Print version

CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #1

Introduction: Basics
Brezonik, pp.1-31

David A. Reckhow   Introduction

Kinetics

2

- Examples
  - Fe^{+2} oxidation by O_2
    - almost instantaneous at high pH
    - quite slow at low pH
    - high D.O. may help
  - Oxidation of organic material
  - Formation of solid phases
    - Aluminum hydroxide
    - Quartz sand

# Utility of Kinetics

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- ☐ Empirical Analysis
  - ◻ Moderate Rate
    - ◼ Estimate reaction time (characteristic time) for;
      - ◾ Engineered systems (size of tanks)
      - ◾ Natural Aquatic Systems (WQ modeling)
      - ◾ Atmospheric systems (air pollution modeling)
  - ◻ Fast Rates
    - ◼ Evaluate simple competitive kinetics
      - ◾ Determine complex reaction stoichiometries
    - ◼ Define complex or cyclic reaction webs
      - ◾ Postulate major pathways
  - ◻ Slow Rates
    - ◼ Reaction time for global processes
      - ◾ Human impacts
- ☐ Theoretical Analysis
  - ◻ All Rates: understand mechanisms
    - ◼ Predict other reaction kinetics

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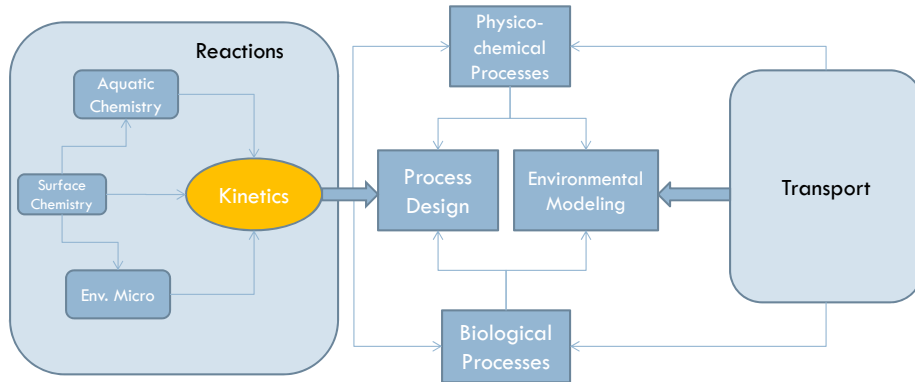# Chemistry and Environmental Engineering

4
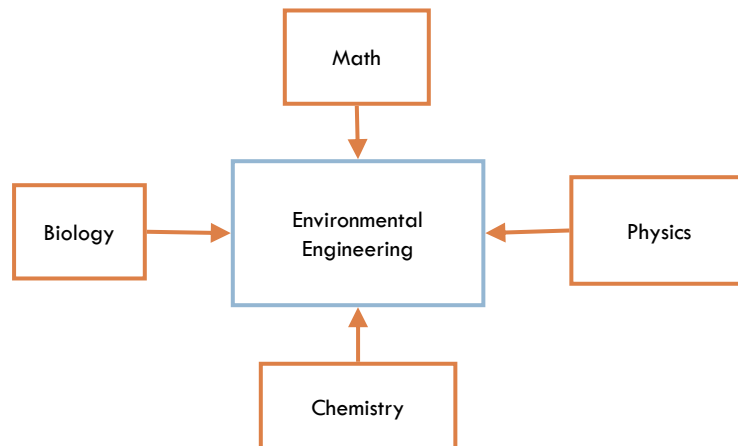
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Engineered & Natural Systems
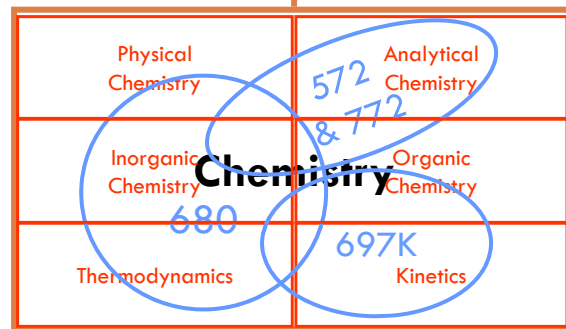
5

☐ Kinetics is the source of reactions and rates

Reactions

Aquatic Chemistry

Surface Chemistry

Kinetics

Env. Micro

Physico-chemical Processes

Process Design

Environmental Modeling

Biological Processes

Transport

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Relation with other Chemistry Disciplines

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Physical Chemistry

Analytical Chemistry

572 & 772

Inorganic Chemistry

Chemistry

Organic Chemistry

680

697K

Thermodynamics

Kinetics

☐ With water chemistry, A cornerstone of the good grad programs in our field

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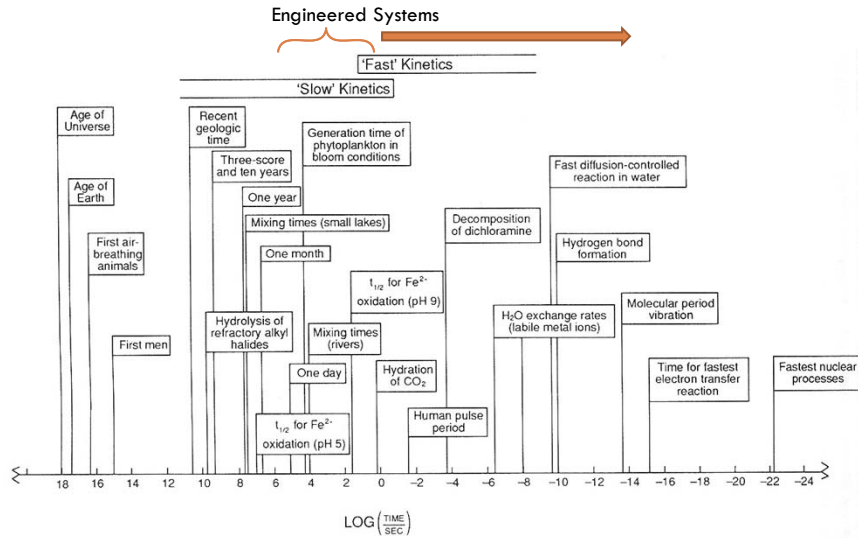
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Time Scales & Kinetics

Figure 1-1. A logarithmic time scale for fast and slow processes in aquatic systems, placed in the context of other important events. [Modified from Onwood, D., *J. Chem. Ed.*, 63, 680 (1986).]
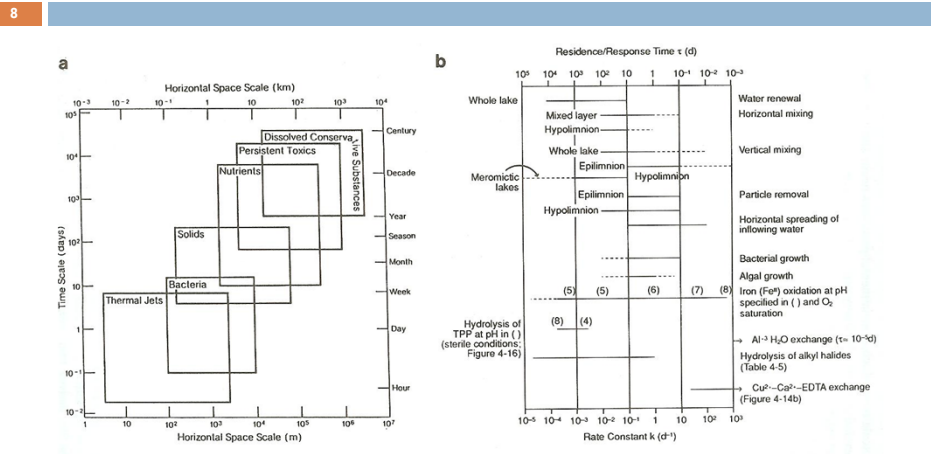
Time and Length scales

Figure 1-2. (a) Correlation between characteristic time and length scales for important water quality problems (Chapra, S. C. and K. H. Reckhow, *Engineering Approaches for Lake Management*, Vol. 2, Ann Arbor Science/Butterworth, Boston, 1983. With permission.); (b) time scales for mixing processes and some chemical and biological processes in aquatic systems. Solid lines: typical range; dashed lines: less common cases. [Based on Imboden, D. M. and R. P. Schwarzenbach, in *Chemical Processes in Lakes*, W. Stumm (Ed.), Wiley-Interscience, New York, 1985, p. 1.]

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Sulfur in lakes I

- Forms
  - Gas: H_2S, SO_2
  - Liquid SO_4^{-2}, HS^-, Amino acids with S
  - Solids: MeS_x, pyrites (FeS_2), elemental S
- Mass Transfer
  - Air:water
  - Sediment:water
- Reactions
  - Chemical: oxidation, reduction, precipitation, complexation, hydrolysis
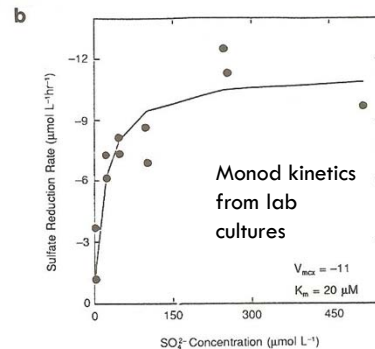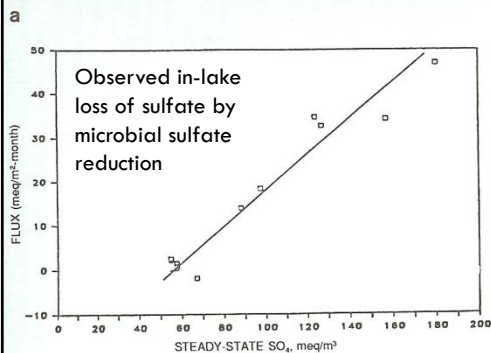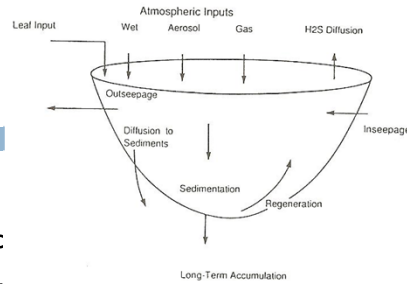 - Biological: biosynthesis, use as TEA, release

Methionine

Cysteine
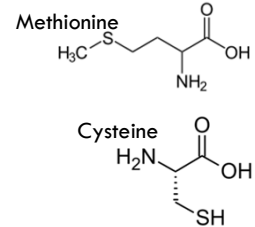
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Sulfur in Lakes II

- Brezonik; example 1-2
  - Sulfur cycling depends on biotic & abiotic redox kinetics, precip, dissolution, complexation, etc.

a

Observed in-lake loss of sulfate by microbial sulfate reduction

FLUX (meq/m²·month)

STEADY-STATE SO_4, meq/m³

b

Sulfate Reduction Rate (µmol L⁻¹·hr⁻¹)

Monod kinetics from lab cultures

$V_{max} = -11$
$K_m = 20$ µM

SO_4^{2-} Concentration (µmol L⁻¹)

Sulfur in lakes (cont.)

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- Typical sulfate depth profile around sediment water interface

July & Sept. 1990
pH 4.7

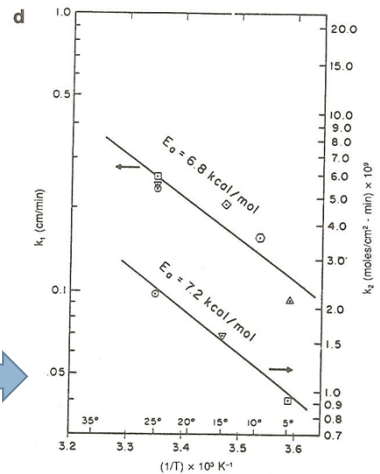- Kinetics of abiotic oxidation of sulfide species
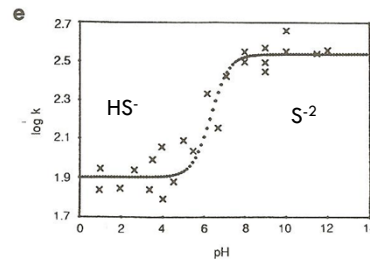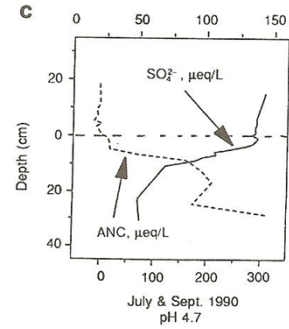
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Sulfur in lakes (cont.)

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- Mackinawite (FeS)
  - Forms in reduced sediments
  - Dissolves by first order rate, also catalyzed by low pH

$$\frac{d[S]_{tot}}{dt} = \frac{A}{V}\left(k_1[H^+] + k_2\right)$$

  - Where A/V is the FeS surface area to total volume ratio
  - Arrhenius temperature plot

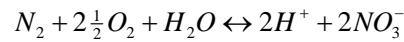

Pankow & Morgan, 1979
[ES&T, 13(10)1248]

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Thermo vs Kinetics

☐ Reaction of oxygen and nitrogen

$$N_2 + 2\tfrac{1}{2}O_2 + H_2O \leftrightarrow 2H^+ + 2NO_3^-$$

- ☐ Thermodynamics tells us:

$$K = 10^{-2.6} = \frac{\{H^+\}_{aq}^2 \{NO_3^-\}_{aq}^2}{p_{N_2} p_{O_2}^{2.5}}$$

- ☐ In the oceans, $\{H^+\}_{aq} \sim 10^{-8}$, and $\{NO_3^-\} \sim 0.26M$
- ☐ Then, considering p_{N2}=0.70, we calculate:

$$p_{O_2} = 2.8x10^{-7} atm$$

- ☐ But the real p_{O2} is 0.21 atm
  - ■ Why does thermo fail us here? the reaction is **very** slow.

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Reaction Kinetics

☐ Irreversible reaction

- ☐ is one in which the reactant(s) proceed to product(s), but there is no significant backward reaction,
- ☐ In generalized for, irreversible reactions can be represented as:
  - ■ **aA + bB ⇒ Products**

i.e., the products do not recombine or change to form reactants in any appreciable amount. An example of an irreversible reaction is hydrogen and oxygen combining to form water in a combustion reaction. We do not observe water spontaneously separating into hydrogen and oxygen.

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Reaction Kinetics: Reversibility

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- A **reversible reaction**
  - is one in which the reactant(s) proceed to product(s), but the product(s) react at an appreciable rate to reform reactant(s).
    - **aA + bB ↔ pP + qQ**
  - Most reactions must be considered reversible

  An example of a reversible biological reaction is the formation of adenosine triphosphate (ATP) and adenosine diphosphate (ADP). All living organisms use ATP (or a similar compound) to store energy. As the ATP is used it is converted to ADP, the organism then uses food to reconvert the ADP to ATP.

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Extent of Reaction I

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- Has the reaction occurred if an so how close to completion is it?
- Consider a generic reaction

$$aA + bB + ... \leftrightarrow pP + qQ + ...$$

- Bringing the reactants to the products side, we get

$$-aA - bB - .... + pP + qQ + ... = 0$$

- And using the Greek, ν, to equal the various stoichiometric coefficients,

$$\nu_A A + \nu_B B + ... + \nu_P P + \nu_Q Q + ... = 0$$

- And the law of conservation of mass requires:

$$\sum_i \nu_i MW_i = 0$$

$$MW \equiv M \equiv molecular\ weight$$

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Extent of Reaction II

☐ Mathematically defined as:

- The change in #moles of a reactant or product as compared to the starting amount divided by the stoichiometric coefficient, ν

$$\xi = \frac{(n_i - n_{io})}{\nu_i}$$

- And therefore:

$$\frac{d\xi}{dt} = \left(\frac{1}{\nu_i}\right)\frac{dn_i}{dt}$$

- And what we call the reaction rate is:

$$rate \equiv \frac{1}{V}\frac{d\xi}{dt} = \left(\frac{1}{\nu_i}\right)\frac{d\left(n_i/V\right)}{dt} \equiv \left(\frac{1}{\nu_i}\right)\frac{d[c_i]}{dt}$$

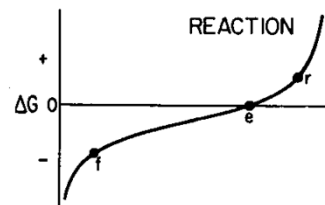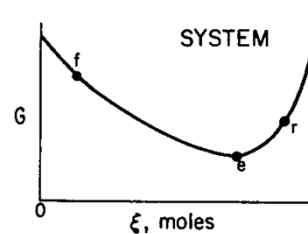Where [c$_i$] is the molar concentration of substance "i"

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Gibbs Energy and reaction extent

Stumm & Morgan Fig. 2.5; Pg. 45

☐ G Changes as reaction progresses due to changing concentrations

☐ G reaches a minimum at the point of equilibrium

$$^\Delta G \equiv \frac{dG}{d\xi}$$

Extent of reaction

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Elementary Reactions

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- When reactant molecules collide with the right orientation and energy level to form new bonds
- Elementary reactions proceed in one step and directly produce product with no intermediates
- Many "observable" reactions are really just combinations of elementary reactions (multi-step reactions)

**Starting out with some A and B, we observe that E and F are the end products**

$$A + B \rightarrow C + D \text{ slow}$$
$$2C \rightarrow E \quad \text{fast}$$
$$A + D \rightarrow C + F \text{ fast}$$

$$2A + B \rightarrow E + F$$
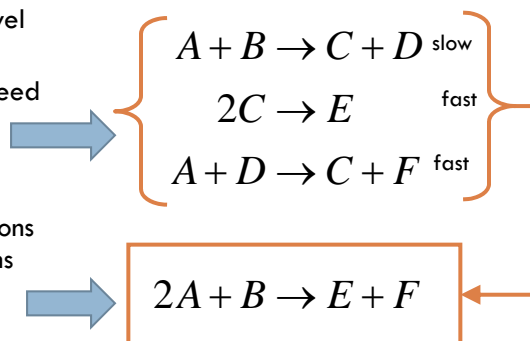
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Cont.

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S&M: Fig. 2.11 Pg. 72

- Elementary reactions
  - A single step in a reaction sequence
  - Involves 1 or 2 reactants and 1 or 2 products
  - Can be described by classical chemical kinetics
    - Law of mass action
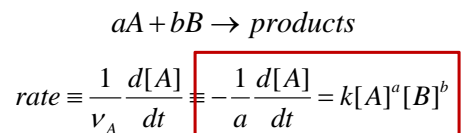 - # of reactant species in an elementary reaction is call the molecularity
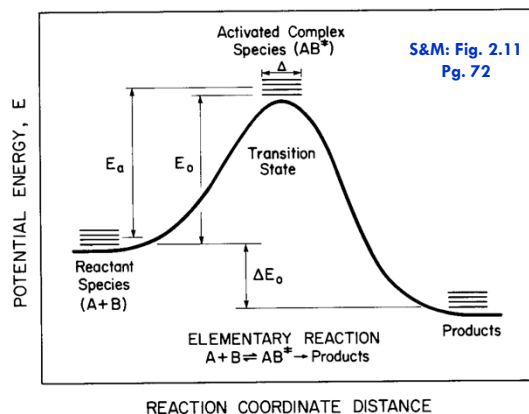
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Law of mass action

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- For elementary reactions, we can write the rate expression directly from the stoichiometry

$$aA + bB \rightarrow products$$

$$rate \equiv \frac{1}{v_A}\frac{d[A]}{dt} \equiv \boxed{-\frac{1}{a}\frac{d[A]}{dt} = k[A]^a[B]^b}$$

- Reaction order
  - Overall order: n=a+b
  - Order with respect to A=a, B=b, C=0.

The rate constant, k, is in units of $c^{1-n}t^{-1}$
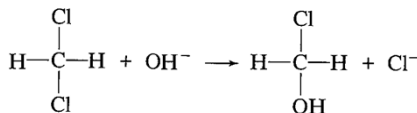
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Elementary vs non-elementary I

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- Base Hydrolysis of dichloromethane (DCM)
  - Forms chloromethanol (CM) and chloride

$$H-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-H + OH^- \longrightarrow H-\underset{\underset{OH}{|}}{\overset{\overset{Cl}{|}}{C}}-H + Cl^-$$

  - Elementary reaction, therefore second order overall (molecularity of 2)

$$\boxed{Rate = k[DCM][OH^-]} = \frac{-d[DCM]}{dt} = \frac{-d[OH^-]}{dt} = \frac{d[CM]}{dt} = \frac{d[Cl^-]}{dt}$$

  - First order in each reactant, second order overall

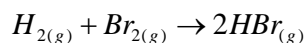CEE697K Lecture #1   David A. Reckhow

Elementary vs non-elementary II

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- The reaction of hydrogen and bromine

$$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$$

- Sometimes used as an example of an elementary reaction in old chemistry textbooks
- Careful study has show the following kinetics

$$\frac{d[HBr]}{dt} = \frac{k[H_{2(g)}][Br_{2(g)}]^{0.5}}{1 + k' \frac{[HBr_{(g)}]}{[Br_{2(g)}]}}$$
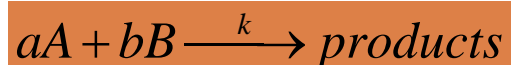
- Thus it is not an elementary reaction!

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Elementary Reactions

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- Recall: Law of Mass Action
  - For elementary reactions

$$aA + bB \xrightarrow{k} products$$

$$rate = kC_A^a C_B^b$$

where,
C_A = concentration of reactant species A, [moles/liter]
C_B = concentration of reactant species B, [moles/liter]
a = stoichiometric coefficient of species A

b = stoichiometric coefficient of species B
k = rate constant, [units are dependent on a and b]

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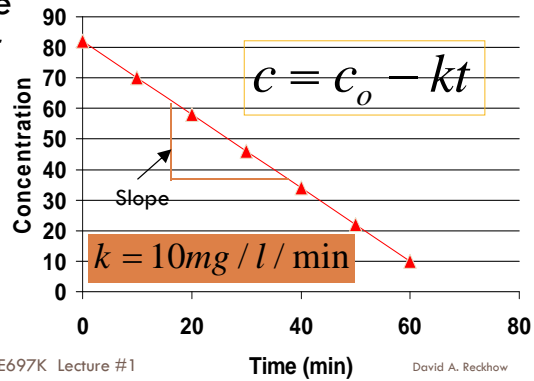
Simple Zero Order

25

- Reactions of order "n" in reactant "c"

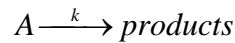$$\frac{dc}{dt} = -kc^n$$

- When n=0, we have a simple zero-order reaction

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

$$c = c_o - kt$$

Slope

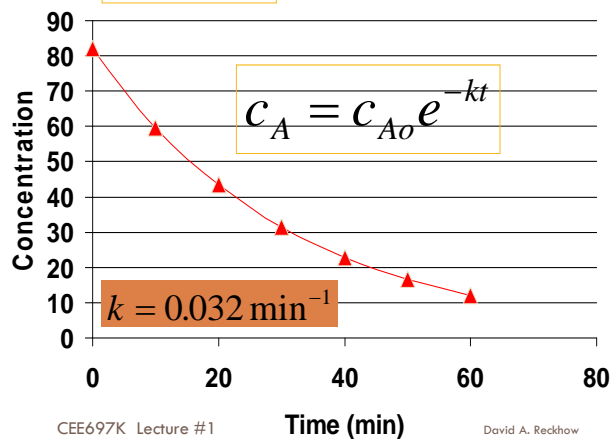$$k = 10\, mg\,/\,l\,/\,\min$$

Concentration vs Time (min)

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Simple first order

$$A \xrightarrow{\ k\ } products$$

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- When n=1, we have a simple first-order reaction

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

- This results in an "exponential decay"

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

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

Concentration vs Time (min)

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First order (cont.)

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

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

$$\ln c_A = \ln c_{Ao} - kt$$

Slope

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

Concentration (log scale): 100, 10
Time (min): 0, 20, 40, 60, 80

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Simple Second Order

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

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$$\frac{1}{v_A}\frac{dc_A}{dt} = -k_2 c_A^2$$
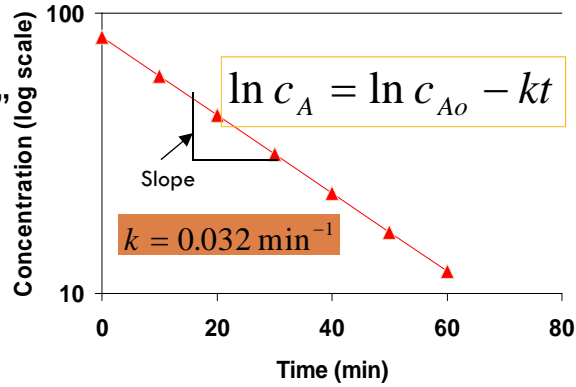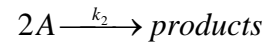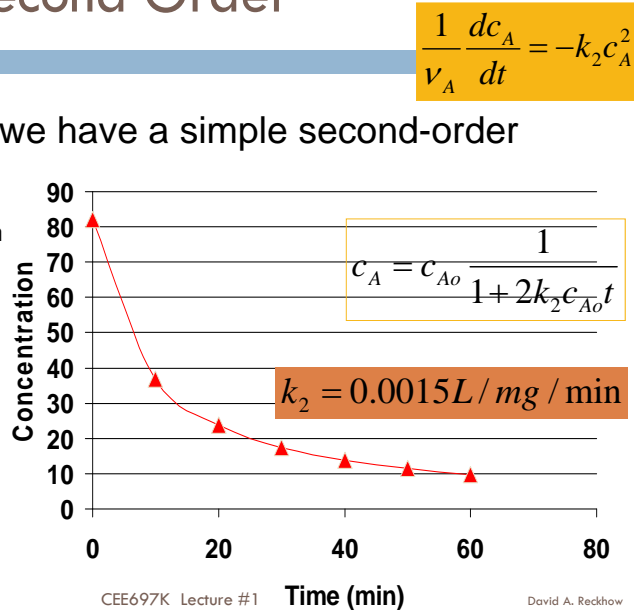
■ When n=2, we have a simple second-order reaction

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

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

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

Concentration: 90, 80, 70, 60, 50, 40, 30, 20, 10, 0
Time (min): 0, 20, 40, 60, 80

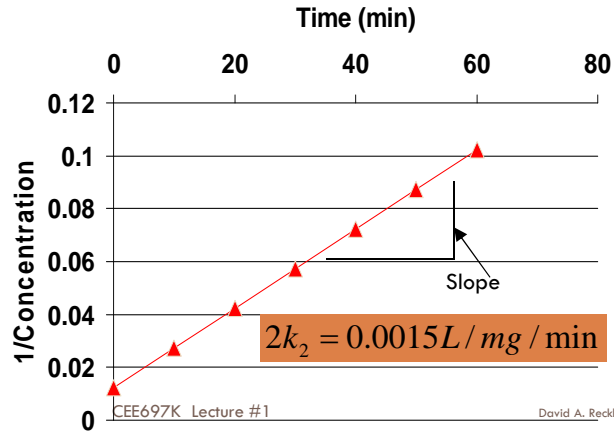CEE697K   Lecture #1   **Time (min)**   David A. Reckhow

Simple Second Order (cont.)

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

$$\frac{1}{v_A}\frac{dc_A}{dt} = -k_2 c_A^2$$
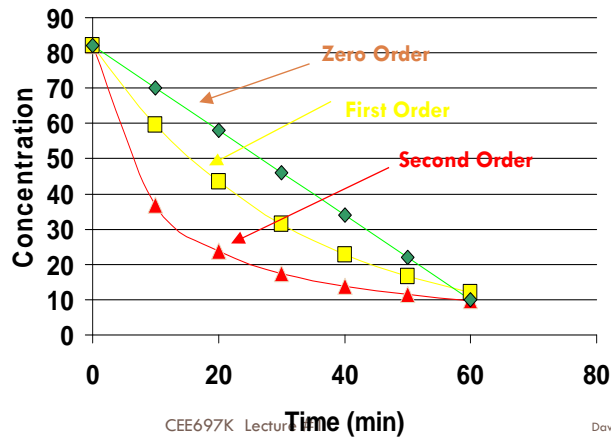
$$\frac{1}{c_A} = \frac{1}{c_{Ao}} + 2k_2 t$$

Time (min)

1/Concentration (y-axis: 0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.12)

x-axis: 0, 20, 40, 60, 80

Slope

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

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Comparison of Reaction Orders

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■ Curvature as order changes: 2nd>1st>zero

Concentration (y-axis: 0, 10, 20, 30, 40, 50, 60, 70, 80, 90)

Zero Order

First Order

Second Order

x-axis: 0, 20, 40, 60, 80
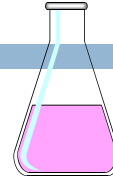
CEE697K Lecture **Time (min)** — David A. Reckhow

Variable Kinetic Order

- Any reaction order, except n=1

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

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

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

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Half-lives

- Time required for initial concentration to drop to half, i.e.., c=0.5c$_o$
  - For a zero order reaction:

$$c = c_o - kt \qquad 0.5c_o = c_o - kt_{1/2} \qquad t_{1/2} = \frac{0.5c_o}{k}$$

  - For a first order reaction:

$$c = c_o e^{-kt} \qquad 0.5c_o = c_o e^{-kt_{1/2}} \qquad t_{1/2} = \frac{\ln(2)}{k}$$

$$= \frac{0.693}{k}$$

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Example: Benzyl Chloride

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□ Use:
  ▪ Manufacture of benzyl compounds, perfumes, pharmaceuticals, dyes, resins, floor tiles

□ Toxicity
  ▪ Intensely irritating to skin, eyes, large doses can cause CNS depression

□ Emission
  ▪ 45,000 lb/yr

□ Fate
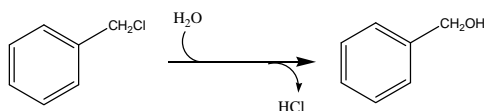 ▪ Benzyl chloride undergoes slow degradation in water to benzyl alcohol

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Benzyl chloride II

Sources:
• Schwarzenbach et al., 1993, Env. Organic Chemistry
• 1972, J. Chem.Soc. Chem. Comm. 425-6
• 1967, Acta Chem. Scand. 21:397-407
• 1961, J. Chem. Soc. 1596-1604

34   (a)

□ **Benzyl chloride to benzyl alcohol**

25°C

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

  ▪ Nucleophilic substitution
    ▪ S_N1 or S_N2?
      ▪ How to distinguish?
        ▪ Salt effects

(b)

$$k = \frac{\ln 2}{t_{1/2}}$$

	Temperature	
	0.1°C	25°C
K	0.042×10^{-5} s^{-1}	1.38×10^{-5}s^{-1}
T$_{1/2}$	19.1 d	0.58 d

CEE690K Lecture #

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□ <u>To next lecture</u>

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