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CEE 697K

ENVIRONMENTAL REACTION KINETICS

Lecture #1

[Introduction:](#) Basics

Brezonik, pp.1-31

Kinetics

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- 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

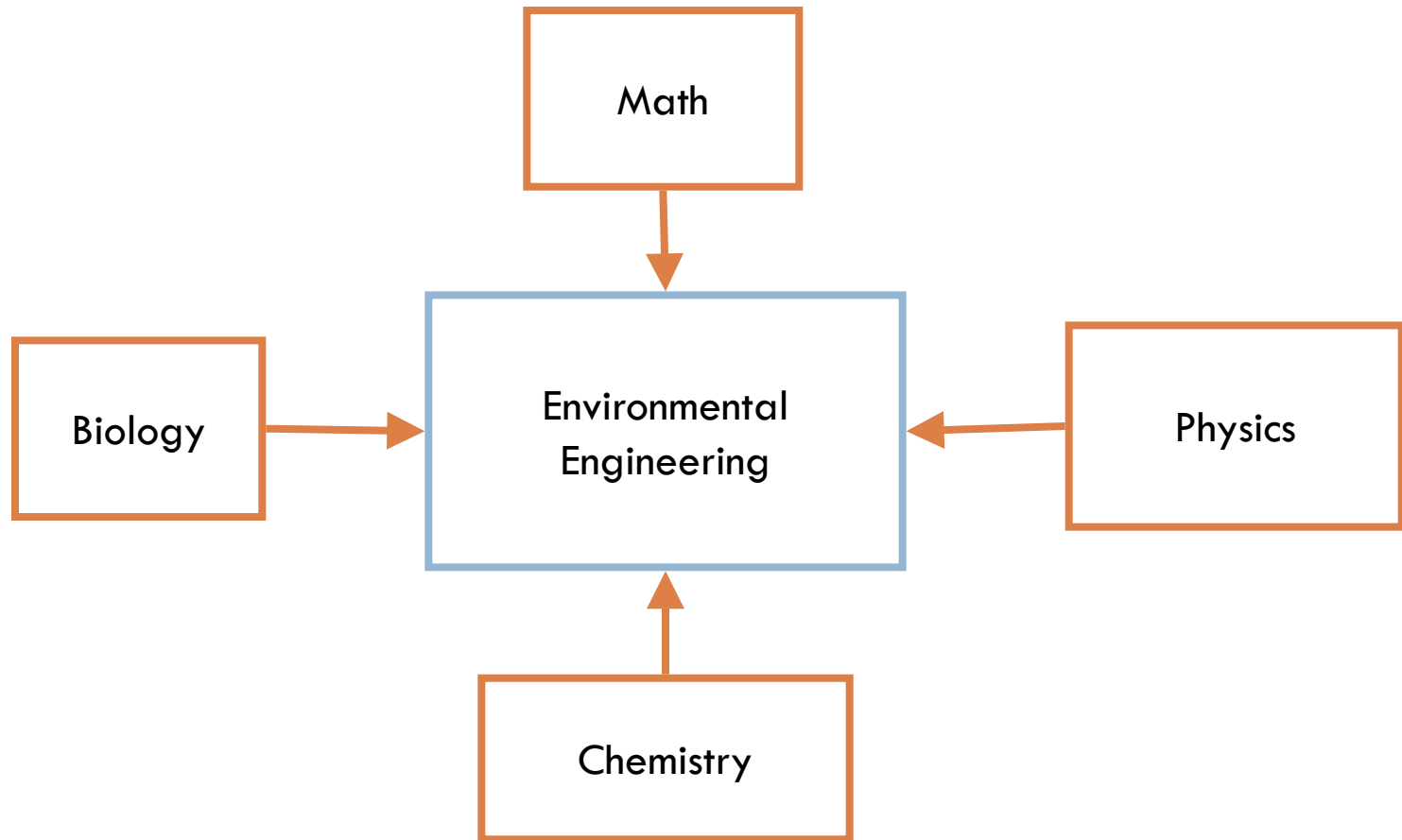
Utility of Kinetics

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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

Chemistry and Environmental Engineering

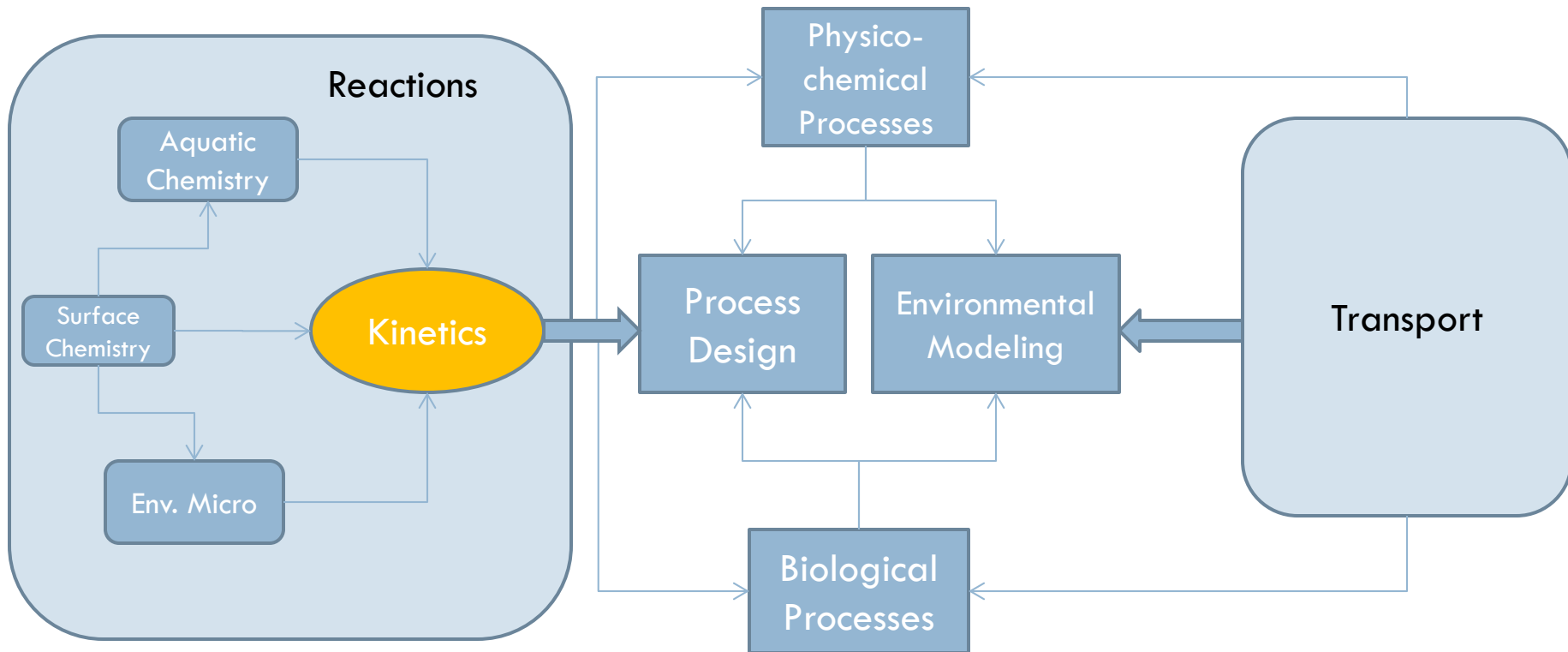
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Engineered & Natural Systems

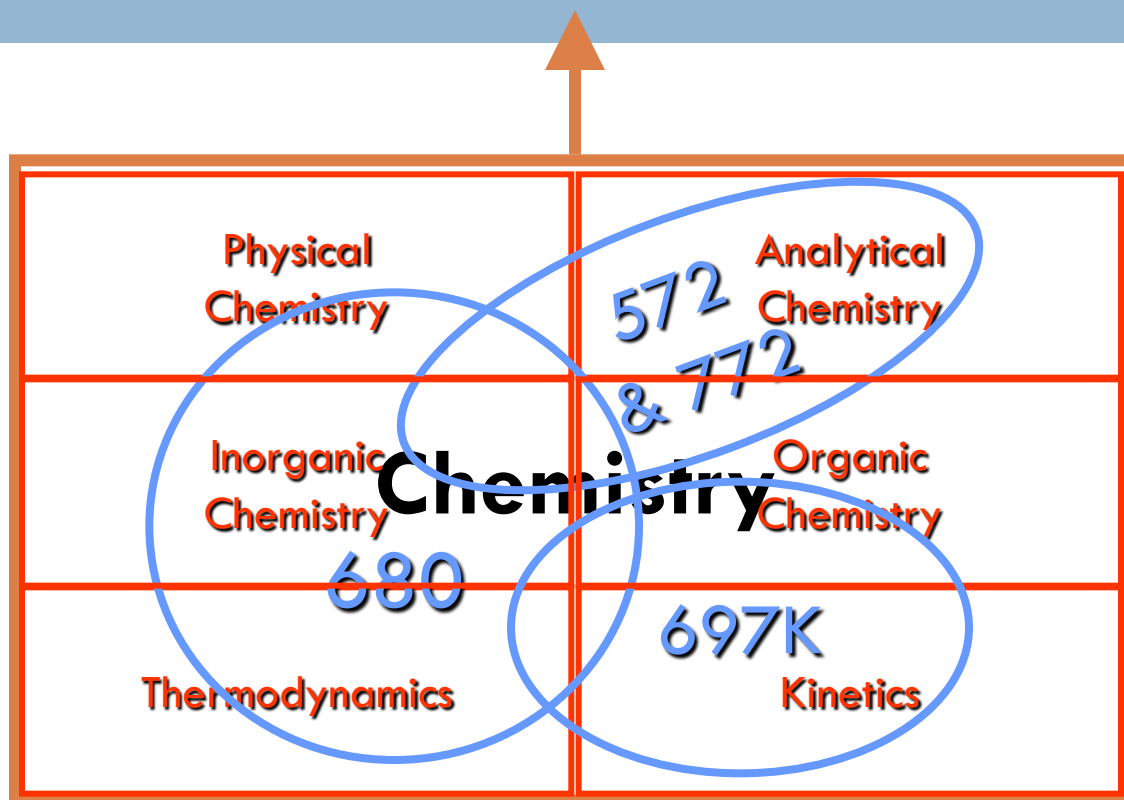
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- Kinetics is the source of reactions and rates



Relation with other Chemistry Disciplines

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

Time Scales & Kinetics

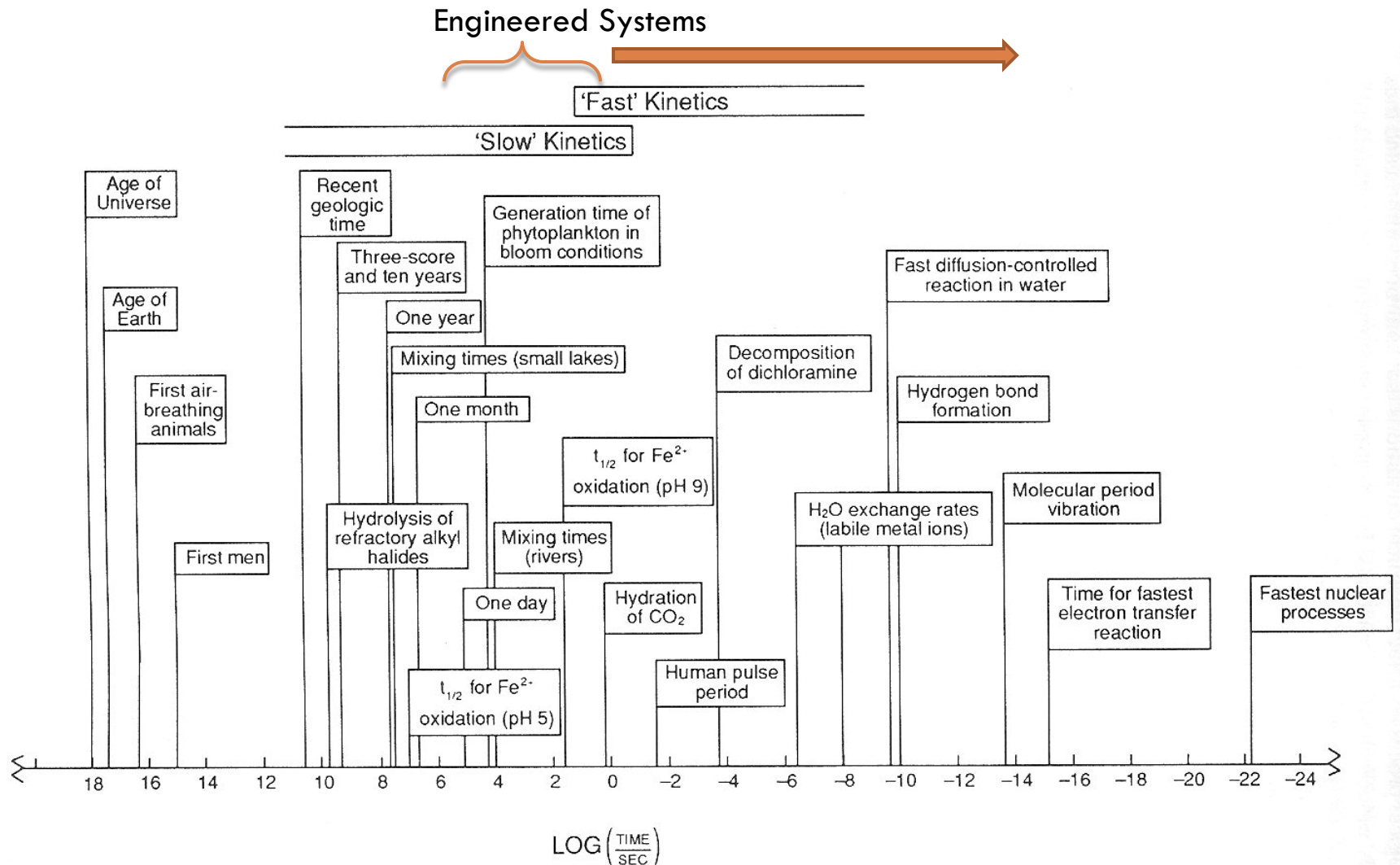


Figure 1-1. A logarithmic time scale for fast and slow processes in aquatic systems, placed in the context of other important events. [Modified from Onwood, D., *J. Chem. Ed.*, 63, 680 (1986).]

Time and Length scales

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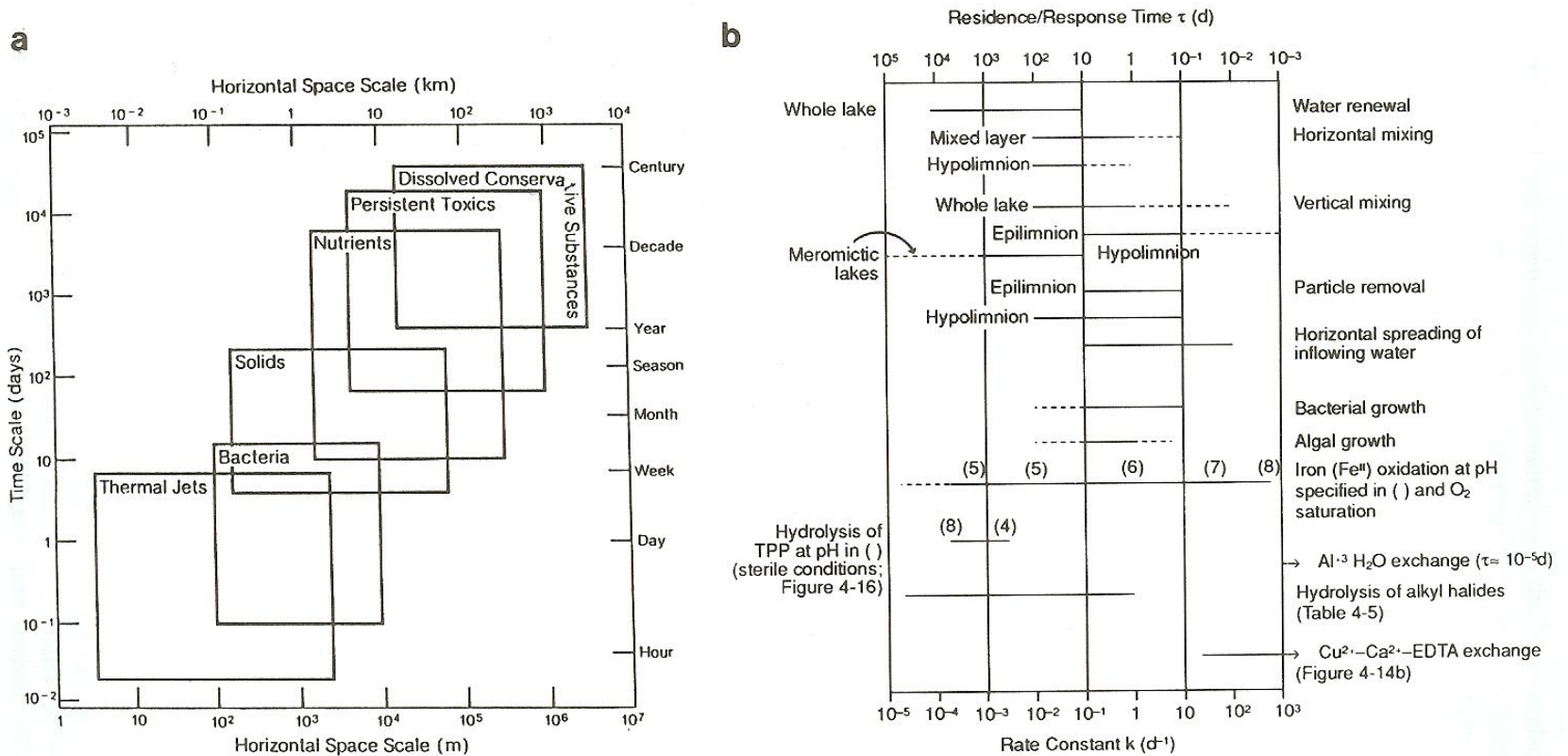


Figure 1-2. (a) Correlation between characteristic time and length scales for important water quality problems (Chapra, S. C. and K. H. Reckhow, *Engineering Approaches for Lake Management*, Vol. 2, Ann Arbor Science/Butterworth, Boston, 1983. With permission.); (b) time scales for mixing processes and 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.]

Sulfur in lakes I

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□ Forms

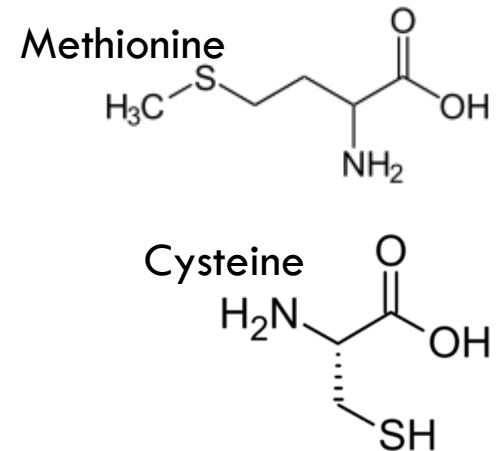
- Gas: H_2S , SO_2
- Liquid SO_4^{-2} , HS^- , Amino acids with S
- Solids: MeS_x , pyrites (FeS_2), elemental S

□ Mass Transfer

- Air:water
- Sediment:water

□ Reactions

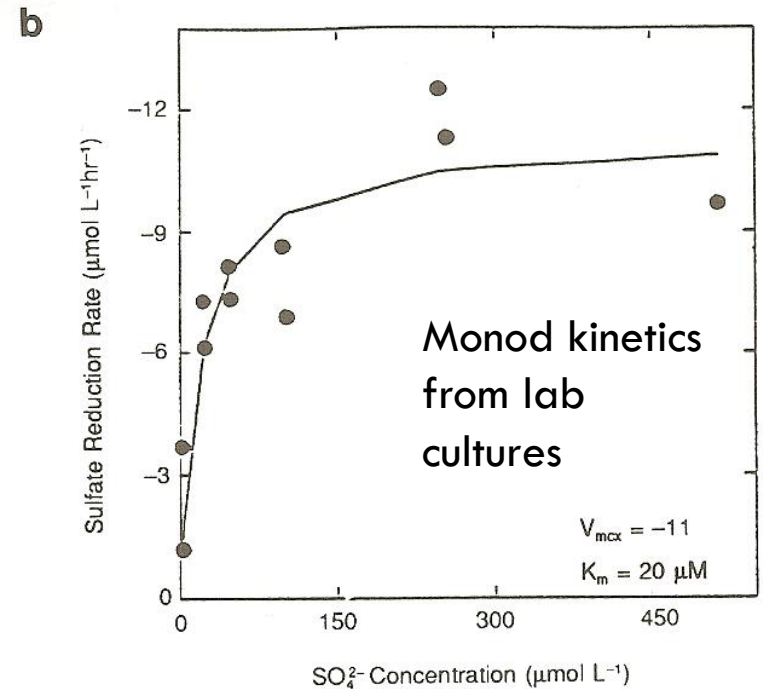
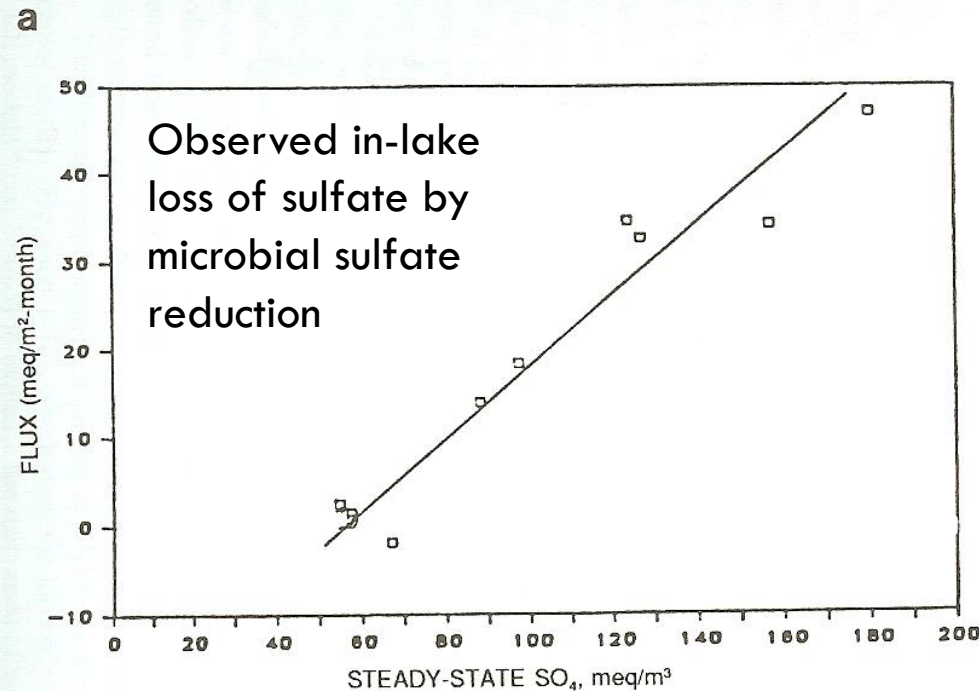
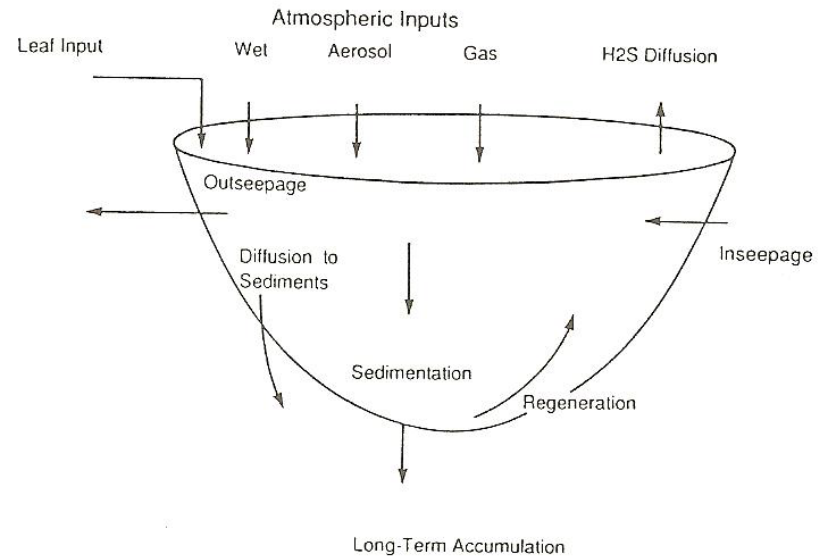
- Chemical: oxidation, reduction, precipitation, complexation, hydrolysis
- Biological: biosynthesis, use as TEA, release



Sulfur in Lakes II

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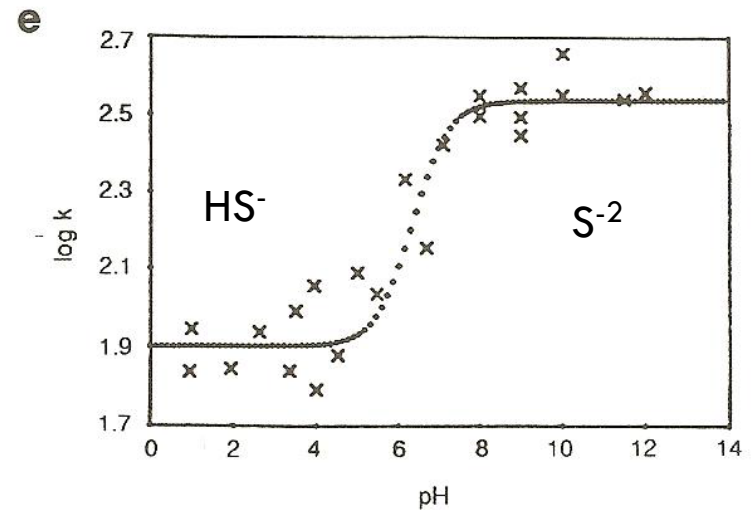
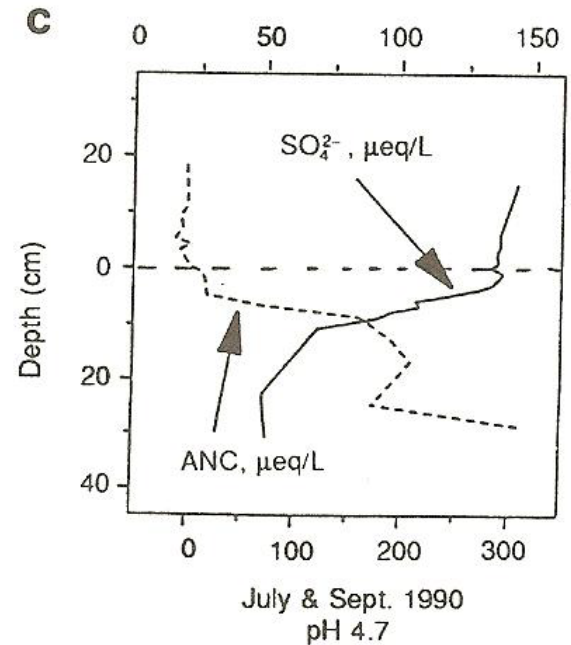
- Brezonik; example 1-2
 - Sulfur cycling depends on biotic & abiotic redox kinetics, precip, dissolution, complexation, etc.



Sulfur in lakes (cont.)

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- Typical sulfate depth profile around sediment water interface
- Kinetics of abiotic oxidation of sulfide species



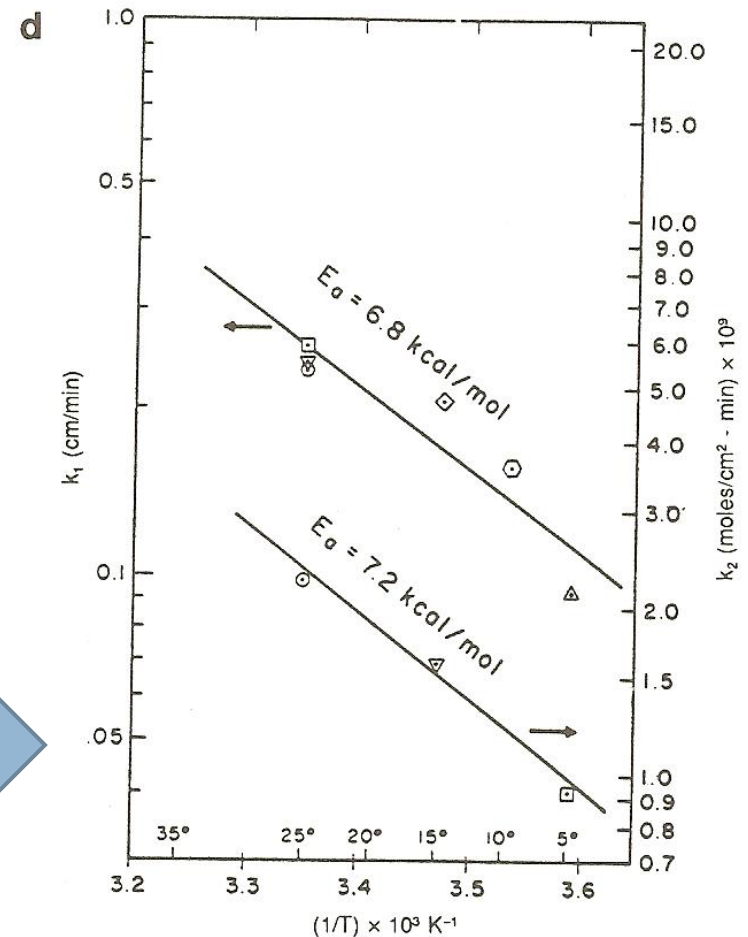
Sulfur in lakes (cont.)

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

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

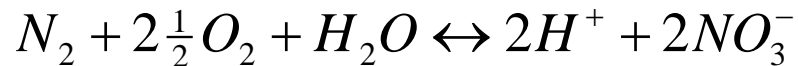
- Where A/V is the FeS surface area to total volume ratio
- Arrhenius temperature plot



Thermo vs Kinetics

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□ Reaction of oxygen and nitrogen



□ 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 $p_{N_2} = 0.70$, we calculate:

$$p_{O_2} = 2.8 \times 10^{-7} \text{ atm}$$

□ But the real p_{O_2} is 0.21 atm

- Why does thermo fail us here? the reaction is **very** slow.

Reaction Kinetics

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□ Irreversible reaction

- ▣ is one in which the reactant(s) proceed to product(s), but there is no significant backward reaction,
- ▣ In generalized form, irreversible reactions can be represented as:



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.

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).



- 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.

Extent of Reaction I

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



- Bringing the reactants to the products side, we get

$$-aA - bB - \dots + pP + qQ + \dots = 0$$

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

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

- And the law of conservation of mass requires:

$$\sum_i \nu_i MW_i = 0$$

MW \equiv *M* \equiv molecular weight

Extent of Reaction II

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□ Mathematically defined as:

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

$$\xi = \frac{(n_i - n_{i0})}{\nu_i}$$

- And therefore:

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

- And what we call the reaction rate is:

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

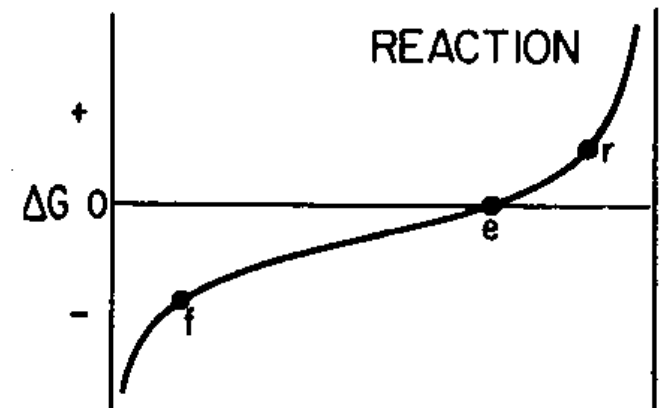
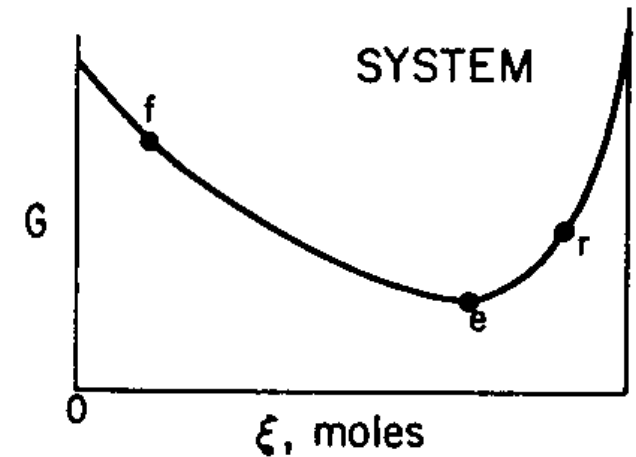
Where $[c_i]$ is the molar concentration of substance “i”

Gibbs Energy and reaction extent

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- G Changes as reaction progresses due to changing concentrations
- G reaches a minimum at the point of equilibrium

Stumm & Morgan
Fig. 2.5; Pg. 45



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

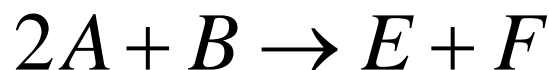
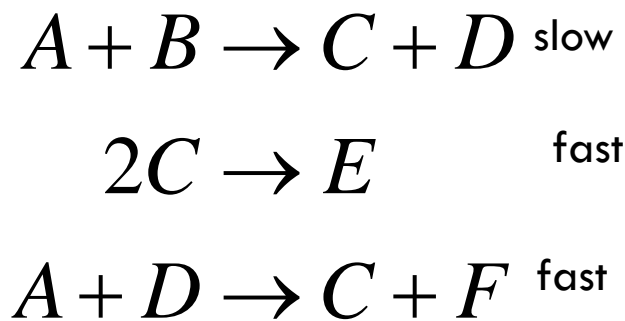
Extent of reaction

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

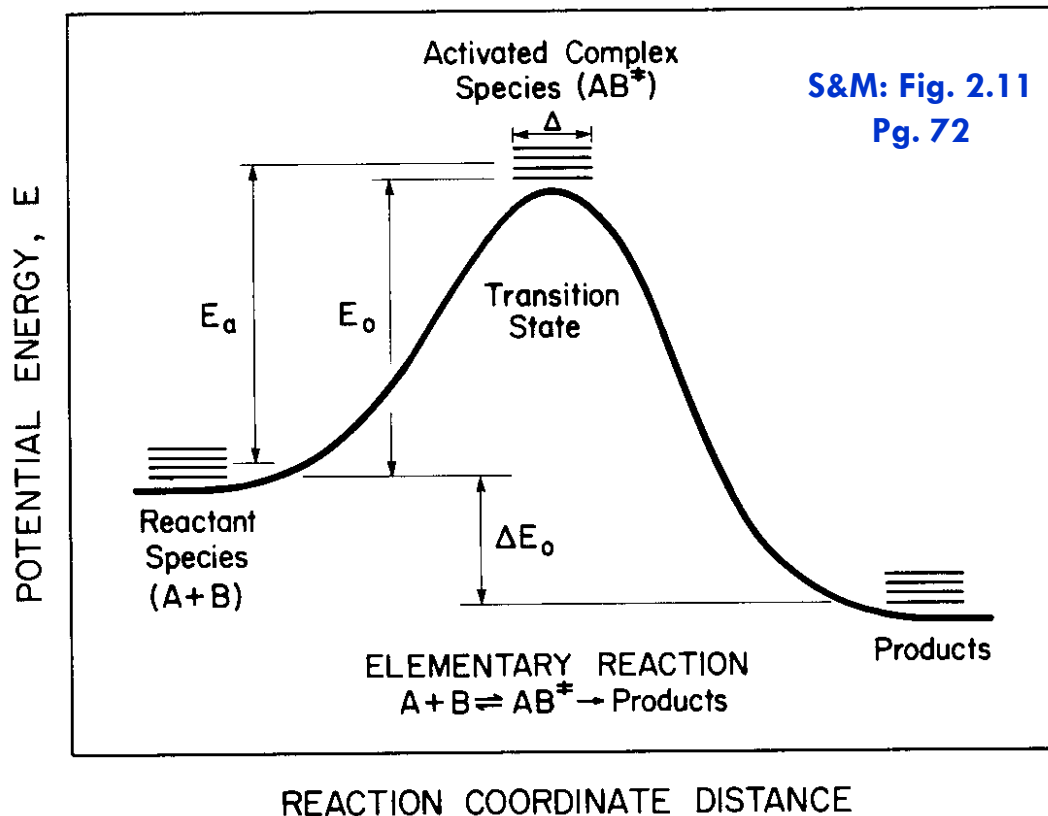


Cont.

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□ Elementary reactions

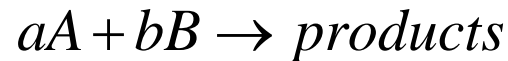
- A single step in a reaction sequence
- Involves 1 or 2 reactants and 1 or 2 products
- Can be described by classical chemical kinetics
 - Law of mass action
- # of reactant species in an elementary reaction is call the molecularity



Law of mass action

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



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

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

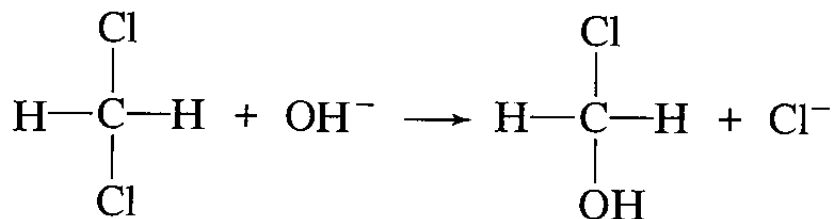
The rate constant, k , is in units of $\text{c}^{1-n}\text{t}^{-1}$

Elementary vs non-elementary I

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□ Base Hydrolysis of dichloromethane (DCM)

- Forms chloromethanol (CM) and chloride



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

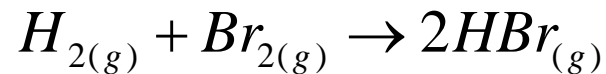
$$\text{Rate} = k[\text{DCM}][\text{OH}^-] = \frac{-d[\text{DCM}]}{dt} = \frac{-d[\text{OH}^-]}{dt} = \frac{d[\text{CM}]}{dt} = \frac{d[\text{Cl}^-]}{dt}$$

- First order in each reactant, second order overall

Elementary vs non-elementary II

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- The reaction of hydrogen and bromine



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

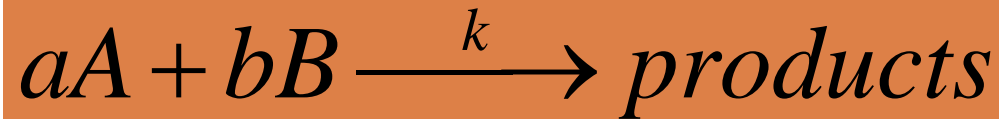
$$\frac{d[HBr]}{dt} = \frac{k[H_{2(g)}][Br_{2(g)}]^{0.5}}{1 + k' \frac{[HBr_{(g)}]}{[Br_{2(g)}]}}$$

- ▣ Thus it is not an elementary reaction!

Elementary Reactions

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- Recall: Law of Mass Action
 - ▣ For elementary reactions



$$\text{rate} = kC_A^a C_B^b$$

where,

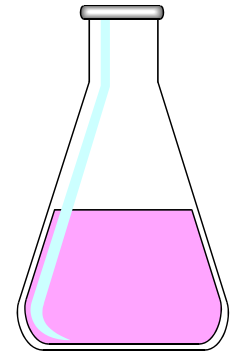
C_A = concentration of reactant species A, [moles/liter]

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]



Simple Zero Order

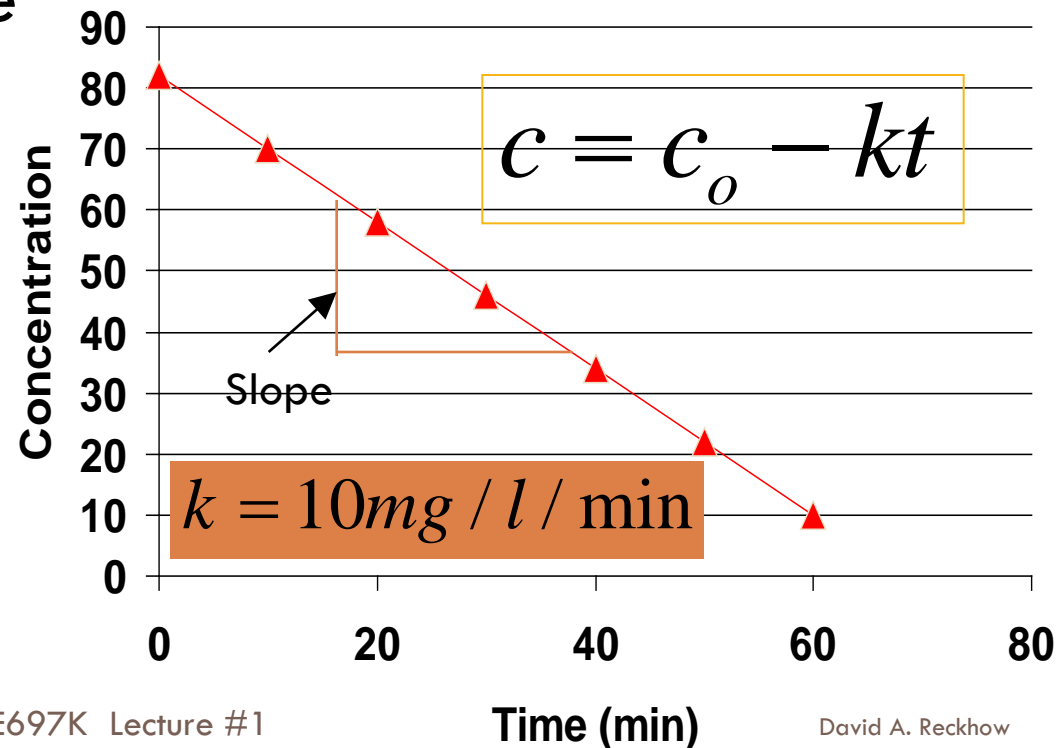
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- Reactions of order “n” in reactant “c”

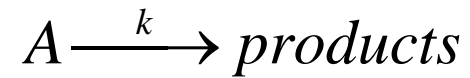
$$\frac{dc}{dt} = -kc^n$$

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

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



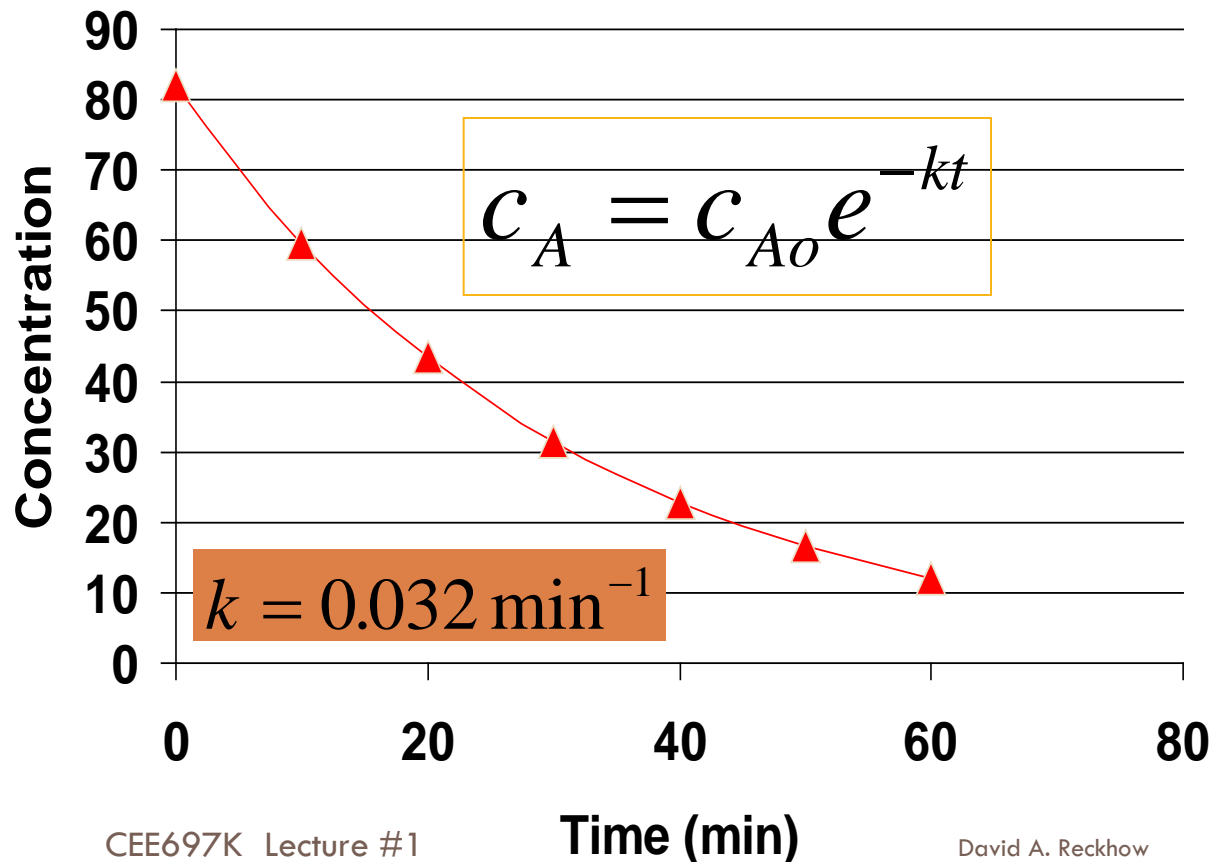
Simple first order



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

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

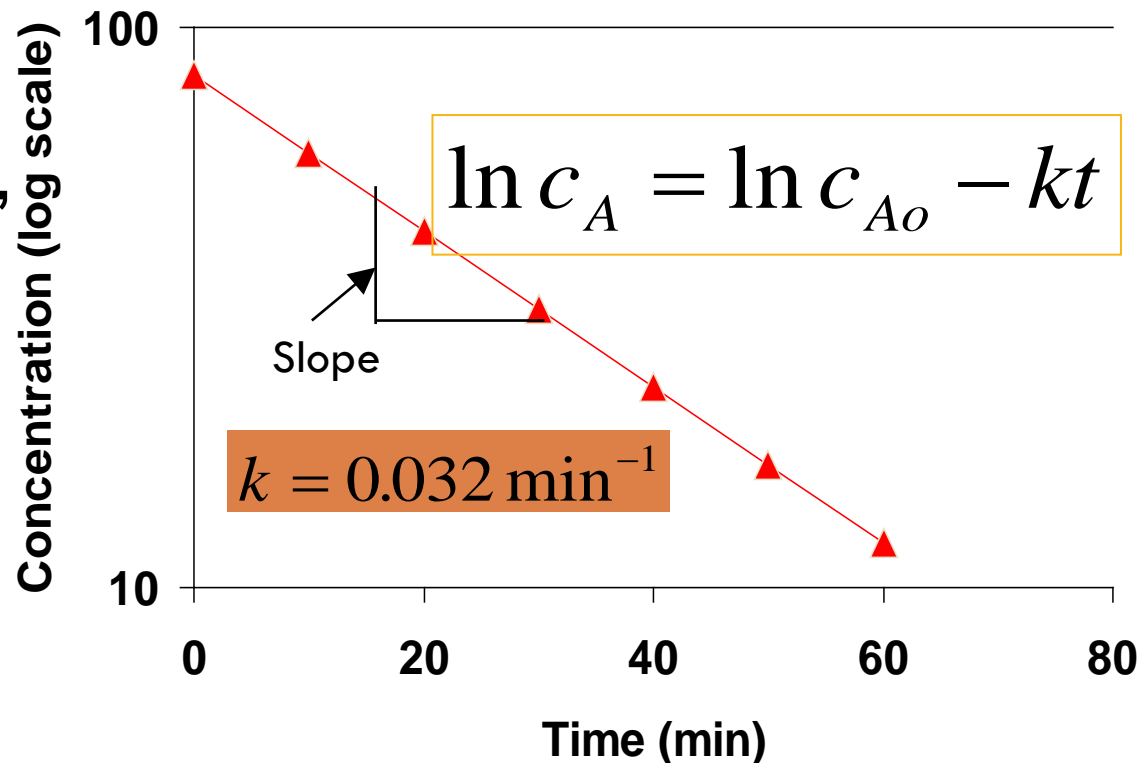


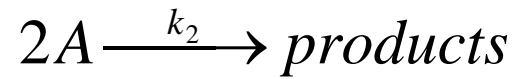
First order (cont.)

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

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





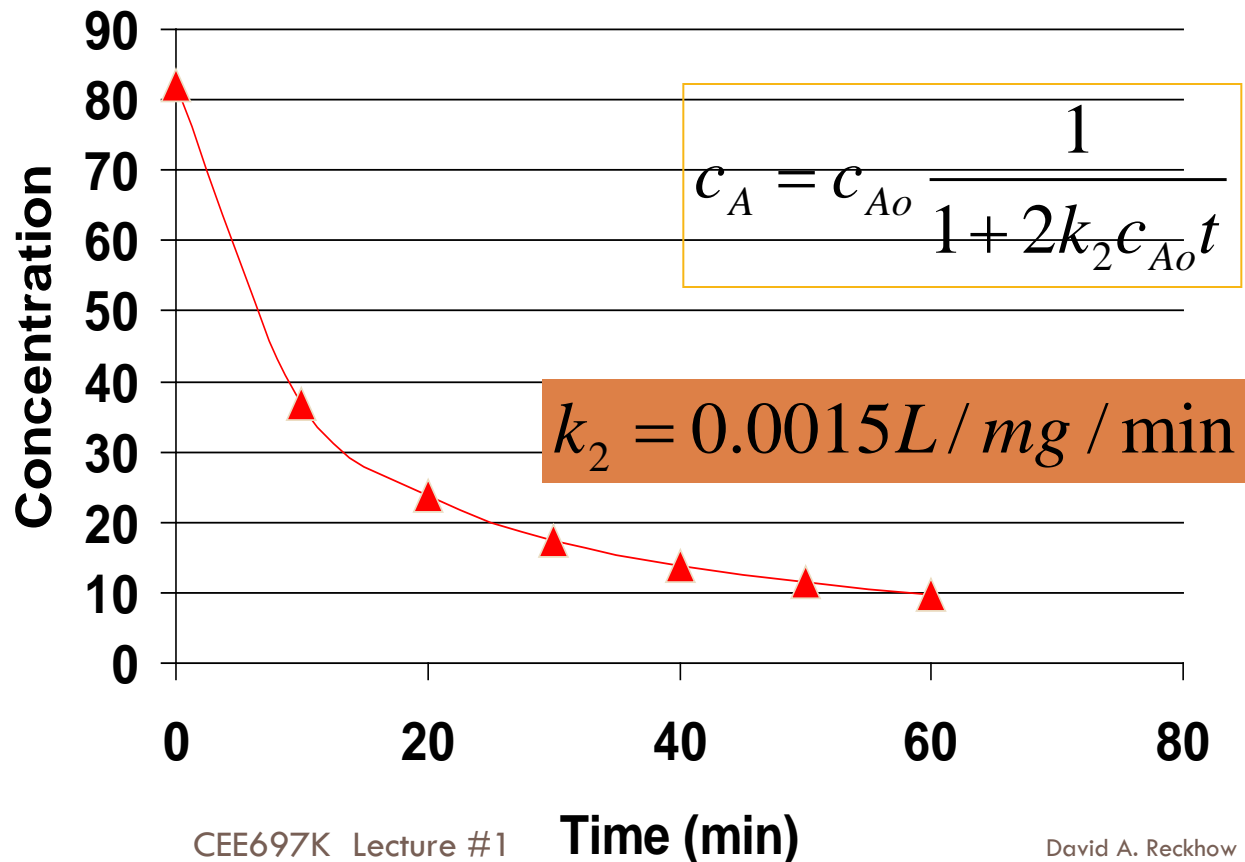
Simple Second Order

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

■ 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



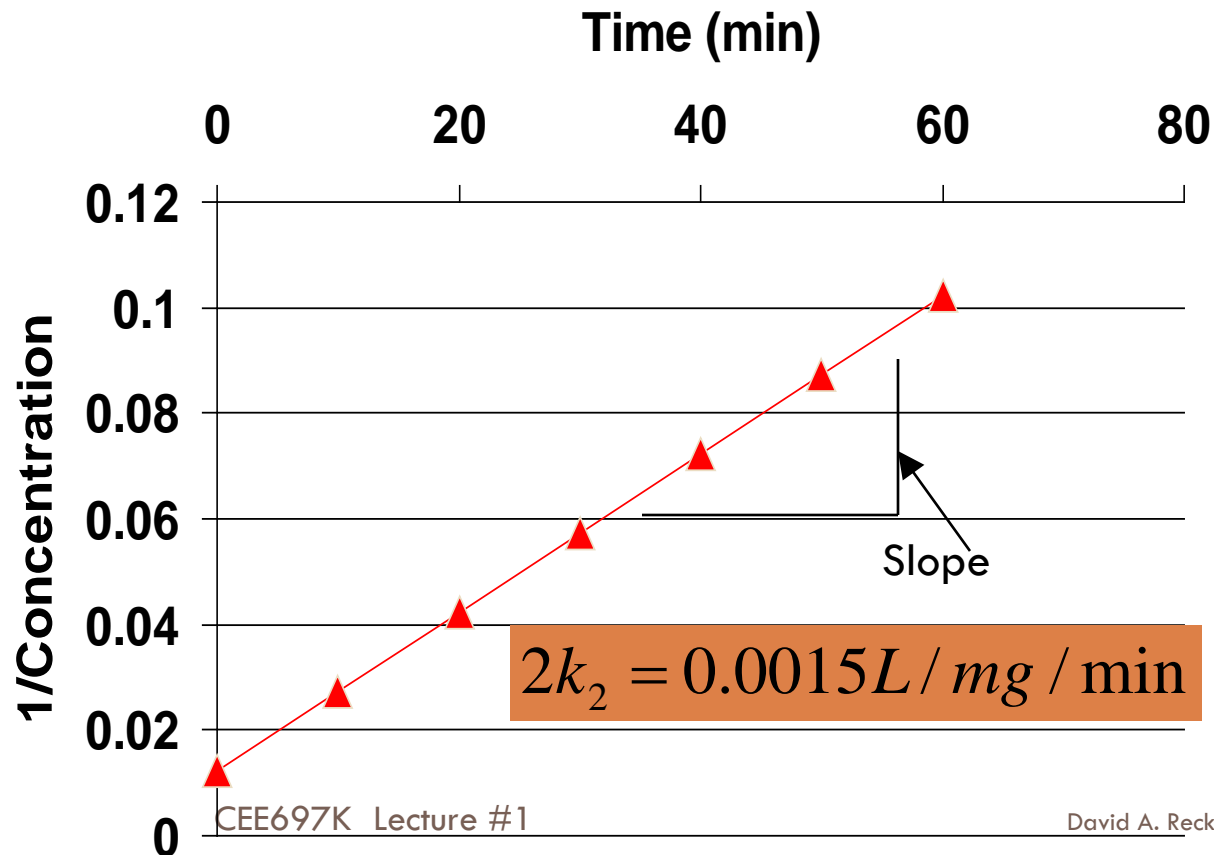
Simple Second Order (cont.)

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

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

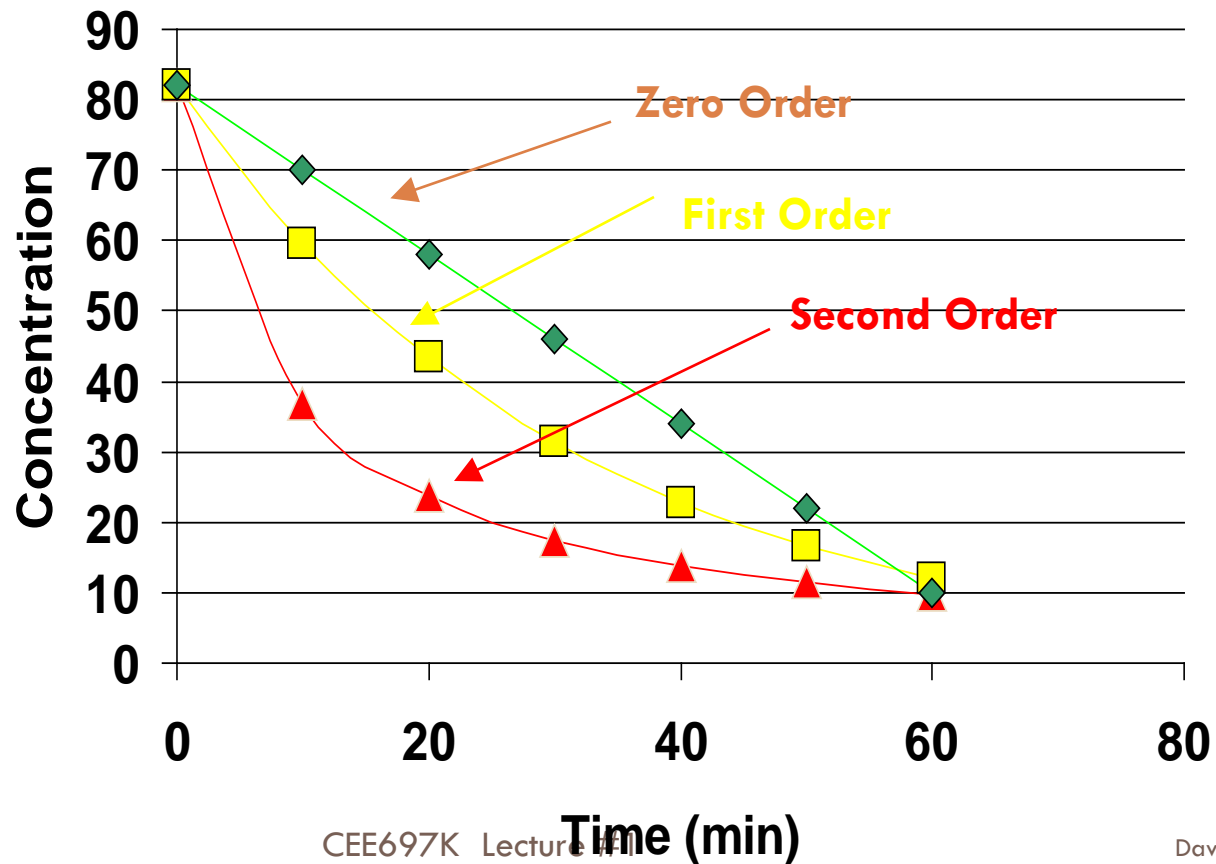
$$\frac{1}{C_A} = \frac{1}{C_{A0}} + 2k_2 t$$



Comparison of Reaction Orders

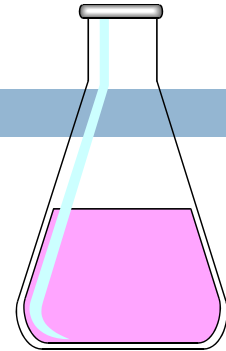
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- Curvature as order changes: $2^{\text{nd}} > 1^{\text{st}} > \text{zero}$



Variable Kinetic Order

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- Any reaction order, except $n=1$

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

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

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

Half-lives

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- Time required for initial concentration to drop to half, i.e., $c=0.5c_o$

- For a zero order reaction:

$$c = c_o - kt$$

$$0.5c_o = c_o - kt_{1/2}$$

$$t_{1/2} = \frac{0.5c_o}{k}$$

- For a first order reaction:

$$c = c_o e^{-kt}$$

$$0.5c_o = c_o e^{-kt_{1/2}}$$

$$t_{1/2} = \frac{\ln(2)}{k}$$
$$= \frac{0.693}{k}$$

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

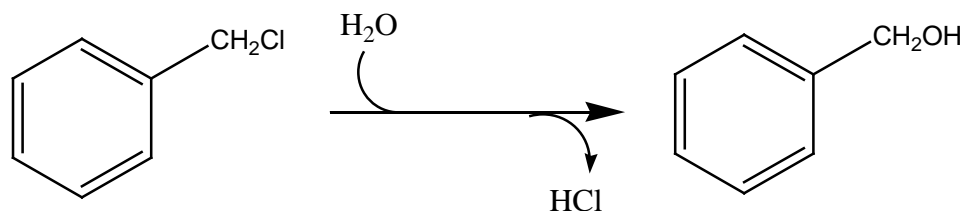
Benzyl chloride II

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

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□ Benzyl chloride to benzyl alcohol



□ Nucleophilic substitution

■ $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$?

■ How to distinguish?

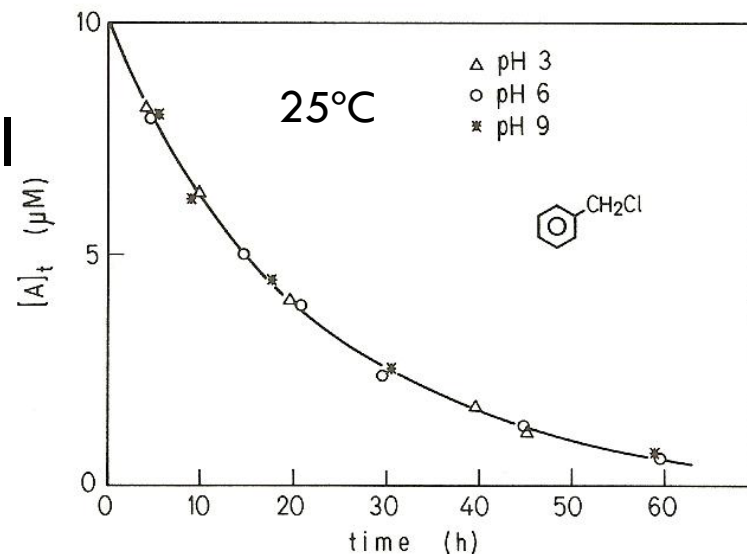
■ Salt effects

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

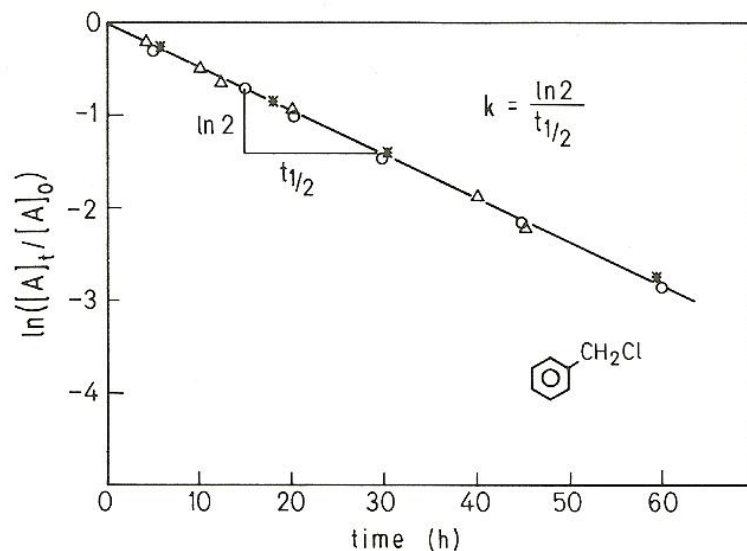
	Temperature	
	0.1°C	25°C
K	$0.042 \times 10^{-5} \text{ s}^{-1}$	$1.38 \times 10^{-5} \text{ s}^{-1}$
$T_{1/2}$	19.1 d	0.58 d

Lecture #

(a)



(b)



- To next lecture