Secular Equilibrium

- If $k_u \gg k_i$
  - The ratio of $[B]/[A]$ approaches a constant
  - Divide equation for $[B]$ by the equation for $[A]$
    \[
    \frac{[B]}{[A]} = \frac{k_i [A]_0}{k_u - k_i} \left( e^{kt} - e^{-kt} \right) \]
    \[
    \left( [A] = [A]_0 e^{kt} \right)
    \]
    \[
    \frac{[B]}{[A]} = \frac{k_i [A]_0}{k_u - k_i} \left( e^{kt} - e^{-kt} \right)
    \]
    \[
    \frac{[B]}{[A]} = \frac{k_i}{k_u - k_i} \left( 1 - e^{-kt} \right)
    \]
  - So when $k_u \gg k_i$, then the exponential approaches zero
    \[
    \frac{[B]}{[A]} \approx \frac{k_i}{k_u - k_i}
    \]
Example: Radium decay I

Natural $^{226}$Ra decays as follows:

$$^{226}\text{Ra} \xrightarrow{k_1} ^{222}\text{Rn} \xrightarrow{k_2} ^{218}\text{Po}$$

$1/2 = 1620 \text{yr}$

$k_1 = 4.28 \times 10^{-4} \text{ yr}^{-1}$

$1/2 = 3.8 \text{ d}$

$k_2 = 6.6 \times 10^{-1} \text{ yr}^{-1}$

Radon is used as a 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

Radon decay II

How long to wait for secular equilibrium?

$$[B] = \frac{k_i}{k_{ii} - k_i} \left[ 1 - e^{-k_{ii}t} \right]$$

$$[Rn] = \frac{4.28 \times 10^{-4}}{66 - 4.28 \times 10^{-1}} \left[ 1 - e^{-(66-4.28 \times 10^{-1})t} \right]$$

$$\equiv 0.0000065 \left[ 1 - e^{-66t} \right]$$

% 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) - promoters
  - Termination (T) - scavengers

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

Chain Reactions II

- **Simple Generic Cycle**
  
  \[
  \begin{align*}
  A_2 & \leftrightarrow 2A \\
  A + B_2 & \leftrightarrow P + B \\
  B + A_2 & \leftrightarrow P + A \\
  A_2 + B_2 & \rightarrow 2P
  \end{align*}
  \]

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

**Hoigne, Strehalin, and Bader mechanism.** Chain decomposition occurs in a chain process that can be represented by the following fundamental reactions (Weiss 1955; Strehalin et al. 1984), including initiation step 1, propagation steps 2 to 6, and break in chain reaction steps 7 and 8.

1. \( \text{O}_2 + \text{OH}^- \xrightarrow{k_1} \text{HO}_2 + \text{O}_2^- \)
   \( k_1 = 7.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \)
   \( \text{HO}_2 \): hydroperoxide radical

2. \( \text{HO}_2 \xrightarrow{k_{2s}} \text{O}_2^- + \text{H}^+ \)
   \( k_{2s} \) (formation constant) = \( 10^{-4.8} \)
   \( \text{O}_2^- \): superoxide radical ion

3. \( \text{O}_3 + \text{O}_2^- \xrightarrow{k_2} \text{O}_4^- + \text{O}_2 \)
   \( k_2 = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \)
   \( \text{O}_4^- \): ozone radical ion

4. \( \text{O}_3 + \text{H}^+ \xrightarrow{k_3} \text{HO}_3 \)
   \( k_3 = 5.2 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1} \)
   \( k_{3s} = 2.3 \times 10^9 \text{ s}^{-1} \)

5. \( \text{O}_3 + \text{OH}^- \xrightarrow{k_1} \text{HO}_2 + \text{O}_2 \)
   \( k_1 = 1.1 \times 10^9 \text{ s}^{-1} \)

6. \( \text{OH} + \text{O}_3 \xrightarrow{k_2} \text{HO}_2 + \text{O}_2 \)
   \( k_2 = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \)

7. \( \text{HO}_3 \xrightarrow{k_3} \text{O}_3 + \text{H}_2 \)
   \( k_3 = 2.8 \times 10^4 \text{ s}^{-1} \)

8. \( \text{O}_3 + \text{HO}_2 \xrightarrow{k_4} \text{H}_2\text{O}_2 + 2\text{O}_2 \)

The overall pattern of the ozone decomposition mechanism is shown in Figure B.

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**Kinetic Modeling**

- **In-class use of Scientist**
  - **Consecutive 2nd order reactions**
    - // 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

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CEE690K Lecture #4
To next lecture