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# CEE 690K

## ENVIRONMENTAL REACTION KINETICS

### Lecture #6

[Estimation of Rates:](#) Practical Methods

Brezonik, pp.50-58

# Chlorination of Phenol

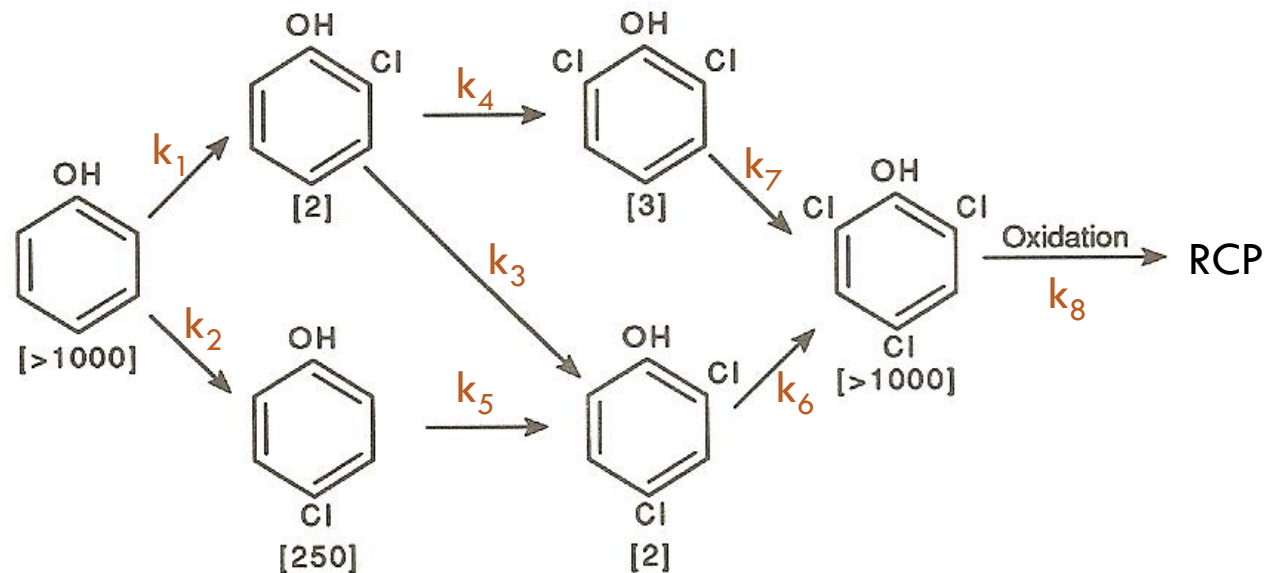
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Table 4-8. Rate Constants ( $k_{\text{obs}}$ ) for Chlorination of Phenols<sup>a</sup>

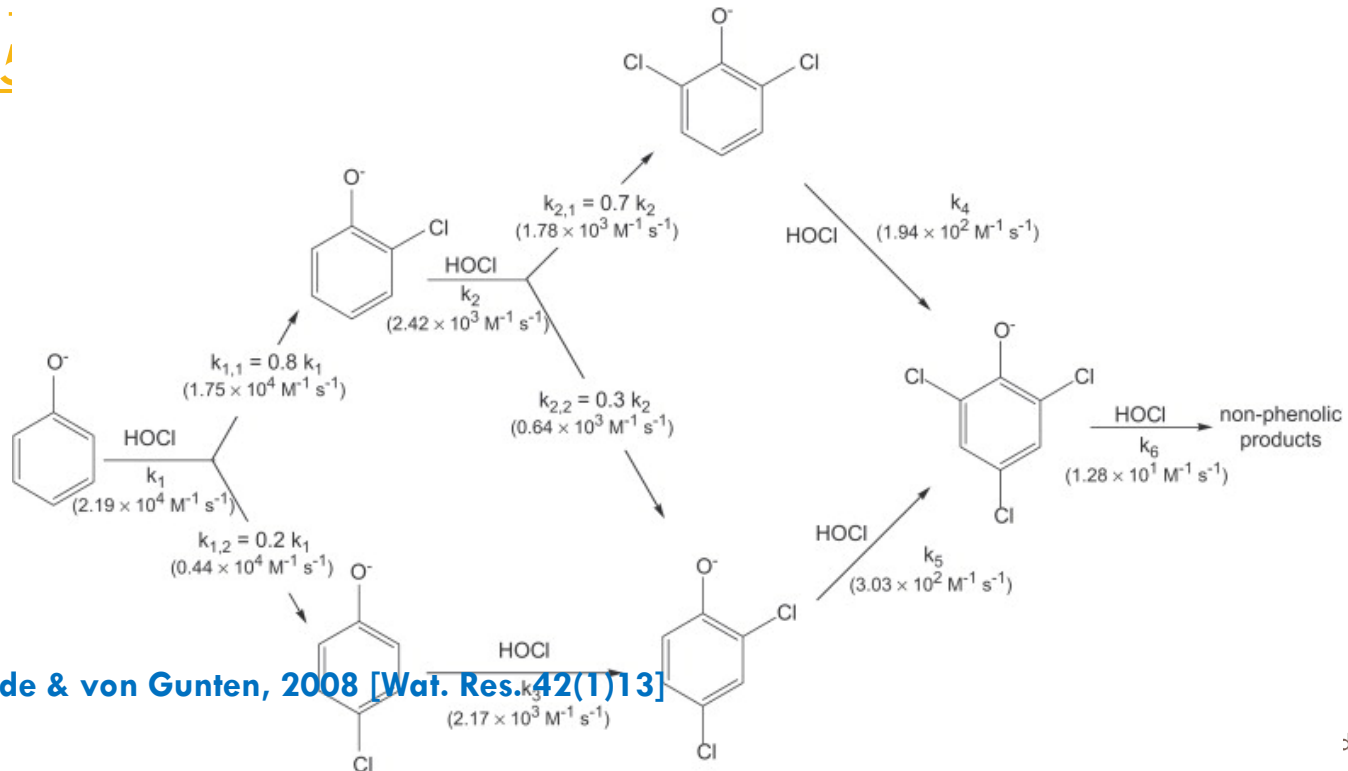
pH	Phenol	2-Chloro-phenol	4-Chloro-phenol	2,4-Dichloro-phenol	2,6-Dichloro-phenol	2,4,6-Tri-chlorophenol
5	2.09E2	4.03E2	9.60E1	2.38E2	6.32E2	1.17E2
6	4.82E2	1.04E3	2.98E2	4.02E2	1.34E3	3.46E2
7	2.23E3	3.16E3	8.93E2	1.76E3	4.95E3	5.16E2
8	6.15E3	8.15E3	1.84E3	2.72E3	2.19E3	1.45E2
9	6.14E3	3.21E3	1.54E3	5.48E2	2.96E2	1.34E1
10	2.84E3	4.30E3	4.15E2	6.32E1	3.09E1	9.05E-1
11	4.73E2	4.60E1	4.70E1	6.37	3.12	5.44E-2
12	4.50E1	4.60	4.54	6.36E-1	3.15E-1	1.81E-3

**How did Morris & Lee get these rate data?**

<sup>a</sup> T = 25°C; I = 0.02; [Cl<sup>-</sup>] = 10<sup>-1</sup> M. From Lee, G.F., in *Principles and Applications of Water Chemistry*, S.D. Faust and J.V. Hunter (Eds.), John Wiley & Sons, New York, 1967.



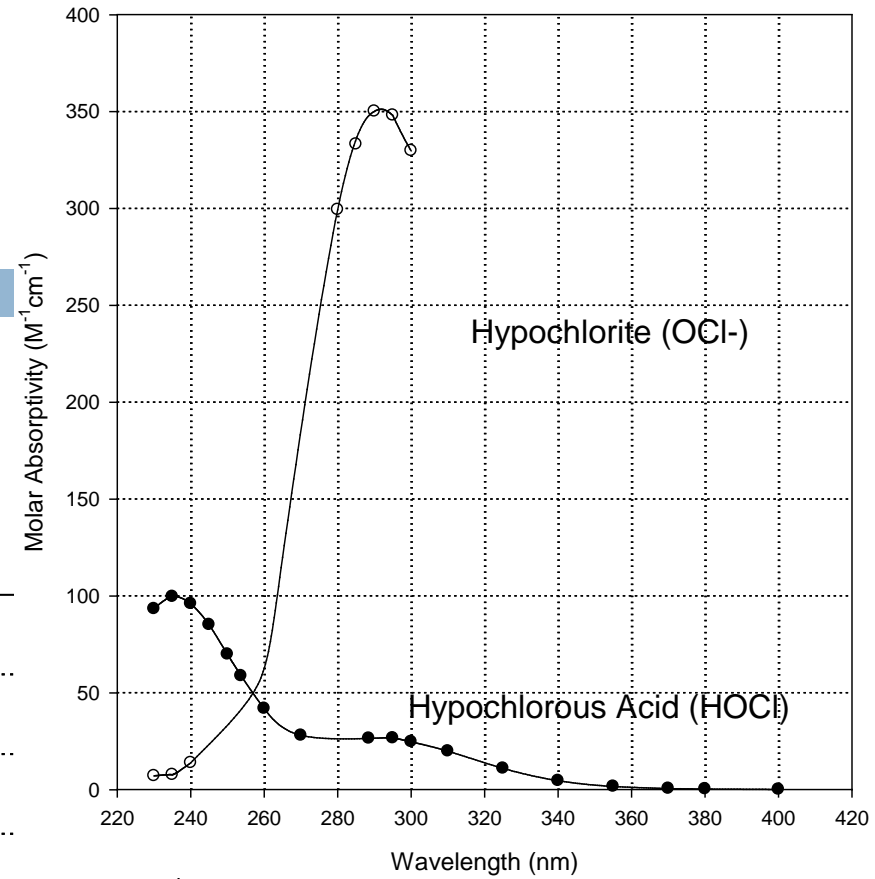
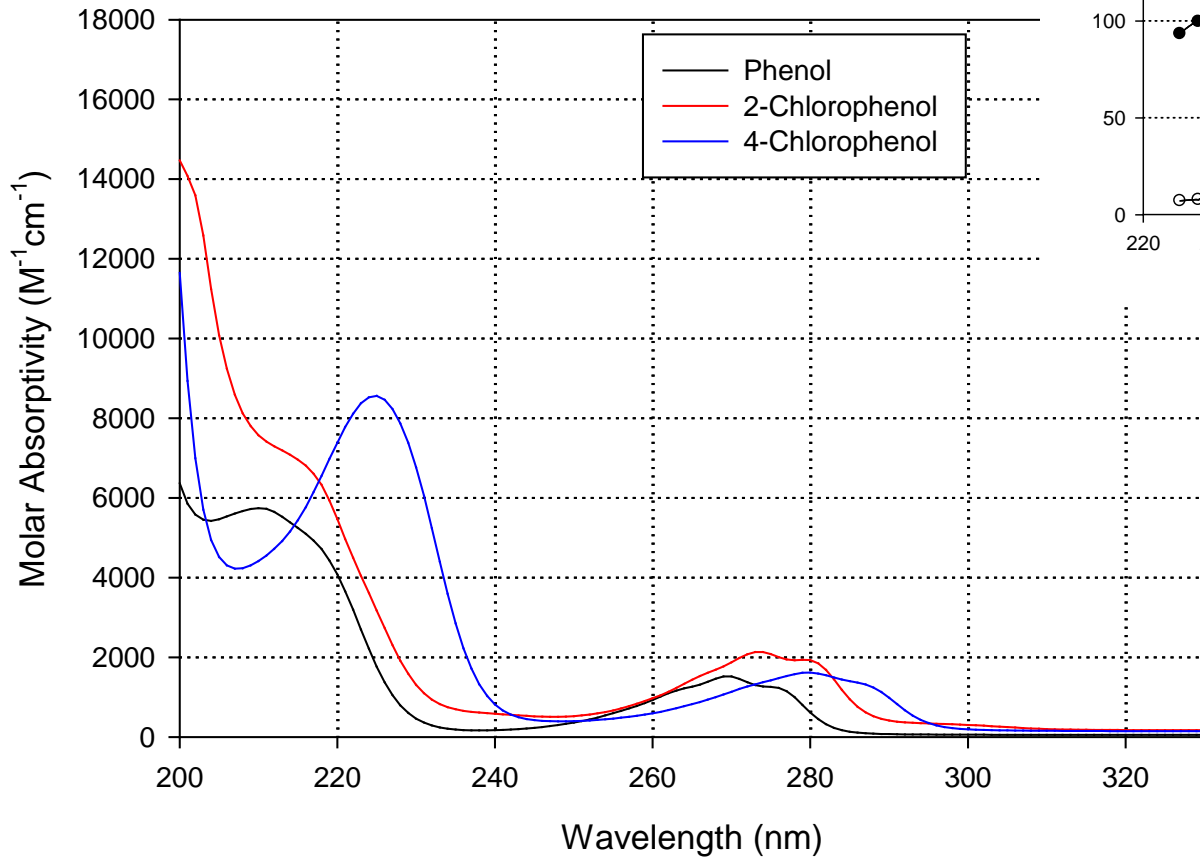
- Reaction scheme for the chlorination of phenoxide ion (adapted from [Lee and Morris \(1962\)](#) and [Burttschell et al. \(1959\)](#)) with rate constants and ratios percentage obtained from [Gallard and von Gunten \(2002\)](#) and [Acero et al. \(2004\)](#)



From: [Deborde & von Gunten, 2008 \[Wat. Res. 42\(1\)13\]](#)

# Absorbance data?

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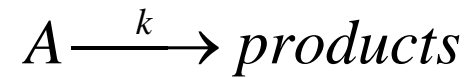


# Kinetic Analysis of Experimental Data

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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

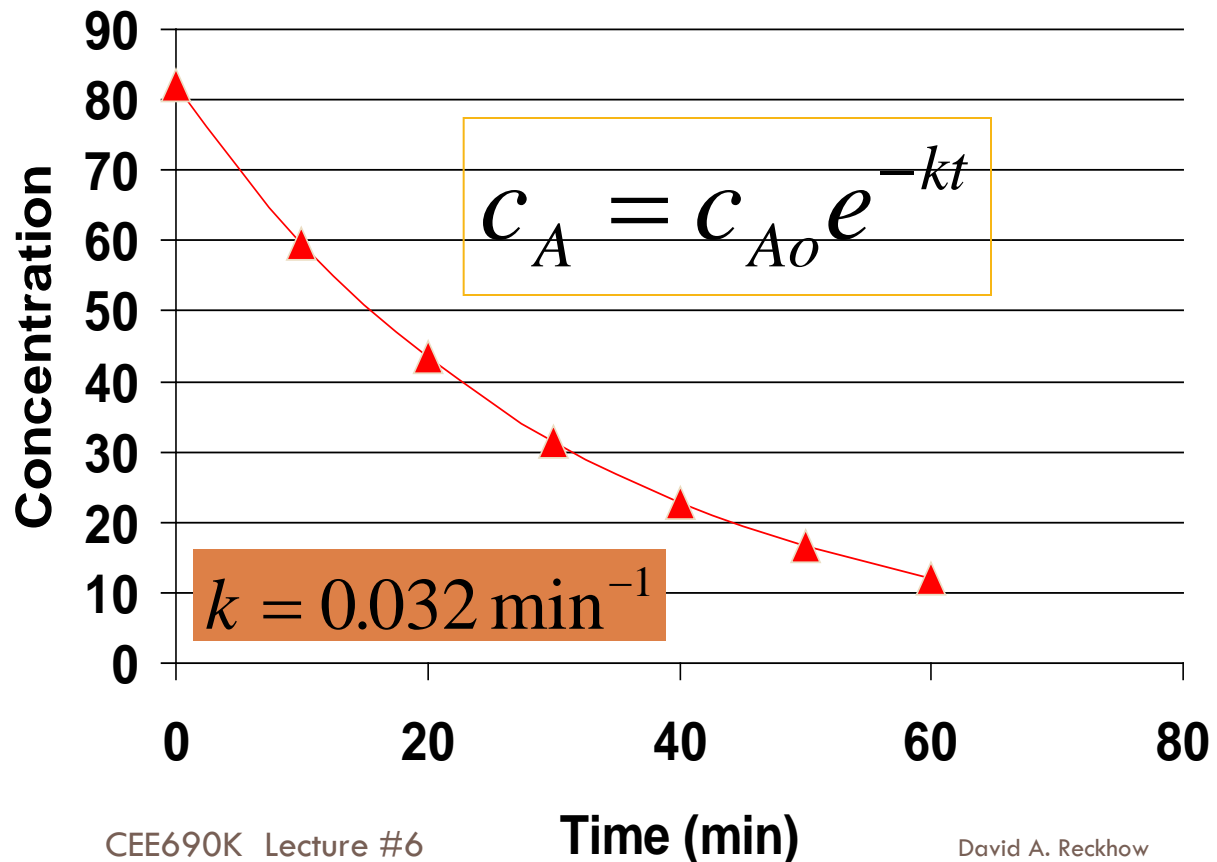
# Simple first order



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

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

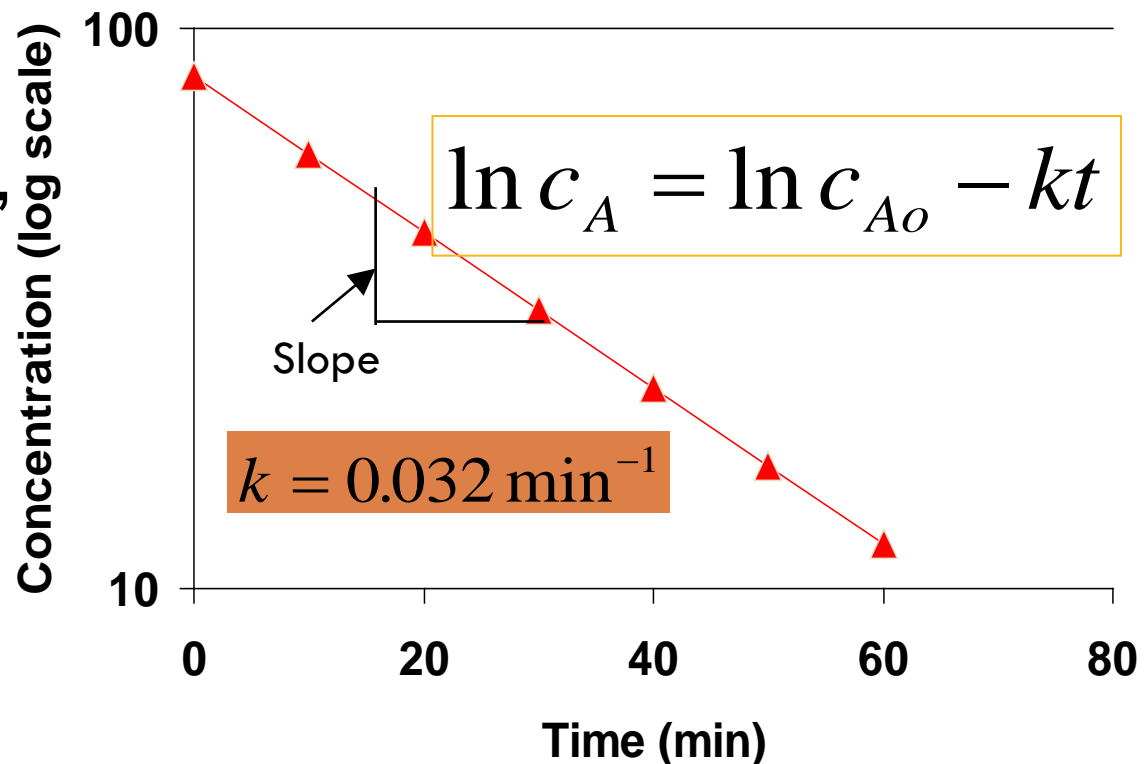


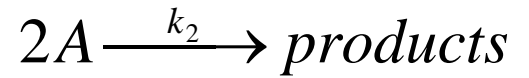
# Integral Method: First order

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

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





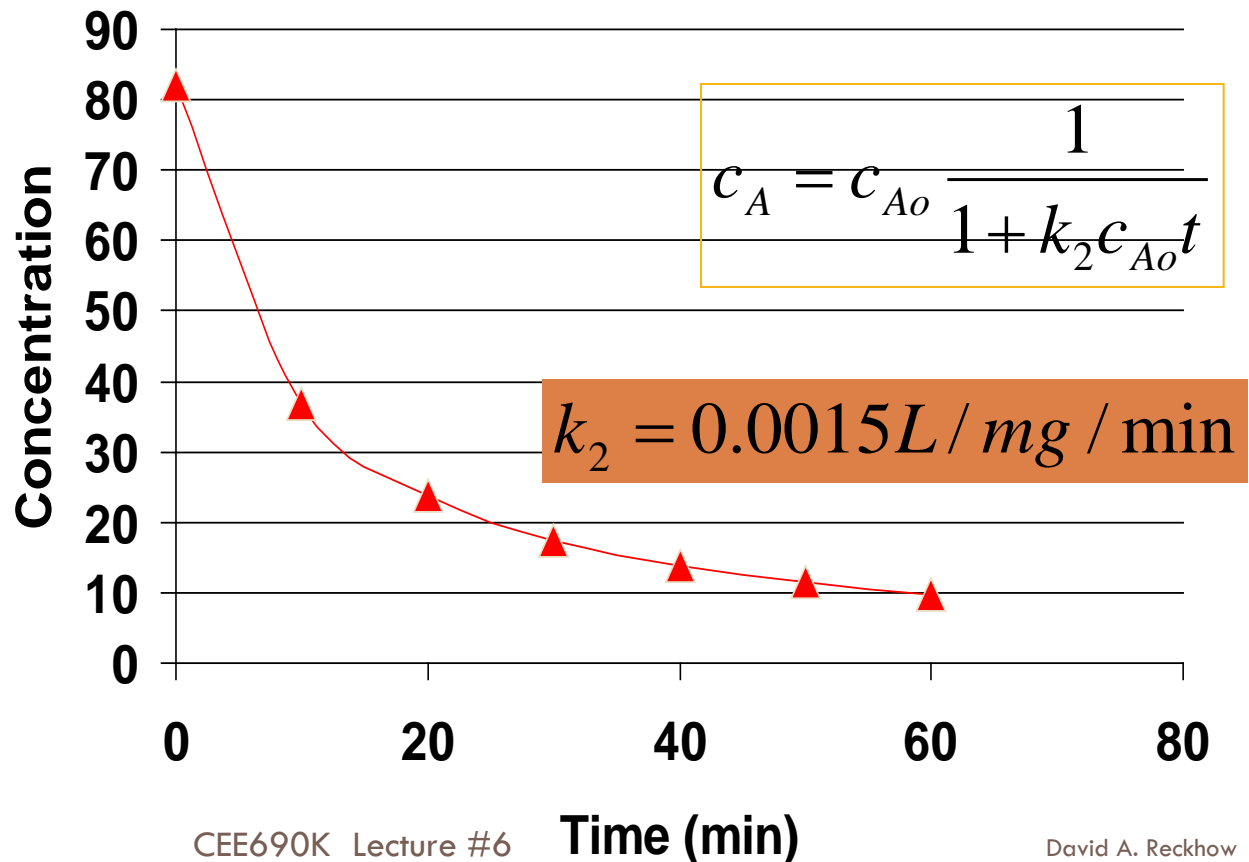
# Simple Second Order

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

■ When  $n=2$ , we have a simple second-order reaction

- This results in an especially wide range in rates
- More typical to have 2<sup>nd</sup> order in each of two different reactants





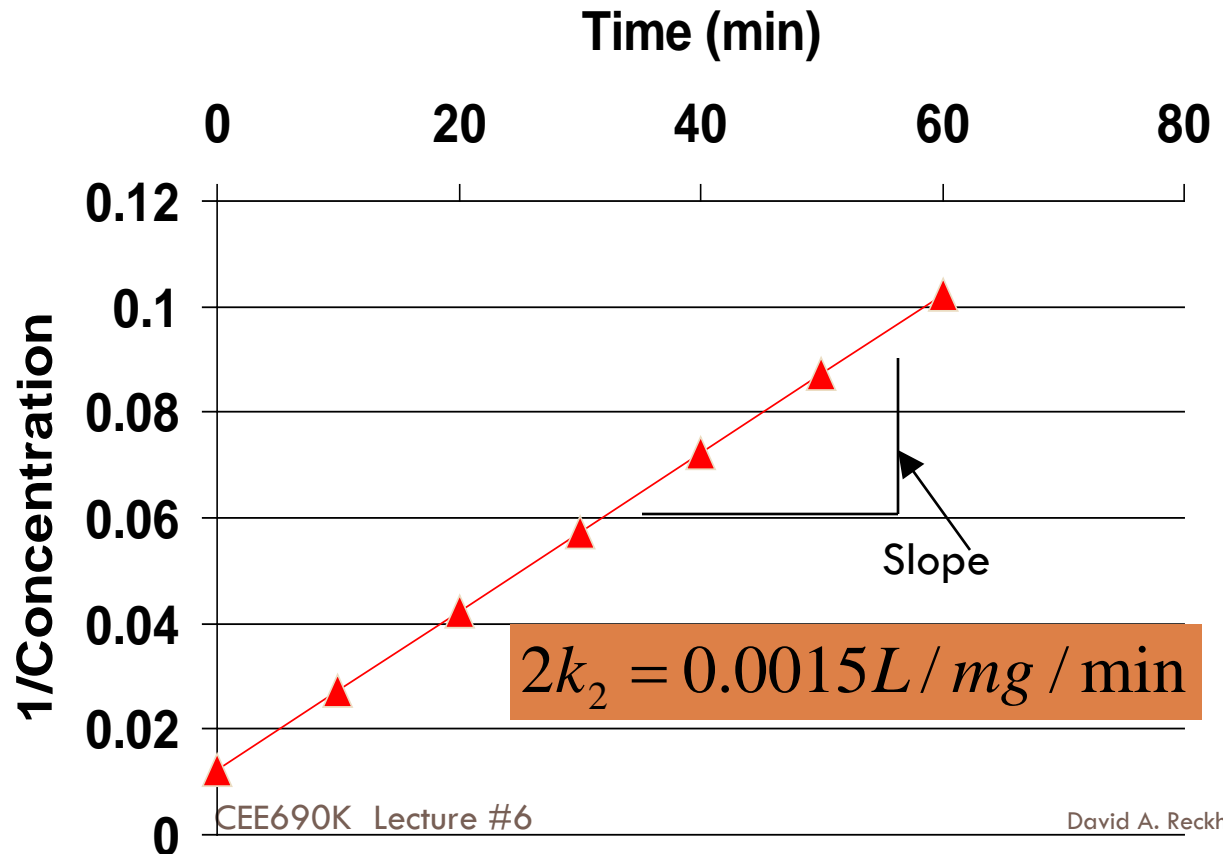
# Integral method: Simple Second Order

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

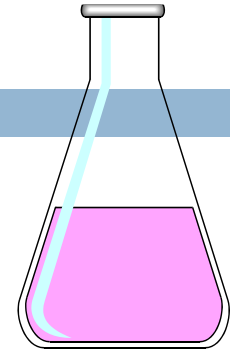
$$\frac{1}{V_A} \frac{dc_A}{dt} = -k_2 c_A^2$$

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



# Variable Kinetic Order

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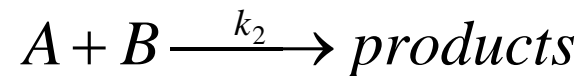
- Any reaction order, except  $n=1$

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

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

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

# Mixed Second Order



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- Two different reactants

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

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

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

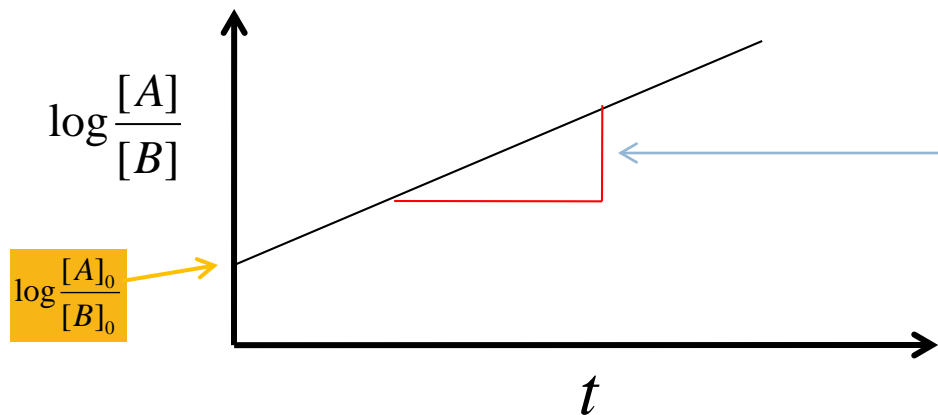
- Initial Concentrations are different;  $[A]_0 \neq [B]_0$

- The integrated form is:

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

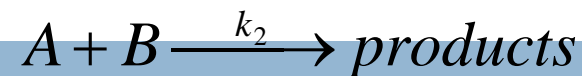
- Which can be expressed as:

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



# Integral Method: Mixed Second Order

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

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

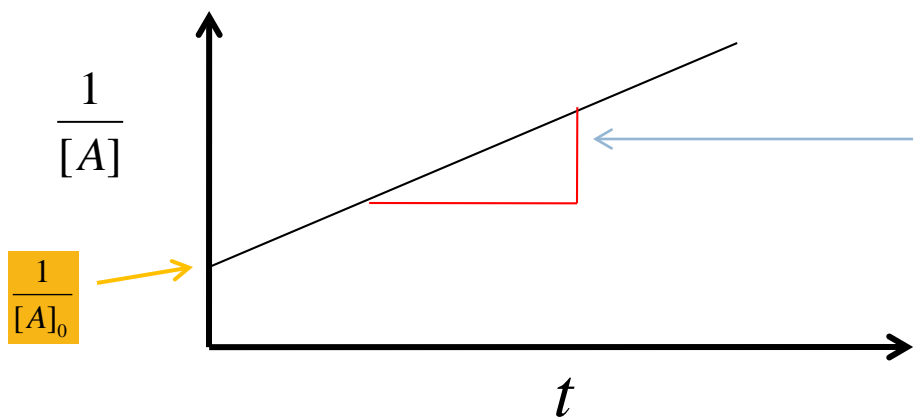
$$[A] = [B] = [A]_0 - x = [B]_0 - x$$

- The integrated form is:

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

- Which can be integrated:

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

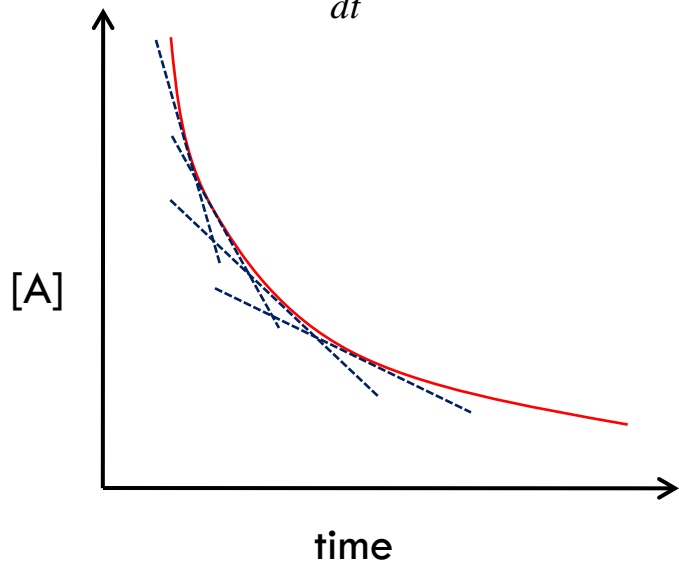


# Differential Methods I

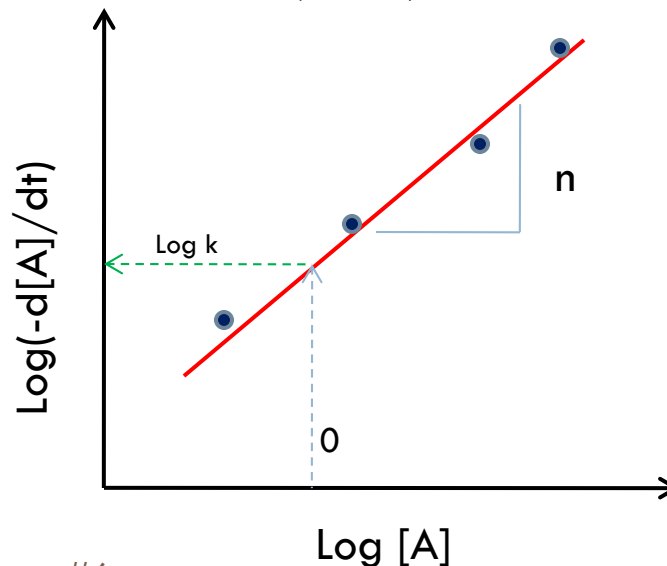
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- Doesn't require assumptions on reaction order
  - ▣ Simple method, doing it by "eye"
    - Get estimates of instantaneous rates by drawing tangents & plotting these slopes

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



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



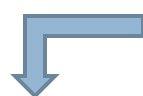
# Differential Methods II

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## □ Finite difference method

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

### □ Start with the general linear solution


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

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

### □ 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

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

# Differential Methods III

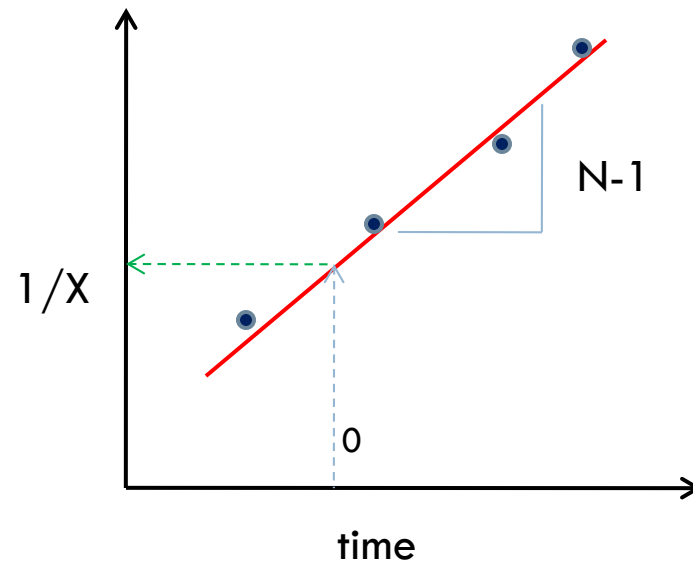
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- Finite difference method (cont.)
  - ▣ Now we can get “X” from a time-centered finite difference approximation

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

- And, for  $t=n$

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



# Initial Rate Methods

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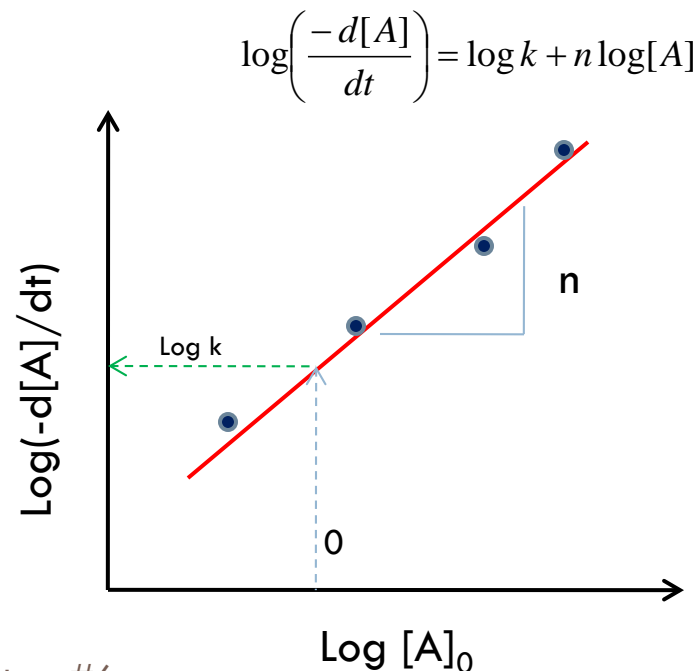
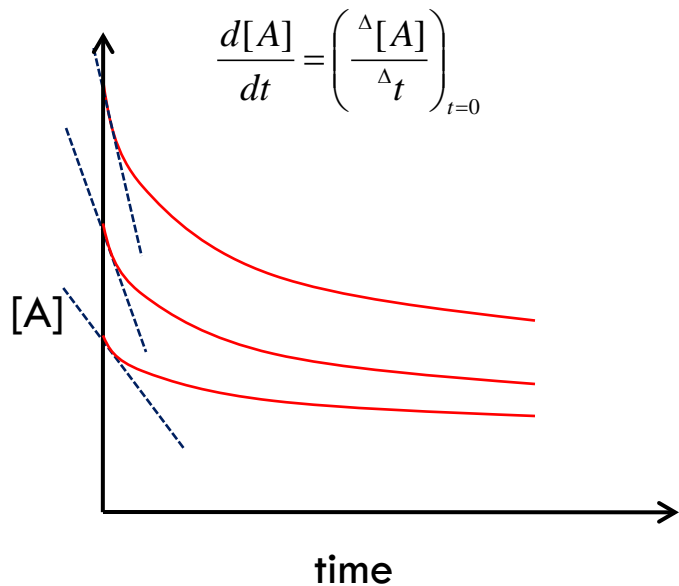
- Evaluated in very early stages of the reaction where:
  - ▣ Only small amounts of products have been formed
  - ▣ Reactants have essentially not changed in concentrations
- Avoids many problems of complex reactions where products continue to react



# Initial Rate II

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- Run multiple reactions at different starting concentrations
- Measure short-term concentrations of starting materials
- Estimate initial rate and plot vs starting concentration



- To next lecture