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Print version

# CEE 577: Surface Water Quality Modeling

Kinetics for CEE 577

Chapra, L2

Begin Chapra "Lecture 2"

# Reaction Kinetics

- Irreversible reaction
  - is one in which the reactant(s) proceed to product(s), but there is no backward reaction,

    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. In generalized form, irreversible reactions can be represented as:
  - **$aA + bB \Rightarrow$ Products**

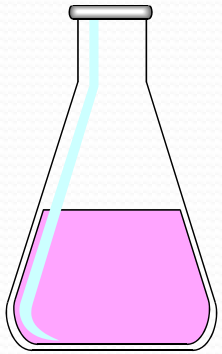
# Reaction Kinetics: Reversibility

- 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).
    - **$aA + bB \leftrightarrow pP + qQ$**

Many biological reactions fit into this category. An example of a reversible 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]

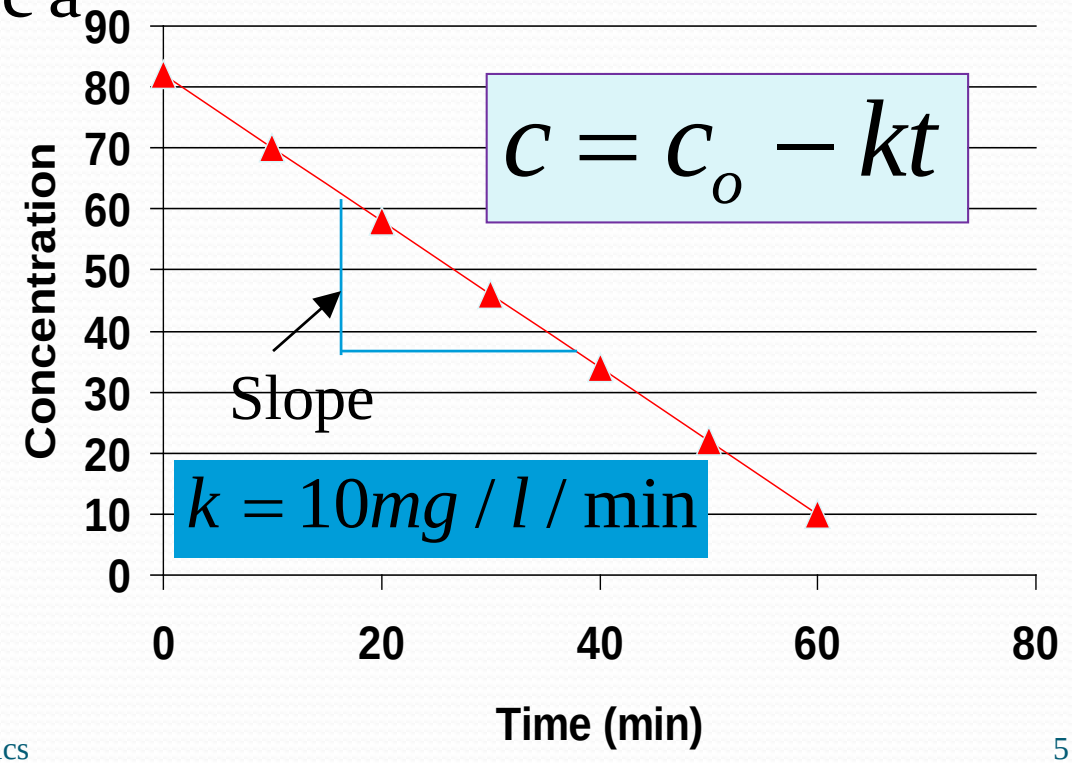
# Reaction Kinetics (cont.)

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

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

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

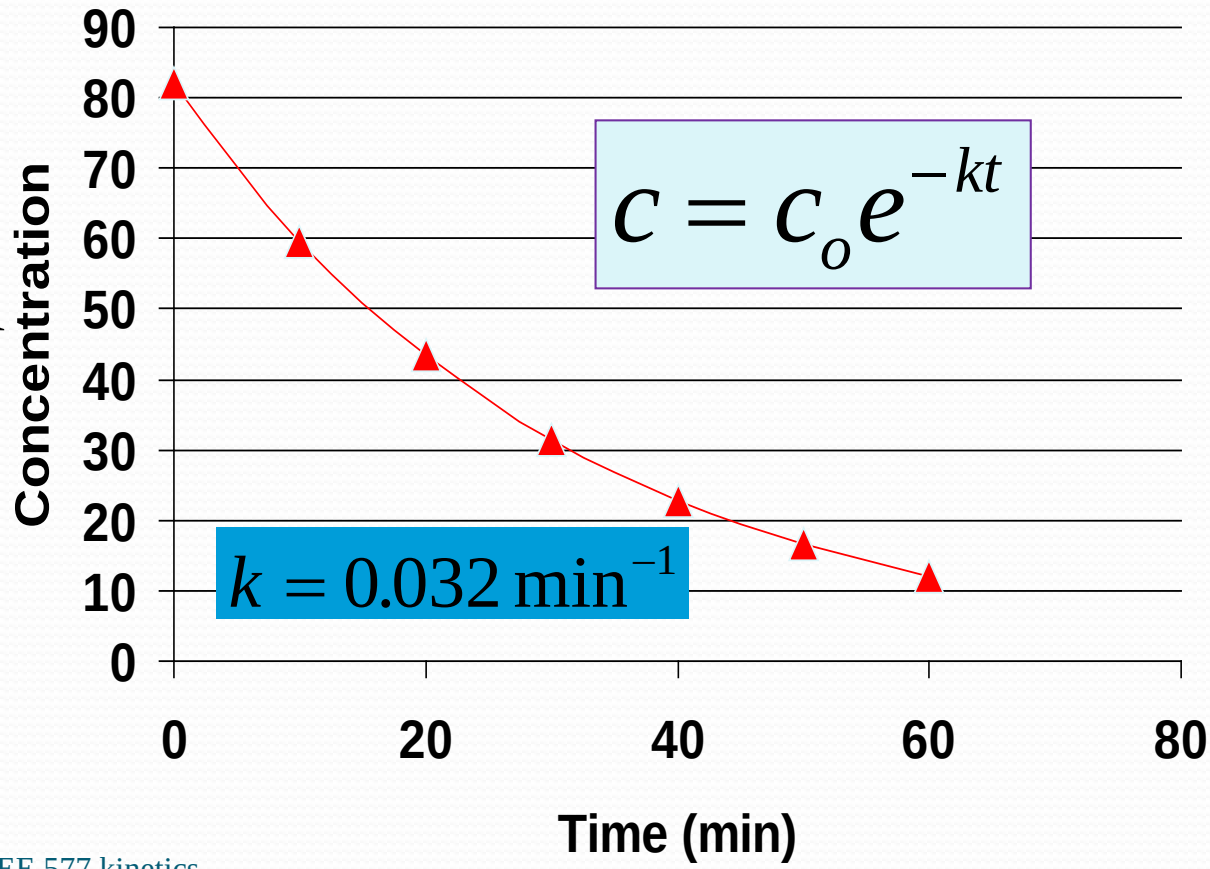
$$\frac{dc}{dt} = -k$$



# Reaction Kinetics (cont.)

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

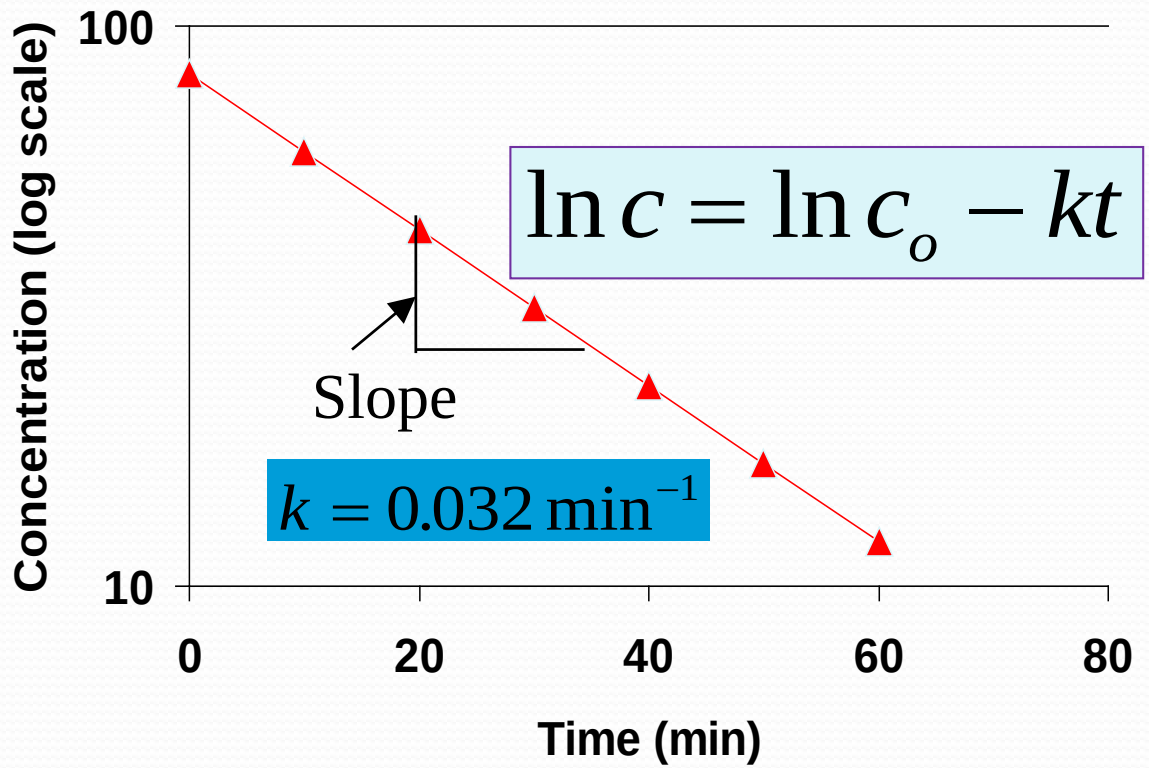
- When n=1, we have a simple first-order reaction
- This results in an "exponential decay"
- Half-life?



# Reaction Kinetics (cont.)

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

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

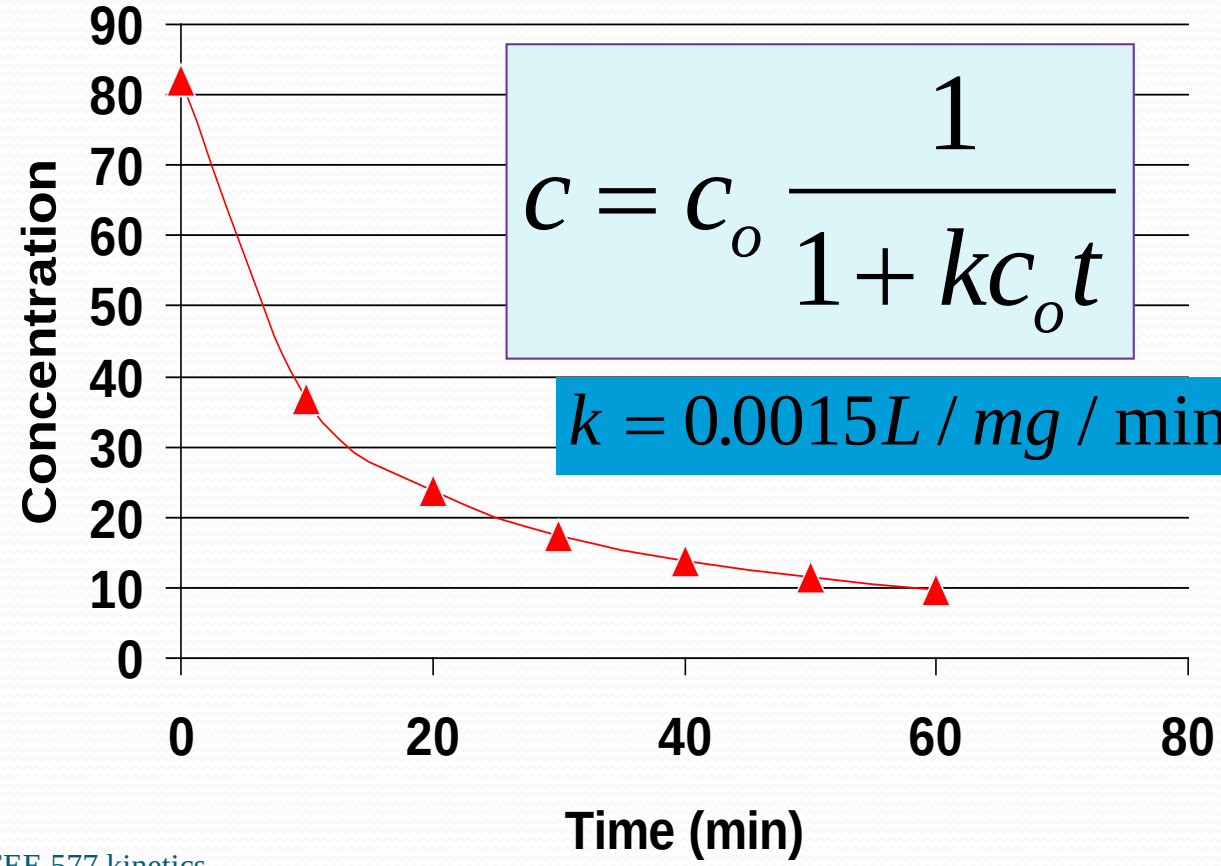


# Reaction Kinetics (cont.)

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

- When n=2, we have a simple second-order reaction

- This results in an especially wide range in rates




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

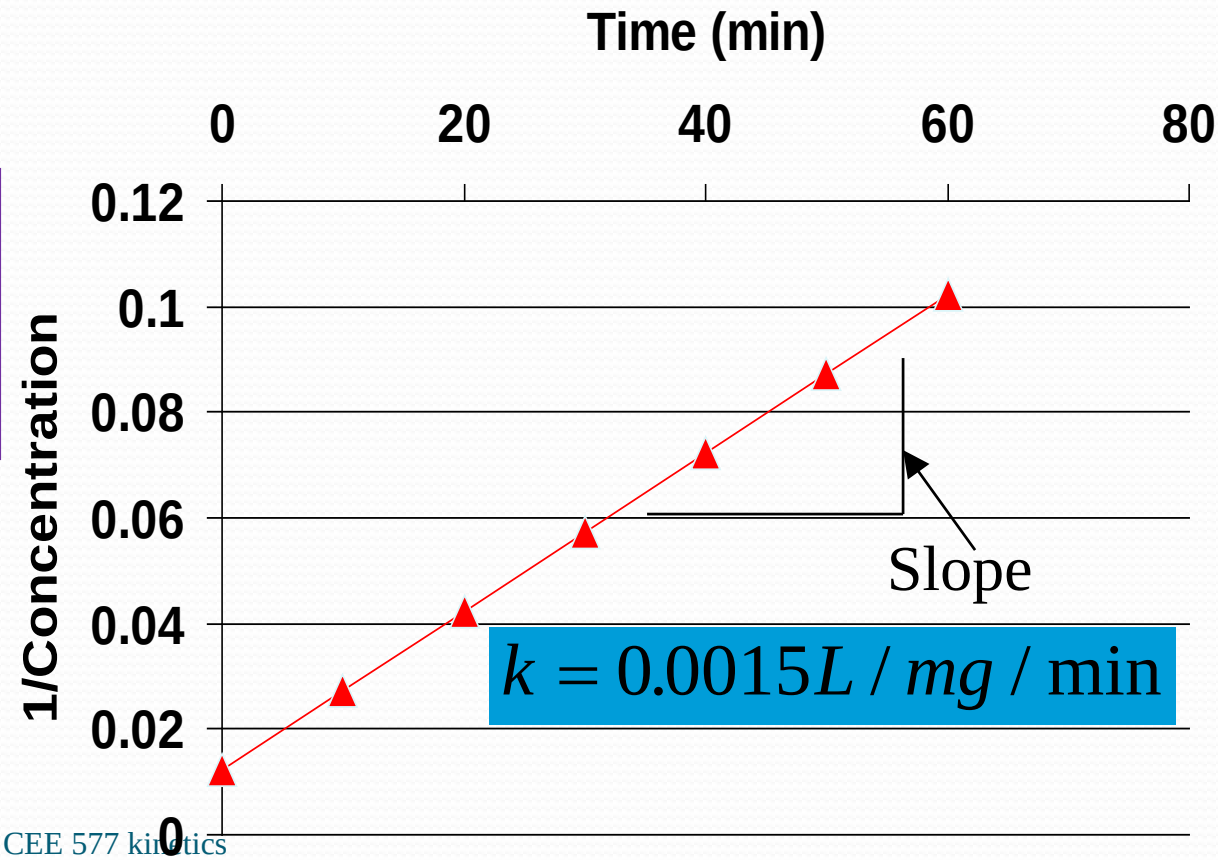
$$k = 0.0015 L / mg / \min$$

# Reaction Kinetics (cont.)

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

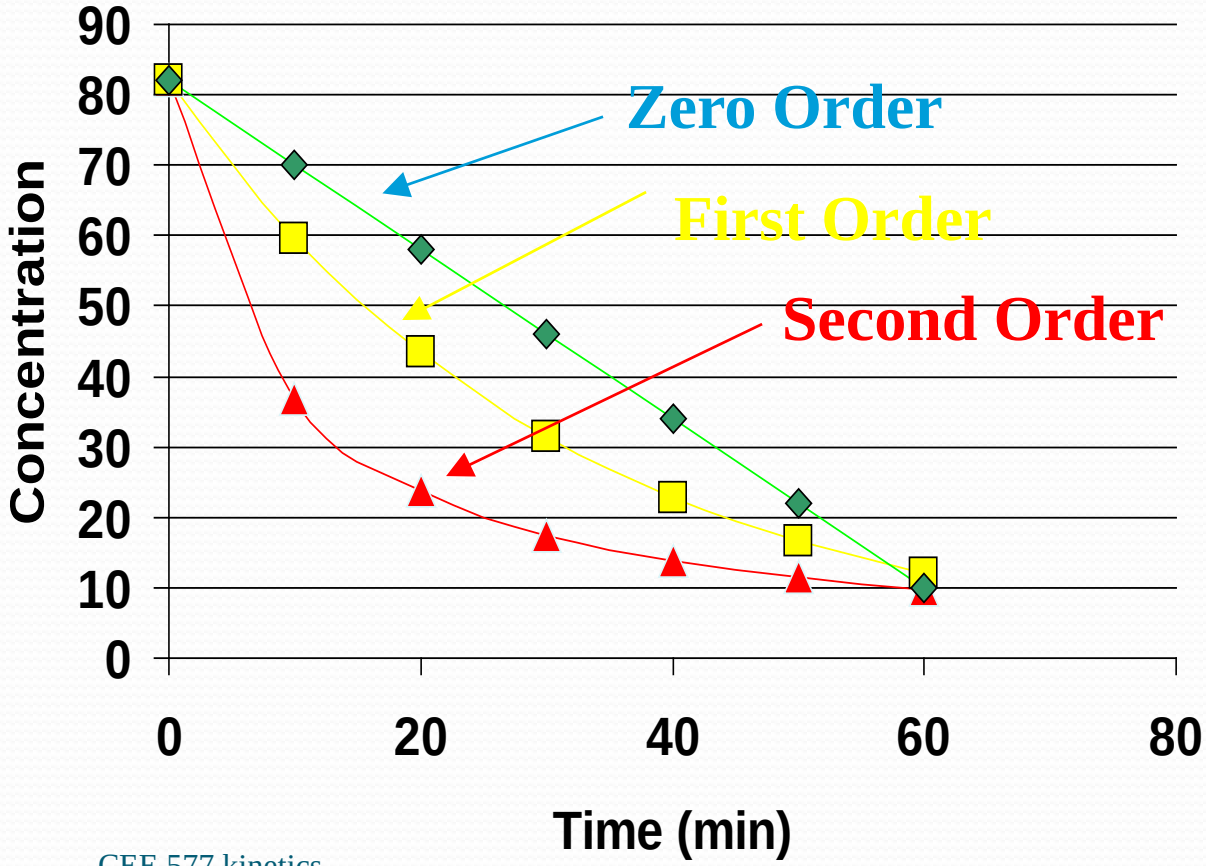
$$\frac{dc}{dt} = -kc^2$$

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

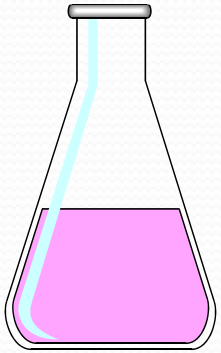


# Comparison of Reaction Orders

- Curvature: 2nd>1st>zero



# Variable Kinetic Order



- Any reaction order, except n=1

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

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

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

# Reversible reaction kinetics

For a general reversible reaction:

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

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

$$\mathbf{r_A = k_f C_A^a C_B^b - k_b C_P^p C_Q^q}$$

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 |

# 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

# Stoichiometry and Temp

- Stoichiometry
  - refer to Chapra or any chemistry book
- Temperature
  - Arrhenius Equation

$$k_{Ta} = Ae^{-E/RTa}$$

  - Engineering Approach:

$$\frac{k_{T_1}}{k_{T_2}} = \theta^{(T_1 - T_2)}$$

# End