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CEE 690K
ENVIRONMENTAL REACTION KINETICS

Lecture #7

Rate Expressions: Chain Reactions

Brezonik, pp.50-58

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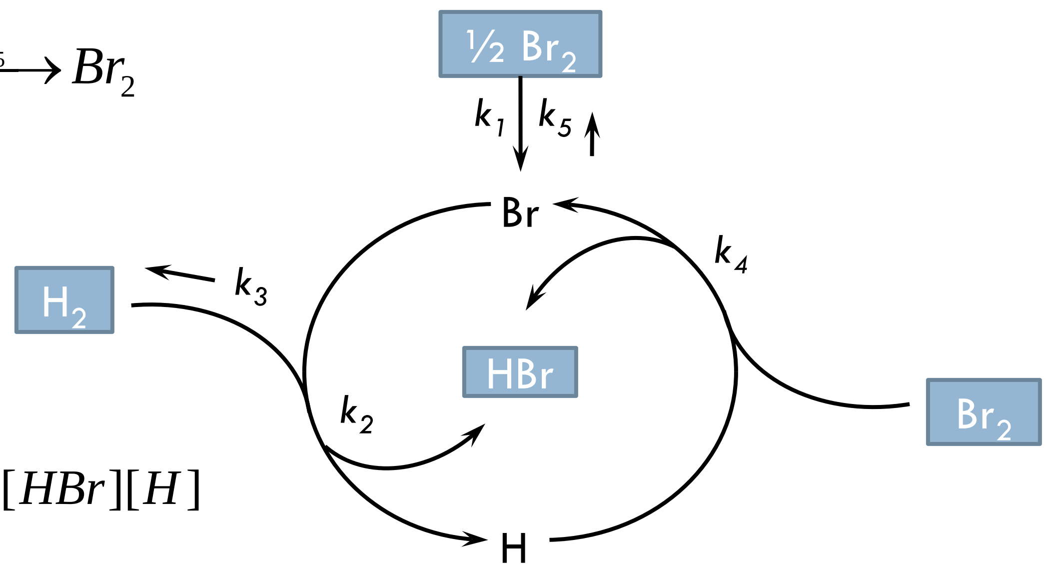
Introduction

HBr Formation I

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{0.5}}{1 + k' \,{}^{[HBr]}\!/_{[Br_2]}}$$

Observed Rate Expression

- Chain Mechanism
  - Initiation $$Br_2 \xrightarrow{k_1} 2Br$$
  - Propagation
    $$Br + H_2 \xrightarrow{k_2} HBr + H$$
    $$H + Br_2 \xrightarrow{k_4} HBr + Br$$
    $$Br + H_2 \xleftarrow{k_3} HBr + H$$
  - Termination $$2Br \xrightarrow{k_5} Br_2$$



"theoretical" Rate Expression

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

HBr Formation II

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

- 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

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

- Solve the H-QSS for [H]

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

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

- And substitute this into the Br-QSS

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

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

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

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

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

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

$k_1/k_5 = K$

for: $Br_2 \leftrightarrow 2Br$

HBr Formation IV

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

- Substituting this back into the equation for [H] gives us expressions without intermediates

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

- 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

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

HBr Formation V

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

- Further simplifying

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

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

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

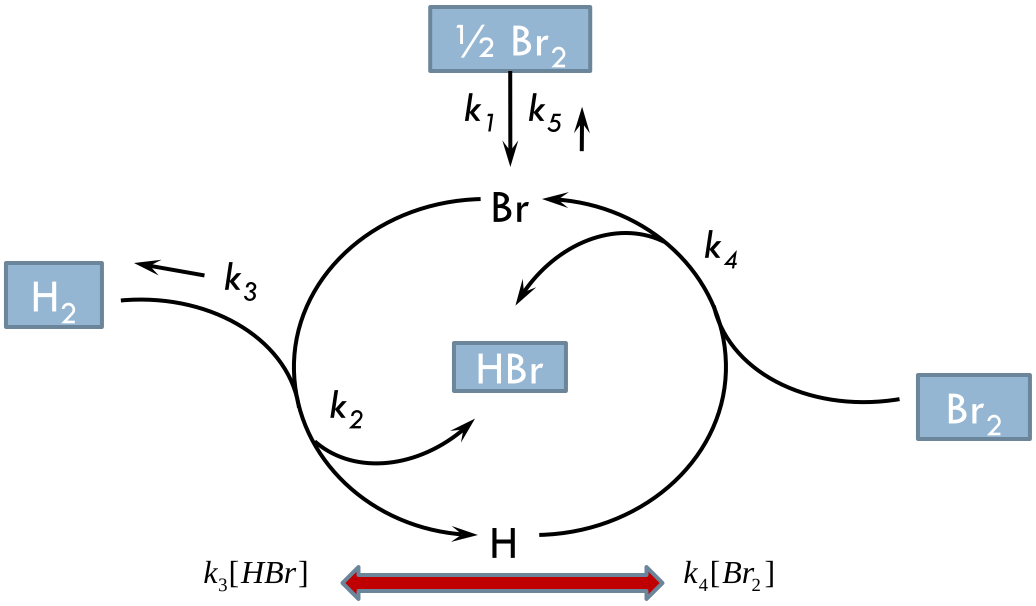
$$\frac{d[HBr]}{dt} = \left(\frac{2k_2[H_2]}{1 + \frac{k_3[HBr]}{k_4[Br_2]}} \right) \left(\frac{k_1}{k_5}[Br_2] \right)^{0.5} \Rightarrow \boxed{\frac{d[HBr]}{dt} = \left(\frac{2k_2 \frac{k_1}{k_2}[H_2][Br_2]^{0.5}}{1 + \frac{k_3[HBr]}{k_4[Br_2]}} \right)}$$

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{0.5}}{1 + k' \, {}^{[HBr]}\!/\!{}_{[Br_2]}}$$

HBr Formation VI

- Quotient in denominator is a form of an inhibition ratio by HBr

$$\frac{d[HBr]}{dt} = \left(\frac{2k_2 \frac{k_1}{k_2}[H_2][Br_2]^{0.5}}{1 + \frac{k_3[HBr]}{k_4[Br_2]}} \right)$$

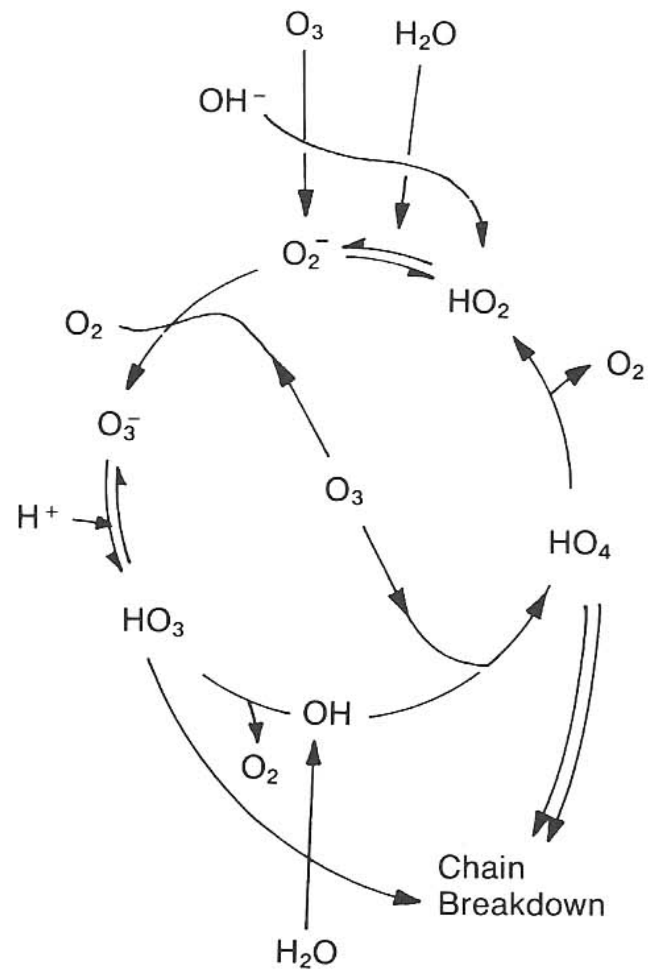


Chain Reactions

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 Analysis of Experimental Data

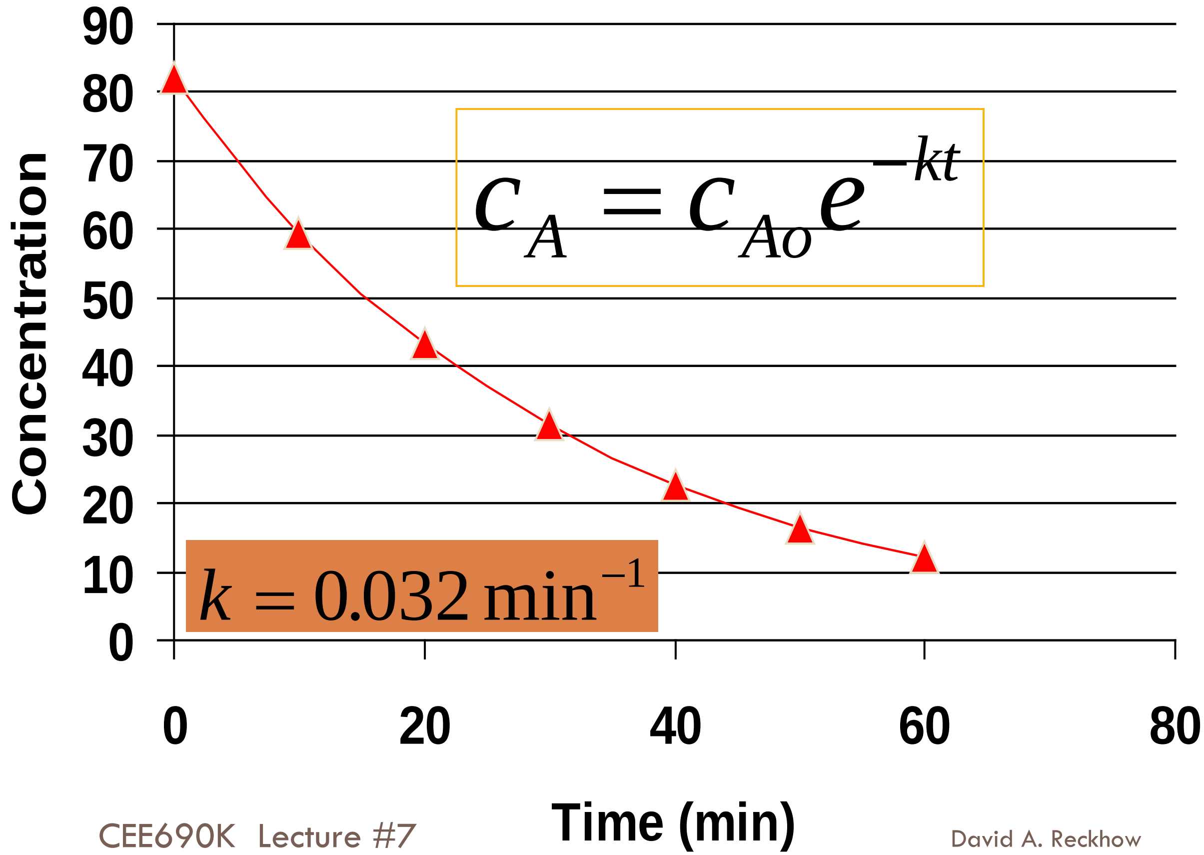
- Fitting the data to rate equations
  - Integral Methods
    - Already discussed; depends on model
    - Uses all data; but not as robust
  - Differential Methods
    - Get simple estimates of instantaneous rates and fit these to a concentration dependent model
    - Quite adaptable
  - Initial Rate Methods
    - Relatively free from interference from products
    - Not dependent on common assumptions

Simple first order

$$A \xrightarrow{k} products$$

- When n=1, we have a simple first-order reaction
- This results in an "exponential decay"

$$\frac{dc}{dt} = -kc_A$$



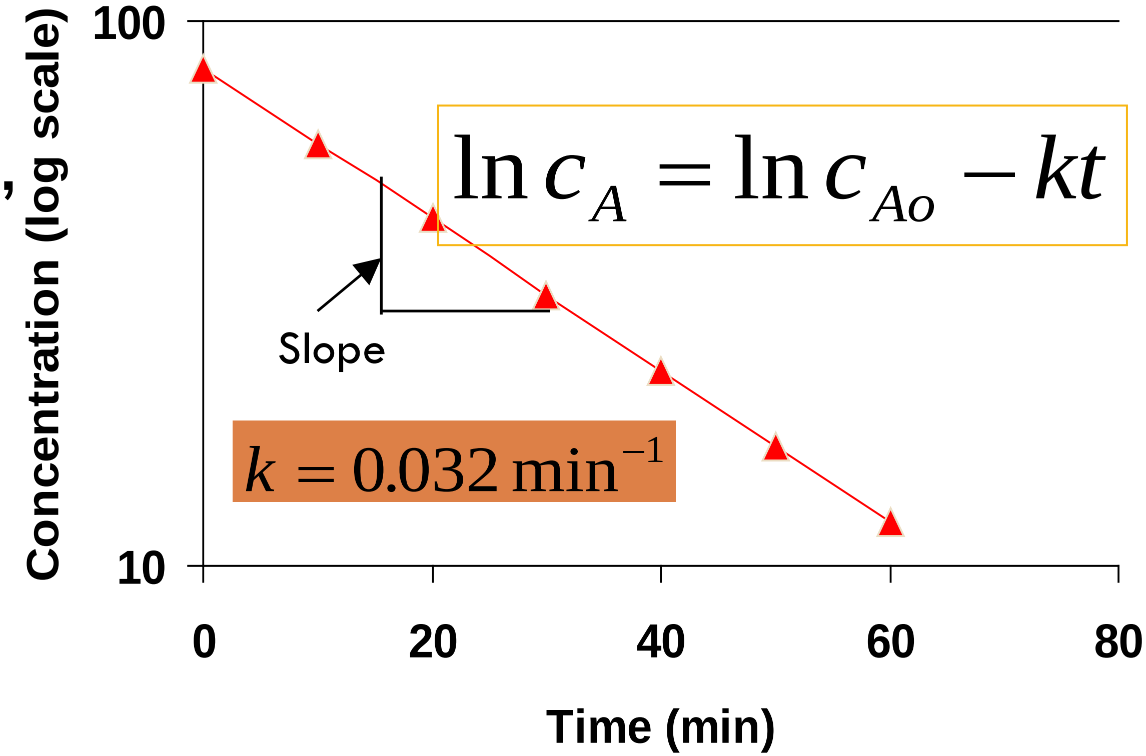
$$c_A = c_{Ao}e^{-kt}$$

$$k = 0.032 \min^{-1}$$

Integral Method: First order

$$\frac{dc_A}{dt} = -kc_A$$

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

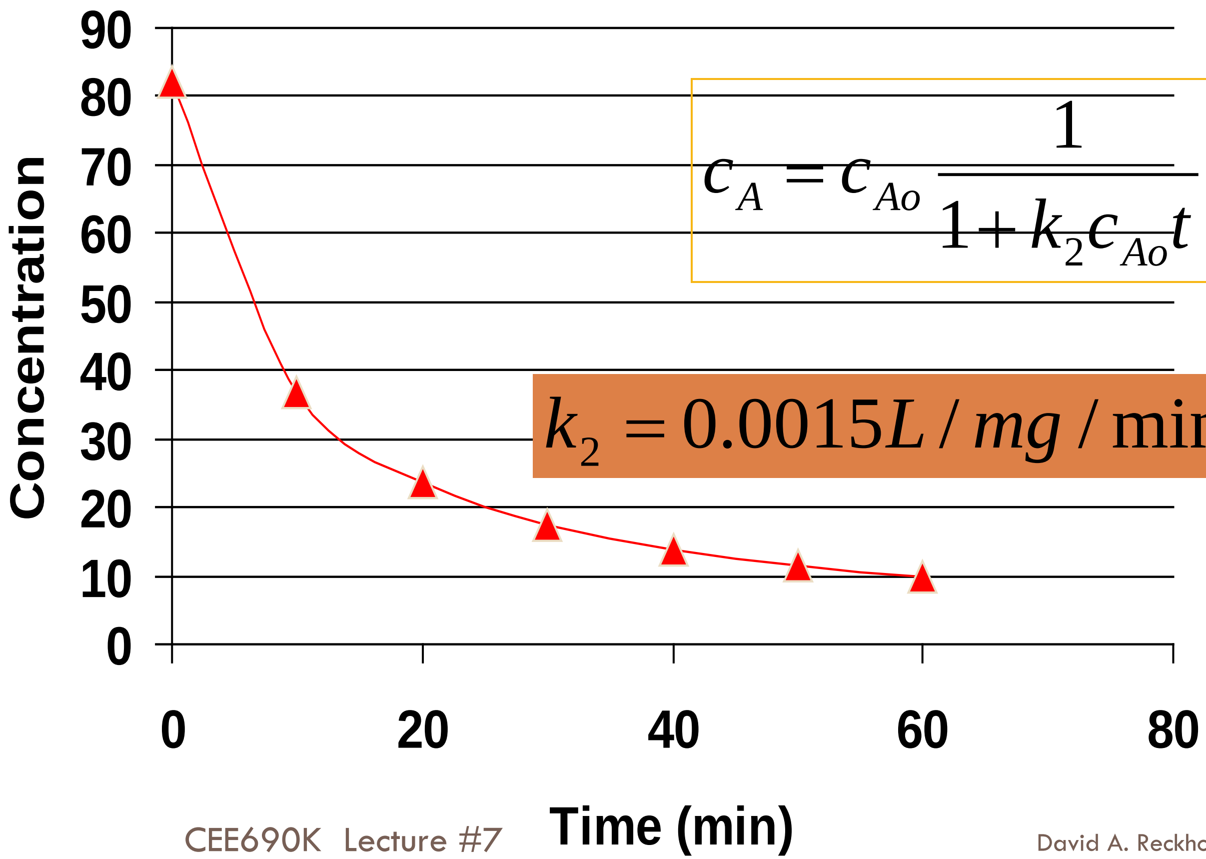


Simple Second Order

$$2A \xrightarrow{k_2} products$$

$$\frac{1}{\nu_A}\frac{dc_A}{dt} = -k_2 c_A^2$$

- 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



$$c_A = c_{Ao}\frac{1}{1 + k_2 c_{Ao} t}$$

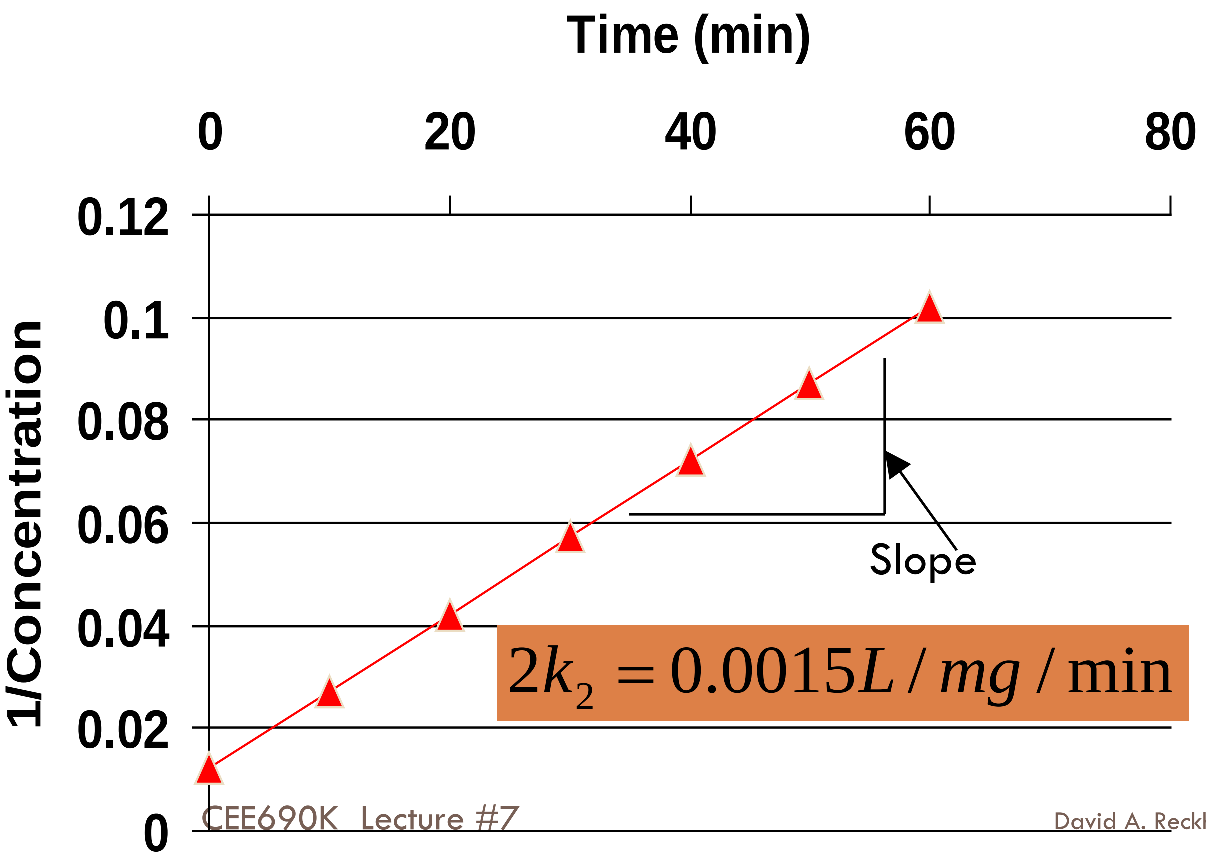
$$k_2 = 0.0015 L / mg / \min$$

Integral method: Simple Second Order

- Again, the equation can be linearized to estimate "k" from data

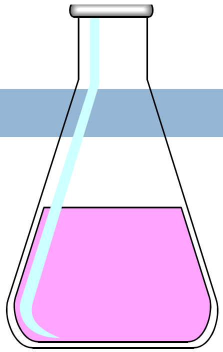
$$\frac{1}{\nu_A}\frac{dc_A}{dt} = -k_2 c_A^2$$

$$\frac{1}{c_A} = \frac{1}{c_{Ao}} + 2k_2 t$$



$$2k_2 = 0.0015 L/mg/\min$$

Variable Kinetic Order



- Any reaction order, except n=1

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

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

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

Mixed Second Order

$$A + B \xrightarrow{k_2} products$$

- Two different reactants

$$rate \equiv \frac{1}{V}\frac{d\xi}{dt} \equiv \frac{1}{\nu_A}\frac{d[A]}{dt} =$$

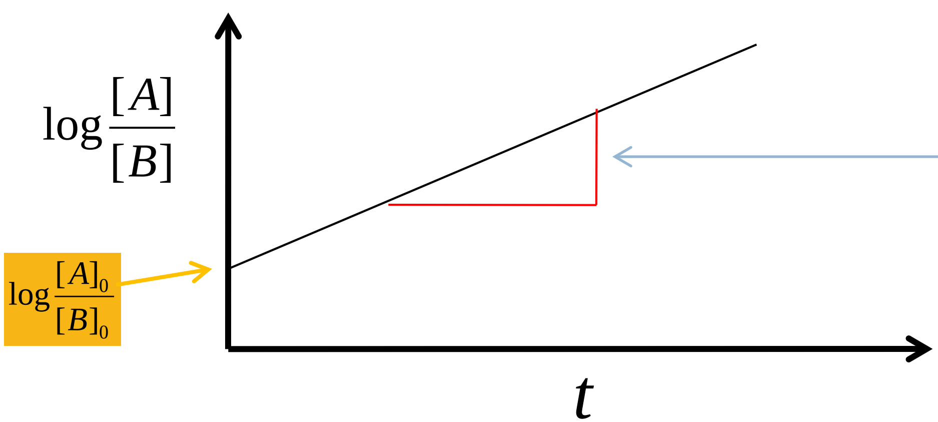
$$\frac{dx}{dt} = k_2[A][B] = k_2\left([A]_0 - x\right)\left([B]_0 - x\right)$$

  - Initial Concentrations are different; $[A]_0 \neq [B]_0$
    - The integrated form is:

$$\frac{1}{[A]_0 - [B]_0}\ln\frac{[B]_0[A]}{[A]_0[B]} = k_2 t$$

    - Which can be expressed as:

$$\log\frac{[A]}{[B]} = 0.43k_2\left([A]_0 - [B]_0\right)t - \log\frac{[B]_0}{[A]_0}$$



Integral Method: Mixed Second Order

$$A + B \xrightarrow{k_2} products$$

- Initial Concentrations are the same; $[A]_0=[B]_0$

$$[A]=[B]=[A]_0 - x = [B]_0 - x$$

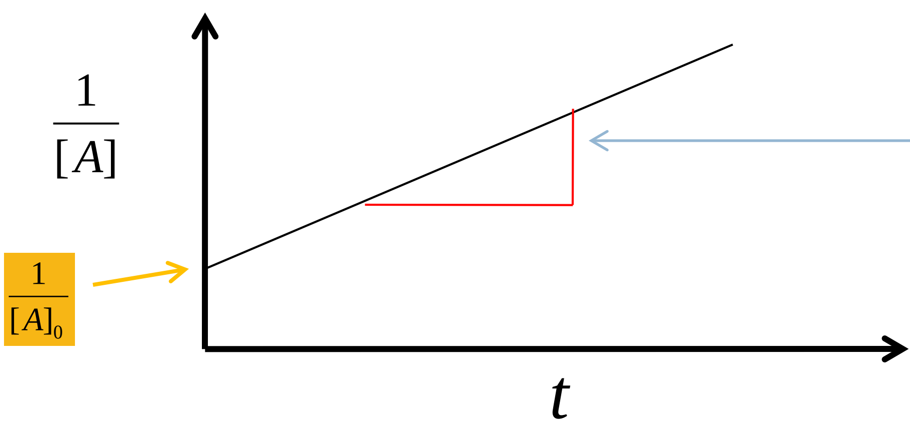
$$\frac{dx}{dt} = k_2[A][A] = k_2([A]_0 - x)([A]_0 - x)$$

- The integrated form is:

$$\int \frac{d[A]}{[A]^2} = \int \nu_A k_2 dt \Rightarrow \frac{1}{[A]} - \frac{1}{[A]_0} = 2k_2 t$$

- Which can be integrated:

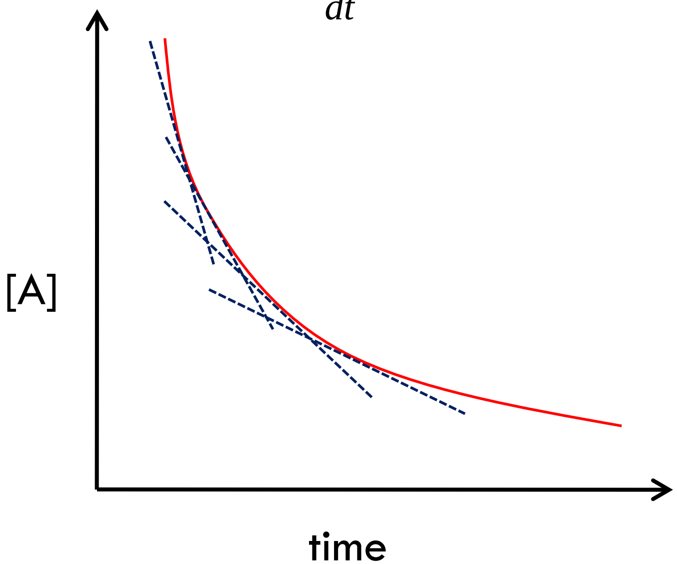
$$\frac{1}{[A]} = 2k_2 t + \frac{1}{[A]_0}$$



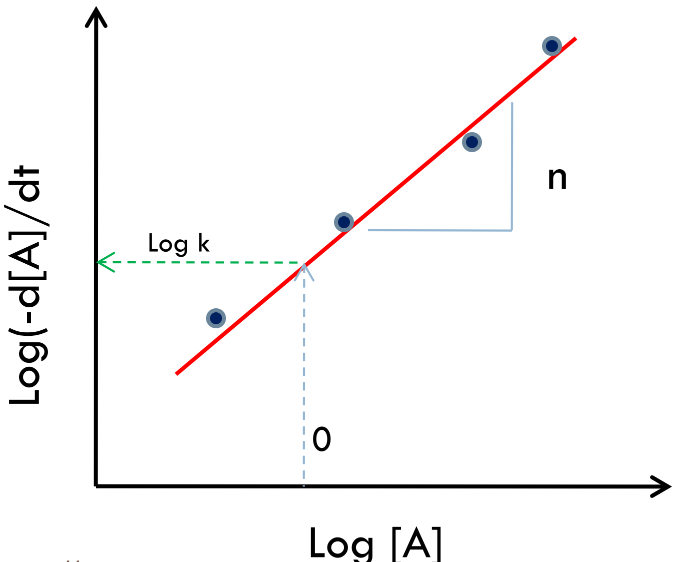
Differential Methods I

- Doesn't require assumptions on reaction order
  - Simple method, doing it by "eye"
    - Get estimates of instantaneous rates by drawing tangents & plotting these slopes

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



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



Differential Methods II

- Finite difference method

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

  - Start with the general linear solution

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

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

  - And substituting back, we get:

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

  - So the reciprocal of "X" is a linear function of time

$$\frac{1}{X} = (n-1)t + \frac{1}{k[A]_0^{n-1}}$$

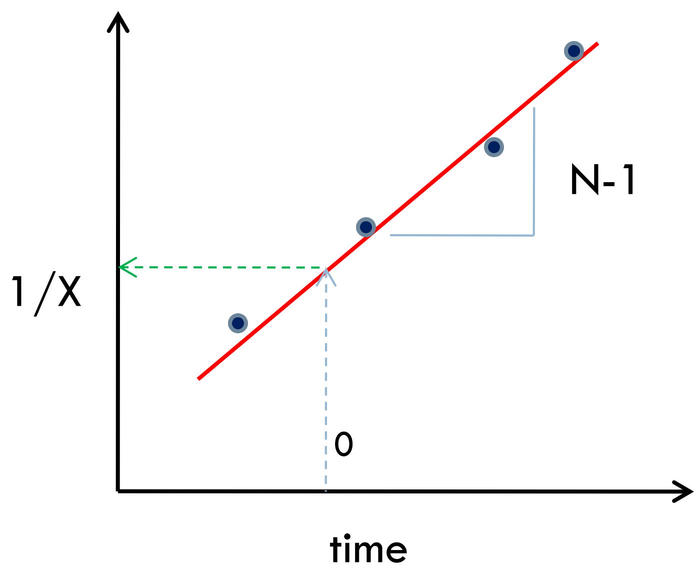
Differential Methods III

- 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