CEE 690K
ENVIRONMENTAL REACTION KINETICS

Lecture #5

Rate Expressions: Chain Reactions
Brezonik, pp.50-58

Introduction
Secular Equilibrium

- If $k_{ii} >> k_i$
  - The ratio of $[B]/[A]$ approaches a constant
  - Divide equation for $[B]$ by the equation for $[A]$
    \[
    [B] = \frac{k_i[A]_0}{k_{ii} - k_i} \left\{ e^{-k_i t} - e^{-k_{ii} t} \right\} \\
    [A] = [A]_0 e^{-k_i t}
    \]
    \[
    \frac{[B]}{[A]} = \frac{k_i e^{k_i t}}{k_{ii} - k_i} \left\{ e^{-k_i t} - e^{-k_{ii} t} \right\}
    \]
    \[
    = \frac{k_i}{k_{ii} - k_i} \left\{ 1 - e^{-(k_{ii} - k_i) t} \right\}
    \]
  - So when $k_{ii} >> k_i$, then the exponential approaches zero
    \[
    \frac{[B]}{[A]} \to \frac{k_i}{k_{ii} - k_i} \approx \frac{k_i}{k_{ii}}
    \]
Natural $^{226}\text{Ra}$ decays as follows:

$$^{226}\text{Ra} \xrightarrow{k_i} ^{222}\text{Rn} \xrightarrow{k_{ii}} ^{218}\text{Po}$$

$t_{1/2} = 1620$ yr
$k_i = 4.28 \times 10^{-4}$ yr$^{-1}$

$t_{1/2} = 3.8$ d
$k_i = 6.6 \times 10^{1}$ yr$^{-1}$

Radon is used as tracer for vertical mixing from sediments to water column; Ra is mostly in sediments

Procedure:

- Collect water column sample & measure purged Rn
- Allow sample to reach secular equilibrium and again measure purged Rn
- Difference is used to calculate amount of Rn diffused from sediments
Radium decay II

How long to wait for secular equilibrium?

\[
\begin{align*}
[B] &= \frac{k_i}{k_{ii} - k_i} \left\{1 - e^{-\left(k_{ii} - k_i\right)t}\right\} \\
[A] &= \frac{k_i}{k_{ii} - k_i} \\
[Rn] &= \frac{4.28 \times 10^{-4}}{66 - 4.28 \times 10^{-4}} \left\{1 - e^{-\left(66 - 4.28 \times 10^{-4}\right)t}\right\} \\
Ra] &= \frac{4.28 \times 10^{-4}}{66 - 4.28 \times 10^{-4}} \left\{1 - e^{-66t}\right\} \\
&\approx 0.0000065 \left\{1 - e^{-66t}\right\}
\end{align*}
\]

% of equilibrium value = 100\%(1 - e^{-66t})

- 92% at 14d
- 98% at 21d
Chain Reactions I

- Description
  - A multi-step reaction mechanism where the reactants form intermediates that react with more reactants that yield products plus more intermediates
  - Quite common for free radical reactions

- Three stages
  - Initiation (I) - initiators
  - Propagation (P) - promotors
  - Termination (T) - scavengers

- Evidence
  - Induction period
  - Unusual catalysis or repression
  - Strange rate equations (product in denominator, fractional order)
  - Unusual surface effects
Simple Generic Cycle

\[
\begin{align*}
A_2 & \leftrightarrow 2A \\
A + B_2 & \leftrightarrow P + B \\
B + A_2 & \leftrightarrow P + A \\
\hline
A_2 + B_2 & \rightarrow 2P
\end{align*}
\]

“A” and “B” are reactive intermediates, or chain carriers.
Chain Reactions

**Hoigné, Stachelin, and Bader mechanism.** Ozone decomposition occurs in a chain process that can be represented by the following fundamental reactions (Weiss 1935; Stachelin et al. 1984), including initiation step 1, propagation steps 2 to 6, and break in chain reaction steps 7 and 8.

1. \[ \text{O}_3 + \text{OH}^- \xrightarrow{k_1} \text{HO}_2 + \text{O}_2^- \]
   \[ k_1 = 7.0 \times 10^1 \text{ M}^{-1} \text{ s}^{-1} \]
   \( \text{HO}_2 \): hydroperoxide radical

1'. \[ \text{HO}_2 \xrightleftharpoons[k_2]{k_2} \text{O}_2^- + H^+ \]
   \[ k_2 \text{ (ionization constant)} = 10^{-4.8} \]
   \[ \text{O}_2^- \]: superoxide radical ion

2. \[ \text{O}_3 + \text{O}_2^- \xrightarrow{k_2} \text{O}_3^- + \text{O}_2 \]
   \[ k_2 = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \]
   \[ \text{O}_3^- \]: ozonide radical ion

3. \[ \text{O}_3^- + H^+ \xrightleftharpoons[k_3]{k_{-3}} \text{HO}_3 \]
   \[ k_3 = 5.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \]
   \[ k_{-3} = 2.3 \times 10^2 \text{ s}^{-1} \]

4. \[ \text{HO}_3 \rightarrow \text{OH} + \text{O}_2 \]
   \[ k_4 = 1.1 \times 10^5 \text{ s}^{-1} \]

5. \[ \text{OH} + \text{O}_3 \xrightarrow{k_5} \text{HO}_4 \]
   \[ k_5 = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \]

6. \[ \text{HO}_4 \xrightarrow{k_6} \text{HO}_2 + \text{O}_2 \]
   \[ k_6 = 2.8 \times 10^4 \text{ s}^{-1} \]

7. \[ \text{HO}_4 + \text{HO}_4 \rightarrow \text{H}_2\text{O}_2 + 2\text{O}_3 \]

8. \[ \text{HO}_4 + \text{HO}_3 \rightarrow \text{H}_2\text{O}_2 + \text{O}_3 + \text{O}_2 \]

The overall pattern of the ozone decomposition mechanism is shown in Figure II. The first fundamental element in the reaction diagram and in the rate const
In-class use of **Scientist**

Constuctive 2\textsuperscript{nd} order reactions

```plaintext
// Example - A --> B --> C Kinetics
// This model describes a system having a second order conversion from A to B.
// B is subsequently converted to C by another second order reaction.

IndVars: TIME
DepVars: A, B, C, D
Params: A0, D0, KAB, KBC,

A' = -KAB*A*D
D' = -KAB*A*D - KBC*B*D
B' = KAB*A*D - KBC*B*D
C' = KBC*B*D

// Initial Conditions
TIME = 0.0
A = A0
D = D0
B = 0.0
C = 0.0
```
To next lecture