

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

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

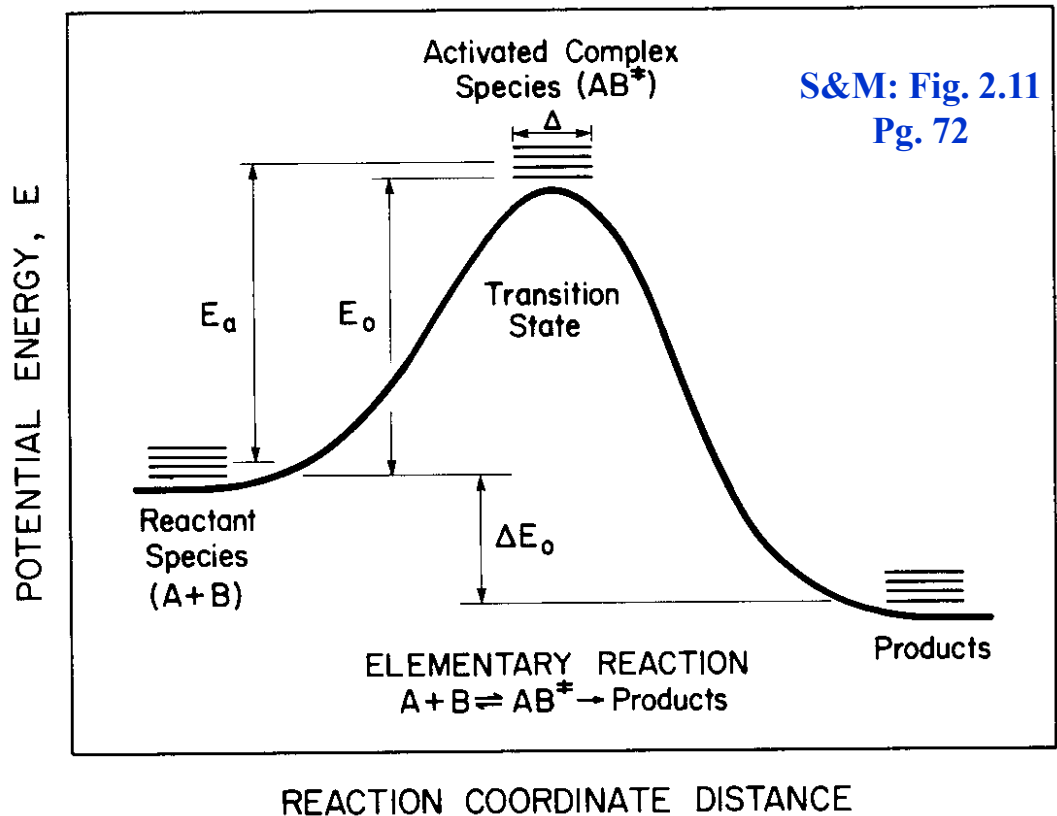
- When reactant molecules collide with the right orientation and energy level to form new bonds
- Many “observable” reactions are really just combinations of elementary reactions



Cont.

- 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

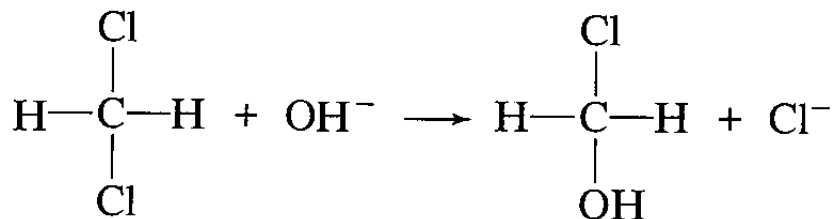


Kinetics

- Examples
 - Fe⁺² oxidation by O₂
 - 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)

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

- First order in each reactant, second order overall

Reaction Kinetics

- 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:
 - **$aA + bB \Rightarrow \text{Products}$**

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).

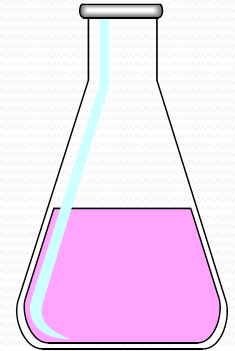


- Most reactions must be considered reversible

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



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

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]

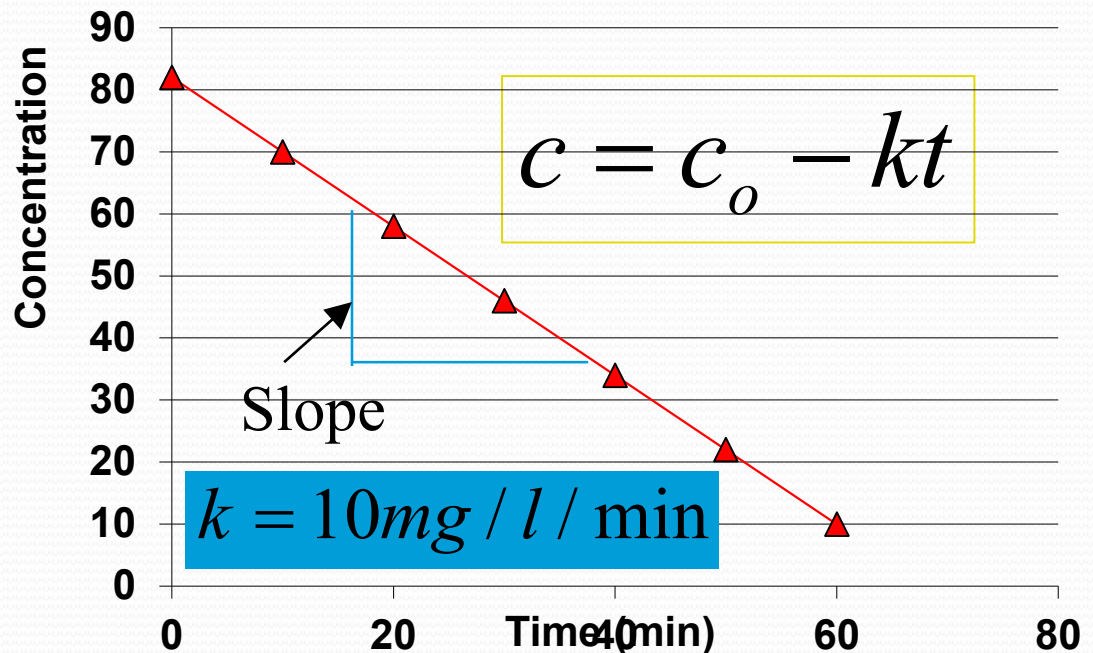
Reaction Kinetics (cont.)

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

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

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

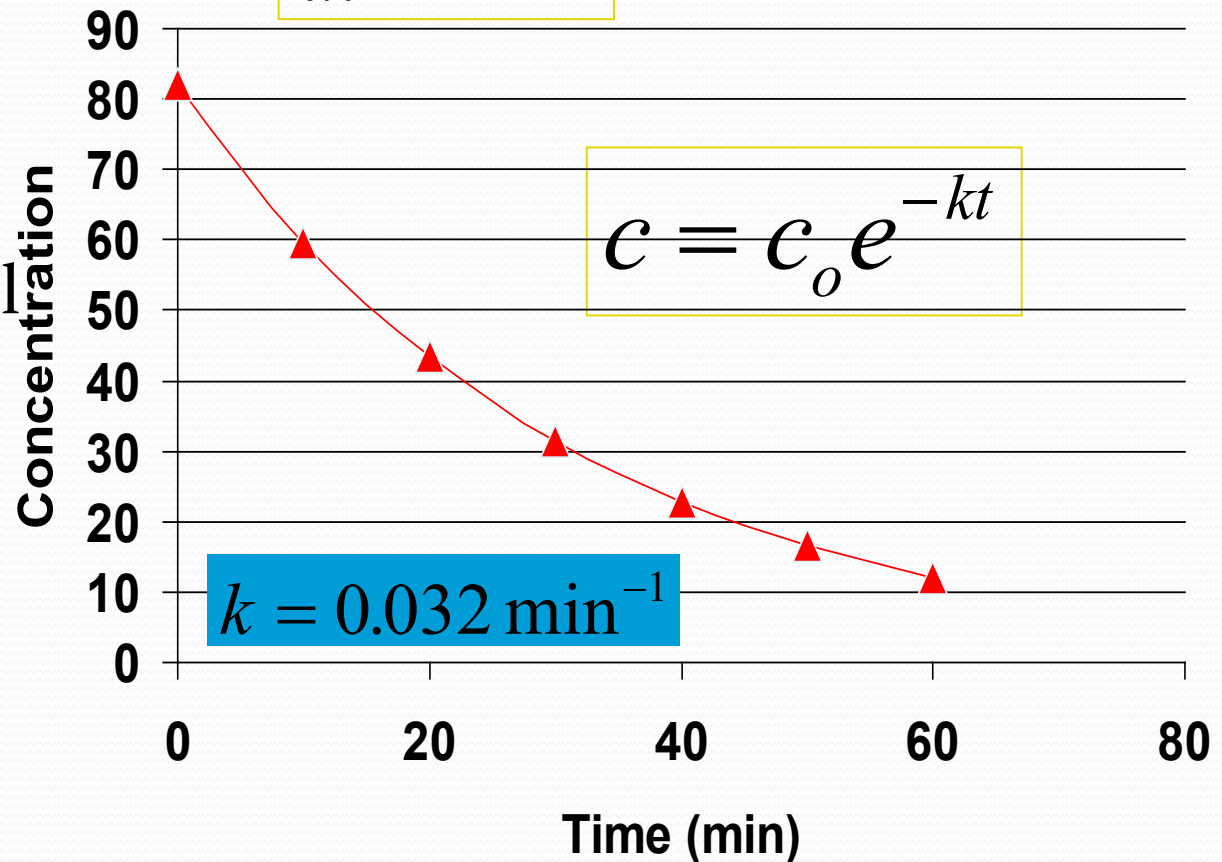
$$\frac{dc}{dt} = -k$$



Reaction Kinetics (cont.)

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

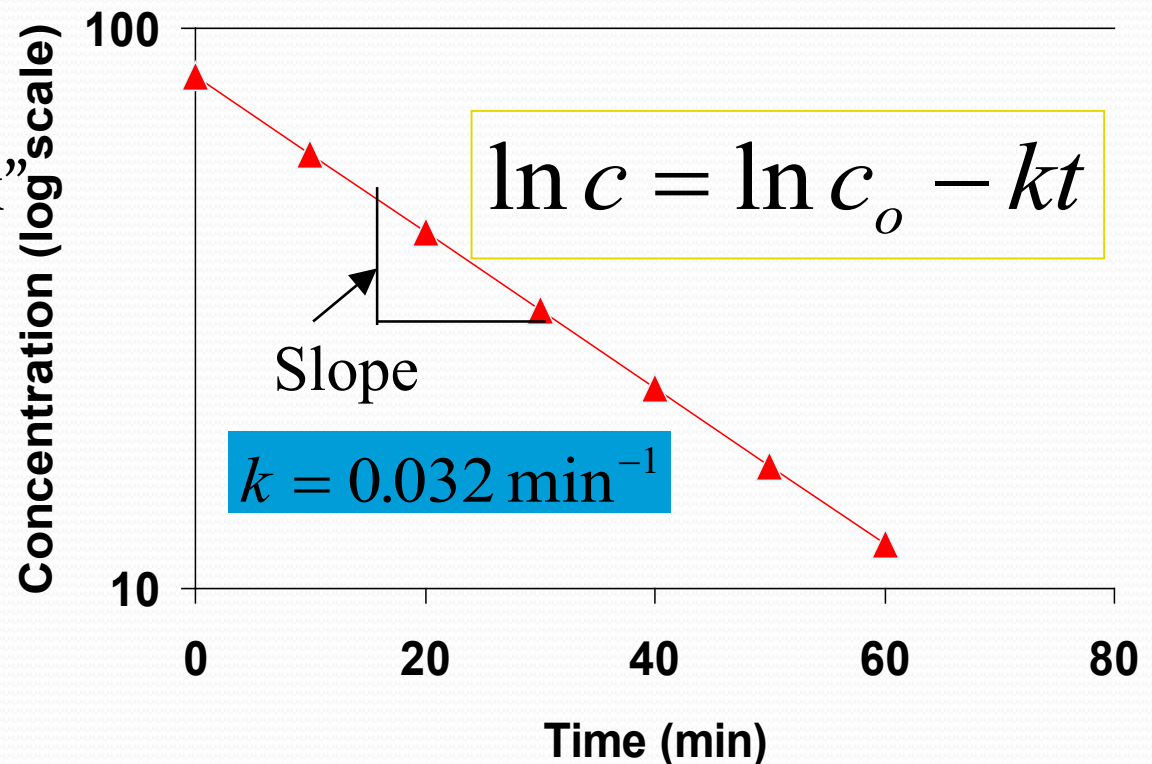
$$\frac{dc}{dt} = -kc^1$$



Reaction Kinetics (cont.)

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

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

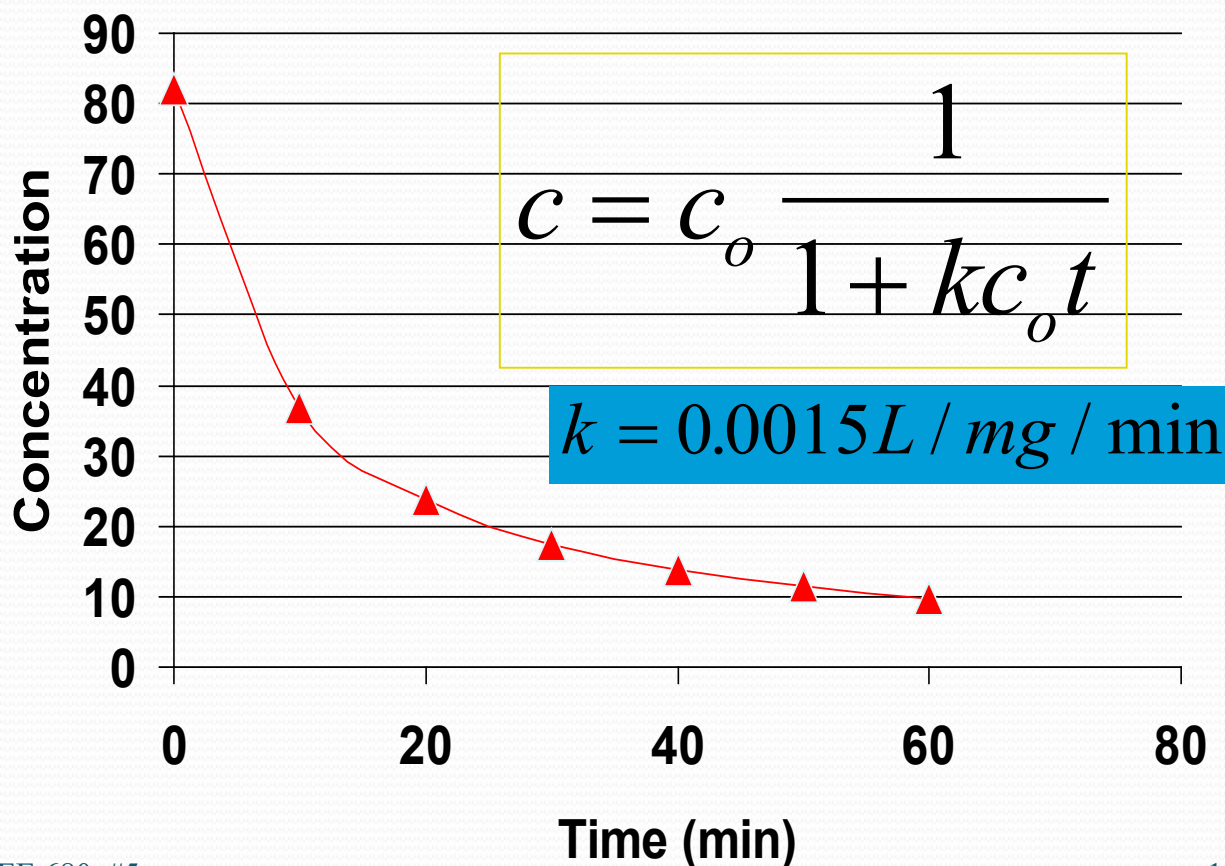


Reaction Kinetics (cont.)

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

■ 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

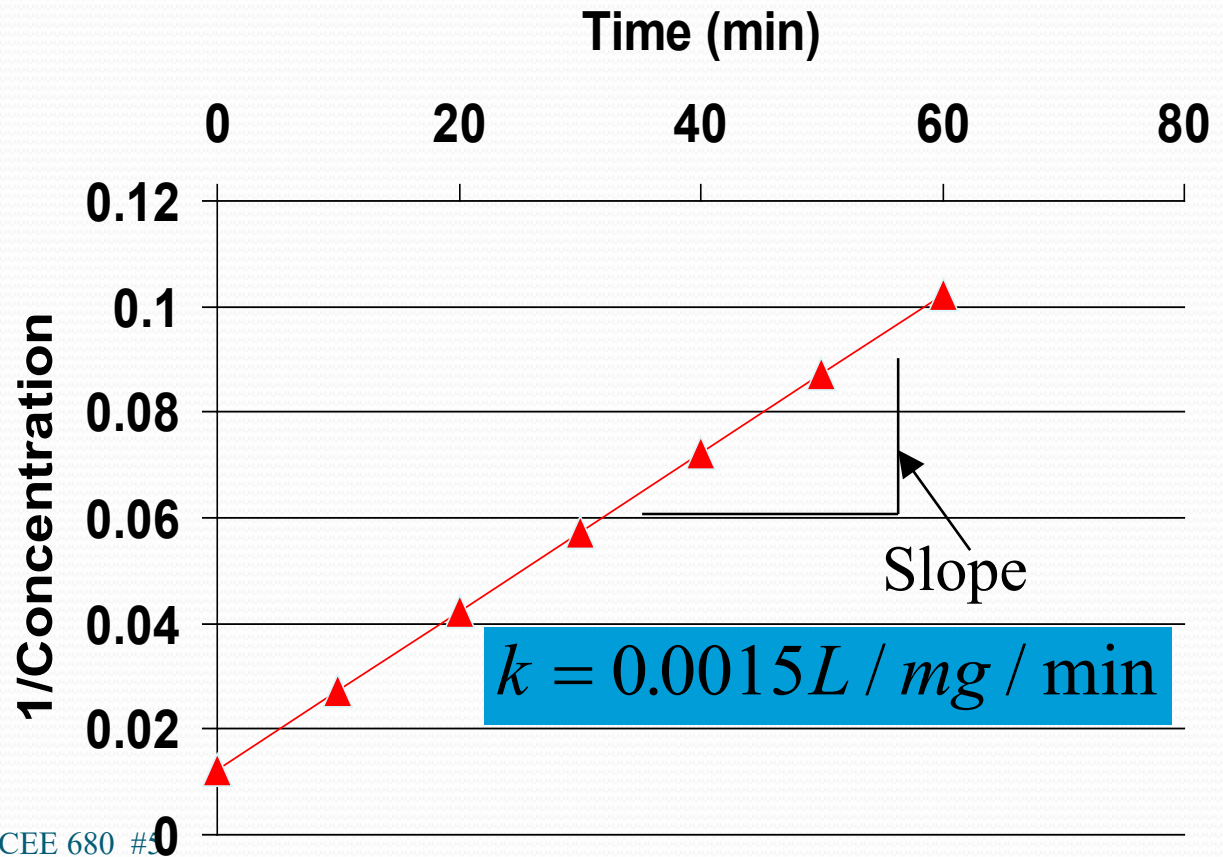


Reaction Kinetics (cont.)

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

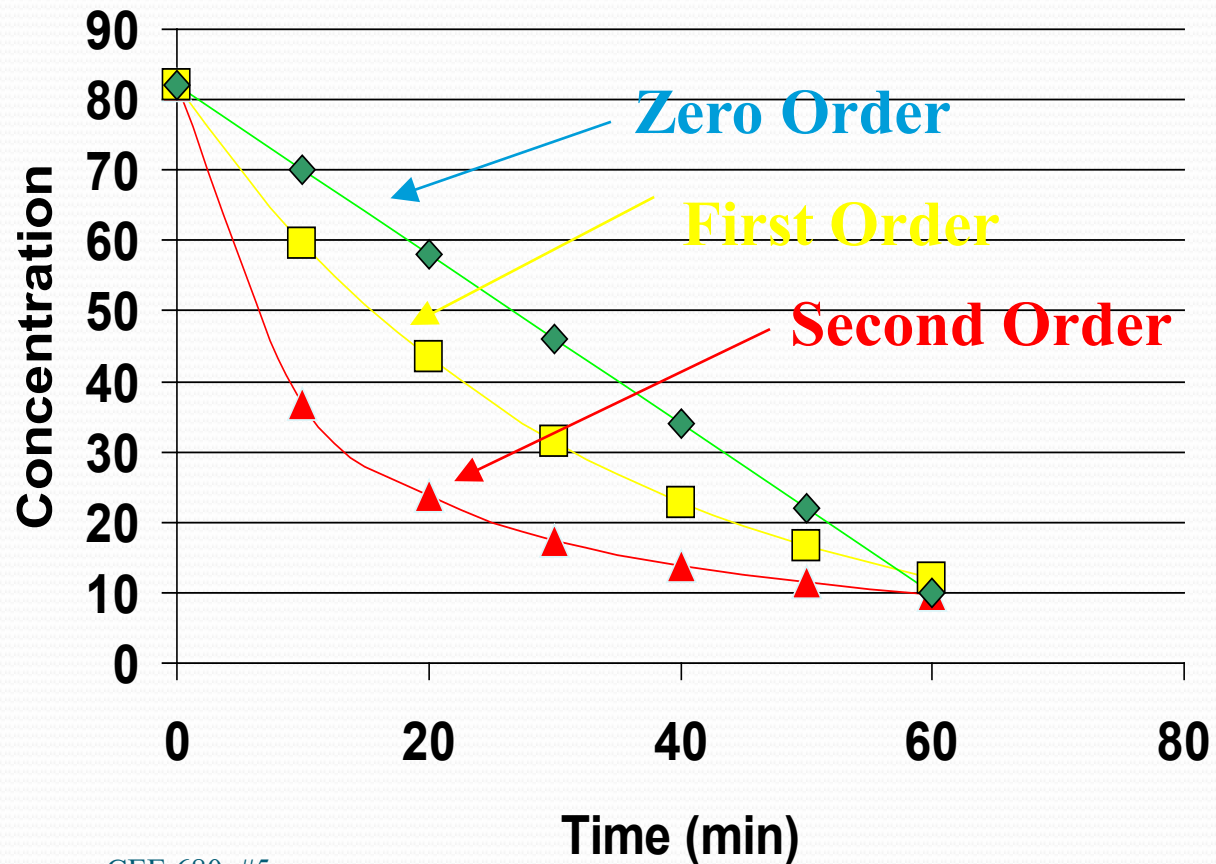
$$\frac{dc}{dt} = -kc^2$$

$$\frac{1}{c} = \frac{1}{c_0} + kt$$



Comparison of Reaction Orders

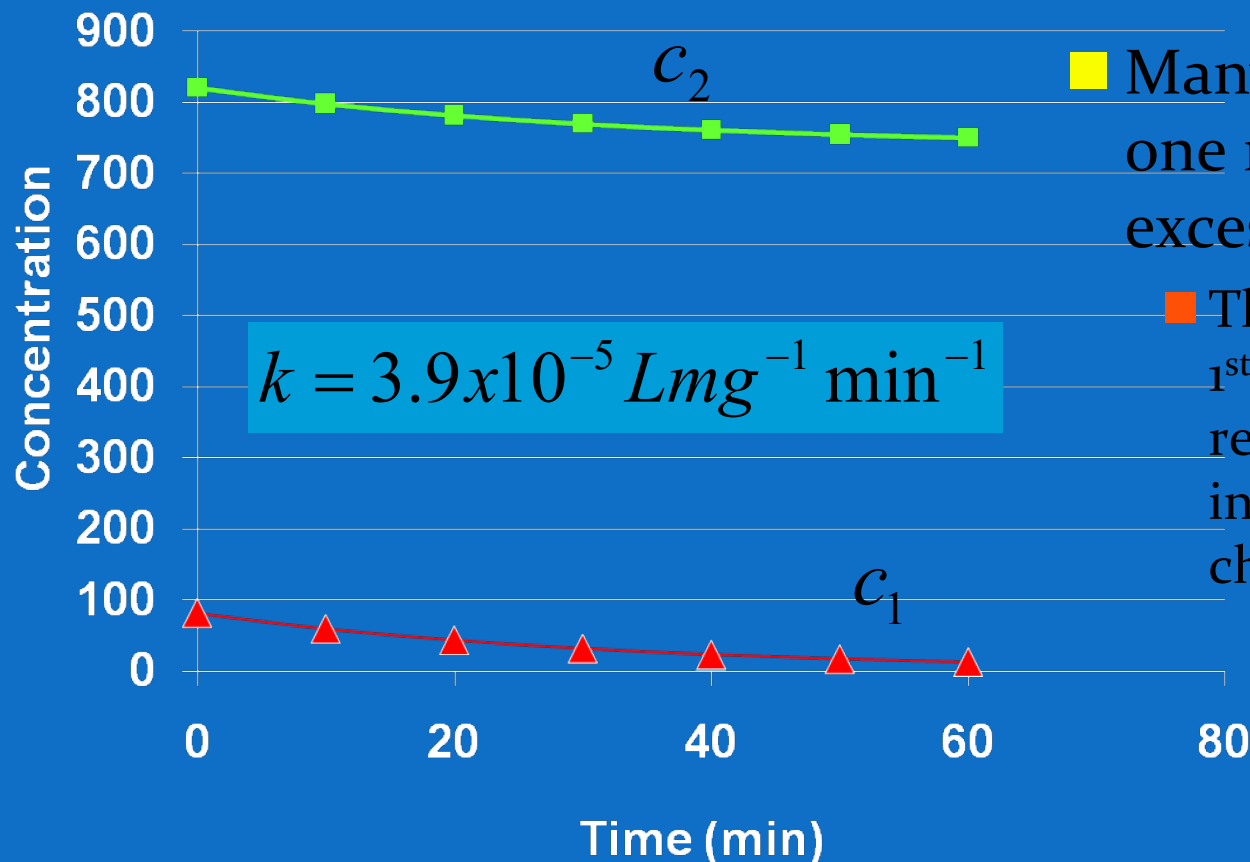
- Curvature as order changes: 2nd > 1st > zero



Reaction Kinetics (cont.)

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

- 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

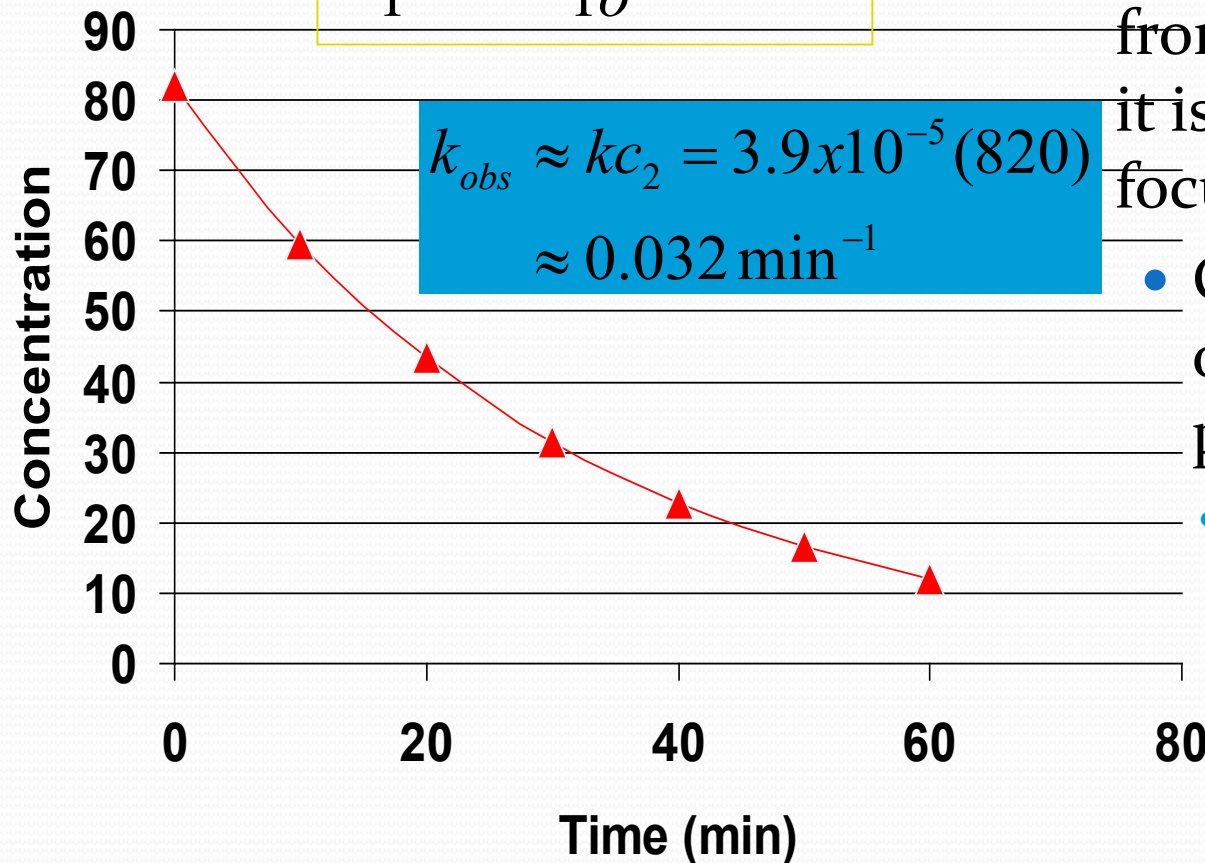
■ These become “pseudo-1st order in the limiting reactant, as the reactant in excess really doesn’t change in concentration

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

Reaction Kinetics (cont.)

$$c_1 = c_{10} e^{-k_{obs}t}$$

$$k_{obs} \approx kc_2 = 3.9 \times 10^{-5} (820) \approx 0.032 \text{ min}^{-1}$$

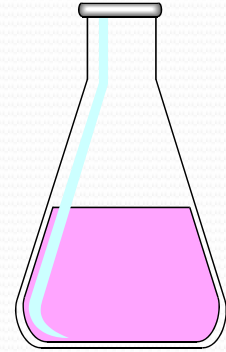


- Since C₂ changes little from its initial 820 mg/L, it is more interesting to focus on C₁

- C₁ 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., $c=0.5c_0$
 - For a zero order reaction:

$$c = c_0 - kt$$

$$0.5c_0 = c_0 - kt_{1/2}$$

$$t_{1/2} = \frac{0.5c_0}{k}$$

- For a first order reaction:

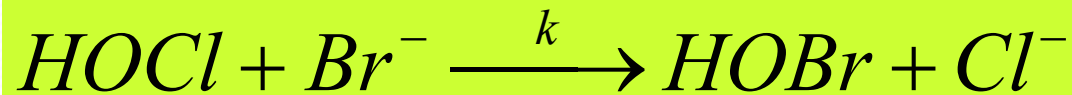
$$c = c_0 e^{-kt}$$

$$0.5c_0 = c_0 e^{-kt_{1/2}}$$

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

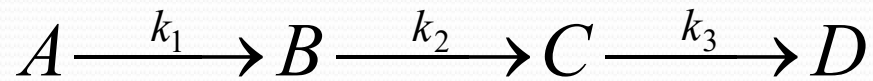
Kinetic problem

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

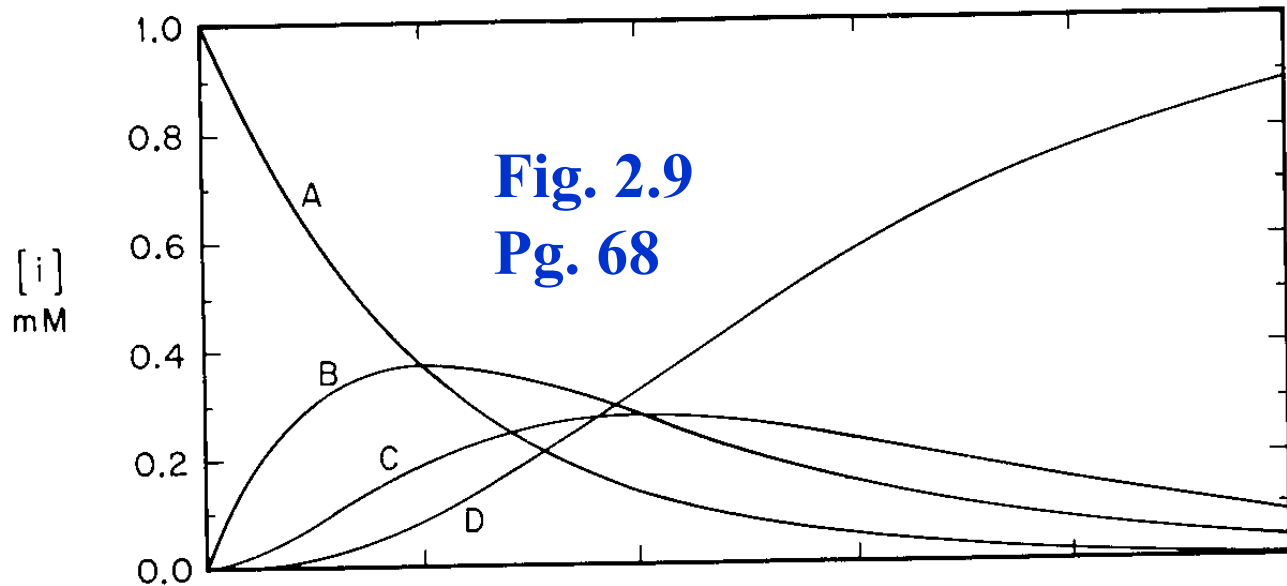


- What is the pseudo-1st order rate constant
- how long does it take for 99% of the bromide to be oxidized?

Reactions in Series

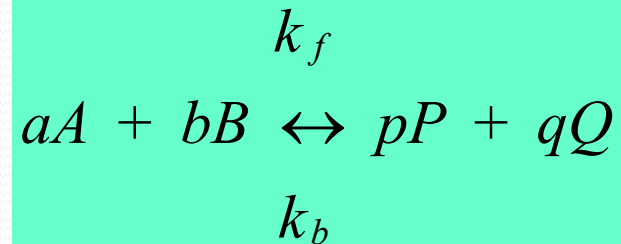


$$k_1 = k_2 = k_3 = 0.1 \text{ day}^{-1}$$



Reversible reaction kinetics

For a general reversible reaction:



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

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

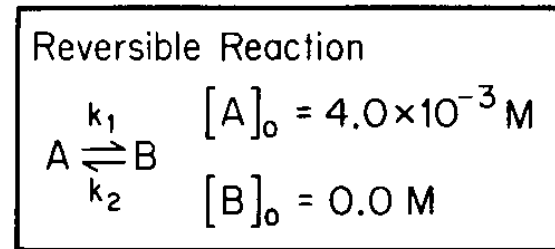
- Eventually the reaction slows and,

- 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



Case 1 $k_1 = 0.15 \text{ day}^{-1}$ $k_2 = 0.05 \text{ day}^{-1}$ $K = \frac{k_1}{k_2} = 3.0$

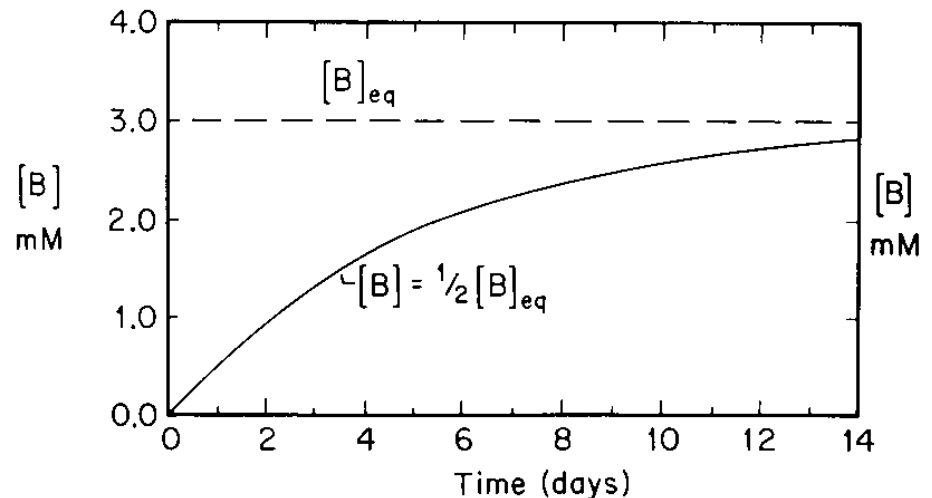


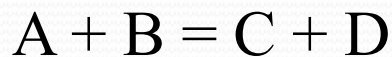
Figure 2.10. Single reversible reaction.

Analysis of Rate Data

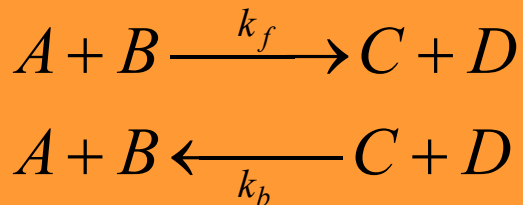
- Integral Method
 - Least squares regression of linearized form
- Differential Method
 - estimate instantaneous rate at known time and reactant concentration
- Initial rate Method
 - more rigorous, but slow
- Method of Excess
 - only when 2 or more reactants are involved

Kinetic model for equilibrium

- Consider a reaction as follows:



- Since all reactions are reversible, we have two possibilities



- 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:

$$r_f = k_f [A] \gamma_A [B] \gamma_B$$

$$r_b = k_b [C] \gamma_C [D] \gamma_D$$

- 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