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CEE 690K
ENVIRONMENTAL REACTION KINETICS

Lecture #5

Rate Expressions: Chain Reactions

Brezonik, pp.50-58

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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]

$$[B] = \frac{k_i[A]_0}{k_{ii} - k_i}\left\{e^{-k_i t} - e^{-k_{ii} t}\right\} \Big/ [A] = [A]_0 e^{-k_i t}$$

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

$$= \frac{k_i}{k_{ii} - k_i}\left\{1 - e^{-(k_{ii} - k_i)t}\right\}$$

  - So when $k_{ii} >> k_i$, then the exponential approaches zero

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

Example: Radium decay I

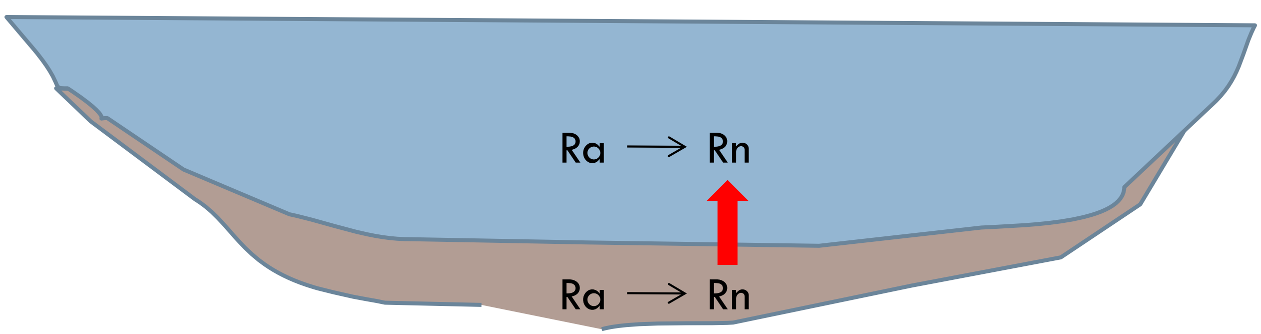
- Natural ^{226}Ra decays as follows:

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

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

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

- 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?

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

$$\frac{[Rn]}{[Ra]} = \frac{4.28x10^{-4}}{66 - 4.28x10^{-4}}\left\{1 - e^{-\left(66 - 4.28x10^{-4}\right)t}\right\}$$

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

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

Chain Reactions II

- Simple Generic Cycle

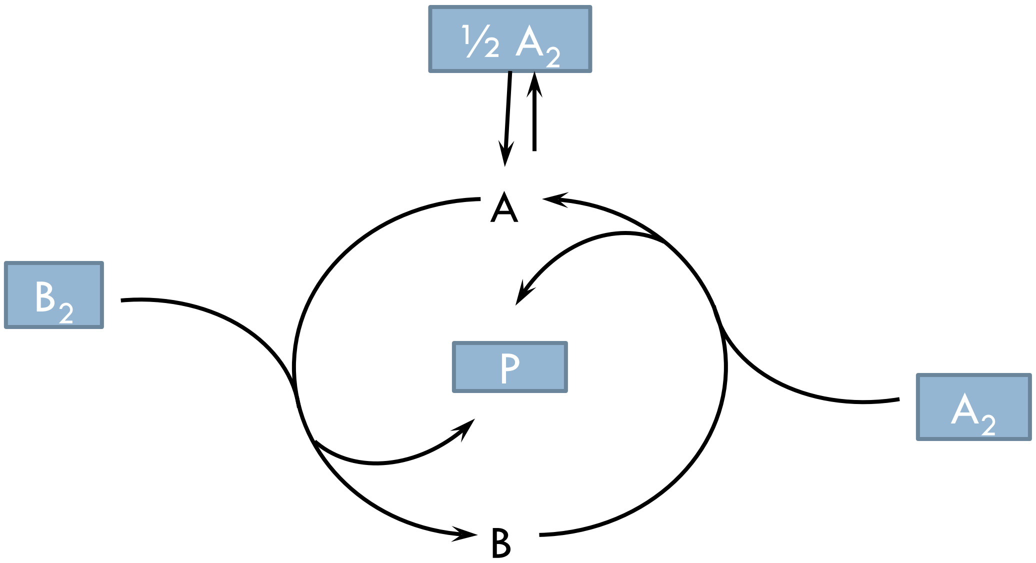
$$A_2 \leftrightarrow 2A$$

$$A + B_2 \leftrightarrow P + B$$

$$B + A_2 \leftrightarrow P + A$$

$$A_2 + B_2 \rightarrow 2P$$

"A" and "B" are reactive intermediates, or chain carriers



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Chain Reactions

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

(1) $O_3 + OH^- \xrightarrow{k_1} HO_2 + O_2^-$ $k_1 = 7.0 \times 10^1\ M^{-1}\ s^{-1}$
HO_2 : hydroperoxide radical

(1′) $HO_2 \overset{k_2}{\rightleftarrows} O_2^- + H^+$ k_2 (ionization constant) $= 10^{-4.8}$
O_2^-: superoxide radical ion

(2) $O_3 + O_2^- \xrightarrow{k_2} O_3^- + O_2$ $k_2 = 1.6 \times 10^9\ M^{-1}\ s^{-1}$
O_3^- : ozonide radical ion

(3) $O_3^- + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} HO_3$ $k_3 = 5.2 \times 10^{10}\ M^{-1}\ s^{-1}$
$k_{-3} = 2.3 \times 10^2\ s^{-1}$

(4) $HO_3 \rightarrow OH + O_2$ $k_4 = 1.1 \times 10^5\ s^{-1}$

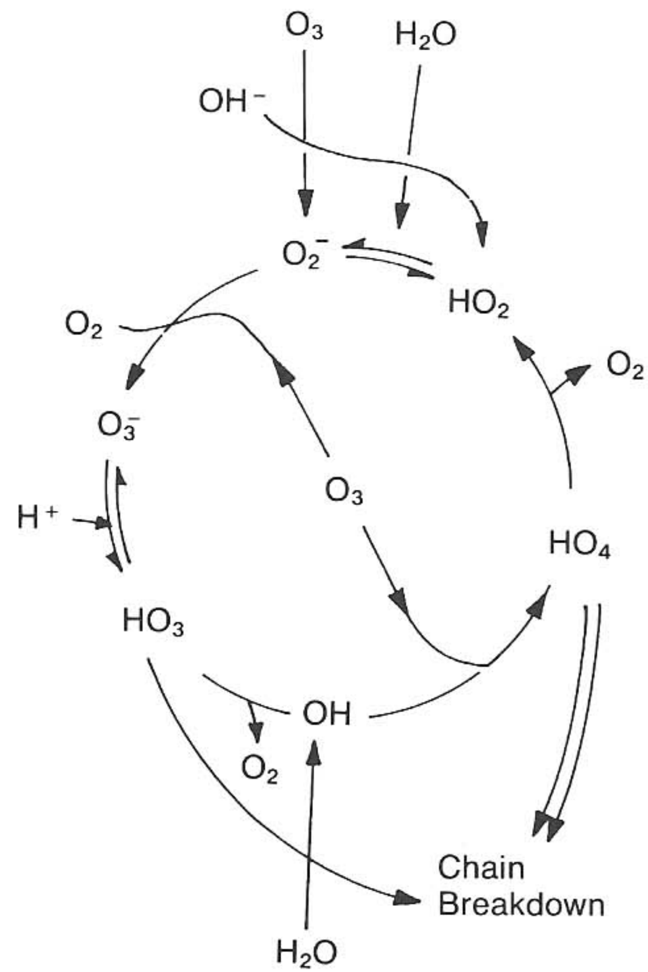
(5) $OH + O_3 \xrightarrow{k_5} HO_4$ $k_5 = 2.0 \times 10^9\ M^{-1}\ s^{-1}$

(6) $HO_4 \xrightarrow{k_6} HO_2 + O_2$ $k_6 = 2.8 \times 10^4\ s^{-1}$

(7) $HO_4 + HO_4 \rightarrow H_2O_2 + 2O_3$

(8) $HO_4 + HO_3 \rightarrow H_2O_2 + O_3 + O_2$

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 consta



Kinetic Modeling

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

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// 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