

# “Transport of Chemicals, Kinetics, and Equilibrium”

## Module 1: Basic Concepts, Lecture 2

*Chemical Fate and Transport in the Environment*, 2<sup>nd</sup> edition. H.F. Hemond and E.J. Fechner-Levy. Academic Press. London. 2000.

## 1.3.2 Consistency of units

- Make sure that you have consistency of units for any calculation; show the units for each parameter, and indicate how they cancel or are converted in order to obtain the desired units:

Rate of chemical inflow (g/sec) = velocity (m/sec) x area (m<sup>2</sup>) x concentration (mg/L) x 0.001g/mg x 1,000 L/m<sup>3</sup>

## 1.4 Physical Transport of Chemicals

Two kinds of physical processes for bulk transport of chemicals:

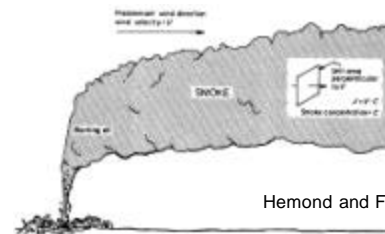
- 1) bulk movement of fluids from one location to another (advection).
- 2) random mixing processes (molecular diffusion is the random motion of the chemical molecules and turbulent diffusion is the random motion of the water or air). Random diffusive transport is often termed Fickian transport. Dispersion transport is movement that is not entirely random, but has a discernible pattern, but is generally too complex to specifically model.

## 1.4.1 Quantification of Advective Transport

- Flux density due to advection is equal to the product of the chemical's concentration in the fluid and the velocity of the fluid:

$$J = CV$$

The units are therefore [M/L<sup>2</sup>T]



Hemond and Fechner-Levy 2000, Fig. 1-5

## 1.4.2 Quantification of Fickian Transport

- Turbulent air and water motions contain constantly changing swirls of fluid, known as eddies.
- These eddies give rise to turbulent (or eddy) diffusion.
- Mixing of the chemicals in the water or air results in the net effect of carrying mass in the direction of decreasing chemical concentration.
- Fick's first law (flux density of mass transport by turbulent diffusion):

$$J = -D (dC/dx) \text{ in one dimension}$$

D is the Fickian mass transport diffusion coefficient [ $L^2/T$ ] and  $dC/dx$  is the change in concentration with distance.

- D can vary for different directions and with time and location.

## Molecular Diffusion

- If a fluid is entirely quiescent and without obstructions, chemicals will still move from regions of high concentration to regions of low concentration (molecular diffusion).
- For a given chemical gradient, usually results in lower flux densities than for other Fickian mass transport processes.
- Molecular diffusion coefficients are mostly dependent on size of molecules.
- For most chemicals at typical environmental temperatures, the molecular diffusion coefficient is about  $0.2 \text{ cm}^2/\text{sec}$  in air and  $10^{-5} \text{ cm}^2/\text{sec}$  in water.
- Increases for higher temperatures and for smaller molecules.

## 1.5 Advection-Dispersion-Reaction Equation

- One dimensional general equation for conservation of mass:

$$\frac{dC}{dt} = -V \cdot \frac{dC}{dx} + \frac{d}{dx} \left( D \cdot \frac{dC}{dx} \right) + r$$

$dC/dt$  is the rate of concentration change at a fixed point in a flowing fluid

$r$  is the input/output associated with internal sources or sinks

- Three dimensional situation using vector notation:

$$\frac{dC}{dt} = -\vec{V} \cdot \nabla C + \nabla \cdot D(\nabla C) + r$$

This equation assumes that D is the same in all directions

## 1.6 Basic Environmental Chemistry

- Chemical reactions involve the formation or breakage of chemical bonds between atoms:
  - Covalent bonds (electrons are shared between atoms)
  - Ionic bonds (bonding force arises from electrical charges of opposite signs on adjacent atoms)
  - Hydrogen bonds (somewhat positively charged hydrogen at one end of a molecule loosely bonds with a somewhat negatively charged atom of another molecule.
  - Other bonds, such as Van der Waals forces (a weak mutual attraction between all molecules).

### 1.6.1 Chemical Kinetics vs. Chemical Equilibrium

- Kinetics describes the rate at which a reaction occurs and is important when comparing rates of different reactions. Example: discharge of degradable pollutant into stream, the contrast between the rate of oxygen consumption with re-aeration rate determines the resulting DO level.
- Equilibrium describes the final expected chemical composition in a control volume. Important when reactions are rapid when compared to other processes of interest (KOH added to drinking water is assumed to result in an instantaneous reaction which lowers the pH of the water, compared to water transport time to consumers).

### 1.6.2 Gibbs Free Energy

- Gibbs free energy helps identify the direction of the reaction and the final equilibrium composition of the system:

$$G = H - TS$$

H is the enthalpy (energy in the system, including bonding forces within and between molecules)

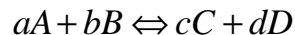
S is the entropy (degree of disorganization or randomness of the system; increases with increasing temperature; takes work to organize molecules)

T is the temperature (expressed in absolute temperature, degrees Kelvin;  $K = ^\circ\text{C} + 273.15$ )

Reactions proceed in a direction that minimizes Gibbs free energy (combination of maximizing disorder and of minimizing energy of the system)

### Calculating Change in Gibbs Free Energy

- The following is a reversible reaction:



A, B, C, and D are chemical compounds

a, b, c, and d are stoichiometric coefficients representing a balanced reaction

The change in Gibbs free energy per additional mole is:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Where R is the gas constant, the standard free energy is  $\Delta G^\circ$ , and:

$$Q = \frac{[C]^c [D]^d}{[B]^b [A]^a}$$

And the values in brackets are the molar concentrations of the chemicals in water.

- If  $\Delta G$  is negative, the reaction will proceed from left to right until  $\Delta G$  becomes zero (at equilibrium)
- $\Delta G$  is positive, the reaction will proceed from right to left until  $\Delta G$  becomes zero
- Therefore, at equilibrium:

$$\Delta G = \Delta G^\circ + RT \ln Q = 0$$

$$\Delta G^\circ = -RT \ln Q$$

$$K = \frac{[C]^c [D]^d}{[B]^b [A]^a} = e^{-\Delta G^\circ / RT}$$

Where K is the equilibrium constant that applies to the final expected chemical composition of the system.

Hemond and Fechner-Levy 2000. Table 1-1

				Approx. log K	$\Delta G^\circ$ (kcal/mol)
Acid-base reactions					
H <sub>2</sub> CO <sub>3</sub> <sup>*</sup> Carbonic acid	→	H <sup>+</sup> Hydrogen ion	+	HCO <sub>3</sub> <sup>-</sup> Bicarbonate ion	-6.3 <sup>b</sup> 8.6
HCO <sub>3</sub> <sup>-</sup> Bicarbonate ion	→	H <sup>+</sup> Hydrogen ion	+	CO <sub>3</sub> <sup>2-</sup> Carbonate ion	-10.3 <sup>b</sup> 14.1
CH <sub>3</sub> COOH Acetic acid	→	H <sup>+</sup> Hydrogen ion	+	CH <sub>3</sub> COO <sup>-</sup> Acetate ion	-4.8 <sup>b</sup> 6.5
NH <sub>3</sub> (g) Ammonia	→	NH <sub>4</sub> <sup>+</sup> Ammonium ion	+	OH <sup>-</sup> Hydroxide ion	-4.8 <sup>b</sup> 6.5
Precipitation-dissolution reactions					
CaCO <sub>3</sub> (s) Calcium carbonate (limestone)	→	Ca <sup>2+</sup> Calcium ion	+	CO <sub>3</sub> <sup>2-</sup> Carbonate ion	-8.3 <sup>b</sup> 11.6
SiO <sub>2</sub> (s) Quartz	+	2H <sub>2</sub> O	→	H <sub>4</sub> SiO <sub>4</sub> Silicic acid	-3.7 <sup>d</sup> 5.0
CaSO <sub>4</sub> (s) Gypsum	→	Ca <sup>2+</sup> Calcium ion	+	SO <sub>4</sub> <sup>2-</sup> Sulfate ion	-4.6 <sup>d</sup> 6.3

### Example Problem 1-4

- What is the ratio of the Cu<sup>2+</sup> (cupric) ion to the CuOH<sup>+</sup> ion in the water if the OH<sup>-</sup> concentration is 10<sup>-4</sup> mol/L?



- From mass action:

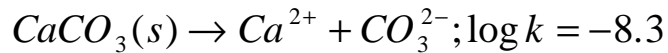
$$\frac{[CuOH^{+}]}{[OH^{-}][Cu^{2+}]} = 10^{6.3}$$

$$\frac{[CuOH^{+}]}{[Cu^{2+}]} = 10^{6.3} \cdot 10^{-4} = 10^{2.3}$$

$$\frac{[Cu^{2+}]}{[CuOH^{+}]} = 0.005$$

### Example 1-5

- Limestone, CaCO<sub>3</sub> (s), is in equilibrium with water in which carbonate, CO<sub>3</sub><sup>2-</sup>, concentration is 10<sup>-5</sup> M. What is the concentration of the calcium ions, Ca<sup>2+</sup>, in the water?



$$\frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]} = 10^{-8.3}$$

$$[\text{solid}] = 1$$

$$[Ca^{2+}] = 10^{-8.3} \cdot \frac{[CaCO_3]}{[CO_3^{2-}]} = 10^{-8.3} \cdot \frac{1}{10^{-5}}$$

$$[Ca^{2+}] = 10^{-3.3} M$$

### 1.6.4 Electroneutrality

- The sum of all positively charged ions (in equivalents) must equal the sum of all negatively charged ions.
- Example 1.7:

An acid mine water flows thru an area having gypsum ( $CaSO_4$ ). The pH of the water is 4.0, the total concentration of sulfate ( $SO_4^{2-}$ ) is  $6 \times 10^{-3}$  M and the total concentration of chloride ( $Cl^-$ ) is  $3 \times 10^{-4}$  M. The only other ion present is assumed to be calcium ( $Ca^{2+}$ ). What is the calcium concentration in the water and will the following precipitation reaction occur downstream?



The electroneutrality equation for this water is:

$$2[Ca^{2+}] + [H^+] = 2[SO_4^{2-}] + [OH^-] + [Cl^-]$$

if the pH is 4.0, the pOH is  $14 - 4.0 = 10$ , and  $[OH^-] = 10^{-10}$

$$2[Ca^{2+}] = -10^{-4} + 2(6 \times 10^{-3}) + 10^{-10} + (3 \times 10^{-4})$$

$$[Ca^{2+}] = 6.1 \times 10^{-3} M$$

From mass action:

$$\frac{[CaSO_4]}{[Ca^{2+}][SO_4^{2-}]} = \frac{1}{(6.1 \times 10^{-3})(6 \times 10^{-3})} = 10^{4.4}$$

Since  $10^{4.4}$  is smaller than  $10^{4.62}$  (the equilibrium constant), the reaction will proceed to the right and solid may form.

### 1.6.6 Kinetics

- For many environmental fate processes (such as the degradation of pollutants), the rate of the reaction is more important to quantify than the final composition.
- It is important to know if the equilibrium (to possibly fully degraded conditions) will take seconds, years, or perhaps centuries.
- Normally have multiple steps that must occur in sequence. The slowest is the rate-limiting step.

## First-Order Kinetics

- In a simple situation, a molecule may react by itself without any collision to form another molecule.
- The number of molecules reacting in a time interval will simply be proportional to the number of molecules present
- The rate at which the concentration of reacting molecules changes with time is described by first-order kinetics:

$$dC/dt = -kC$$

C is the concentration of the parent compound [M/L<sup>3</sup>], t is the time [T], and k is the rate constant [T<sup>-1</sup>]

- This is called a first-order reaction because the rate at which the chemical concentration changes is proportional to the concentration raised to the first power.
- First-order kinetics may lead to exponential decay, or first-order decay, of the chemical concentration. The integration of the previous equation leads to:

$$C_t = C_o e^{-kt}$$

## Half-Life ( $t_{1/2}$ )

- These expressions lead to the definition of half-life, the amount of time it takes for the parent compound to decay to half its initial concentration:

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

$$\ln(0.5) = -kt_{1/2}$$

$$t_{1/2} = 0.693/k$$

- Half lives for different decay processes can be compared to identify which mechanism is the most significant and to estimate the downstream concentration after a specific flow time.

## Example Problem 1.9

- What is the remaining source strength for a radioactive source in 1993, if the 1940 source strength was 10 microcuries ( $\mu\text{Ci}$ ) for cobalt-60 ( $^{60}\text{Co}$ ). The half-life is 1900 days for this material.

$$t_{1/2} = \frac{0.693}{1900 \text{ days}} = 3.6 \times 10^{-4} / \text{day}$$

$$C_t = 10e^{-(3.6 \times 10^{-4} / \text{day})(53 \text{ years})(365 \text{ days / year})}$$

$$C_t = 8.6 \times 10^{-3} \text{ mCi}$$

- Can simplify in some cases, because one of the chemicals may remain in relatively constant concentration (such as water).
- In these cases, it is possible to multiply the rate constant,  $k$ , by the constant chemical concentration to obtain a new rate constant,  $k'$ , resulting in:

$$dA/dt = -k'A$$

$$\text{where } k' = kB$$

Also, the Arrhenius rate law:  $k = Ae^{-E_a/RT}$  is used to correct the rates for different temperatures (see example 1-10).

## Two Chemical System

- If two different types of chemicals, A and B, must collide to cause a reaction to occur, then the (identical) rates at which the concentrations decrease will be:

$$dA/dt = -kAB$$

$$dB/dt = -kAB$$

- $k$  [ $L^3/MT$ ] is the rate constant for the reaction and is (different from the first-order rate constants).
- The rate at which a chemical disappears is proportional not only to its own concentration, but also to the concentration of the other chemical with which it reacts. Increasing the concentration of either will increase the rate.

## 1.7 Errors in Measurements of Environmental Quantities

- You need to understand measurements of central tendencies (mean, mode, average, median, etc.) along with measures of variance (variance, standard deviation, standard error, coefficient of variation), and intervals.
- Also understand “significant figures” and how to round, etc. and when to round.

## Homework Problems

- Chapter 1: 1, 4, 7, 11, 12, and 22