CHEMICAL CONCEPTS
Part 2

CE 370 – Lecture 4

Physical Chemistry

- Chemical Kinetics
- Gas Laws
- Colloidal Dispersions

Chemical Kinetics

- Is concerned with the rate at which reaction occur.
  - Zero-order Reactions
  - First-order Reactions
  - Second-order Reactions

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Zero-Order Reactions

- The rate is independent of the concentration of the reactant or product. Consider the following reaction:

  A (reactant) → P (product)

  If C represent the concentration of A, the change in concentration of the reactant A with time is linear and given by:

$$-\frac{dC}{dt} = k = -r$$

where:

r = rate of change in conc with time, mg/l-day

k = reaction constant, mg/l-day

Integrating the above equation gives:

$C = C_o - kt$ where C = conc of A at any time, t, mg/l

C_o = initial conc of A, mg/l

t = time, days or hours

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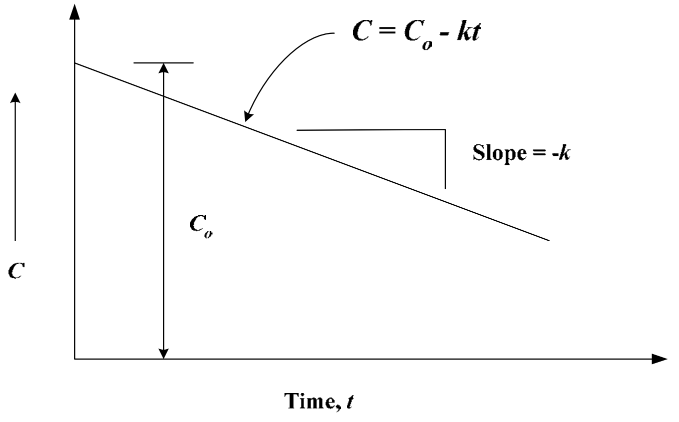
Plot of data for Zero-Order Reaction



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First-Order Reactions

The rate is proportional to the concentration of a one reactant. Consider the following reaction:

A (reactant) → P (product)

If C represent the concentration of A at any time, t, the change in concentration of the reactant A with time is given by:

$$-\frac{dC}{dt} = kC = -r$$

where:

r = rate of change in conc with time, mg/l-day or hour

k = rate constant, day^{-1} or hour^{-1}

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First-Order Reactions

Integrating the first-order equation gives:

$\ln C = \ln C_o - kt$

where:

C = conc of A at any time, t, mg/l

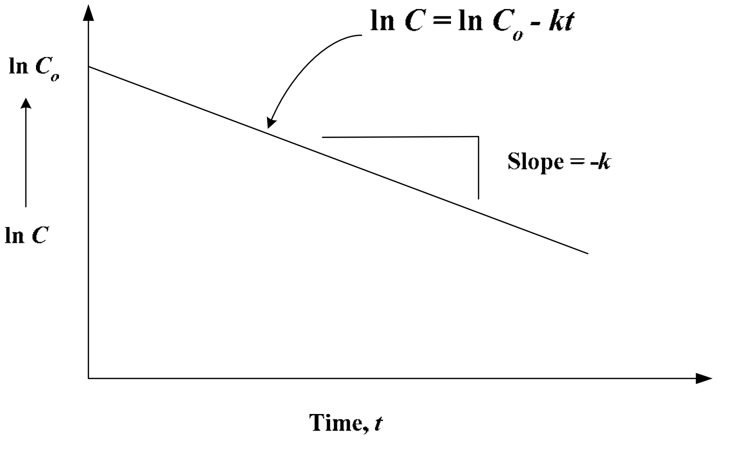
C_o = initial conc of A, mg/l

t = time, days or hours

Another common form of the first-order equation:

$$\frac{C}{C_o} = e^{-kt}$$

Plot of data for First-Order Reaction



Second-Order Reactions

The rate is proportional to the second power of a single reactant being converted to a single product. Consider the following reaction:

2A (reactant) → P (product)

If C represent the concentration of A at any time, t, the change in concentration of the reactant A with time is given by:

$$-\frac{dC}{dt} = kC^2 = -r$$

where:

r = rate of change in conc with time, mg/l-day

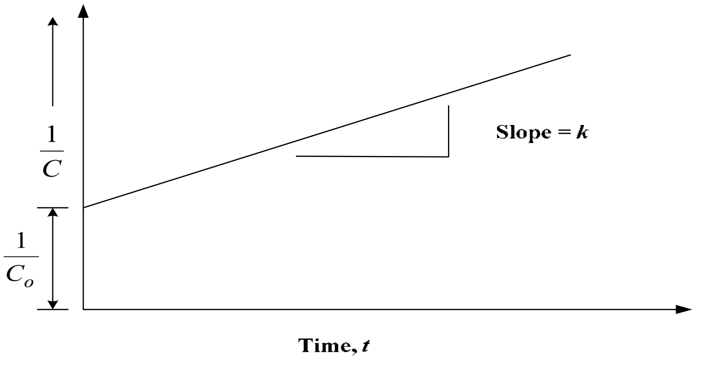
k = rate constant, l/mg-day

c = concentration of A at any time, t, mg/l

Second-Order Reactions

Integrating the second-order equation gives:

$$\frac{1}{C} = \frac{1}{C_o} + kt$$



Effect of Temperature on Reaction Rate

- In most chemical reactions, an increase in temperature will increase the reaction rate.
- The following relationship that relates temperature to reaction-rate constant is used:

$$k_2 = k_1 \theta^{T_2 - T_1}$$

- Where:
- k_1 = rate constant at temperature T_1
- k_2 = rate constant at temperature T_2
- θ = temperature coefficient. A common value of θ is 1.072.
- T_1, T_2 = Temperatures, °C.

Gas Laws

- General Gas Law
- Dalton's law
- Henry's Law

General Gas Law

- Gives the relationship between pressure, volume, and temperature of a gas at two different conditions. The law states that:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

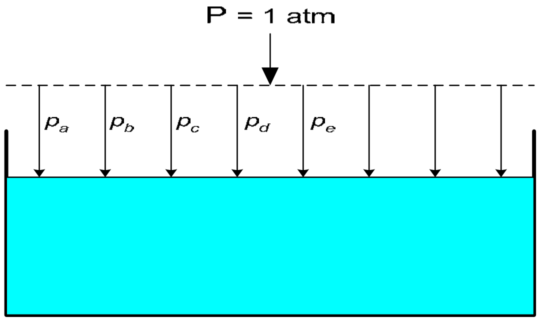
  - Where:
  - P_1, P_2 = absolute gas pressures
  - V_1, V_2 = gas volumes
  - T_1, T_2 = absolute gas temperature, °R, °K

Dalton's law

- In a mixture of gases, such as air, each gas exerts a pressure independent of the others.

- The partial pressure of each gas is proportional to the percent by volume of that gas in the mixture.

Dalton's law



P = $p_a + p_b + p_c$ + etc….= 1 atm

p_a is proportional to the volume percent of the mixture.

Example: Air contains 20.9% by volume of oxygen. Determine its partial pressure.

Solution: 20.9% $\times$ 1 atm = 0.209 atm

Henry's Law

- The weight of any gas that would dissolve in a given volume of a liquid, at a constant temperature, is directly proportional to the pressure the gas exerts above the liquid. In equation form:
  - $C_s = H\,p_g$

    where:

    C_s = the concentration of the gas dissolved in the liquid at equilibrium

    H = Henry's law constant for the gas at the given temperature

    p_g = the partial pressure of the gas above the liquid

Henry's Law

- Example: Calculate the equilibrium concentration of oxygen in water at 20 °C and an elevation of 610 m above sea level, given that Henry's law constant for oxygen in water at 20 °C and 1 atm is 43.8 mg/*l*-atm and that the partial pressure (p_{O2}) is 0.209 atm.
- Solution:

  At sea level atmospheric pressure (P) = 1 atm (760 mm Hg)

  At 610 m P = 706 mm Hg or = 706/760 = 0.929 atm

  $C_s = H\, p_{O2}$

  C_s = 43.8 mg/*l*-atm × 0.209 atm × 0.929 = 8.5 mg/*l*

Applications in Environmental Engineering

- Aeration
  - The rate of transfer of oxygen into solution is proportional to the difference between equilibrium concentration as given by Henry's Law and the actual concentration in the liquid. Therefore:

$$\frac{dC}{dt} \propto (C_s - C_a)$$

Where:

dC/dt = rate of oxygen transfer into solution

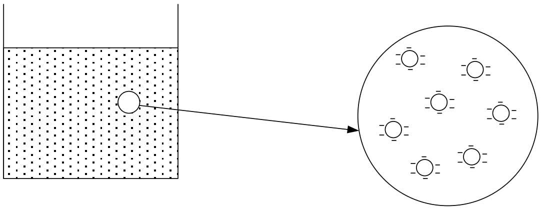
C_s = equilibrium concentration of oxygen

C_a = actual concentration of oxygen

Colloidal Dispersions

Definition:

A system in which particles of *colloidal* size are held in suspension due to their extremely small size and surface electric charge. Colloidal particles do not settle by gravity.



Particles do not settle

Colloidal Dispersions

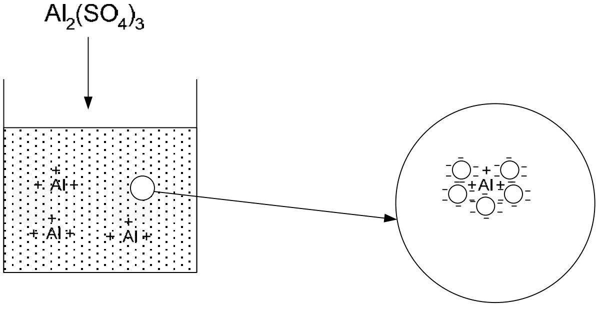
Properties of colloids:

- Range in size from 1 millimicron (mμ) to 1 micron (μ).
- Not visible individually to the naked eye.
- They could be of solid material (clay, organic debris, or waste material) or liquid such as oil.
- Electrically charged (usually negatively charged), therefore, they repel each other and stay in suspension.

Removal of colloids:

- Removal is accomplished by adding a chemical coagulant to suppress the charge, therefore, bringing the particles together so that they grow in size and settle out of solution by gravity.

Removal of colloids



Particles Agglomerate and settle