CEE 690K
ENVIRONMENTAL REACTION KINETICS

Lecture #7

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

David A. Reckhow
Introduction
**HBr Formation I**

- **Chain Mechanism**
  - **Initiation**
    \[ \text{Br}_2 \xrightarrow{k_1} 2\text{Br} \]
  - **Propagation**
    \[
    \begin{align*}
    \text{Br} + \text{H}_2 & \xrightarrow{k_2} \text{HBr} + \text{H} \\
    \text{H} + \text{Br}_2 & \xrightarrow{k_4} \text{HBr} + \text{Br}
    \end{align*}
    \]
  - **Termination**
    \[ 2\text{Br} \xrightarrow{k_5} \text{Br}_2 \]

**Observed Rate Expression**

\[
\frac{d[\text{HBr}]}{dt} = \frac{k[H_2][\text{Br}_2]^{0.5}}{1 + k'[\text{HBr}] / [\text{Br}_2]}
\]

**“theoretical” Rate Expression**

\[
\frac{d[\text{HBr}]}{dt} = k_2[H_2][\text{Br}] + k_4[\text{Br}_2][\text{H}] - k_3[\text{HBr}][\text{H}]
\]
But radical species (H & Br) are really intermediates

- They are not easily measured, and they are not the starting materials
- They are also extremely reactive and never build up to any appreciable concentration

Thus we can make the quasi-steady state (QSS) assumption:

\[ 0 \approx \frac{d[Br]}{dt} = 2k_1[Br_2] + k_3[HBr][H] + k_4[Br_2][H] - k_2[H_2][Br] - 2k_5[Br]^2 \]

\[ 0 \approx \frac{d[H]}{dt} = k_2[H_2][Br] - k_3[HBr][H] - k_4[Br_2][H] \]

Now we combine the two QSS equations with the HBr formation rate expression
HBr Formation III

- **Solve the H-QSS for \([H]\)**

\[
[H] = \frac{k_2[H_2][Br]}{k_3[HBr] + k_4[Br_2]}
\]

- **And substitute this into the Br-QSS**

\[
0 \approx \frac{d[H]}{dt} = k_2[H_2][Br] - k_3[HBr][H] - k_4[Br_2][H]
\]

\[
0 \approx \frac{d[Br]}{dt} = 2k_1[Br_2] + k_3[HBr][H] + k_4[Br_2][H] - k_2[H_2][Br] - 2k_5[Br]^2
\]

\[
2k_5[Br]^2 = 2k_1[Br_2] + (k_3[HBr] + k_4[Br_2])[H] - k_2[H_2][Br]
\]

\[
2k_5[Br]^2 = 2k_1[Br_2] + (k_3[HBr] + k_4[Br_2])\frac{k_2[H_2][Br]}{k_3[HBr] + k_4[Br_2]} - k_2[H_2][Br]
\]

\[
2k_5[Br]^2 = 2k_1[Br_2] + k_2[H_2][Br] - k_2[H_2][Br]
\]

\[
2k_5[Br]^2 = 2k_1[Br_2]
\]

\[
[Br] = \left(\frac{k_1}{k_5}[Br_2]\right)^{0.5}
\]

\[
k_1/k_5 = K
\]

For: \(Br_2 \leftrightarrow 2Br\)
Substituting this back into the equation for \([H]\) gives us expressions without intermediates

\[
[H] = \frac{k_2[H_2]}{k_3[HBr] + k_4[Br_2]} \left( \frac{k_1}{k_5} [Br_2] \right)^{0.5}
\]

and

\[
[Br] = \left( \frac{k_1}{k_5} [Br_2] \right)^{0.5}
\]

Now we can substitute back into the original HBr expression

\[
\frac{d[HBr]}{dt} = k_2[H_2] \left( \frac{k_1}{k_5} [Br_2] \right)^{0.5} + \left( k_4[Br_2] - k_3[HBr] \right) \frac{k_2[H_2]}{k_3[HBr] + k_4[Br_2]} \left( \frac{k_1}{k_5} [Br_2] \right)^{0.5}
\]

And simplify

\[
\frac{d[HBr]}{dt} = \left( k_2[H_2] + \left( k_4[Br_2] - k_3[HBr] \right) \right) \frac{k_2[H_2]}{k_3[HBr] + k_4[Br_2]} \left( \frac{k_1}{k_5} [Br_2] \right)^{0.5}
\]
Further simplifying
\[
\frac{d[HBr]}{dt} = \left( k_2[H_2] + \frac{k_2[H_2]k_4[Br_2] - k_2[H_2]k_3[HBr]}{k_3[HBr] + k_4[Br_2]} \right) \left( \frac{k_1}{k_5} \right)^{0.5}[Br_2]
\]

\[
\frac{d[HBr]}{dt} = \left( k_2[H_2] + \frac{k_2[H_2] - k_2[H_2]}{1 + \frac{k_3[HBr]}{k_4[Br_2]}} \right) \left( \frac{k_1}{k_5} \right)^{0.5}[Br_2]
\]

\[
\frac{d[HBr]}{dt} = \left( \frac{2k_2[H_2]}{1 + \frac{k_3[HBr]}{k_4[Br_2]}} \right) \left( \frac{k_1}{k_5} \right)^{0.5}[Br_2]
\]
Quotient in denominator is a form of an inhibition ratio by HBr

\[
\frac{d[HBr]}{dt} = \frac{2k_2 \frac{k_1}{k_2} [H_2][Br_2]^{0.5}}{1 + \frac{k_3[HBr]}{k_4[Br_2]}}
\]
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. \( \text{O}_3 + \text{OH}^- \xrightleftharpoons{k_1} \text{HO}_2 + \text{O}_2^- \)
   \( k_1 = 7.0 \times 10^1 \text{ M}^{-1} \text{ s}^{-1} \)
   \( \text{HO}_2 \) : hydroperoxide radical

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

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

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

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 consti...
Fitting the data to rate equations

Integral Methods
- Already discussed; depends on model
- Uses all data; but not as robust

Differential Methods
- Get simple estimates of instantaneous rates and fit these to a concentration dependent model
- Quite adaptable

Initial Rate Methods
- Relatively free from interference from products
- Not dependent on common assumptions
Simple first order

- When $n=1$, we have a simple first-order reaction.
- This results in an “exponential decay”

\[
\frac{dc}{dt} = -k c_A
\]

\[
c_A = c_{A0} e^{-kt}
\]

\[k = 0.032 \text{ min}^{-1}\]
Integral Method: First order

- This equation can be linearized
- good for assessment of “k” from data

\[ \frac{dc_A}{dt} = -kc_A \]

\[ \ln c_A = \ln c_{Ao} - kt \]

\[ k = 0.032 \text{ min}^{-1} \]
Simple Second Order

- When \( n = 2 \), we have a simple second-order reaction.
  - This results in an especially wide range in rates.
  - More typical to have 2\(^{nd}\) order in each of two different reactants.

\[
2A \overset{k_2}{\rightarrow} \text{products}
\]

\[
\frac{1}{v_A} \frac{dc_A}{dt} = -k_2 c_A^2
\]

\[
c_A = c_{A_0} \frac{1}{1 + k_2 c_{A_0} t}
\]

\[
k_2 = 0.0015 L/mg/min
\]
Again, the equation can be linearized to estimate “k” from data.

\[
\frac{1}{C_A} = \frac{1}{C_{Ao}} + 2k_2t
\]
Variable Kinetic Order

- Any reaction order, except \( n = 1 \)

\[
\frac{dc}{dt} = -k_n c^n
\]

\[
\frac{1}{c^{n-1}} = \frac{1}{c_o^{n-1}} + (n-1)k_n t
\]

\[
c = c_o \frac{1}{\left[1 + (n-1)k_n c_o^{n-1} t\right]^{1/(n-1)}}
\]
Two different reactants
rate $= \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{\nu_A} \frac{d[A]}{dt} = \frac{dx}{dt} = k_2[A][B] = k_2([A]_0 - x)([B]_0 - x)$

Initial Concentrations are different; $[A]_0 \neq [B]_0$

The integrated form is:
$$\frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A][B]} = k_2 t$$

Which can be expressed as:
$$\log \frac{[A]}{[B]} = 0.43 k_2 ([A]_0 - [B]_0) t - \log \frac{[B]_0}{[A]_0}$$
Integral Method: Mixed Second Order

\[ A + B \overset{k_2}{\longrightarrow} \text{products} \]

- Initial Concentrations are the same; \([A]_0 = [B]_0\)

\[
\frac{dx}{dt} = k_2[A][A] = k_2([A]_0 - x)([A]_0 - x)
\]

- The integrated form is:

\[
\int \frac{d[A]}{[A]^2} = \int v_A k_2 dt \quad \Rightarrow \quad \frac{1}{[A]} - \frac{1}{[A]_0} = 2k_2t
\]

- Which can be integrated:

\[
\frac{1}{[A]} = 2k_2t + \frac{1}{[A]_0}
\]
Doesn’t require assumptions on reaction order

Simple method, doing it by “eye”

Get estimates of instantaneous rates by drawing tangents & plotting these slopes

\[
\frac{-d[A]}{dt} = k[A]^n
\]

\[
\log\left(\frac{-d[A]}{dt}\right) = \log k + n \log [A]
\]
Finite difference method

Start with the general linear solution

\[
\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt
\]

\[ [A]^{n-1} = \left( (n-1)kt + \frac{1}{[A]_0^{n-1}} \right)^{-1} \]

And substituting back, we get:

\[
\frac{d[A]}{dt} = k[A]^{n-1} = k \left( (n-1)kt + \frac{1}{[A]_0^{n-1}} \right)^{-1}
\]

So the reciprocal of “X” is a linear function of time

\[
\frac{1}{X} = (n-1)t + \frac{1}{k[A]_0^{n-1}}
\]
Finite difference method (cont.)

Now we can get “X” from a time-centered finite difference approximation

\[
\left( \frac{d[A]}{dt} \right)_n \approx \frac{[A]_{n-1} - [A]_{n+1}}{t_{n+1} - t_{n-1}}
\]

And, for \( t=n \)

\[
\frac{1}{X} \equiv \frac{[A]}{d[A]/dt}
\]
Initial Rate Methods

- Evaluated in very early stages of the reaction where:
  - Only small amounts of products have been formed
  - Reactants have essentially not changed in concentrations
- Avoids many problems of complex reactions where products continue to react
To next lecture