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CEE690K Lecture #7 1

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CEE 690K

ENVIRONMENTAL REACTION KINETICS

Lecture #7

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

David A. Reckhow

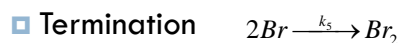
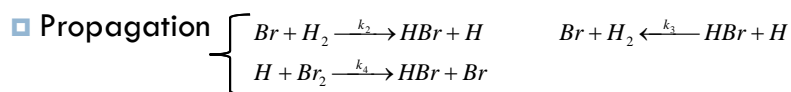
Introduction

HBr Formation I

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

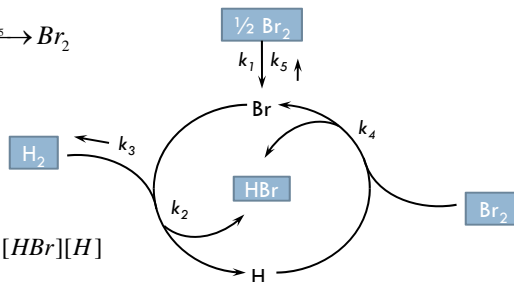
Observed Rate Expression

Chain Mechanism



"theoretical" Rate Expression

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2][\text{Br}] + k_4[\text{Br}_2][\text{H}] - k_3[\text{HBr}][\text{H}]$$



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HBr Formation II

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2][\text{Br}] + k_4[\text{Br}_2][\text{H}] - k_3[\text{HBr}][\text{H}]$$

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- 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:

$$0 \approx \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] + k_3[\text{HBr}][\text{H}] + k_4[\text{Br}_2][\text{H}] - k_2[\text{H}_2][\text{Br}] - 2k_5[\text{Br}]^2$$

$$0 \approx \frac{d[\text{H}]}{dt} = k_2[\text{H}_2][\text{Br}] - k_3[\text{HBr}][\text{H}] - k_4[\text{Br}_2][\text{H}]$$

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

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HBr Formation III

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2][\text{Br}] + k_4[\text{Br}_2][\text{H}] - k_3[\text{HBr}][\text{H}]$$

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- Solve the H-QSS for [H]

$$[\text{H}] = \frac{k_2[\text{H}_2][\text{Br}]}{k_3[\text{HBr}] + k_4[\text{Br}_2]}$$

$$0 \approx \frac{d[\text{H}]}{dt} = k_2[\text{H}_2][\text{Br}] - k_3[\text{HBr}][\text{H}] - k_4[\text{Br}_2][\text{H}]$$

- And substitute this into the Br-QSS

$$0 \approx \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] + k_3[\text{HBr}][\text{H}] + k_4[\text{Br}_2][\text{H}] - k_2[\text{H}_2][\text{Br}] - 2k_5[\text{Br}]^2$$

$$2k_5[\text{Br}]^2 = 2k_1[\text{Br}_2] + (k_3[\text{HBr}] + k_4[\text{Br}_2])[\text{H}] - k_2[\text{H}_2][\text{Br}]$$

$$2k_5[\text{Br}]^2 = 2k_1[\text{Br}_2] + (k_3[\text{HBr}] + k_4[\text{Br}_2]) \frac{k_2[\text{H}_2][\text{Br}]}{k_3[\text{HBr}] + k_4[\text{Br}_2]} - k_2[\text{H}_2][\text{Br}]$$

$$2k_5[\text{Br}]^2 = 2k_1[\text{Br}_2] + k_2[\text{H}_2][\text{Br}] - k_2[\text{H}_2][\text{Br}]$$

$$2k_5[\text{Br}]^2 = 2k_1[\text{Br}_2]$$



$$[\text{Br}] = \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5}$$

$$k_1/k_5 = K$$

for: $\text{Br}_2 \leftrightarrow 2\text{Br}$

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HBr Formation IV

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2][\text{Br}] + k_4[\text{Br}_2][\text{H}] - k_3[\text{HBr}][\text{H}]$$

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

$$[\text{H}] = \frac{k_2[\text{H}_2]}{k_3[\text{HBr}] + k_4[\text{Br}_2]} \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5} \quad \text{and} \quad [\text{Br}] = \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5}$$

- Now we can substitute back into the original HBr expression

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2] \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5} + (k_4[\text{Br}_2] - k_3[\text{HBr}]) \frac{k_2[\text{H}_2]}{k_3[\text{HBr}] + k_4[\text{Br}_2]} \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5}$$

- And simplify

$$\frac{d[\text{HBr}]}{dt} = \left(k_2[\text{H}_2] + (k_4[\text{Br}_2] - k_3[\text{HBr}]) \frac{k_2[\text{H}_2]}{k_3[\text{HBr}] + k_4[\text{Br}_2]} \right) \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5}$$

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HBr Formation V

$$\frac{d[\text{HBr}]}{dt} = \left(k_2[\text{H}_2] + (k_4[\text{Br}_2] - k_3[\text{HBr}]) \frac{k_2[\text{H}_2]}{k_3[\text{HBr}] + k_4[\text{Br}_2]} \right) \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5}$$

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- Further simplifying

$$\frac{d[\text{HBr}]}{dt} = \left(k_2[\text{H}_2] + \frac{k_2[\text{H}_2]k_4[\text{Br}_2] - k_2[\text{H}_2]k_3[\text{HBr}]}{k_3[\text{HBr}] + k_4[\text{Br}_2]} \right) \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5}$$

$$\frac{d[\text{HBr}]}{dt} = \left(k_2[\text{H}_2] + \frac{k_2[\text{H}_2] - k_2[\text{H}_2] \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}}{1 + \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}} \right) \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5}$$

$$\frac{d[\text{HBr}]}{dt} = \left(\frac{k_2[\text{H}_2] + k_2[\text{H}_2] \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}}{1 + \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}} + \frac{k_2[\text{H}_2] - k_2[\text{H}_2] \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}}{1 + \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}} \right) \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5}$$

$$\frac{d[\text{HBr}]}{dt} = \left(\frac{2k_2[\text{H}_2]}{1 + \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}} \right) \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{0.5} \quad \Rightarrow \quad \boxed{\frac{d[\text{HBr}]}{dt} = \left(\frac{2k_2 \frac{k_1}{k_5} [\text{H}_2][\text{Br}_2]^{0.5}}{1 + \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}} \right)}$$

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

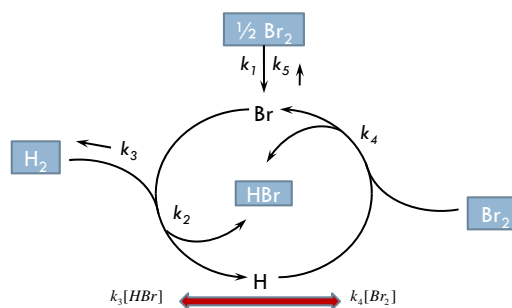
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HBr Formation VI

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

$$\frac{d[\text{HBr}]}{dt} = \left(\frac{2k_2 \frac{k_1}{k_2} [\text{H}_2][\text{Br}_2]^{0.5}}{1 + \frac{k_3[\text{HBr}]}{k_4[\text{Br}_2]}} \right)$$



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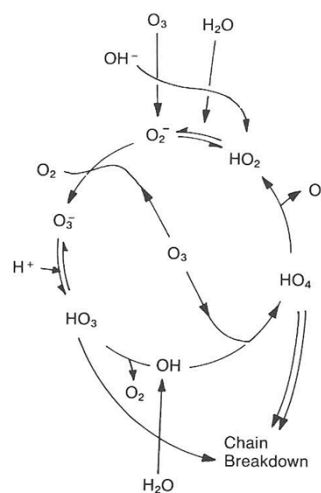
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Chain Reactions

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) | $\text{O}_3 + \text{OH}^- \xrightarrow{k_1} \text{HO}_2 + \text{O}_2^-$ | $k_1 = 7.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
HO_2 : hydroperoxide radical |
| (1') | $\text{HO}_2 \xrightleftharpoons[k_2]{k_2} \text{O}_2^- + \text{H}^+$ | k_2 (ionization constant) = $10^{-4.8}$
O_2^- : superoxide radical ion |
| (2) | $\text{O}_3 + \text{O}_2^- \xrightarrow{k_2} \text{O}_3^- + \text{O}_2$ | $k_2 = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
O_3^- : ozonide radical ion |
| (3) | $\text{O}_3^- + \text{H}^+ \xrightleftharpoons[k_{-3}]{k_3} \text{HO}_3$ | $k_3 = 5.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
$k_{-3} = 2.3 \times 10^2 \text{ s}^{-1}$ |
| (4) | $\text{HO}_3 \xrightarrow{k_4} \text{OH} + \text{O}_2$ | $k_4 = 1.1 \times 10^5 \text{ s}^{-1}$ |
| (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 const



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Kinetic Analysis of Experimental Data

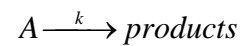
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- Fitting the data to rate equations
 - Integral Methods
 - Already discussed; depends on model
 - Uses all data; but not as robust
 - Differential Methods
 - Get simple estimates of instantaneous rates and fit these to a concentration dependent model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

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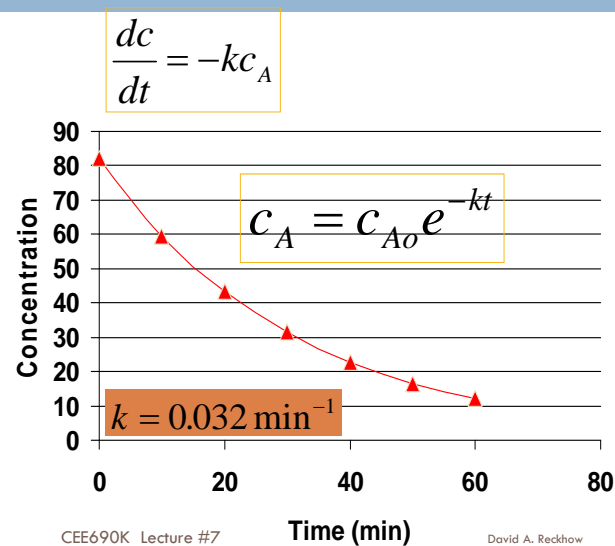
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Simple first order



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



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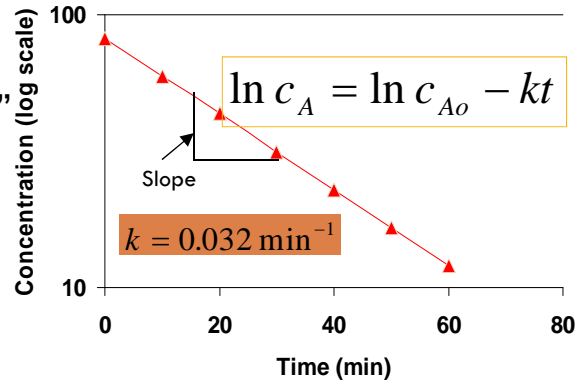
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Integral Method: First order

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

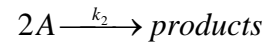
$$\frac{dc_A}{dt} = -kc_A$$



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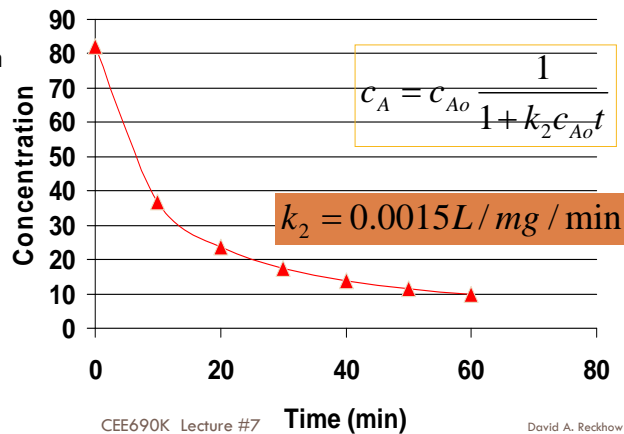
Simple Second Order



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- When $n=2$, we have a simple second-order reaction
- This results in an especially wide range in rates
- More typical to have 2nd order in each of two different reactants

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



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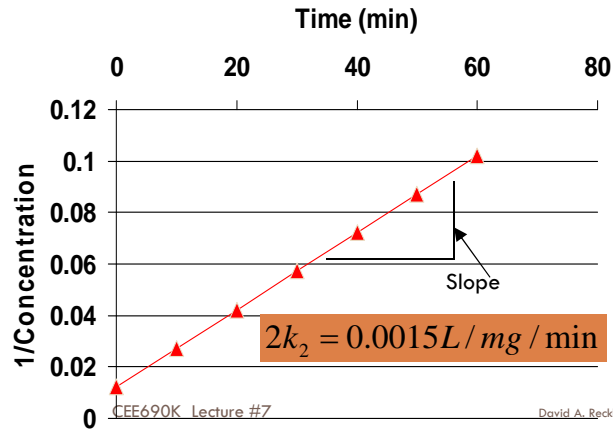
Integral method: Simple Second Order

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

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

$$\frac{1}{c_A} = \frac{1}{c_{A0}} + 2k_2 t$$



Variable Kinetic Order

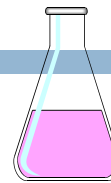
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- Any reaction order, except $n=1$

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

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

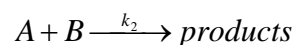
$$c = c_o \frac{1}{\left[1 + (n-1)k_n c_o^{n-1} t\right]^{1/(n-1)}}$$



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Mixed Second Order



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Two different reactants

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

$$\frac{dx}{dt} = k_2[A][B]$$

$$= k_2([A]_0 - x)([B]_0 - x)$$

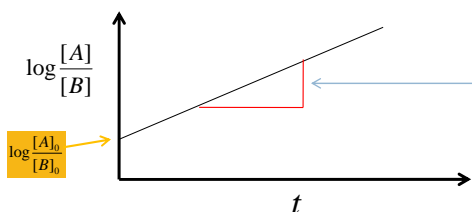
Initial Concentrations are different; $[A]_0 \neq [B]_0$

The integrated form is:

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

Which can be expressed as:

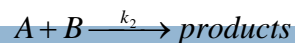
$$\log \frac{[A]}{[B]} = \underbrace{0.43 k_2 ([A]_0 - [B]_0) t}_{\text{slope}} - \log \frac{[B]_0}{[A]_0}$$



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Integral Method: Mixed Second Order



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

$$\frac{dx}{dt} = k_2[A][A]$$

$$= k_2([A]_0 - x)([A]_0 - x)$$

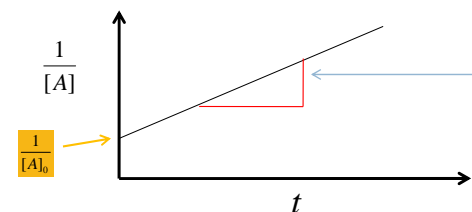
$$[A] = [B] = [A]_0 - x = [B]_0 - x$$

The integrated form is:

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

Which can be integrated:

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



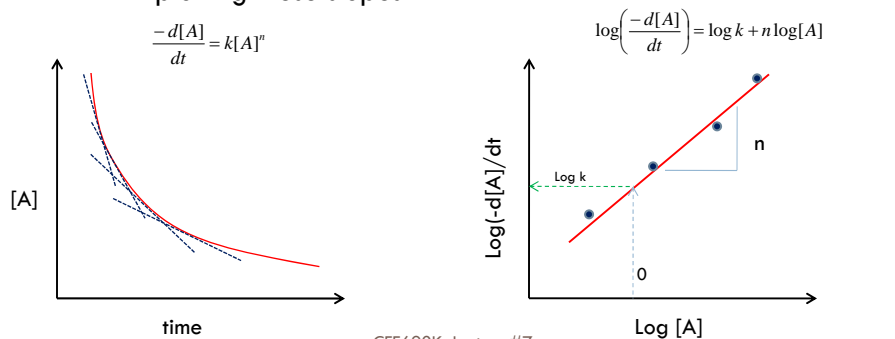
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Differential Methods I

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



Differential Methods II

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- Finite difference method
 - Start with the general linear solution
 - $$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt$$
 - $$[A]^{n-1} = \left\{ (n-1)kt + \frac{1}{[A]_0^{n-1}} \right\}^{-1} \quad \longrightarrow \quad [A]^n = [A] \left\{ (n-1)kt + \frac{1}{[A]_0^{n-1}} \right\}^{-1}$$
 - 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

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

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Differential Methods III

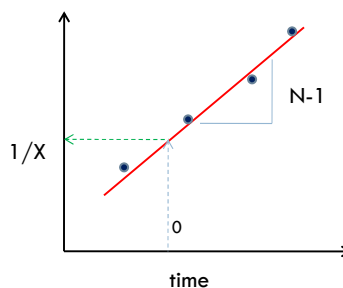
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- Finite difference method (cont.)
 - Now we can get “X” from a time-centered finite difference approximation

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

- And, for $t=n$

$$\frac{1}{X} \equiv \frac{[A]}{d[A]/dt}$$



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Initial Rate Methods

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- 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

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□ To next lecture