</tr>
</tbody>
</table>
Example 1: sucrose hydrolysis: reaction rate constants at different temperatures

The reaction rates at different temperatures for the hydrolysis of 50% sucrose solution in 0.1N HCl are given in the International Critical Tables (1).

<table>
<thead>
<tr>
<th>Temptures (T) (°C)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>273</td>
<td>288</td>
<td>303</td>
<td>313</td>
<td>323</td>
</tr>
<tr>
<td>(1/K)</td>
<td>3.67x10⁻³</td>
<td>3.47x10⁻³</td>
<td>3.30x10⁻³</td>
<td>3.19x10⁻³</td>
<td>3.10x10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction rate (k) (min⁻¹)</th>
<th>7.7x10⁻⁶</th>
<th>9.2x10⁻⁵</th>
<th>8.7x10⁻⁴</th>
<th>3.3x10⁻³</th>
<th>1.2x10⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>ln k</td>
<td>-11.77</td>
<td>-9.29</td>
<td>-7.05</td>
<td>-5.71</td>
<td>-4.42</td>
</tr>
</tbody>
</table>

In k is plotted against 1/K to get the Arrhenius plot for sugar hydrolysis.
Sucrose Hydrolysis - Arrhenius Plot

![Arrhenius Plot](image)
Example 1 (contd)

this is a straight-line relationship, so the slope gives the value of:

\[
E/R = (11.77 - 4.42)/(3.67 \times 10^{-3} - 3.1 \times 10^{-3}) = 7.35/0.57 \times 10^{-3} \\
= 12.9 \times 10^{3} K
\]

R, the gas constant, is 8.314 joules/mol K
so \(E\) = 107 \times 10^{3} J/mol
= 107 kJ/mol

To estimate the reaction rate at 110°C, that is 383 K,
\[
k_{383}/k_{323} = \exp \{-E/RT_{383}\}/\exp \{-E/RT_{323}\}
\]
so \(k_{383}/1.2 \times 10^{-2} = \exp \{ER(1/323-1/383)\}
\]
= \exp (12.99 \times 10^{3} (3.096 \times 10^{-3} - 2.611 \times 10^{-3})
\]
= \exp (6.30)
\]
= 545

and so \(k_{383} = 545 \times 1.2 \times 10^{-2}
\]
= 6.54 min\(^{-1}\)

To estimate the time for 50% hydrolysis at 110°C, that is 383 K
\[
-t_{0.5} = (1/6.54)(\ln \frac{1}{2})
\]
= 0.153 \times -0.693
= 0.11 min
In a continuous liquid sterilizing operation, the product need to be heated at a holding temperature of 118 deg C for 7 min. One morning you discover from the product output that fluid pumps has unaccountably increased the flowrate by 30%. The only available way to rectify it in the short term to get usable product is to increase the reaction rate of spore destruction by 30%. This can be done by lifting the holding temperature. To what temperature should you lift it?

- E for bacteria spore destruction = 298 KJ/mol
- R = 8.314 J/mol/K
Other Temperature Coefficients used in Food Industry

- **D value**: Decimal Reduction Time
- The time needed for the amount of reactant to be reduced to 1/10 of its original value (assuming first order reaction)

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

\[
\ln(0.1) = -kD
\]

\[
D = \frac{2.303}{k}
\]
Other Temperature Coefficients used in Food Industry

- z value
- Temperature increase to multiply the rate of the reactions ten fold
- $z$ is defined by $10 = \frac{k_{T+z}}{k_T}$
- $z = 2.303 \frac{RT^2}{E}$
Other Temperature Coefficients used in Food Industry

- Sensitivity

\[
\frac{(k_{T+1})}{(k_T)} = 1 + \text{sensitivity}
\]

The Arrhenius equation is

\[
k = A e^{-ERT}
\]

Taking the derivative \( \frac{dk}{dT} = \frac{d(Ae^{-ERT})}{dT} = \frac{E}{(RT^2)} = k \left[ \frac{E}{(RT^2)} \right] \)

Therefore, \( \frac{dk}{dT} = d(\ln k)/dT = \frac{E}{RT^2} \)

And since \( d(\ln k)/dT = \ln \left[ \frac{(k_{T+1})}{(k_T)} \right] \)

Therefore \( \frac{E}{RT^2} = \ln \left[ \frac{(k_{T+1})}{(k_T)} \right] \)

\[
\exp \left( \frac{E}{RT^2} \right) = \frac{(k_{T+1})}{(k_T)} = 1 + \text{sensitivity}
\]

or \( \exp \left( \frac{E}{RT^2} \right) - 1 = \text{sensitivity} \)
### Activation energies for typical food processing reactions

| Reaction Type                                      | Activation Energy (kJ/mol) | Sensitivity
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical reactions</td>
<td></td>
<td>(40°C)</td>
</tr>
<tr>
<td>General chemical reactions</td>
<td>40-100</td>
<td>13°/°C</td>
</tr>
<tr>
<td>Hydrolysis reactions</td>
<td>60-120</td>
<td>16°/°C</td>
</tr>
<tr>
<td>Lipid oxidations</td>
<td>40-100</td>
<td>13°/°C</td>
</tr>
<tr>
<td>Browning (non-enzymic) reactions</td>
<td>100-200</td>
<td>28°/°C</td>
</tr>
<tr>
<td>Vitamin destruction</td>
<td>70-150</td>
<td>18°/°C</td>
</tr>
<tr>
<td>Protein denaturation/ coagulation</td>
<td>200-500</td>
<td>84°/°C</td>
</tr>
<tr>
<td>Microbiological changes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microorganism growth</td>
<td>100-150</td>
<td>18°/°C</td>
</tr>
<tr>
<td>Vegetative microorganism death</td>
<td>300-500</td>
<td>84°/°C</td>
</tr>
<tr>
<td>Spore death</td>
<td>250-350</td>
<td>53°/°C</td>
</tr>
</tbody>
</table>
Tutorial 1: Loss of ascorbic acid on storage: Arrhenius plot

The reaction rate constants for an investigation of ascorbic acid deterioration in a multivitamin mix during storage at different temperatures were:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>293</td>
<td>303</td>
<td>323</td>
<td>333</td>
<td>343</td>
</tr>
</tbody>
</table>

Reaction rate constant (k)

mg/ml/day⁻¹  6.2x10⁻³  2.4x10⁻²  2.4x10⁻¹  6.6x1⁻¹  1.8x1⁻¹

Determine the activation energy, E, the z value and the sensitivity at 20 deg C and 70 deg C.
Tutorial 2

For three activation energies: 100, 200 and 400 kJ/mol

- Work out the sensitivities at temperatures of 100°C and 110°C
- Determine the ratio of reaction rate constants, \( k_{110}/k_{100} \)
- Reflect on the magnitudes of these numbers and of their significance in a food process in
Tutorial 3

- A batch process is being used for cooking the food product, but the process also cause the breakdown of vitamin C. At present the process is carried out at 121 deg C for 20 min in order to achieve satisfactory cooking. What percentage of vitamin C is destroyed in the current process? (assume first order reaction for both cooking and vitamin)
  - $k_{121} = 3.2 \times 10^{-3} \text{ s}^{-1}$ (for cooking)
  - $k_{121} = 1.57 \times 10^{-4} \text{ s}^{-1}$ (for vitamin C destruction)
- A modification of the process is considered to improve the process with less destruction of vitamin C by reducing the cooking time and increasing the temperature to 130 deg C. What is the new cooking time and what do the changes have on the percentage of vitamin C reduction
  - $z_{\text{cooking}} = 21 \text{ deg C}$
  - $z_{\text{vitamin C}} = 51 \text{ deg C}$
Topic 5

Combining Effect of Time and Temperature
Outcome/Time-Temperature Chart

Following the Arrhenius equation, \( k = k(T) = A \exp(-E/RT) \)

and so \( \frac{dC}{f(C)} = -k(T) \, dt = -A \exp(-E/RT) \, dt \)

\[
\int_{C_0}^{C} \frac{dC}{C} = - \int_{0}^{t} kd\tau = -kt \quad \text{if } k \text{ is constant}
\]

= \ln \frac{C}{C_0} \text{ for a first order reaction}

= \left( \frac{1}{C} - \frac{1}{C_0} \right) \text{ for a second order reaction, and so on.}

For a defined change between the concentrations \( C_0 \) and \( C \), and irrespective of the form that the relationship takes (zero, first, … order), the LHS is constant between any particular limits \( C_0, C \), and therefore the RHS must total to that same constant sum.
Outcome/Time-Temperature Chart

- The product $kt$ is a constant

$$K = kt$$

$$\ln k = \frac{\ln K}{t} = \ln (K) - \ln (t)$$

A plot of $\ln(t)$ versus $1/T$ will produce a straight line with slope $E/R$ but displace vertically by $\ln (K)$
Combining effect of time and temperature

Sucrose hydrolysis – “Arrhenius” plot for time
Data from International Critical Tables (3)

Sucrose hydrolysis – OTT chart
Tutorial 1

- Construct an OTT chart if the processing specifications is 15 s at 72 deg C and assuming a z value of 8 deg C
Application OTT Chart: Pasteurization

- Microbial death confirm to first order kinetics
- Bacterial reduction ratios are much higher than normal reaction requirement
- Typically $10^9$ to $10^{12}$ reduction ratios
- Conveniently abbreviated by 9D or 12D reductions
- OTT chart at different reductions enable the operator to use a combination of time and temperature to get adequate pasteurization
Pasteurization reduces spoilage organisms and pathogens

- 63°C for 30 minutes
- 72°C for 15 seconds
- 140°C for 1 second
OTT chart: pasteurization of milk
Exercise:
If the critical requirement is mesophilic spores must be reduced to 9D, flavour limit and the protease destruction is 90% determine the allowable area for the process.

Destruction of A 50% thiamin; B 10% lysine; C 90% lipase; D 90% protease. Just noticeable appearance of colour and cooked flavour, E. Destruction of F 1% lysine; G 3% thiamine. Reduction by 10° of H thermophilic spores; I mesophilic spores.

Data from Kessler (7)

High-temperature processing of liquid milk OTT chart
Example OTT chart: Food pasteurization

**INTERNAL TEMPERATURES AND TIMES FOR FOOD PASTEURIZATION**

<table>
<thead>
<tr>
<th>Center Temperature, °F</th>
<th>Time, 5D kill (Hamburger)</th>
<th>Time, 6.5D kill (Roast Beef)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>86.42 minutes</td>
<td>112.34 minutes</td>
</tr>
<tr>
<td>135</td>
<td>27.33 minutes</td>
<td>35.53 minutes</td>
</tr>
<tr>
<td>140</td>
<td>8.64 minutes</td>
<td>11.23 minutes</td>
</tr>
<tr>
<td>145</td>
<td>2.73 minutes</td>
<td>3.55 minutes</td>
</tr>
<tr>
<td>150</td>
<td>51.85 seconds</td>
<td>1.12 minutes</td>
</tr>
<tr>
<td>155</td>
<td>16.40 seconds</td>
<td>21.32 seconds</td>
</tr>
<tr>
<td>160</td>
<td>5.19 seconds</td>
<td>6.74 seconds</td>
</tr>
<tr>
<td>165</td>
<td>1.64 seconds</td>
<td>2.13 seconds</td>
</tr>
</tbody>
</table>
Example OTT Chart: Juice pasteurization

For apple juice at pH values of 4.0 or less, FDA recommends the following thermal processes to achieve a 5-log reduction for oocysts of Cryptosporidium parvum. Because this parasite is believed to be more heat resistant than E. coli O157:H7, these parameters will also control bacterial pathogens.

- 160 degrees F for at least 6 seconds
- 165 degrees F for at least 2.8 seconds,
- 170 degrees F for at least 1.3 seconds,
- 175 degrees F for at least 0.6 seconds, or
- 180 degrees F for at least 0.3 seconds

Exercise:
Develop the OTT chart for this data and determine the E value
OTT Chart: pasteurization of liquid whole eggs

Data from Swartzel et al. (19)
Application: Canning/Sterilization

- Killing of *c. botulinum* spores typically up to 12 D
- Reference canning temperature 121.1 deg C (boiling temperature at 2 atmospheric pressure)
- \( D_{121} \) *c. botulinum* = 0.2 min
- \( F_0 \) value is usually encountered in canning = time taken to reduce the spore concentration to 12 D at 121.1 deg C with \( z = 10 \) deg C

Exercise:
- Find a \( F_0 \) value of a sterilization process taking 1 min at 128 deg C
Topic 6

Application of Kinetics Model: Shelf Life Prediction
How LONG Does Food Last?
“the amount of time that a food product is considered acceptable for consumption when stored at the appropriate storage conditions.”
What affects shelf-life of food?

- Composition
  - Water
  - Fat
  - Protein
  - Carbohydrate
  - Other components
- Storage Conditions

Food

Perishable

Shelf Stable
Vitamin Loss

SOURCE: Institute of Food Technologists
Common modes of food deterioration

- Microbial decay - pH, aw
- Senescence - Normal enzymatic reactions in post-harvest physiology of food stuffs
- Non-enzymatic browning - aw, pH, temperature, etc.
- Lipid oxidation - rancidity
- **Hydrolytic Rancidity** - Hydrolysis of triglycerides into fatty acids and glycerol, resulting in a distinctive “soapy” flavor when the product has spoiled
- **Oxidative Rancidity** - Lipid oxidation of unsaturated fatty acids into hydroperoxides, which later form aldehydes, causing a distinctive “cardboard” flavor/aroma when the product has spoiled
- Off flavor - Loss of solubility and biological value of proteins - Bleaching of fat-soluble pigments (carotenoids)
- Loss of efficacy of fat soluble vitamins (A, D, E, and K)
Common modes of food deterioration

- Vitamin loss - Hydrolysis - Light - Heat - Acid - Oxidation • Vitamin C is most labile
- Color changes - Loss of Mg from chlorophyll
- Enzymatic activity - PPO - Pectic enzymes - Lipase
- Sensory changes
- Physical deterioration - Decreased solubility of certain constituents - Mushiness - Freezing-thawing - Melting-recrystallization of fat - Bread staling
Shelf Life Studies

- Direct Method
- Indirect Method (Predictive Model)

  Direct method) for a ‘best-before’ date

This requires the food to be stored for a period of time that is longer than the expected shelf life, in order to observe, test and record changes in the products characteristics.

From this information a shelf life can be estimated.

The shelf life will need to take into account possible variability between product batches and in storage conditions, including whether the product is intended to be consumed over a period of time and so will be subjected to a number of temperature cycles.

For some products it will be important to take into account conditions that could impact unfavourably during normal storage and transport.
Indirect method: General methodology

- Select the major mode of deterioration to study
- Measure some quality factor related to this mode
- Apply mathematical models to make predictions
Kinetics and food deterioration

Why is this technique needed?

- Evaluation of new ingredients -
- Setting of “use by” and best before dates -
- To insure nutritional labelling
Selecting what to measure

In selecting what to measure, consider

- Key labile ingredients
- Characteristics of the packaging material
- How the product will be shipped and stored
- Relative humidity
- Temperature
- Susceptibility to light
- If no chemical test exists, would a sensory test work?
Kinetic approach to accelerating shelf life deterioration

Accelerated shelf life testing is needed to reduce the time needed for study especially during the early stage of product development to evaluate the effect of various parameters

- Concentration acceleration
- Moisture or relative humidity acceleration
- Temperature acceleration - This is usually done
  - The food product is conditioned and stored at elevated temperature and the quality changes of the product are evaluated at a specific sampling rate. The accelerated shelf life study could significantly shorten the duration of shelf life study to ½ or ¼ of the standard shelf life study.
Accelerated Shelf Life Test

- Using the Arrhenius equation
- We can find \( k \) at several higher temperatures (accelerated shelf life study) than the one in which we are interested.
- Then, plot \( \ln k \) vs. \( 1/T \) to get a straight line which you can extrapolate to lower temperatures.
Case study

Asceptic packaged simulated orange drink product

Simulated orange drink product

Use by: ???????

How do I establish my “use by” date?
Case Study

- On the label of my asceptic packaged orange drink product it states that each serving provides 100% of the % DV for vitamin C. I know that vitamin C is the most labile constituent of my product, therefore I can use it as a marker.

- %DV = 60 mg
Case Study

- Number of servings per package = 6
- Total minimum vitamin C needed in package at time of consumption = 360 mg
- To account for breakdown, I add enough vitamin C to make the total at manufacture = 720 mg
- Question: How do I determine my “use by” date?
Case Study

- Answer: Do an accelerated shelf life study. Measure k at C (323, 333, and 343°K)
- Do an Arrhenius plot
Case Study

Extrapolate to storage temperature, in this case 25 degrees C (298 deg K).
Case Study

- At 25 C (298 °K), $k_1 = 3.1 \times 10^{-3}$ days$^{-1}$
- My maximum allowable loss occurs when the [vitamin C] reaches one-half of its initial level, that is, at the half-life for vitamin C under these conditions.
- First order equation
  - $t_{1/2} = \frac{0.693}{k_1} = \frac{0.693}{3.1 \times 10^{-3}}$
- $t_{1/2} = 224$ days
Case Study: Shelf Life of Frozen Fish

- How to measure fish quality?
- One method: Formation of trimethylamine - results in off-odor from bacterial growth and activity in fish flesh

Data from Lovern, quoted in Bate-Smith & Morris (25)

*Storage of fish on ice – generation of trimethylamine*
Case Study: Shelf Life of Frozen Fish

Grades: A = Excellent to very good, B = Good, C = Satisfactory
Data from Kuprianoff (26)

Storage of chilled fish: OTT plot of time and temperature
Example: Time-temperature chart

Shelf life of frozen strawberry

Shelf life plot for frozen strawberries from Guadagni (1968)
Nutrition is an important part of ready-to-eat cereal. To make cereal healthier many nutrients are added. Unfortunately, nutrients degrade over time, making it necessary to add more than the declared amount to assure enough for the life of the cereal. Vitamin V1 is declared at a level of 20% of the Recommended Daily Allowance per serving (serving size = 30 g). The recommended daily allowance is 6500 IU (1.7 \times 10^6 \text{ IU} = 1 \text{ g}). It has been found that the degradation of this nutrient is first order in the amount of nutrients. Accelerated storage tests have been conducted on this cereal, with the following results:

- Temp (deg C) 45 55 65
- k (week^{-1}) 0.0061 0.0097 0.0185

Given this information and the fact that the cereal needs to have a vitamin level above the declared value of 6500 IU for 1 year at 25 deg C, what IU should be present in the cereal at the time it is manufactured?
Biochemical Reactions

Topic 7-8
INTRODUCTION OF BIOCHEMICAL REACTIONS

Biochemical reactions

Fermentation
- yeast
- bacteria
- algae
- molds
- protozoa

Enzymatic reactions
- high molecule weight compound protein, has specific active site for converting substrate to desired product
Microbial Fermentation

(organic feed, $A$) \( \rightarrow \) (product, $R$) + (more cells, $C$)

In fermentation, the cell or microbe, reproduces itself.

Enzymatic Reactions

(organic feed, $A$) \( \rightarrow \) (product, $R$)

Enzyme as biocatalyst, which does not reproduce itself.
Enzymatic Reactions

Michaelis-Menten kinetics

\[ A \rightarrow E \rightarrow R \]

\[ -r_A = r_R = k \frac{C_{E0}C_A}{C_M + C_A} \]

Total enzyme

Michaelis constant

Proposed reaction mechanisms

\[ A + E \xrightarrow{1} X \xrightarrow{3} R + E \]

Intermediate

\[ C_{E0} = C_E + C_X \]

Free enzyme

Enzyme attached to reactant
M-M Kinetics

Assumptions

\[ [E_0] = [E] + [X] \]

\[
\frac{d[R]}{dt} = k_3[X]
\]

\[
\frac{d[X]}{dt} = k_1[A][E] - k_2[X] - k_3[X] = 0
\]

\[
\frac{dX}{dt} \approx 0
\]

\[
[X] = \frac{k_1[A][E_0]}{(k_2 + k_3) + k_1[A]}
\]

\[
\frac{d[R]}{dt} = \frac{k_1k_3[A][E_0]}{(k_2 + k_3) + k_1[A]} = \frac{k_3[A][E_0]}{[M] + [A]}
\]

\[ [M] = \left(\frac{k_2 + k_3}{k_1}\right) \]

is called the Michaelis constant
Rate: \(-r_A = r_R\)

First order behavior when \(C_A \ll C_M\)

Zero order behavior when \(C_A \gg C_M\)

Rate-concentration curve for Michaelis–Menten kinetics

\[ r = \frac{r_{\text{max}}}{2} = \frac{k_3 C_{E0}}{2} \]

Initial slope:

\[ = \left( \frac{k_1 k_3}{k_2 + k_3} \right) C_{E0} \]

\[ C_A = C_M = \frac{k_2 + k_3}{k_1} \]
Michaelis-Menten kinetics (Batch/Plug flow bioreactors) Integration gives

\[-r_A = r_R = \frac{k_3 C_{E0}}{C_M} \frac{C_A}{1 + \frac{C_A}{C_M}}\]

\[c_M \ln \frac{C_{A0}}{C_A} + (C_{A0} - C_A) = k_3 C_{E0} t\]

See page 59 (O. Levenspiel)

1st order

Zero order

First order is approached at low \(C_A\)

Shift at \(C_A = C_M\)

Zero-order is approached at high \(C_A\)

Eq. 5
Michaelis-Menten kinetics (Batch/Plug flow bioreactor)

After rearranging, it gives

\[
\frac{c_{A0} - c_A}{\ln \frac{c_{A0}}{c_A}} = -c_M + k_3 c_{E0} \frac{t}{\ln \frac{c_{A0}}{c_A}}
\]
Michaelis-Menten kinetics (Mixed flow bioreactors)

\[ \tau_m = \frac{c_{A0} - c_A}{-r_A}, \text{ thus } k_3 c_{E0} \tau_m = \frac{(c_{A0} - c_A)(c_M + c_A)}{c_A} \]

Rearranged as

\[ c_A = -c_M + k_3 \left( \frac{c_{E0} c_A \tau_m}{c_{A0} - c_A} \right) \]
ENZYMATIC REACTIONS

Competitive and noncompetitive inhibition by a foreign substance

Foreign substance (B) causes slowdown of the enzyme-substrate reaction of A to R, B is called inhibitor
Kinetic of competitive inhibition

\[ A + E \xrightarrow{1} X \xrightarrow{3} R + E \]

\[ B + E \xrightarrow{2,4} Y \xrightarrow{5} \]

\[ -r_A = r_R = \frac{k_3 c_{E0} c_A}{c_M + c_A + N c_{B0} c_M} = \frac{k_3 c_{E0} c_A}{c_M (1 + N c_{B0}) + c_A} \]

where \( c_M = \frac{k_2 + k_3}{k_1} \), \( N = \frac{k_4}{k_5} \)
ENZYMATIC REACTIONS

Kinetic of competitive inhibition
Compared to system without inhibition, replace $c_M$ by $c_M(1+Nc_{B0})$, thus

For batch/plug flow bioreactor

$$
\frac{c_{A0} - c_A}{\ln \frac{c_{A0}}{c_A}} = -c_M (1 + Nc_{B0}) + k_3 c_E0 \frac{t}{\ln \frac{c_{A0}}{c_A}}
$$

For mixed flow bioreactor

$$
c_A = -c_M (1 + Nc_{B0}) + k_3 \left( \frac{c_E0 c_A \tau_m}{c_{A0} - c_A} \right)
$$
Kinetic of noncompetitive inhibition

\[ \begin{align*}
A + E & \xrightarrow{1} X \xrightarrow{3} R + E \\
\xleftarrow{2} B + E & \xrightarrow{4} Y, \quad B + X \xrightarrow{6} Z \\
\xleftarrow{5} & \xleftarrow{7}
\end{align*} \]

\[ -r_A = r_R = \frac{k_3 c_{E0} c_A}{c_M + c_A + N c_{B0} c_M + L c_A c_{B0}} = \frac{k_3}{1 + L c_{B0}} \frac{c_{E0} c_A}{c_M \left( \frac{1 + N c_{B0}}{1 + L c_{B0}} \right) + c_A} \]

where \( c_M = \frac{k_2 + k_3}{k_1}, \quad N = \frac{k_4}{k_5}, \quad L = \frac{k_6}{k_7} \)
Kinetic of noncompetitive inhibition
Compared to system without inhibition, replace $k_3$ and $c_M$ by $k_3/(1+Lc_{B0})$ and $c_M(Nc_{B0})/(1+Lc_{B0})$, thus

For batch/plug flow bioreactor

$$
\frac{c_{A0} - c_A}{\ln \frac{c_{A0}}{c_A}} = -c_M \left( \frac{1 + Nc_{B0}}{1 + Lc_{B0}} \right) + \frac{k_3}{1 + Lc_{B0}} c_{E0} \frac{t}{\ln \frac{c_{A0}}{c_A}}
$$

For mixed flow bioreactor

$$
c_A = -c_M \left( \frac{1 + Nc_{B0}}{1 + Lc_{B0}} \right) + \frac{k_3}{1 + Lc_{B0}} \left( \frac{c_{E0}c_A \tau_m}{c_{A0} - c_A} \right)
$$
Kinetic of competitive and noncompetitive inhibition for batch/plug flow bioreactors

**Competitive**

\[
\frac{C_{A_0} - C_A}{\ln \frac{C_{A_0}}{C_A}} = \frac{C_M}{k_3} + \frac{k_3 C_M (1 + NC_{B_0})}{k_3}
\]

This curve from Fig. 5

No inhibition

Slope = \(k_3\)

**Noncompetitive**

\[
\frac{C_{E_0}t}{\ln \frac{C_{A_0}}{C_A}} = \frac{C_M}{k_3} + \frac{k_3 C_M (1 + NC_{B_0})}{k_3}
\]

This curve from Fig. 5

No inhibition

Slope = \(\frac{k_3}{1 + LC_{B_0}}\)
Kinetic of competitive and noncompetitive inhibition for mixed flow bioreactors
Microbial Fermentation

Cell is reproducible, the composition of the substrate changes, and product which can be toxic to the cells forms

\[ A \rightarrow cC + rR \]

![Graph showing the life cycle of microbial fermentation with stages: Lag, Exponential growth, Stationary, and Cells start dying.] (Time)

Cells start to die because depletion of food or accumulation of toxic material to the cells (product or biomass)
Microbial Fermentation

\[
A \rightarrow cC + rR
\]

After the time lag, the cells growth rate is given by Monod as

\[
r_C = \frac{kc_A c_C}{c_A + c_M}
\]

\[
\begin{align*}
A + C_{\text{resting}} & \rightleftharpoons C_{\text{pregnant}} \\
C_{\text{pregnant}} & \rightarrow 2C_{\text{resting}} + R \\
\text{and } C_{\text{total}} &= C_{\text{pregnant}} + C_{\text{resting}}
\end{align*}
\]
Limiting Mechanism

**Substrate limiting**
(final $C_C$ depends on the initial amount of food. Product does not affect the rate)

- **Start with much food**
- **Rapid growth**
- **Curve for high $C_{A0}$**
- **Start with little food**
- **Slow growth**
- **Low $C_{A0}$**

**Poison limiting**
($C_C$ never exceeds a certain value. Product slows and then stops the reaction)

- **High $C_{A0}$**
- **Rapid growth**
- **Low $C_{A0}$**
- **Slow growth**
Microbial Fermentation

The instantaneous fractional yields are defined as

\[ A \rightarrow cC + rR \]

\[ \varphi(C/A) = \frac{dc}{-dA} \]

\[ \varphi(R/A) = \frac{dR}{-dA} \]

\[ \varphi(R/C) = \frac{dR}{dc} \]

For the reaction rates,

\[ r_C = -r_A \varphi(C/A) \]

\[ r_R = -r_A \varphi(R/A) \]

\[ r_R = r_C \varphi(R/C) \]

When \( \varphi \) values stay constant, can be written as,

\[ c_c - c_{c0} = \varphi(C/A)(c_{A0} - c_A) \]

\[ c_R - c_{R0} = \varphi(R/A)(c_{A0} - c_A) \]

\[ c_R - c_{R0} = \varphi(R/C)(c_c - c_{c0}) \]
Effects of Harmful Waste

• As Harmful product increase, the observed rate constant starts to decrease

\[ k_{\text{obs}} = k \left( 1 - \frac{C_R}{C_R^*} \right)^n \]

order of product poisoning

rate constant in the absence of harmful waste material

\[ r_C = -r_A \frac{C}{A} = r_R \frac{C}{R} = k_{\text{obs}} \frac{C_A C_C}{C_A + C_M} \]

generalized Monod equation

\[ k_{\text{obs}} \text{ decreases as } C_R \text{ rises} \]

...where...

\[ k_{\text{obs}} = k \left( 1 - \frac{C_R}{C_R^*} \right)^n \]

concentration where all reaction stops

Activity stays high until close to \(C_R^*\)

Linear decrease in rate constant as \(R\) builds up

\(n = \frac{1}{2}\)

Rapid initial drop in \(k\)

\(n = 1\)

\(n = 2\)

Concentration of waste where all cell activity stops
Substrate Limiting Microbial Fermentation

\[ A \rightarrow cC + rR \]

\[ r_C = \varphi \left( \frac{C}{A} \right)(-r_A) = \frac{kc_A c_C}{c_A + c_M}, \]

\[ c_C - c_{C0} = \varphi \left( \frac{C}{A} \right)(c_{A0} - c_A) \]
Substrate Limiting: Batch Plug Flow Fermentors

**Performance equation:**

\[ t_b = \tau_p = \int_{c_{c0}}^{c_c} \frac{dc_C}{r_c} = \frac{1}{k} \int_{c_{c0}}^{c_c} \frac{c_A + c_M}{c_C c_A} dc_C \]

**Integration gives:**

\[ kt_b = k\tau_p = \left( \frac{c_M}{c_{A0} + \varphi(A/C)c_{c0}} + 1 \right) \ln \frac{c_C}{c_{c0}} - \left( \frac{c_M}{c_{A0} + \varphi(A/C)c_{c0}} \right) \ln \frac{c_A}{c_{A0}} \]
\[ kt_b = k\tau_p = \left( \frac{c_M}{c_{A0} + \varphi(A/C)c_{C0}} + 1 \right) \ln \frac{c_C}{c_{C0}} - \left( \frac{c_M}{c_{A0} + \varphi(A/C)c_{C0}} \right) \ln \frac{c_A}{c_{A0}} \]

After rearranging, it gives

\[ \frac{t_b}{\ln(c_C/c_{C0})} = \frac{M + 1}{k} + \frac{M}{k} \frac{\ln(c_{A0}/c_A)}{\ln(c_C/c_{C0})} \]

with \( M = \frac{c_M}{c_{A0} + \varphi(A/C)c_{C0}} \)
Substrate Limiting: Mix Flow Fermentors

Design Equation

\[ \tau_m = \frac{\Delta c_i}{r_i} \]

\[ c_{c0} = 0, \]

Feed stream contains no cells:

\[ k\tau_m = \frac{c_A + c_M}{c_A} \]

Term of \( c_A \)

\[ k\tau_m = \frac{\varphi(C/A)(c_A + c_M) - c_C}{\varphi(C/A)c_{A0} - c_C} \]

Term of \( c_C \)

\[ k\tau_m = \frac{\varphi(R/A)(c_{A0} + c_M) - c_R}{\varphi(R/A)c_{A0} - c_R} \]

Term of \( c_R \)
Substrate Limiting: Mix Flow Fermentors

\[ \tau_m = \frac{\Delta c_i}{r_i} \]

Feed stream contains cells, \( c_{c0} \neq 0 \), the performance equation gives

\[ k \tau_m = \frac{(c_{A0} - c_A)(c_A + c_M)}{\varphi(A/C)c_{c0}c_A + c_A(c_{A0} - c_A)} \]

Term of \( c_A \)

\[ k \tau_m = \frac{\varphi(C/A)(c_{A0} - c_A)(c_A + c_M)}{c_{c0}c_A + \varphi(C/A)c_A(c_{A0} - c_A)} \]

Term of \( c_C \)
Substrate Limiting: Mix Flow Fermentors

Substrate-limiting (Mixed flow fermentors)

\[ k \tau_m = \frac{C_A + C_M}{C_A} \]

After rearranging, it becomes

\[ \frac{1}{C_A} = \frac{k}{C_M} \tau_m - \frac{1}{C_M} \]
Substrate Limiting: Mix Flow Fermentors

**Substrate-limiting (Mixed flow fermentors)**

Optimum operations of a single mixed flow fermentor

\[
\frac{c_A}{c_{A0}} = \frac{1}{N + 1}
\]

\[
\frac{c_C}{c_{C, \text{max possible}}} = \frac{N}{N + 1}
\]

\[
k\tau_{opt} = \frac{N}{N - 1}
\]
Product Limiting: Microbial Fermentation

$$A \rightarrow cC + rR$$

$$r_C = \varphi \left( C / R \right) (-r_R) = k \left( 1 - \frac{c_R}{c_R^*} \right)^n \frac{c_A c_C}{c_A + c_M}$$

If $c_A \gg c_M$, $n = 1$, it becomes

$$r_C = \varphi \left( C / R \right) (-r_R) = k \left( 1 - \frac{c_R}{c_R^*} \right) c_C$$

Term of $c_R$, it becomes

$$r_R = k \left( 1 - \frac{c_R}{c_R^*} \right) \left( c_R - c_{R0} + \varphi \left( R / C \right) c_{C0} \right)$$
Product Limiting: Microbial Fermentation

Maximum rate, where \( \frac{dr_R}{dc_R} = 0 \)

\[
c_{R, \text{max rate}} = \frac{1}{2} \left( c_{R0} + c^* - \varphi \left( \frac{R}{C} \right) c_{C0} \right)
\]
Product Limiting: Microbial Fermentation
(Batch/Plug Flow Reactor)

Product-limiting (Batch/Plug flow fermentors)
\( n = 1 \)

**High** \( c_{A0} \)
\( c_{c0} \neq 0 \)
Any \( c_{r0} \)

\( c_{A} \approx c_{A0} \)
\( c_{C} \)
\( c_{R} \)

\[ t_b = \tau_P = \int_{c_{R0}}^{c_R} \frac{dc_R}{r_R} = \int_{c_{R0}}^{c_R} \frac{dc_R}{k \left(1 - \frac{c_R}{c_R^*}\right) \left(c_R - c_{R0} + \varphi \left(\frac{R}{C}\right) c_{C0}\right)} \]

After integration, it becomes

\[ k\tau_P = \frac{c_R^*}{c_R - c_{R0} + \varphi \left(\frac{R}{C}\right) c_{C0}} \ln \frac{c_C \left(c_R^* - c_{R0}\right)}{c_{C0} \left(c_R^* - c_R\right)} \]
Product Limiting: Microbial Fermentation
(Batch/Plug Flow Reactor)
Product Limiting: Microbial Fermentation (Mixed Flow Reactor)

\[ n = 1 \]

With negligible time lag and for high \( c_A \)

\[
\tau_m = \frac{c_R - c_{R0}}{r_R} = \frac{c_R - c_{R0}}{k \left(1 - \frac{c_R^*}{c_R}\right) \left(c_R - c_{R0} + \varphi \left(\frac{R}{C}\right)c_{C0}\right)}
\]

When \( c_{C0} = 0 \) and \( c_{R0} = 0 \), it is simplified as

\[
k\tau_m = \frac{c_R^*}{c_R - c_R} = \frac{1}{1 - \frac{c_R^*}{c_R}}, \quad \text{for } k\tau_m > 1
\]
Product Limiting: Microbial Fermentation (Mixed Flow Reactor)

After rearranging, it becomes

\[ C_R = C_R^* - \frac{C_R}{k} \frac{1}{\tau_m} \]
Product Limiting: Microbial Fermentation (Mixed Flow Reactor)

\[ k\tau_m = \frac{C_R^*}{C_R - C_R} \]

This graph only for \( C_{C0} = 0 \) and \( C_{R0} = 0 \)

Maximum possible \( C_R \)

Initial slope

Largest slope (the tangent to the curve) gives the highest production rate of \( R \)

Best operating conditions are represented by this point. Here

\[ F_R, \text{max} = (vC_R)_{\text{opt}} = \frac{kV C_R^*}{4}, \quad \left[ \text{mol R} \right] \]

Optimum \( \tau \) is just double \( \tau_{\text{washout}} \)
Topic 9  Reactor Design

• Elements of reaction kinetics
  – Rates of which different reaction occurs
  – Factors that affect reaction rates
  – Reactions mechanisms
  – Rate limiting steps that control the reaction
  – Mathematical model describing reaction rate

  ‣ Elements of Reactor Design
    – Exploitation of chemical reaction in commercial scale
    – Sizing of chemical reactor
    – Determination of best process conditions i.e flow, temperature, pressure for optimum performance
    – Types of reactors: Flow patterns
    – Arrangement of reactors: staged, recycle etc
    – How materials behave (chemically and physically) within a reactor
Figure 5.1 The three types of ideal reactors: (a) batch reactor, or BR; (b) plug flow reactor, or PFR; and (c) mixed flow reactor, or MFR.
Mole Balances and Energy Balances

• Fundamental principle
• Starting point to develop design equation for different type of reactors
Mole balances

\[
\text{rate of reactant flow into element of volume} = \text{rate of reactant flow out of element of volume} + \text{rate of reactant loss due to chemical reaction within the element of volume} + \text{rate of accumulation of reactant in element of volume}
\]
Reactants are initially charged into a container, are well mixed, and are left to react for a certain period. Finally, the products are discharged.

Unsteady-state operation
**IDEAL BATCH REACTOR**

**Mass balance of A**

\[
\text{input} = \text{output} + \text{disappearance} + \text{accumulation}
\]

\[
\begin{align*}
\left(\text{Disappearance of A by reaction}\right) = (-r_A) V &= \left( \text{moles A reacting} \right) \left( \frac{\text{time}}{\text{volume of fluid}} \right) \\
\left(\text{Accumulation of A}\right) &= \frac{dN_A}{dt} = \frac{d \left[ N_{A0} (1 - X_A) \right]}{dt} = -N_{A0} \frac{dX_A}{dt}
\end{align*}
\]

\[
(-r_A) V = N_{A0} \frac{dX_A}{dt}
\]
Rearranging and integrating then gives

\[ t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)V} \]

\[ t = \text{residence time, time required to achieve a conversion, } X_A \]

For constant volume/density, plot a graph \( 1/(-r_A) \) vs \( X_A \) or \( c_A \) from equation

\[ t = c_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} = - \int_{c_{A0}}^{c_A} \frac{dc_A}{-r_A}, \quad \varepsilon_A = 0 \]

For varying volume/density, plot a graph \( 1/\left[(-r_A)(1+\varepsilon_A X_A)\right] \) vs \( X_A \) from equation

\[ t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)V_0(1+\varepsilon_A X_A)} = c_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)}, \quad \varepsilon_A \neq 0 \]
IDEAL BATCH REACTOR

General case

\[ \frac{1}{(-r_A)V} \]

Area = \( t/N_{AO} \)

\[ \frac{1}{r_A} \left( 1 + \varepsilon X_A \right) \]

Area = \( t_C \)

Constant density

\[ -\frac{1}{r_A} \]

Area = \( t_C \)
Tutorial 1

• Liquid A decomposed by a second order kinetics. In batch reactor 50% of A is converted in a 5 minute run. How much longer would it take to reach 75 % conversion?
Example

• Liquid reaction $A \rightarrow R$ is to be performed in a batch reactor. The rate of the reaction is given in the table below. If the initial $A$ concentration is 1.3 mol/L, how long does it need to reduce the concentration to 0.3 mol/L?

<table>
<thead>
<tr>
<th>$C_A$ (mol/L)</th>
<th>$-r_A$ mol/L.min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.6</td>
<td>0.25</td>
</tr>
<tr>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>0.8</td>
<td>0.06</td>
</tr>
<tr>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>1.3</td>
<td>0.045</td>
</tr>
<tr>
<td>2</td>
<td>0.042</td>
</tr>
</tbody>
</table>
With a bit more thought we see that we were not asked to find a rate equation, we were just asked for $t$, and that this could be done by solving the general design equation, Eq 4 directly by graphical procedures. Let us do this.

\[
\text{Area} = t = \int \frac{C_{a0}}{r_A} \frac{dC_A}{C_{Af}}
\]

thus

\[
t = \left[12.75 \ \text{lit. min/mol} \right] \cdot \left[1.3 - 0.3 \ \text{mol/Lit} \right]
\]

or

\[
t = 12.75 \ \text{min}
\]

This is the more general way of solving this problem since it does not require that we describe the rate by an equation.
It is assumed that the inlet is completely and instantly mixed into the reactor.

Reactor and the outlet have identical, homogenous composition at all times.

Continuous operation.
Mass balance

\[ \text{input} = \text{output} + \text{disappearance} + \text{accumulation} = 0 \]

\[ F_{A0} = \nu_0 c_{A0} \]

\[
\begin{align*}
\text{Input of A} \\
\text{(moles/time)}
\end{align*}
\] = \( F_{A0}(1 - X_{A0}) = F_A \)

\[
\begin{align*}
\text{Output of A} \\
\text{(moles/time)}
\end{align*}
\] = \( F_A = F_{A0}(1 - X_A) \)

\[
\begin{align*}
\text{(Disappearance of A)} \\
\text{by reaction} \\
\text{(moles/time)}
\end{align*}
\] = \((-r_A)V = \left( \frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right)(\text{volume of reactor}) \]

\[ F_{A0}X_A = (-r_A)V \]
Rearranging then gives

\[
\frac{V}{F_{A0}} = \tau = \frac{\Delta X_A}{-r_A} = \frac{X_A}{-r_A}
\]

\(\tau = \) space time, time required to process a reactor volume of feed measured at specific conditions

For any \(\varepsilon_A\), space time is determined by

\[
\tau = \frac{V}{\nu_0} = \frac{Vc_{A0}}{F_{A0}} = \frac{c_{A0}X_A}{-r_A}
\]

For \(\varepsilon_A = 0\), space time is determined by

\[
\tau = \frac{V}{\nu_0} = \frac{c_{A0}X_A}{-r_A} = \frac{c_{A0} - c_A}{-r_A}
\]
Space-time:

\[
\tau = \frac{1}{s} = \left( \frac{\text{time required to process one reactor volume of feed measured at specified conditions}}{\text{[time]}} \right)
\]
General case

\[
\text{Area} = \frac{V}{F_{A0}} = \frac{\tau}{C_{A0}}
\]
from Eq. 11

\[
\frac{-1}{r_A}
\]

Conditions within reactor and at exit

Constant density

\[
\text{Area} = \tau = \frac{VC_{A0}}{F_{A0}}
\]
from Eq. 13

\[
\frac{-1}{r_A}
\]
**Tubular (Plug Flow) Reactor (PFR):**

\[
\begin{align*}
\text{reactants} & \quad \rightarrow \quad \Delta V \\
\Delta y & \quad \rightarrow \quad \text{products}
\end{align*}
\]

\[
F_A(y) \quad \rightarrow \quad \Delta V \\
\rightarrow \quad F_A(y+\Delta y)
\]
Mole Balance Applied to Flow Reactors

- Tubular (Plug Flow) Reactor (PFR):

Input = output + dissapearance + accumulation

\[ F_{Ao} = F_A - \int_{0}^{\Delta V} r_A dV + \frac{dN_A}{dt} \]

\[ F_{Ao} + r_A \Delta V - F_A = 0 \quad \text{spatially uniform } \Delta V \]

\[ F_A(y) - F_A(y + \Delta y) + r_A(A\Delta y) = 0 \quad \text{uniform cross-section} \]
Mole Balance Applied to Flow Reactors

- **Tubular (Plug Flow) Reactor (PFR):**

\[
\begin{align*}
- \left[ \frac{F_A (y + \Delta y) - F_A (y)}{\Delta y} \right] = -r_A A \\
\frac{dF_A}{dy} = r_A A = r_A \frac{dV}{dy}
\end{align*}
\]

\[
\lim_{\Delta x \to 0} \left[ \frac{f(x + \Delta x) - f(x)}{\Delta x} \right] = \frac{df}{dx}
\]

\[
\begin{align*}
\frac{dF_A}{dV} = r_A
\end{align*}
\]
Conversion

\[
\frac{dF_A}{dV} = r_A \\
F_A = F_{A_0}(1 - X)
\]

\[
F_{A_0} \frac{dX}{dV} = -r_A \\
V = F_{A_0} \int_0^X \frac{dX}{-r_A}
\]

differential form \hspace{1cm} \text{integral form}
Rate law

\[ F_{Ao} \frac{dX}{dV} = -r_A \]

\[ -r_A = kC_A = kC_{Ao}(1 - X) \]

\[ -r_A = kC_A C_B \]

Relate \( C_A \) and \( C_B \) using stoichiometric table
Graphical Representation

\[ V = F_{Ao} \int_{0}^{X} \frac{dX}{-r_{A}} \]

**General case**

Area = \( \frac{V}{F_{A0}} = \frac{t}{C_{A0}} \),
from Eq. 17

**Constant density**

Area = \( t = \frac{C_{A0}V}{F_{A0}} \),
from Eq. 19

\( r-C \) curve for the reaction
Reaction Kinetics and Introduction to Reactor Design in Food Production

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Required Text: Earle, R. Earle ,M., Fundamentals of Food Reaction Technology


Course Description: This course covers the fundamental of reaction kinetics and its application in food processing. The kinetic models of various reaction types are developed. Evaluation of kinetics parameters are made. Effect of temperature, concentration and time on the kinetic models are discussed. The kinetics models are then applied to various processes in the food production. The design of ideal reactors are also treated at an introductory level.

Course Objectives:

1. Students will learn the kinetics models of various types of reaction and the method to determine the kinetic parameters from batch reactor data.
2. Students will learn to predict the concentration, temperature and processing time requirement based on the kinetics model.
3. Students will apply the kinetics models of various food processes particularly pasteurization, sterilization, cooking and shelf life study.
4. Students will have basic knowledge of the design of ideal reactors used in food processing.

Topical Outline of the Course Content:

SUBJECTS

Introduction to Reaction Kinetics in Food Processing
Changes and Reactions in Food Material during Processing
Important Application of Kinetics in Food Processing
Factors Affecting Rate of Reactions

**Determination of Kinetics Parameters**
- Zero Order Reaction
- First Order Reaction
- Second Order Reaction
- Reversible Reaction
- Parallel Reactions
- Reaction of Shifting Order

**Effect of Concentration**
- Determination of Time and Concentration
- Half life of Reaction
- Effect of Reaction Order on Rate

**Effect of Temperature**
- Dependency on Temperature: Arrhenius Equation
- Activation Energy
- \( z, D, F, \) sensitivity and \( Q \) values

**Combining Effect of Temperature and Time**
- Outcome Time and Temperature Chart
- Application in Food Processes

**Case Studies: Pasteurization, Sterilizations and Shelf Life of Food**
- Application of kinetics models to predict Pasteurization/Sterilization Time and Temperature
- Shelf Life Prediction using Kinetics Model: Accelerated Storage Test

**Kinetics of Enzymatic Reaction**
- Michaelis Menten Kinetics
- Inhibition Effect

**Kinetics of Microbial Growth**
- Monod Kinetics
- Substrate Limiting
- Product Limiting

**Design of Mixed Flow Reactor**
- Mass Balance Fundamental
- Determination of Reactor Size and Conversion

**Design of Plug Flow Reactor**
- Mass Balance Fundamental
- Determination of Reactor Size and Conversion
Grading Policy

Class participation: Attendance is required as all exam questions will come directly from class discussion. Attendance will constitute 10% of the grades.

Tests: There will be a Test 1 that constitute 20% of your grade and a Final Exam that constitute 70% of your grade. The Final is Cumulative!

If you have any question – ASK!!! If I am going too fast, please ask me to slow down.

To help encourage the proper educational environment and out of courtesy for your fellow classmates, please turn of all cell phones prior to entering the classroom and be on time.