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CEE 690K

ENVIRONMENTAL REACTION KINETICS

Lecture #5

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

David A. Reckhow

Introduction

Secular Equilibrium

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- If $k_{ii} \gg k_i$
 - ▣ The ratio of $[B]/[A]$ approaches a constant
 - ▣ Divide equation for $[B]$ by the equation for $[A]$

$$\boxed{[B] = \frac{k_i [A]_0}{k_{ii} - k_i} \{e^{-k_i t} - e^{-k_{ii} t}\}} \quad / \quad \boxed{[A] = [A]_0 e^{-k_i t}}$$

$$\begin{aligned} \frac{[B]}{[A]} &= \frac{k_i e^{k_i t}}{k_{ii} - k_i} \{e^{-k_i t} - e^{-k_{ii} t}\} \\ &= \frac{k_i}{k_{ii} - k_i} \{1 - e^{-(k_{ii} - k_i)t}\} \end{aligned}$$

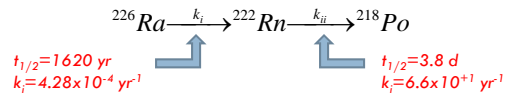
- ▣ So when $k_{ii} \gg k_i$, then the exponential approaches zero

$$\frac{[B]}{[A]} \rightarrow \frac{k_i}{k_{ii} - k_i} \approx \frac{k_i}{k_{ii}}$$

Example: Radium decay I

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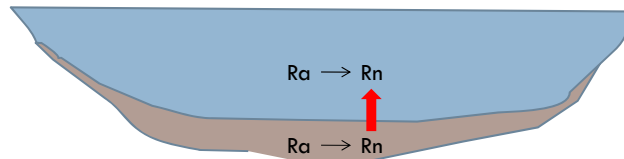
- Natural ^{226}Ra decays as follows:



- 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



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Radium decay II

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- How long to wait for secular equilibrium?

$$\frac{[B]}{[A]} = \frac{k_i}{k_{ii} - k_i} \{1 - e^{-(k_{ii} - k_i)t}\}$$

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

$$\cong 0.0000065 \{1 - e^{-66t}\}$$

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

- 92% at 14d
- 98% at 21d

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Chain Reactions I

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- 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

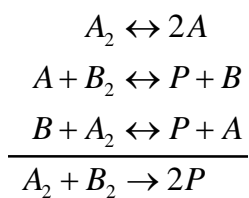
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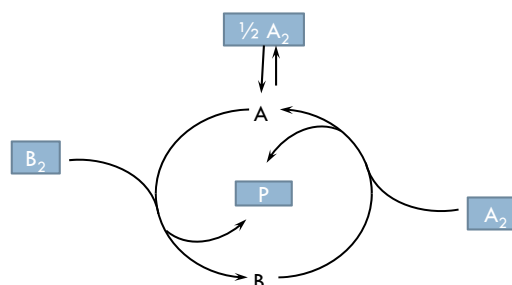
Chain Reactions II

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□ Simple Generic Cycle



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

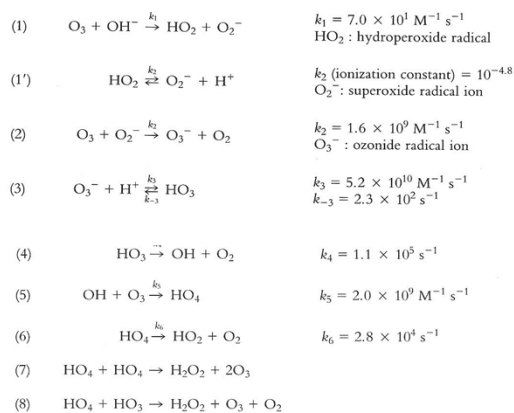


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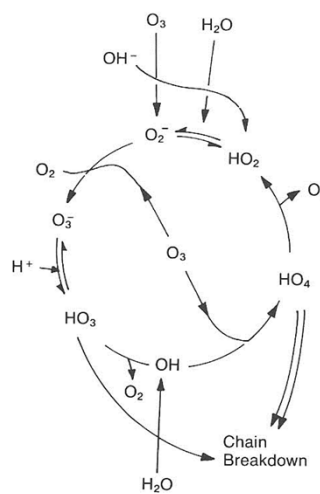
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Chain Reactions

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.



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:



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Kinetic Modeling

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□ 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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□ To next lecture