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CEE690K Lecture #6 1

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# CEE 690K

## ENVIRONMENTAL REACTION KINETICS

### Lecture #6

**Estimation of Rates:** Practical Methods  
Brezonik, pp.50-58

David A. Reckhow

Introduction

## Chlorination of Phenol

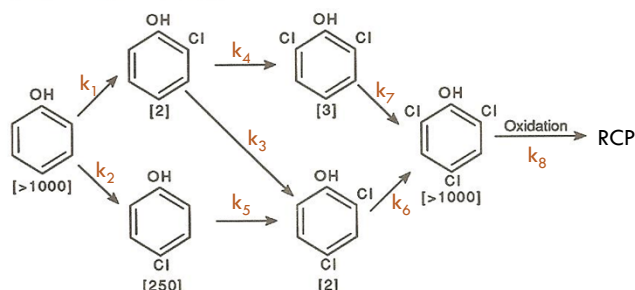
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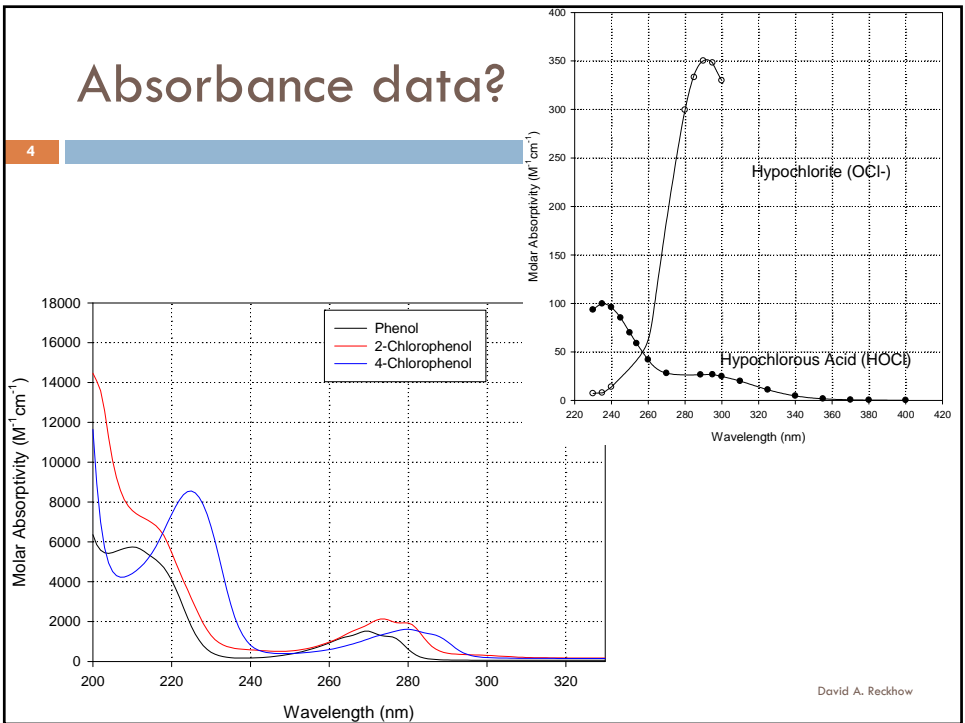
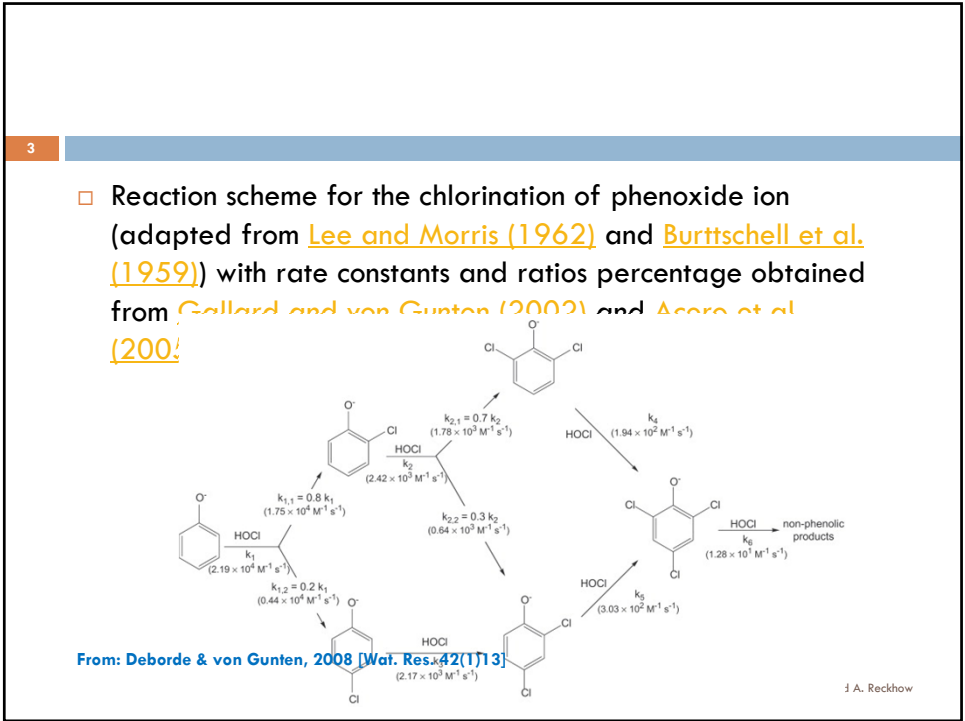
Table 4-8. Rate Constants ( $k_{\text{obs}}$ ) for Chlorination of Phenols<sup>a</sup>

pH	Phenol	2-Chloro-phenol	4-Chloro-phenol	2,4-Dichloro-phenol	2,6-Dichloro-phenol	2,4,6-Trichlorophenol
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.





## Kinetic Analysis of Experimental Data

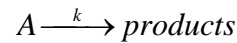
5

- 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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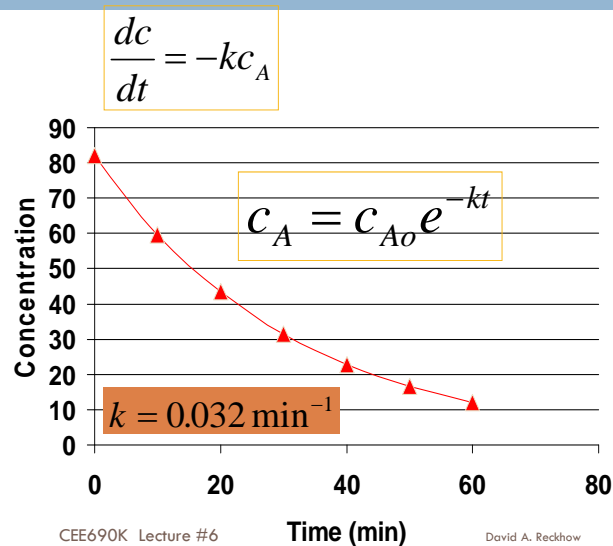
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## Simple first order



6

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



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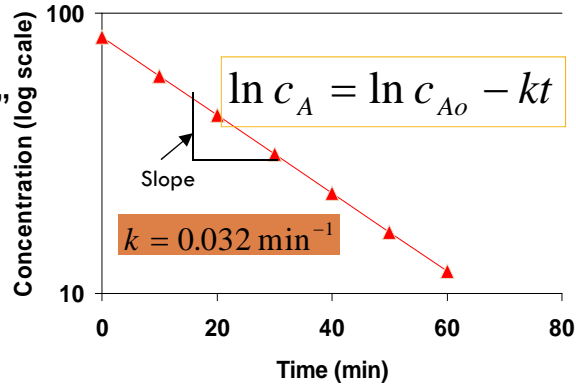
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## Integral Method: First order

7

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

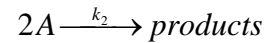
$$\frac{dc_A}{dt} = -kc_A$$



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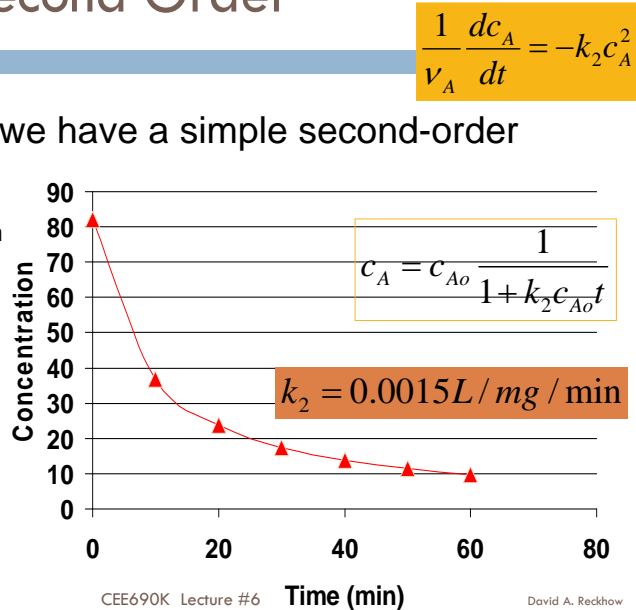
## Simple Second Order



8

- 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



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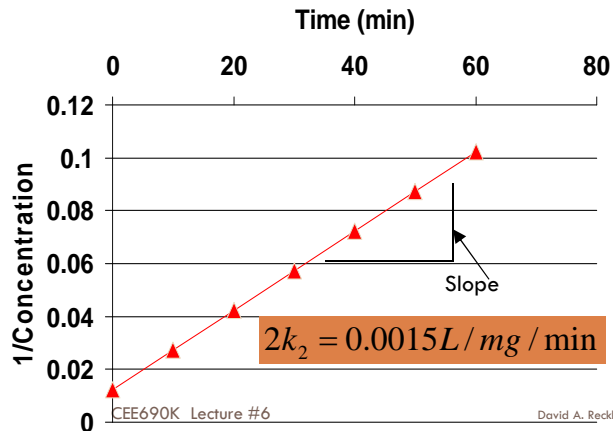
## Integral method: Simple Second Order

9

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

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

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



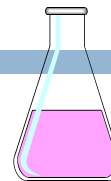
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## Variable Kinetic Order

10

- Any reaction order, except n=1



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

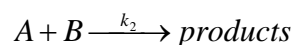
$$\frac{1}{c^{n-1}} = \frac{1}{c_o^{n-1}} + (n-1)k_n t$$

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

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## Mixed Second Order



11

### Two different reactants

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

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

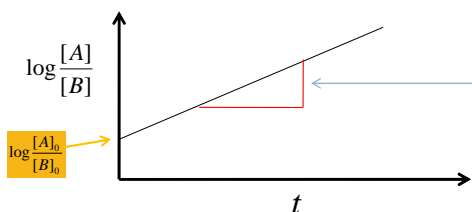
### Initial Concentrations are different; $[A]_0 \neq [B]_0$

#### 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:

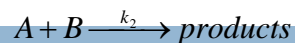
$$\log \frac{[A]}{[B]} = 0.43 k_2 ([A]_0 - [B]_0) t - \log \frac{[B]_0}{[A]_0}$$



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## Integral Method: Mixed Second Order



12

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

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

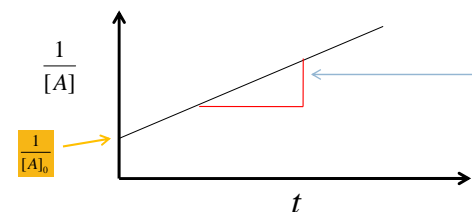
$$[A] = [B] = [A]_0 - x = [B]_0 - x$$

#### The integrated form is:

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

#### Which can be integrated:

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



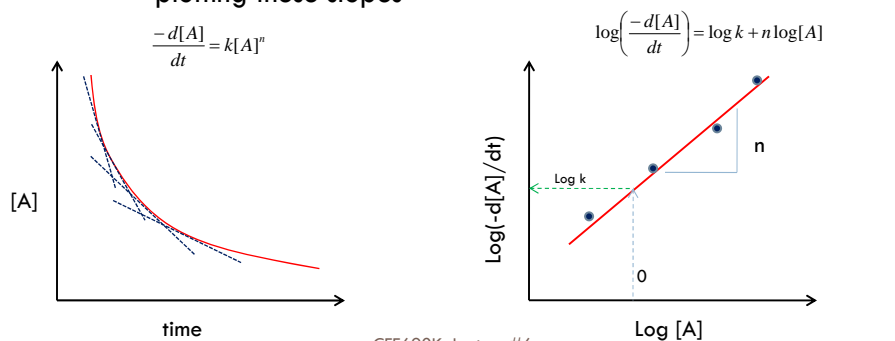
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## Differential Methods I

13

- 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

14

- 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

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

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## Differential Methods III

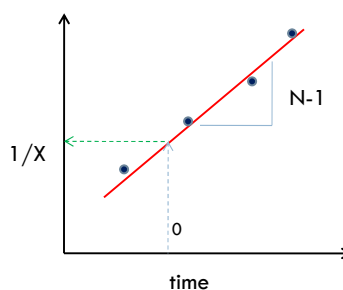
15

- 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

16

- 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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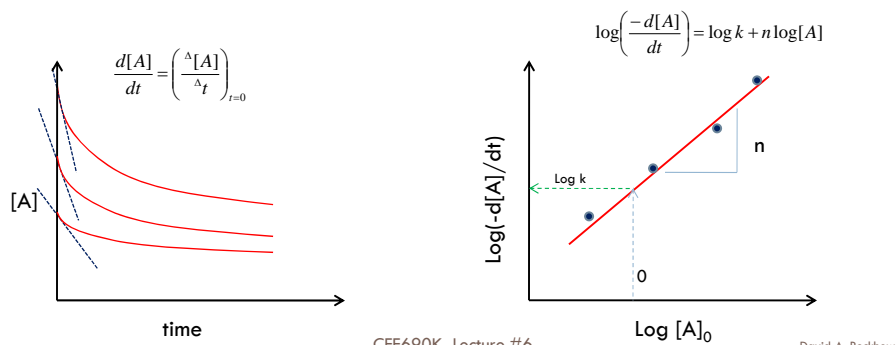
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## Initial Rate II

17

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



18

- To next lecture

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