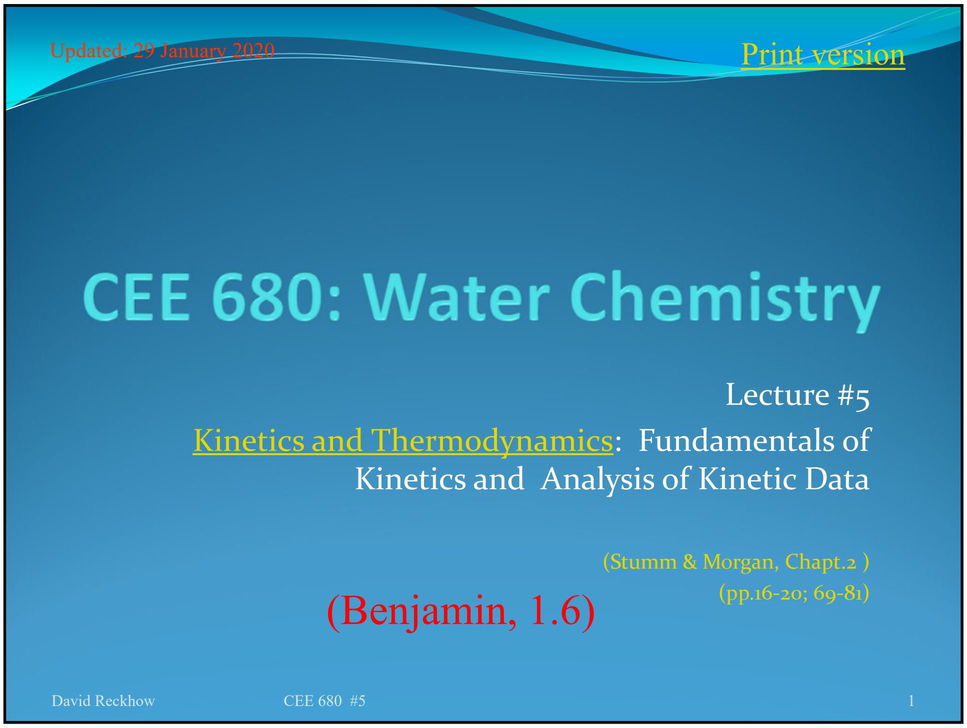

Updated: 29 January 2020

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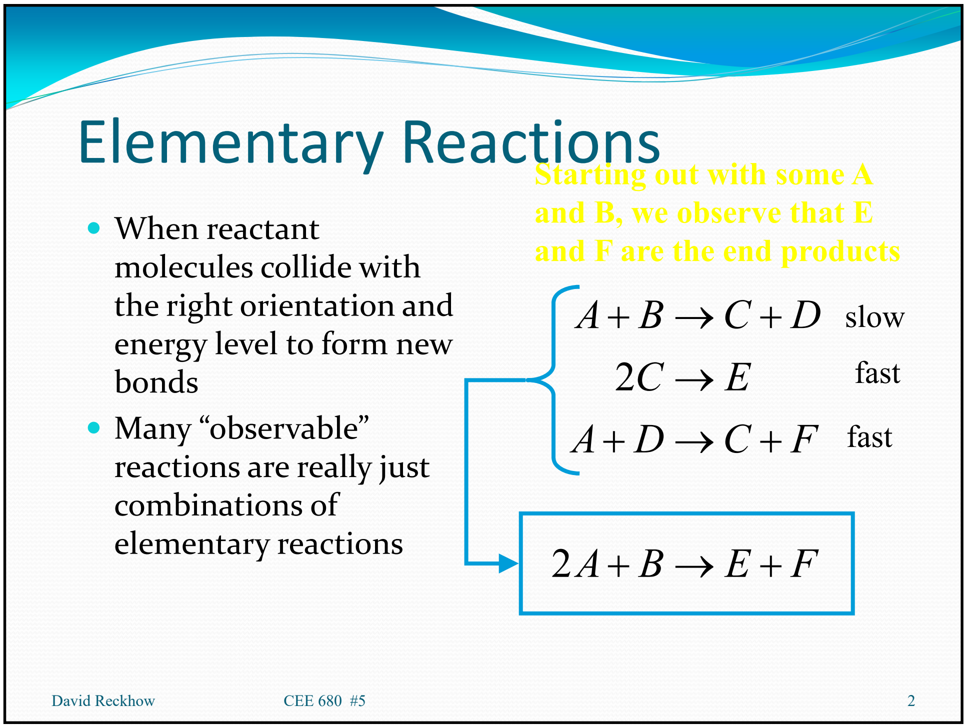
CEE 680: Water Chemistry

Lecture #5

Kinetics and Thermodynamics: Fundamentals of Kinetics and Analysis of Kinetic Data

(Stumm & Morgan, Chapt.2)
(pp.16-20; 69-81)

(Benjamin, 1.6)



Elementary Reactions

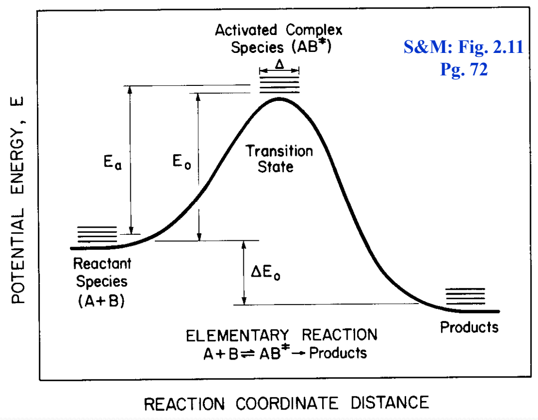
- When reactant molecules collide with the right orientation and energy level to form new bonds
- Many "observable" reactions are really just combinations of elementary reactions

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

$$\left\{\begin{array}{ll} A + B \rightarrow C + D & \text{slow} \\ 2C \rightarrow E & \text{fast} \\ A + D \rightarrow C + F & \text{fast} \end{array}\right.$$

$$\boxed{2A + B \rightarrow E + F}$$

Cont.

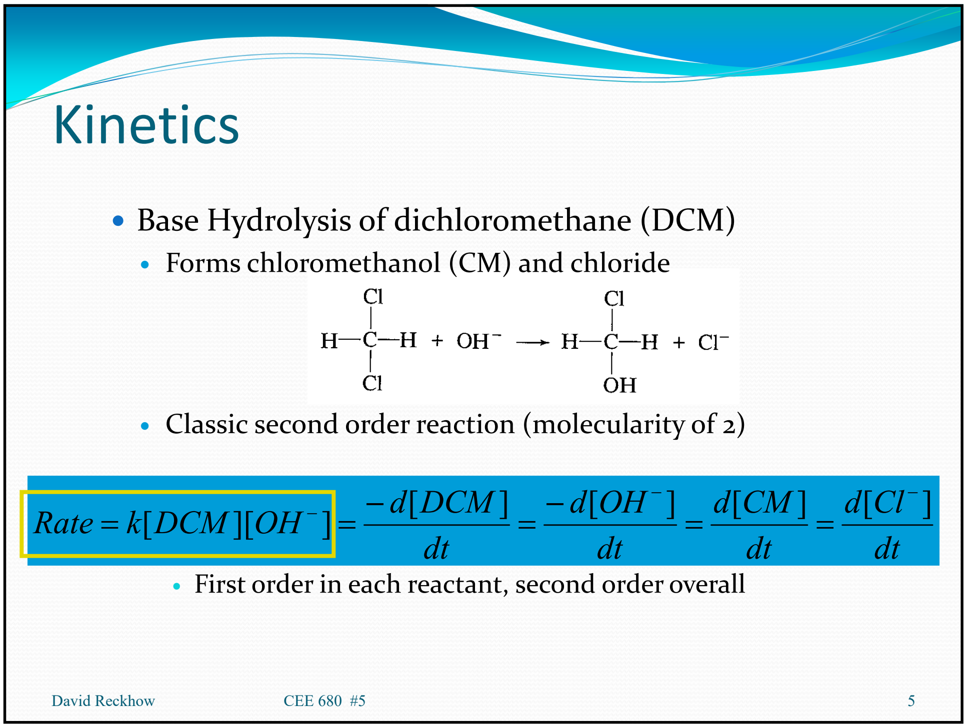


S&M: Fig. 2.11
Pg. 72

- 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

Kinetics

- 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



Kinetics

- Base Hydrolysis of dichloromethane (DCM)
  - Forms chloromethanol (CM) and chloride
  - Classic second order reaction (molecularity of 2)

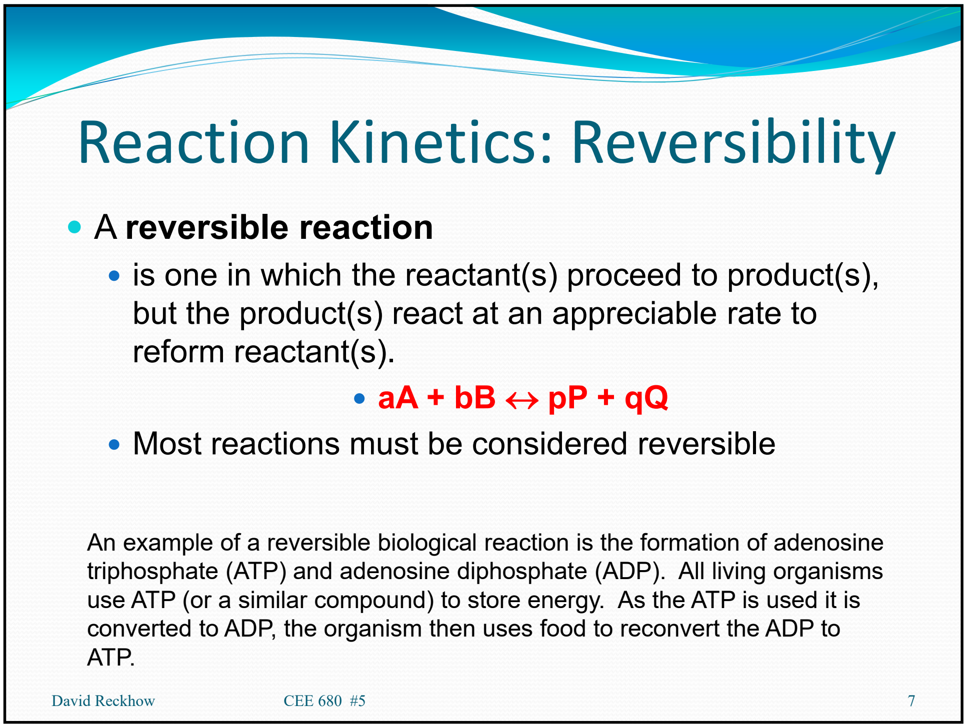
$$\boxed{Rate = k[DCM][OH^-]} = \frac{-d[DCM]}{dt} = \frac{-d[OH^-]}{dt} = \frac{d[CM]}{dt} = \frac{d[Cl^-]}{dt}$$

- First order in each reactant, second order overall

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**

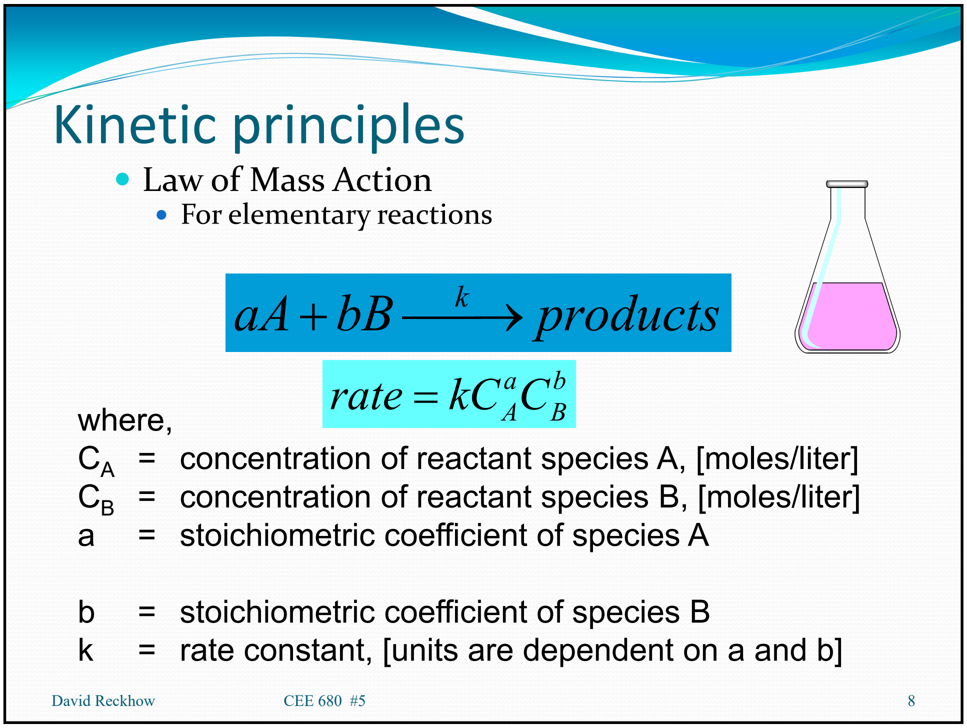
i.e., the products do not recombine or change to form reactants in any appreciable amount. An example of an irreversible reaction is hydrogen and oxygen combining to form water in a combustion reaction. We do not observe water spontaneously separating into hydrogen and oxygen.



Reaction Kinetics: Reversibility

- 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.



Kinetic principles

- Law of Mass Action
  - For elementary reactions

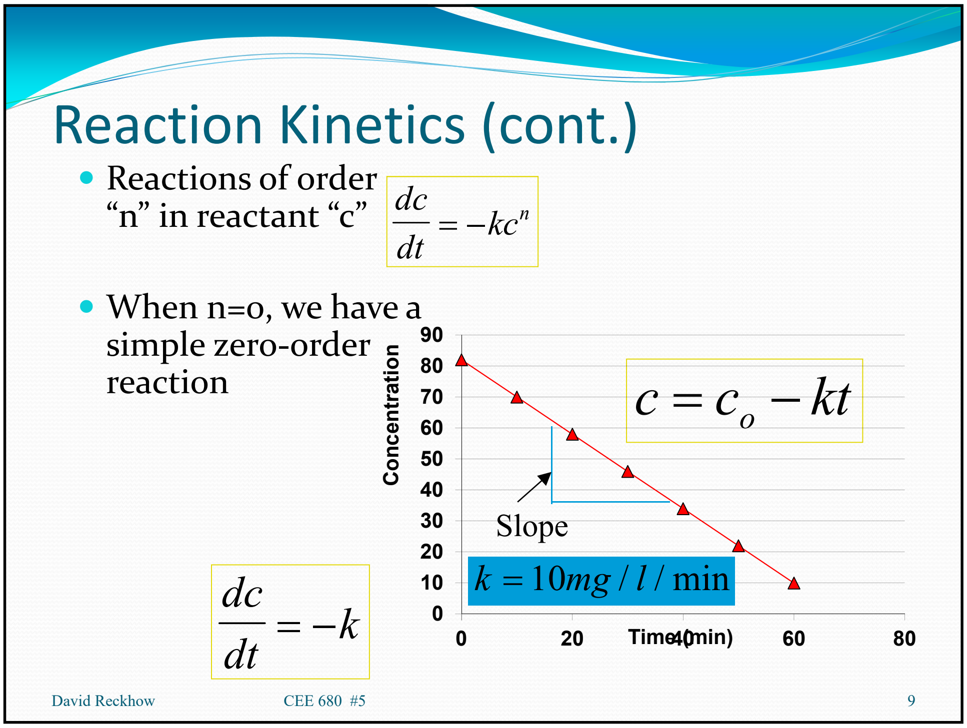
$$aA + bB \xrightarrow{k} products$$

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

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]



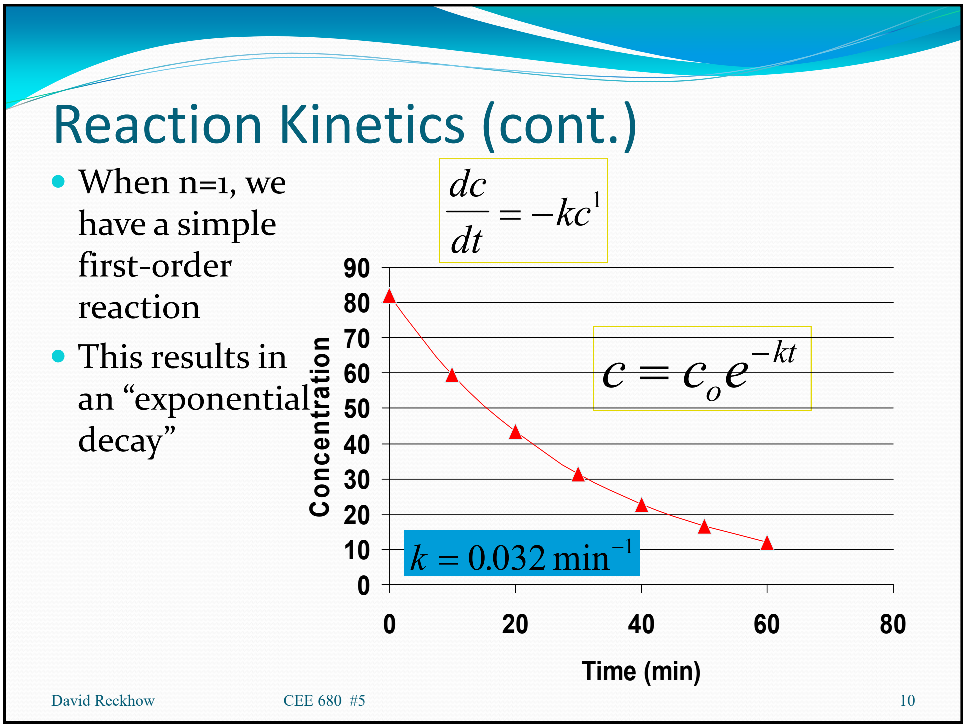
Reaction Kinetics (cont.)

- Reactions of order "n" in reactant "c" $\frac{dc}{dt} = -kc^n$
- When n=0, we have a simple zero-order reaction

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

$$c = c_o - kt$$

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



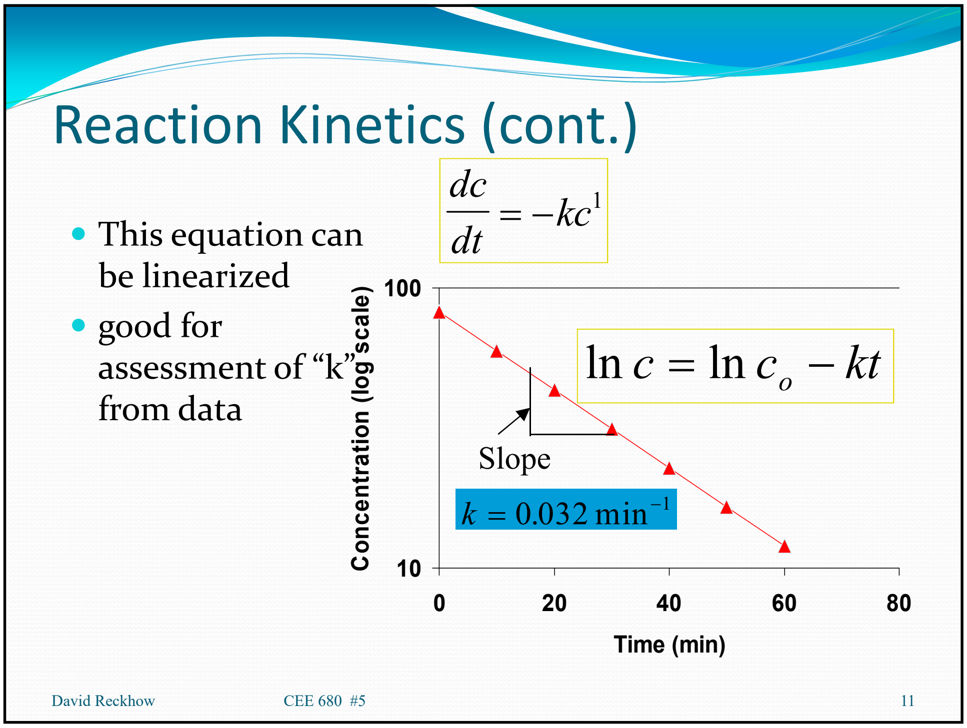
Reaction Kinetics (cont.)

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

$$\frac{dc}{dt} = -kc^1$$

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

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



Reaction Kinetics (cont.)

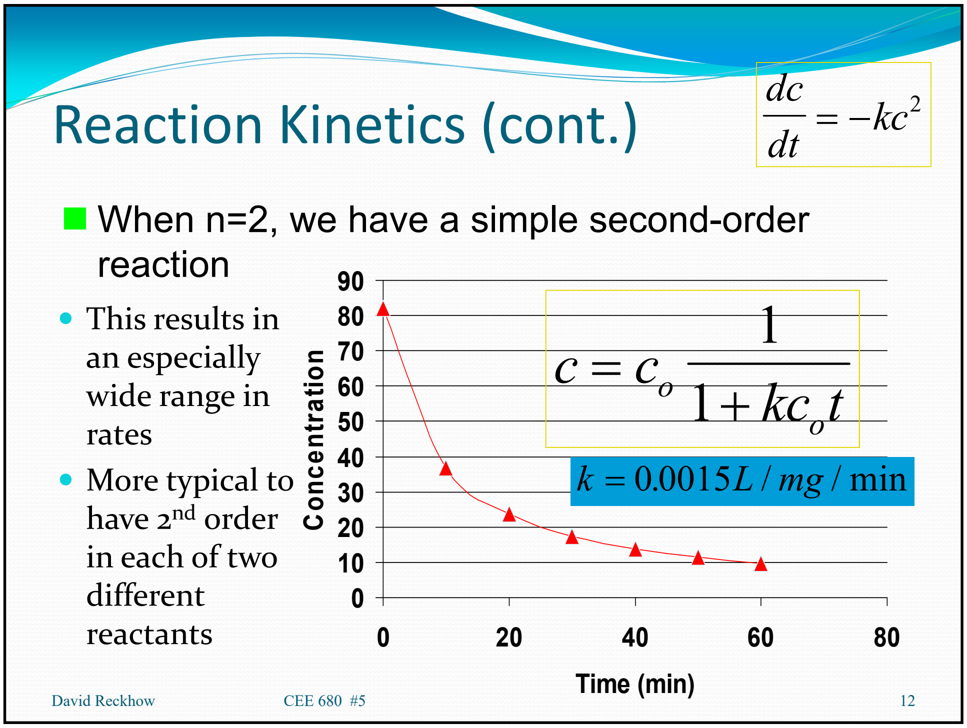
$$\frac{dc}{dt} = -kc^1$$

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

$$\ln c = \ln c_o - kt$$

Slope

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



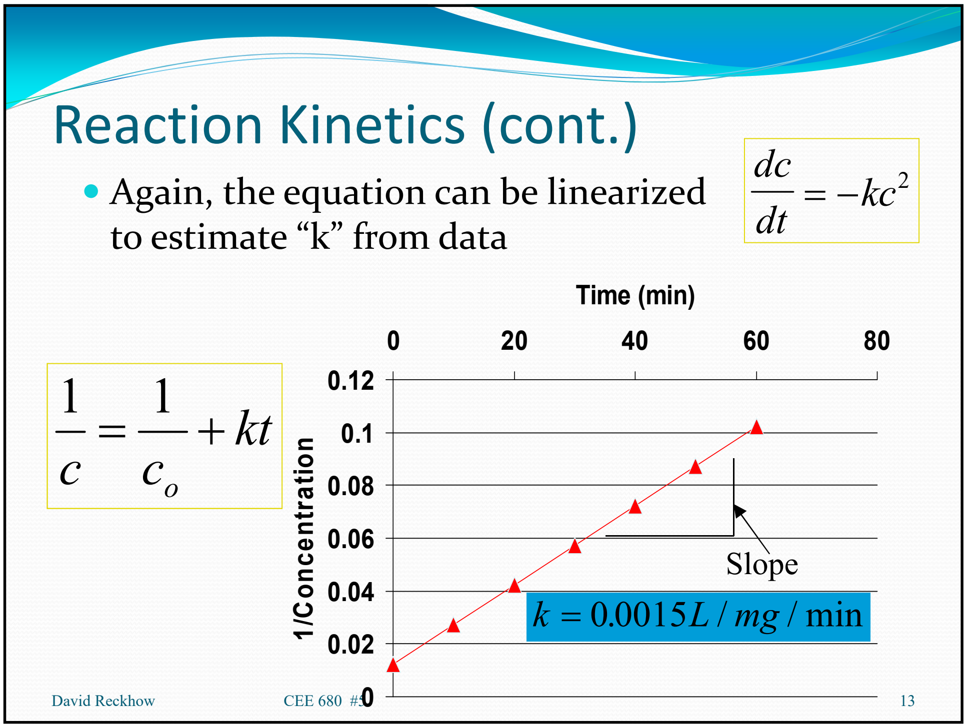
Reaction Kinetics (cont.)

$$\frac{dc}{dt} = -kc^2$$

- 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

$$c = c_o \frac{1}{1 + kc_o t}$$

$k = 0.0015 L / mg / \text{min}$



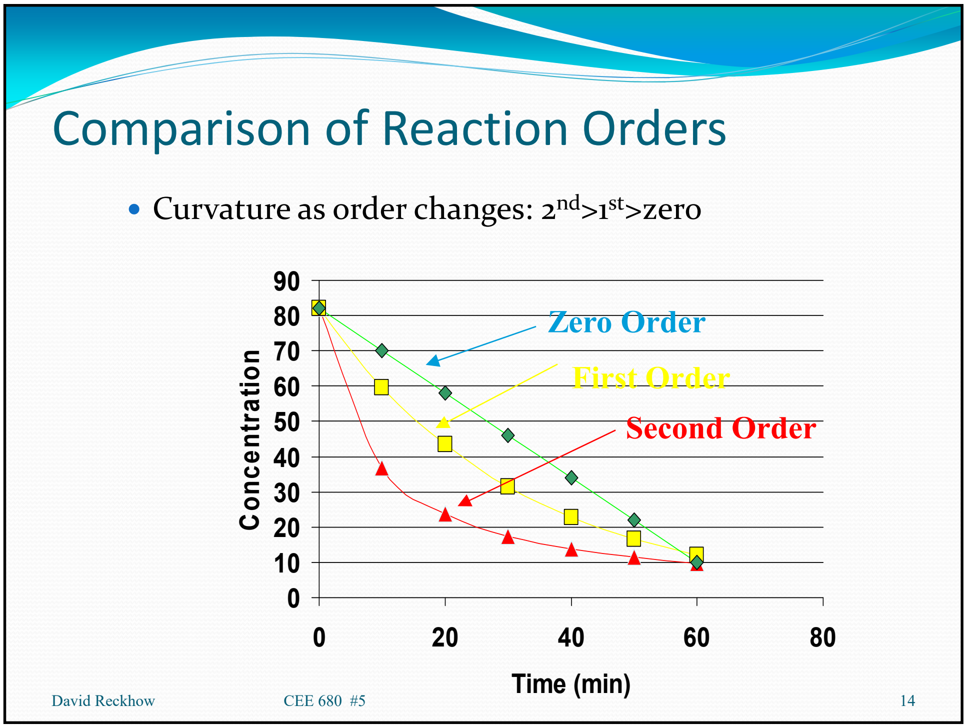
Reaction Kinetics (cont.)

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

$$\frac{dc}{dt} = -kc^2$$

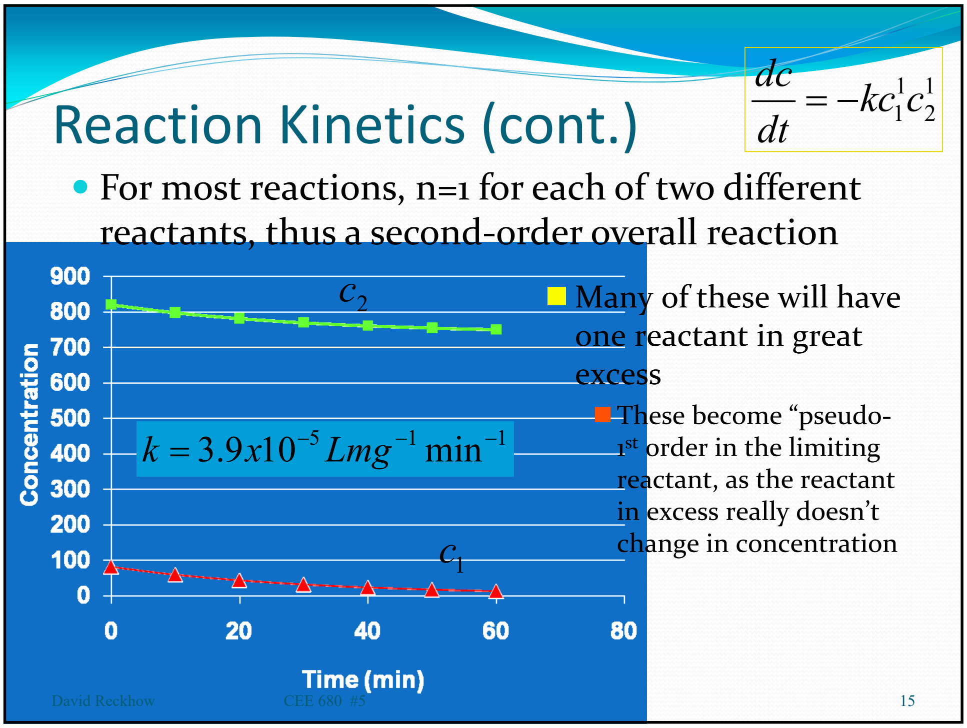
$$\frac{1}{c} = \frac{1}{c_o} + kt$$

$$k = 0.0015 L / mg / \min$$



Comparison of Reaction Orders

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

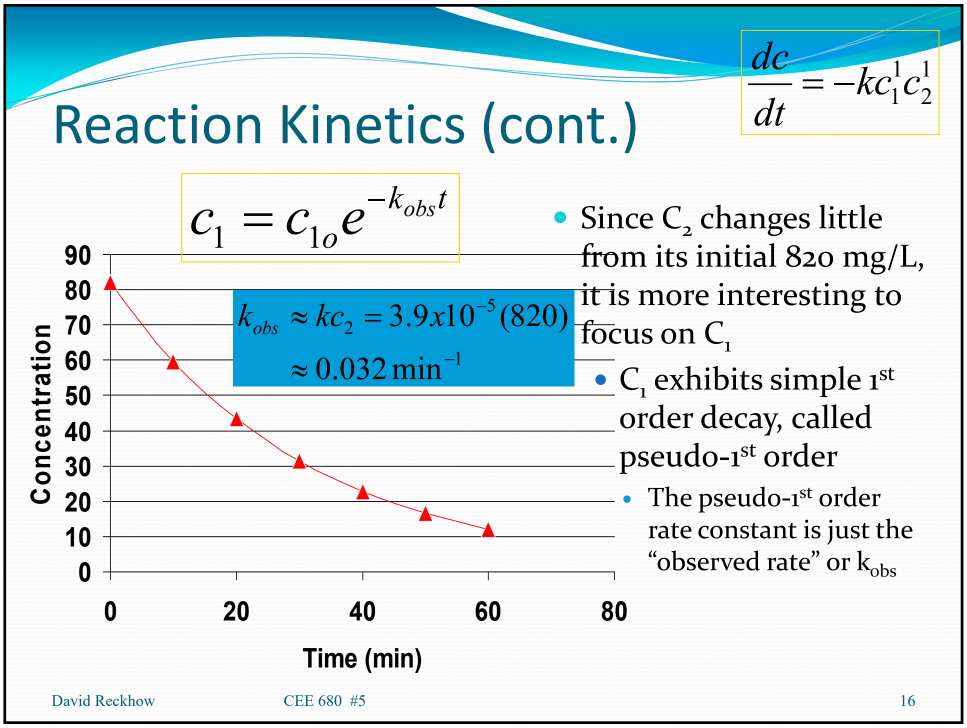


Reaction Kinetics (cont.)

$$\frac{dc}{dt} = -kc_1^1 c_2^1$$

- For most reactions, n=1 for each of two different reactants, thus a second-order overall reaction
  - Many of these will have one reactant in great excess
    - These become "pseudo-1st order in the limiting reactant, as the reactant in excess really doesn't change in concentration

$$k = 3.9x10^{-5}\, Lmg^{-1}\, \min^{-1}$$



Reaction Kinetics (cont.)

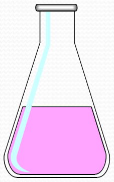
$$\frac{dc}{dt} = -kc_1^1 c_2^1$$

$$c_1 = c_{1o} e^{-k_{obs} t}$$

$$k_{obs} \approx kc_2 = 3.9x10^{-5}(820)$$
$$\approx 0.032\,\min^{-1}$$

- Since C_2 changes little from its initial 820 mg/L, it is more interesting to focus on C_1
  - C_1 exhibits simple 1st order decay, called pseudo-1st order
    - The pseudo-1st order rate constant is just the "observed rate" or k_{obs}

Variable Kinetic Order



- Any reaction order, except n=1

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

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

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

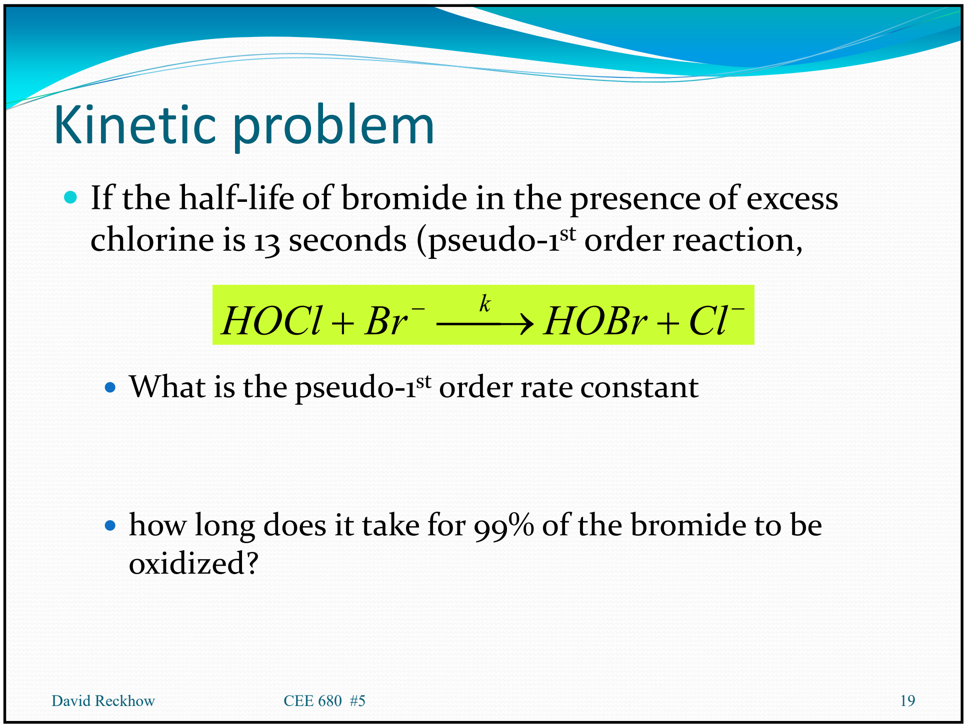
Half-lives

- 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:

$$c = c_o e^{-kt} \qquad 0.5c_o = c_o e^{-kt_{1/2}} \qquad t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

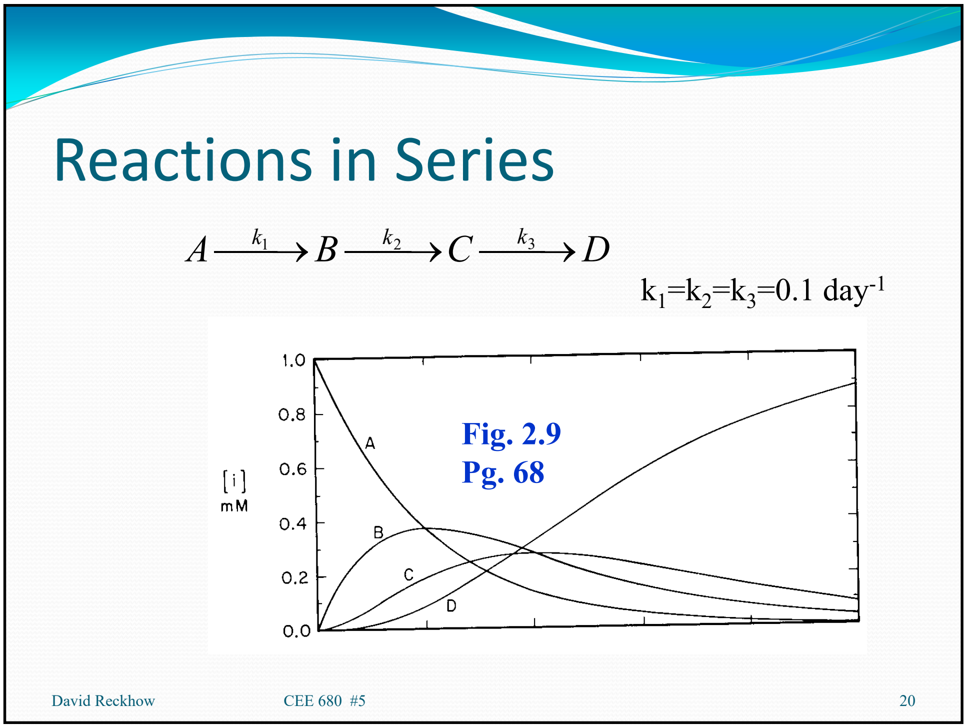


Kinetic problem

- If the half-life of bromide in the presence of excess chlorine is 13 seconds (pseudo-1st order reaction,

$$HOCl + Br^- \xrightarrow{k} HOBr + Cl^-$$

  - What is the pseudo-1st order rate constant
  - how long does it take for 99% of the bromide to be oxidized?



Reactions in Series

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

$k_1=k_2=k_3=0.1$ day^{-1}

Fig. 2.9
Pg. 68

Reversible reaction kinetics

For a general reversible reaction:

$$aA + bB \overset{k_f}{\underset{k_b}{\leftrightarrow}} pP + qQ$$

And the rate law must consider both forward and reverse reactions:

$$r_A = k_f C_A^a C_B^b - k_b C_P^p C_Q^q$$

where,

k_f = forward rate constant, [units depend on a and b]

k_b = backward rate constant, [units depend on a and b]

C_P = concentration of product species P, [moles/liter]

C_Q = concentration of product species Q, [moles/liter]

p = stoichiometric coefficient of species P

q = stoichiometric coefficient of species Q

Reversible 1st order reactions

- Kinetic law

$$\frac{dB}{dt} = k_1[A] - k_2[B]$$

- Eventually the reaction slows and,
  - Reactant concentrations approach the equilibrium values

$$\frac{dB}{dt} = 0 = k_1[A] - k_2[B]$$

$$\frac{[B]}{[A]} = \frac{k_1}{k_2} \equiv K_{eq}$$

Fig. 2.10
Pg. 69

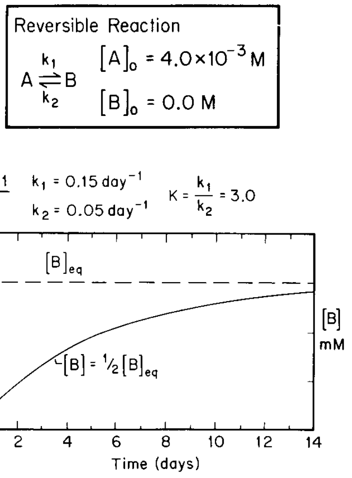


Figure 2.10. Single reversible reaction.

Analysis of Rate Data

- Integral Method
  - Least squares regression of linearized form
- Differential Method
  - estimate instantaneous rate at known time and reactant concentration
- Initial rate Method
  - more rigorous, but slow
- Method of Excess
  - only when 2 or more reactants are involved

Kinetic model for equilibrium

- Consider a reaction as follows:

$$A + B = C + D$$

- Since all reactions are reversible, we have two possibilities

$$A + B \xrightarrow{k_f} C + D$$
$$A + B \xleftarrow[k_b]{} C + D$$

- The rates are:

$$r_f = k_f \{A\}\{B\} \qquad r_b = k_b \{C\}\{D\}$$

- And at equilibrium the two are equal, $r_f = r_b$

$$k_f \{A\}\{B\} = k_b \{C\}\{D\}$$

- We then define an equilibrium constant (K_{eq})

$$K_{eq} \equiv \frac{k_f}{k_b} = \frac{\{C\}\{D\}}{\{A\}\{B\}}$$

Kinetic model with moles

- In terms of molar concentrations, the rates are:

$$r_f = k_f[A]\gamma_A[B]\gamma_B \qquad r_b = k_b[C]\gamma_C[D]\gamma_D$$

- And at equilibrium the two are equal, $r_f = r_b$

$$k_f[A]\gamma_A[B]\gamma_B = k_b[C]\gamma_C[D]\gamma_D$$

- And solving for the equilibrium constant (K_{eq})

$$K_{eq} \equiv \frac{k_f}{k_b} = \frac{[C]\gamma_C[D]\gamma_D}{[A]\gamma_A[B]\gamma_B} = \frac{[C][D]}{[A][B]}\left(\frac{\gamma_C\gamma_D}{\gamma_A\gamma_B}\right)$$

- To next lecture