Kinetics and Rates of Reactions

CEE 373
Roadmap

SANDBOX

Modeling concepts, scales and approaches

SANDBOX

Programming languages, software engineering & numerical methods

DESIGN

Project Proposal

IMPLEMENTATION

Examination of Equilibrium-based Code

IMPLEMENTATION

Examination of Reaction Rate-based Code

IMPLEMENTATION

Examination of Existing Models for Complex Systems

IMPLEMENTATION

Visualization, Interface Design and Usability

READINESS

Internal Testing and Code Freeze

RELEASE

Final Presentations ("Rollout")
OBJECTIVES
1. Build a modeling framework for reaction rate-limited chemistry.
2. Examine and understand computer code.
3. Produce model results and interpret critically.
1. Rate-Limited Reactions
2. Kinetics of Nitrification in a Batch Reactor
   • Derivation of expressions used in model
   • Temperature effect on rate constant
   • Implementation in computer code
3. Kinetics of Nitrification in a Column Reactor
   • Expressions used in model
4. Michaelis-Menten Kinetics
   • Substrate-limited reaction rates
# Rate-Limited Reactions

## SIMPLE IRREVERSIBLE REACTION EXAMPLES

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Order</th>
<th>Rate Law</th>
<th>Concentration Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A \rightarrow B$</td>
<td>Zero</td>
<td>$-\frac{d[A]}{dt} = k_0$</td>
<td>$[A] = [A]_0 - k_0 t$</td>
</tr>
<tr>
<td>$A \rightarrow B$</td>
<td>First</td>
<td>$-\frac{d[A]}{dt} = k_1[A]$</td>
<td>$\ln \frac{[A]}{[A]_0} = k_1 t$</td>
</tr>
</tbody>
</table>
Reaction Mechanisms
The Added Complexity of Reality

CONSECUTIVE IRREVERSIBLE
$A_0 \rightarrow A_1 \rightarrow A_2$

PARALLEL IRREVERSIBLE
$A_0 \leftrightarrow A_1$

REVERSIBLE
$A_0 \leftrightarrow A_1$

CONSECUTIVE REVERSIBLE
$A_0 \leftrightarrow A_1 \leftrightarrow A_2$

PARALLEL CONSECUTIVE
$A_0 \leftrightarrow A_1 \leftrightarrow A_2$

PARALLEL CONSECUTIVE
$A_0 \leftrightarrow A_1 \leftrightarrow A_2 \leftrightarrow A_3$
Nitrification Kinetics
Nitrification in a Batch Reactor

DERIVATION

Pair of irreversible, first order kinetic reactions

\[
\begin{align*}
\text{NH}_4^+ & \xrightarrow{k_1, \text{nitrosomonas}} \text{NO}_2^- \\
& \xrightarrow{k_2, \text{nitrobacter}} \text{NO}_3^-
\end{align*}
\]

First order rate law for step 1

\[
\frac{d[\text{NH}_4^+]}{dt} = -k_1[\text{NH}_4^+]
\]

Integrated form for step 1

\[
[\text{NH}_4^+] = [\text{NH}_4^+]_0 e^{-k_1 t}
\]

First order rate law expression for consecutive first order steps

\[
\frac{d[\text{NO}_2^-]}{dt} = k_1[\text{NH}_4^+] - k_2[\text{NO}_2^-]
\]

Integrated form for consecutive steps

\[
[\text{NO}_2^-] = \frac{k_1[\text{NH}_4^+]_0}{k_2 - k_1} \left\{ e^{-k_1 t} - e^{-k_2 t} \right\}
\]

Mass balance expression

\[
[\text{NO}_3^-] = [\text{NH}_4^+]_0 - [\text{NH}_4^+] - [\text{NO}_2^-]
\]
Nitrification in a Batch Reactor
RELATING TO COMPUTER CODE

Temperature Effect Adjustments
\[ k'_i = k_i e^{a(T - 20)} \]

where \( a = \frac{E_a}{RT_1T_2} \)

\[ [NH_4^+] = [NH_4^+]_0 e^{-k_1t} \]

\[ [NO_2^-] = \frac{k_1[NH_4^+]_0}{k_2 - k_1} \left\{ e^{-k_1t} - e^{-k_2t} \right\} \]

\[ [NO_3^-] = [NH_4^+]_0 - [NH_4^+] - [NO_2^-] \]

Temperature Effect Adjustments

\[ K_1 = LA \cdot \exp(A \cdot (TA - 20)) \]
\[ K_2 = LB \cdot \exp(B \cdot (TA - 20)) \]

\[ TC = TC + (TB / 10) \]
\[ S = S + 1 \]
\[ DA = \exp(-K1 \cdot TC) \]
\[ DB = \exp(-K2 \cdot TC) \]
\[ N1(S) = CA \cdot DA \]
\[ J = K1 \cdot CA / (K2 - K1) \]
\[ N2(S) = J \cdot (DA - DB) \]
\[ N3(S) = CA - N1(S) - N2(S) \]

Temperature Effect Adjustments

\[ \left\{ \right\} \]

20°C Reference State

Constant

\[ E_a = \frac{RT}{T_1T_2} \]

where \( a = \frac{E_a}{RT_1T_2} \)

\[ k'_i = k_i e^{a(T - 20)} \]

\[ [NH_4^+] = [NH_4^+]_0 e^{-k_1t} \]

\[ [NO_2^-] = \frac{k_1[NH_4^+]_0}{k_2 - k_1} \left\{ e^{-k_1t} - e^{-k_2t} \right\} \]

\[ [NO_3^-] = [NH_4^+]_0 - [NH_4^+] - [NO_2^-] \]

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\[ N3(S) = CA - N1(S) - N2(S) \]

Temperature Effect Adjustments

\[ \left\{ \right\} \]
Nitrification in a Column

NUMERICAL SOLUTIONS (STEADY STATE)

Simple Transport \[ x = vt \]

where \( x \) = distance, \( v \) = velocity, \( t \) = time

Velocity in porous media \[ v = \frac{Q}{\theta A} \]

where \( Q \) = application rate, \( v \) = pore water velocity, \( \theta \) = volumetric water content, \( A \) = cross-sectional area

Temperature Effect Adjustments \[ K_i' = K_i'e^{a(T-20)} \]

where \( K_i = \frac{k_i}{v} \)

\[
\begin{align*}
[NH_4^+] &= [NH_4^+]_0 e^{-K_1'x} \\
[NO_2^-] &= \frac{K'_1[NH_4^+]_0}{K'_2 - K'_1} \left\{ e^{-K'_1x} - e^{-K'_2x} \right\} \\
[NO_3^-] &= [NH_4^+]_0 - [NH_4^+] - [NO_2^-]
\end{align*}
\]
Reaction Mechanisms
The Added Complexity of Reality

**Consecutive Irreversible**

\[ A_0 \rightarrow A_1 \rightarrow A_2 \]

**Parallel Irreversible**

\[ A_0 \leftrightarrow A_1 \leftrightarrow A_2 \]

**Reversible**

\[ A_0 \leftrightarrow A_1 \]

**Consecutive Reversible**

\[ A_0 \leftrightarrow A_1 \leftrightarrow A_2 \]

**Parallel Consecutive**

\[ A_0 \leftrightarrow A_{11} \leftrightarrow A_{12} \leftrightarrow A_{13} \]

\[ A_{21} \leftrightarrow A_{22} \leftrightarrow A_{23} \]
Biologically Controlled Reactions

Growth, Decay, and Biodegradation

\[ E + S \overset{k_i}{\underset{k_{-i}}{\rightleftharpoons}} ES \overset{k_p}{\rightarrow} P + E \]

Michaelis-Menten Kinetics

\[ \mu = \frac{\mu_{\text{max}}[S]}{K_m + [S]} \]

Examples
- Biodegradation of pesticides
- Algal growth
<table>
<thead>
<tr>
<th>Visual Basic type</th>
<th>Common language runtime type structure</th>
<th>Nominal storage allocation</th>
<th>Value range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boolean</td>
<td>System.Boolean</td>
<td>2 bytes</td>
<td><strong>True</strong> or <strong>False</strong>.</td>
</tr>
<tr>
<td>Byte</td>
<td>System.Byte</td>
<td>1 byte</td>
<td>0 through 255 (unsigned).</td>
</tr>
<tr>
<td>Char</td>
<td>System.Char</td>
<td>2 bytes</td>
<td>0 through 65535 (unsigned).</td>
</tr>
<tr>
<td>Date</td>
<td>System.DateTime</td>
<td>8 bytes</td>
<td>0:00:00 on January 1, 0001 through 11:59:59 PM on December 31, 9999.</td>
</tr>
<tr>
<td>Decimal</td>
<td>System.Decimal</td>
<td>16 bytes</td>
<td>0 through +/-79,228,162,514,264,337,593,543,950,335 with no decimal point; 0 through +/-7.9228162514264337593543950335 with 28 places to the right of the decimal; smallest nonzero number is +/-0.0000000000000000000000000001 (+/-1E-28).</td>
</tr>
<tr>
<td>Double (double-precision floating-point)</td>
<td>System.Double</td>
<td>8 bytes</td>
<td>-1.79769313486231570E+308 through -4.9406545841246544E-324 for negative values; 4.9406545841246544E-324 through 1.79769313486231570E+308 for positive values.</td>
</tr>
<tr>
<td>Integer</td>
<td>System.Int32</td>
<td>4 bytes</td>
<td>-2,147,483,648 through 2,147,483,647.</td>
</tr>
<tr>
<td>Object</td>
<td>System.Object (class)</td>
<td>4 bytes</td>
<td>Any type can be stored in a variable of type <strong>Object</strong>.</td>
</tr>
<tr>
<td>Short</td>
<td>System.Int16</td>
<td>2 bytes</td>
<td>-32,768 through 32,767.</td>
</tr>
<tr>
<td>Single (single-precision floating-point)</td>
<td>System.Single</td>
<td>4 bytes</td>
<td>-3.4028235E+38 through -1.401298E-45 for negative values; 1.401298E-45 through 3.4028235E+38 for positive values.</td>
</tr>
</tbody>
</table>