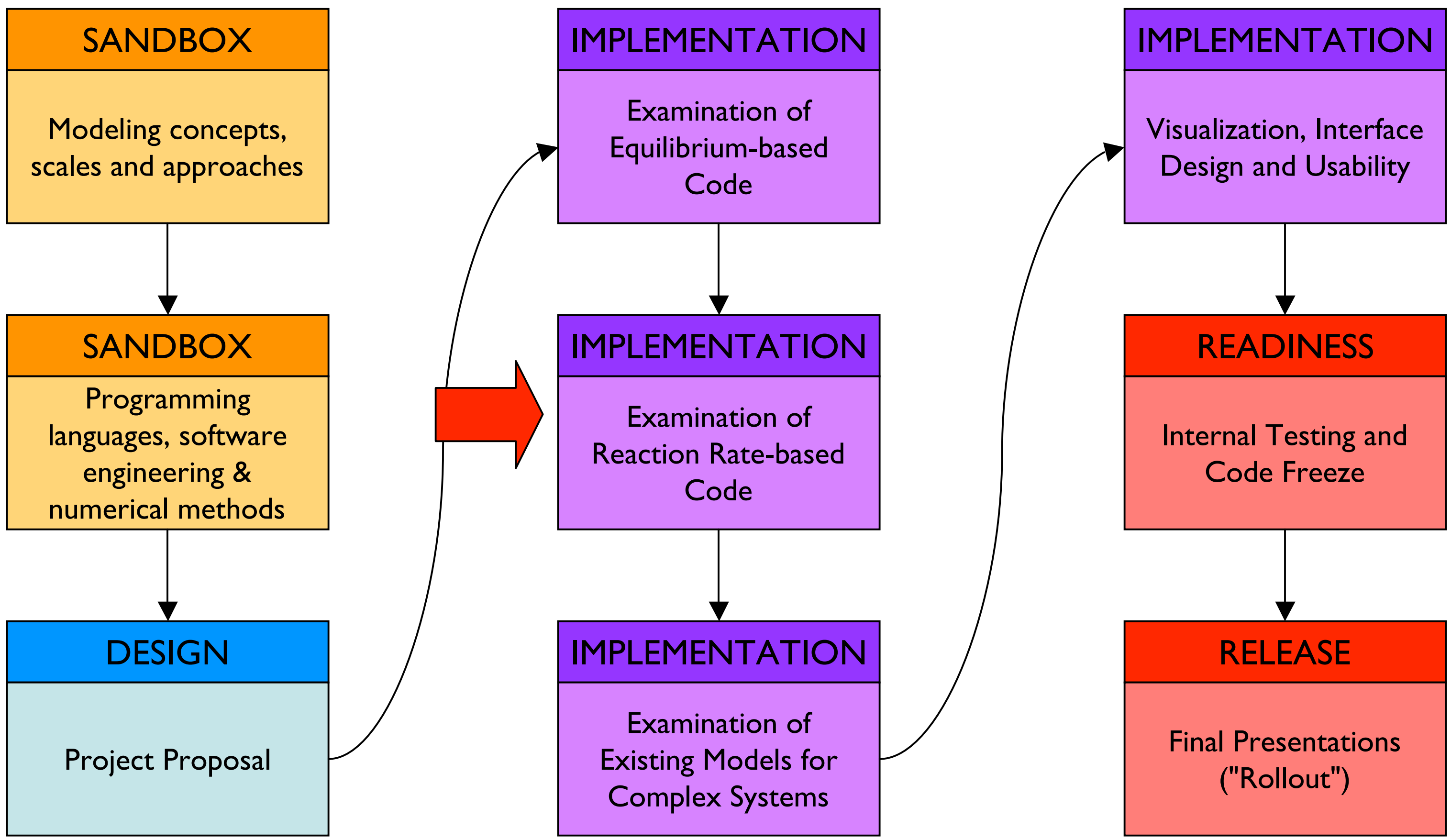
Kinetics and Rates of Reactions

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")

KINETICS AND RATE LIMITED REACTIONS

OBJECTIVES

1. Build a modeling framework for reaction rate-limited chemistry.
2. Examine and understand computer code.
3. Produce model results and interpret critically.

KINETICS AND RATE LIMITED REACTIONS

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

$A \rightarrow B$	Zero	$-\frac{d[A]}{dt} = k_0$	$[A] = [A]_0 - k_0 t$ $t_{1/2} = \frac{[A]_0}{2k_0}$
$A \rightarrow B$	First	$-\frac{d[A]}{dt} = k_1[A]$	$\ln\frac{[A]}{[A]_0} = k_1 t$ $t_{1/2} = \frac{1}{k_1}\ln 2$

Reaction Mechanisms

The Added Complexity of Reality

CONSECUTIVE IRREVERSIBLE

$$A_0 \rightarrow A_1 \rightarrow A_2$$

PARALLEL IRREVERSIBLE

$$\begin{tikzcd} & A_1 \\ A_0 \arrow[ur] \arrow[dr] & \\ & A_2 \end{tikzcd}$$

REVERSIBLE

$$A_0 \rightleftarrows A_1$$

CONSECUTIVE REVERSIBLE

$$A_0 \rightleftarrows A_1 \rightleftarrows A_2$$

PARALLEL CONSECUTIVE

$$\begin{tikzcd} & A_{11} \arrow[r] & A_{12} \arrow[r] & A_{13} \\ A_0 \arrow[ur] \arrow[dr] & & & \\ & A_{21} \arrow[r] & A_{22} \arrow[r] & A_{23} \end{tikzcd}$$

PARALLEL CONSECUTIVE

$$\begin{tikzcd} & A_{11} \arrow[r] \arrow[ddr] & A_{12} \arrow[r] \arrow[ddr] & A_{13} \\ A_0 \arrow[ur] \arrow[dr] & & & \\ & A_{21} \arrow[r] \arrow[uur] & A_{22} \arrow[r] \arrow[uur] & A_{23} \end{tikzcd}$$

Nitrification Kinetics

Nitrification in a Batch Reactor

DERIVATION

Pair of irreversible, first order kinetic reactions

$$NH_4^+ \xrightarrow{k_1,\,nitrosomonas} NO_2^- \xrightarrow{k_2,\,nitrobacter} NO_3^-$$

First order rate law for step 1 →

$$\frac{d[NH_4^+]}{dt} = -k_1[NH_4^+]$$

Integrated form for step 1 →

$$[NH_4^+] = [NH_4^+]_0 e^{-k_1 t}$$

First order rate law expression for consecutive first order steps →

$$\frac{d[NO_2^-]}{dt} = k_1[NH_4^+] - k_2[NO_2^-]$$

Integrated form for consecutive steps →

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

Mass balance expression →

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

Nitrification in a Batch Reactor

RELATING TO COMPUTER CODE

Temperature Effect Adjustments

$$k_i' = k_i e^{a(T-20)}$$

20°C Reference State Constant

$$\text{where } a = \frac{E_a}{RT_1T_2}$$

```
K1 = LA * Exp(A * (TA - 20))
K2 = LB * Exp(B * (TA - 20))
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$$[NH_4^{\,+}] = [NH_4^{\,+}]_0 e^{-k_1 t}$$

$$[NO_2^{\,-}] = \frac{k_1[NH_4^{\,+}]_0}{k_2 - k_1}\left\{e^{-k_1 t} - e^{-k_2 t}\right\}$$

$$[NO_3^{\,-}] = [NH_4^{\,+}]_0 - [NH_4^{\,+}] - [NO_2^{\,-}]$$

```
TC = TC + (TB / 10)
S = S + 1
DA = Exp(-K1 * TC)
DB = Exp(-K2 * TC)
N1(S) = CA * DA
J = K1 * CA / (K2 - K1)
N2(S) = J * (DA - DB)
N3(S) = CA - N1(S) - N2(S)
```

Nitrification in a Column

NUMERICAL SOLUTIONS (STEADY STATE)

Simple Transport $x = vt$ where x = distance, v = velocity, t = time

Velocity in porous media $v = \dfrac{Q}{\theta A}$ where Q = application rate, v = pore water velocity, θ = volumetric water content, A = cross-sectional area

Temperature Effect Adjustments $K_i' = K_i' e^{a(T-20)}$ *where* $K_i = \dfrac{k_i}{v}$

$$[NH_4^{\,+}] = [NH_4^{\,+}]_0 e^{-K_1' x}$$

$$[NO_2^{\,-}] = \frac{K_1'[NH_4^{\,+}]_0}{K_2' - K_1'}\left\{e^{-K_1' x} - e^{-K_2' x}\right\}$$

$$[NO_3^{\,-}] = [NH_4^{\,+}]_0 - [NH_4^{\,+}] - [NO_2^{\,-}]$$

Reaction Mechanisms

The Added Complexity of Reality

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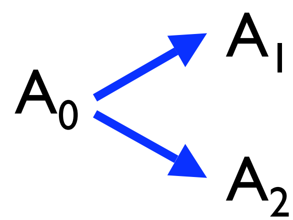


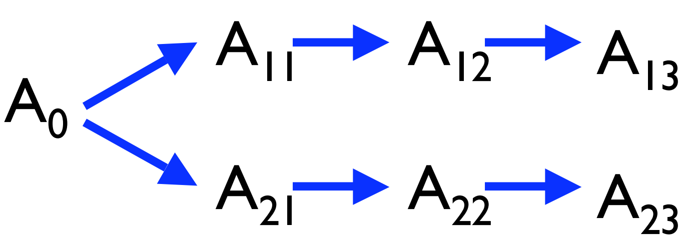
REVERSIBLE

$$A_0 \rightleftharpoons A_1$$

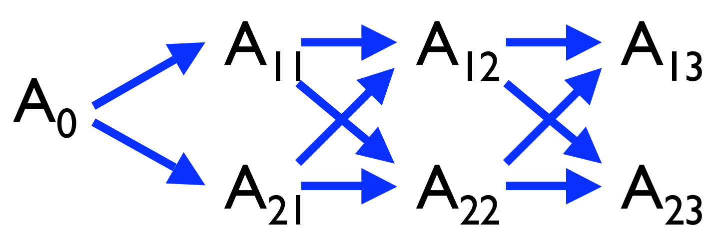
CONSECUTIVE REVERSIBLE

$$A_0 \rightleftharpoons A_1 \rightleftharpoons A_2$$

PARALLEL CONSECUTIVE



PARALLEL CONSECUTIVE



Biologically Controlled Reactions

Growth, Decay, and Biodegradation

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_p} P + E$$

Michaelis-Menten Kinetics

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

Examples

- Biodegradation of pesticides
- Algal growth

Numeric Types: Visual BASIC

Visual Basic type	Common language runtime type structure	Nominal storage allocation	Value range
Boolean	**System.Boolean**	2 bytes	**True** or **False.**
Byte	**System.Byte**	1 byte	0 through 255 (unsigned).
Char	**System.Char**	2 bytes	0 through 65535 (unsigned).
Date	**System.DateTime**	8 bytes	0:00:00 on January 1, 0001 through 11:59:59 PM on December 31, 9999.
Decimal	**System.Decimal**	16 bytes	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).
Double (double-precision floating-point)	**System.Double**	8 bytes	-1.79769313486231570E+308 through -4.94065645841246544E-324 for negative values; 4.94065645841246544E-324 through 1.79769313486231570E+308 for positive values.
Integer	**System.Int32**	4 bytes	-2,147,483,648 through 2,147,483,647.
Long (long integer)	**System.Int64**	8 bytes	-9,223,372,036,854,775,808 through 9,223,372,036,854,775,807.
Object	**System.Object** (class)	4 bytes	Any type can be stored in a variable of type **Object**.
Short	**System.Int16**	2 bytes	-32,768 through 32,767.
Single (single-precision floating-point)	**System.Single**	4 bytes	-3.4028235E+38 through -1.401298E-45 for negative values; 1.401298E-45 through 3.4028235E+38 for positive values.