Fundamental
of
Environmental Engineering

Chapter 2: Environmental Chemistry

Activity vs. Concentration

Activity: can be thought of as the effective or apparent concentration in water or that portion of the true mole-based concentration of species that participates in a chemical reaction.

$$\{C_i\} = \gamma_i[C_i]$$

where $\{C_i\}$ = activity of species i

γ_i = activity coefficient of species i

$[C_i]$ = concentration of species i

Ionic Strength

Ionic Strength (I or μ) of the solution, mole/L: is used to determine the effect of other dissolved species or composition of the solution which affect a solute of interest.

$$\mu = \frac{1}{2} \sum_i C_i Z_i^2$$

where Z_i = the change of the ion

Chemical Kinetics

There are two very different approaches used in evaluating a chemical's fate and treatment.

- Kinetics: deals with the rates of reactions.

- Equilibrium: deals with the final result or stopping place of reactions.

Kinetics Approach:

- Used to understand how fast the reaction will occur.

- Applied for reactions either occur relatively slowly or are prevented from reaching equilibrium.

For examples, biologically mediated reactions, light-driven (photochemical) reactions, redox reactions, and decay of radioactive elements etc.

"For kinetics approach, we need to know about the rate law".

Equilibrium Approach:

- Used to determine to the final conditions that result from the reaction when they are likely to be of more interest than the rates at which the reaction occurs.

- Applied for reactions happen very rapidly relative to the time frame of our interest.

For examples, acid-base reactions, complexation reactions, and some phase-transfer reactions (e.g., volatilization, dissolution etc.) etc.

"Both the equilibrium and kinetic approaches are based on thermodynamics".
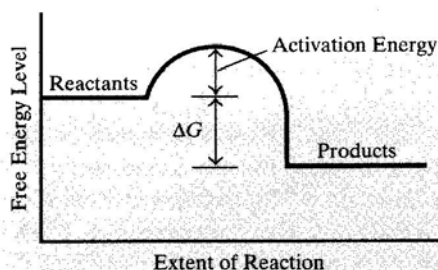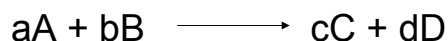

Figure 3-3. The energetic relationships required for a reaction to occur.

Only reactions that result in thermodynamically favorable changes in their energy state can occur. This change in energy state is called Gibb's free energy change (ΔG).
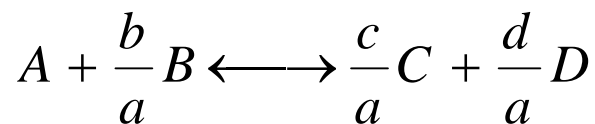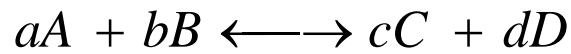

Rate Law

$$aA + bB \longrightarrow cC + dD$$

$$Rate \; \alpha \quad [A]^m[B]^n$$

$$Rate \; = \quad K[A]^m[B]^n$$

K   = specific rate constant

m, n   = reaction order with respect to
        A and B, respectively

m + n = overall reaction order

[A], [B] = concentrations of A and B,
        respectively

The relationship between the rates of reaction for a single reaction step

$$aA + bB \longleftrightarrow cC + dD$$

$$A + \frac{b}{a}B \longleftrightarrow \frac{c}{a}C + \frac{d}{a}D$$

$$\frac{-r_a}{1} = \frac{-r_b}{b/a} = \frac{r_c}{c/a} = \frac{r_d}{d/a}$$
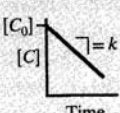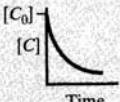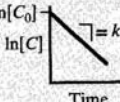
Zero- and First-Order Reactions

Reaction Order	Rate Law	Integrated Form of Rate Law	Plot of Conc. versus Time	Linearized Plot of Conc. versus Time	Half-Life $t_{1/2}$	Example Units of Rate Constant, k
Zero	$\frac{d[C]}{dt} = -k$	$[C] = [C_0] - kt$	$[C_0]$, $[C]$ vs Time, slope $= k$	Same as $[C]$ vs. time	$\frac{0.5[C_0]}{k}$	moles/L-s, mg/L-s
First	$\frac{d[C]}{dt} = -k[C]$	$[C] = [C_0]e^{-kt}$	$[C_0]$, $[C]$ vs Time	$\ln[C_0]$, $\ln[C]$ vs Time, slope $= k$	$\frac{0.693}{k}$	$s^{-1}, min^{-1}, h^{-1}, day^{-1}$

Figure 3-4. Summary of zero and first-order rate expressions. Note the differences between each of these expressions.

Example: How long will it take the carbon monoxide (CO) concentration in a room to decrease by 99% after the source of CO is removed and the windows are opened? Assume the first-order rate constant for CO removal (due to dilution by incoming clean air) is 1.2 hr^{-1}.
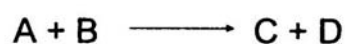
Solution
This is a first-order reaction. Let $[CO_0]$ equal the initial CO concentration. When 99% of the CO goes away, $[CO] = 0.01[CO_0]$. Therefore,

$$0.01[CO_0] = [CO_0]e^{-kt}$$

where $k = 1.2 \ hr^{-1}$. Solve for t, which equals 3.8 hr.

Pseudo-First-Order Reaction

$$A + B \longrightarrow C + D$$

$$Rate = k[A][B]$$

If the concentration of A does not change significantly during the reaction (i.e. $[A_0] >> [B_0]$ or $[A] \approx [A_0]$, the concentration of A may be assumed to remain constant and can be incorporated into the rate constant, k. The rate law then becomes:

$$Rate = k'[B]$$

where k' is the pseudo-first-order rate constant and equals $k[A_0]$.

Example: Lake Silbersee is located in the German city of Nuernberg. The lake's water quality has been diminished because of high hydrogen sulfide concentrations (the rotten egg smell) that originates from a nearby leaking landfill. To combat the problem, the city decided to aerate the lake in an attempt to oxidize the odorous H_2S to nondorous sulfate ion according to the following oxidation reaction:

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$
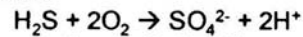
It has been determined experimentally that the reaction follows first-order kinetics with respect to both oxygen and hydrogen sulfide concentrations:

$$\frac{d[H_2S]}{dt} = -k[H_2S][O_2]$$

The present rate of aeration maintains the oxygen concentration in the lake at 2 mg/L. The rate constant (k) for the reaction was determined experimentally to be 1,000 L/mole-day. If the aeration completely inhibited anaerobic respiration and thus stopped the production of sulfide, how long would it take to reduce the H_2S concentration in the lake from 500 μM to 1 μM?

Solution

The dissolved oxygen of the lake is maintained at a constant value and therefore is a constant. It can be combined with the rate constant to make a pseudo - first - order rate constant. Thus

$$[H_2S] = [H_2S_0]e^{-k't}$$

where $k' = k[O_2]$.

$$1\,\mu M = 500\mu M \exp\left\{-\frac{1000L}{mole - day} \times \frac{2mg}{L} \times \frac{g}{1000mg} \times \frac{mole}{32g} \times t\right\}$$

The time, t, can be calculated to equal 100 days.

Effect of Temperature on Rate Constants

The Arrhenius equation is used to adjust rate constants for changes in temperature. It is written as

$$k = Ae^{-(Ea/RT)}$$

where k is the rate constant of a particular order, A is termed the preexponential factor (same units as k), E_a is the activation energy (kcal/mole), R is the gas constant, and T is the absolute temperature (K).

Catalysis

Catalysts are substances that increase the rate of reaction. They act by modifying The reaction or the nature of the activated complex so that the reaction may proceed through an activated complex with a lower activation energy.

Chemical Equilibrium

$$aA + bB \xleftrightarrow{\quad k_f,k_b \quad} cC + dD$$
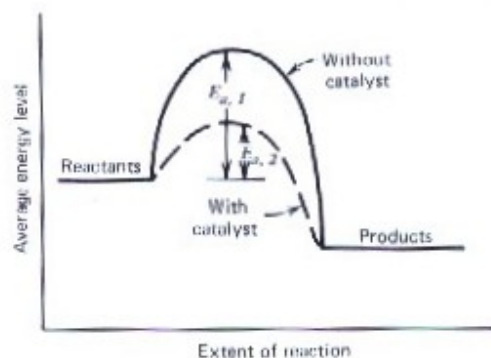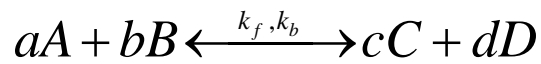
$r_f = k_f[A]^a[B]^b$ $\qquad\qquad$ $r_b = k_b[C]^c[D]^d$

At equilibrium

$$r_f = r_b$$

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

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

The Thermodynamics Basis of Chemical Equilibrium

Thermodynamics : the study of the flow of energy in matter. There are two ways of transferring energy to a system: heat the system or do work on the system.

For a closed system at constant pressure and temperature, the thermodynamic expression for free energy can be expressed as:

G = H-TS

Where G = Gibbs free energy , kcal
$\qquad$ T = absolute temperature, K
$\qquad$ S = entropy, kcal/K
$\qquad$ H = enthalpy, kcal

Enthalpy (H)

The enthalpy (heat content of a substance) :
is the amount of energy in the system capable
of doing mechanical work. Natural systems
tend to go from a state of higher energy to a
state of lower energy.

Entropy (S)

The entropy (energy of a substance that spreads
out in a process): is the way to measure all kind of
energy spontaneously spread out from where
they are concentrated to where they are more
dispersed.

Free Energy (G)

The free energy (chemical potential of a
substance) : a comparison of the changes of
enthalpy and entropy during a chemical reaction.
All spontaneous processes move toward
equilibrium.

"If the enthalpy and entropy for a chemical reaction
have the same sign, there will be some temperature
at which ΔH and $T\Delta S$ will be numerically equal and
ΔG will be exactly zero".
**This state is the thermodynamic definition of a
system at equilibrium**.

Exothermic reactions usually take place spontaneously. The products of an exothermic reaction have less energy than the reactants, therefore the reaction occurs naturally to reach a lower state of energy.

Endothermic reactions do not take place spontaneously.

Isothermal reactions take place at a constant temperature.

Isobaric reactions take place at a constant pressure.

As any reaction proceeds an incremental amount, the change in G_T, is proportional to ΔG

$$\Delta G = \left(\sum_i v_i \overline{G}_i \right)_{products} - \left(\sum_i v_i \overline{G}_i \right)_{reactants}$$

Where v_i is the stoichiometric coefficient and $\overline{G}_i$ is the free energy per mole.

1. ΔG is < 0 the reaction may proceed spontaneously as written.

2. ΔG is > 0 the reaction can not proceed spontaneously as written. Conversely, it may proceed spontaneously in the opposite direction to which it is written.

3. ΔG = 0 the reaction is at equilibrium

$$\overline{G}_i = \Delta\overline{G}^o_{f,i} + RT\ln\{i\}$$

where $\overline{G}_i$ = the free energy per mole of substance i in a state other than standard measured relative to our established datum

{i} = the active concentration, or activity, of species i

* For ions and molecules in solution, {i} is related to the molar concentration, [i], by {i} = γ_i where γ_i is activity coefficient. As the solution becomes dilute, γ_i approaches 1 and {i} approaches [i]

* For the solvent in a solution, {i} =$\gamma_i X_i$ where X_i is the mole fraction. As the solution becomes more dilute, γ_i approaches 1.

* For pure solids and liquids in equilibrium with a solution, {i} =1

* For gases in equilibrium with a solution, {i} = $\gamma_i P_i$ where P_i is the partial pressure of the gas in atmospheres. As the total pressure decreases, γ_i approaches 1. When reactions take place at atmospheric pressure, the activity of a gas can be approximated closely by its partial pressure.

* For mixtures of liquids, {i} = X_i where X_i is the mole fraction.

ΔG for the general reaction can be calculated using the following equation:

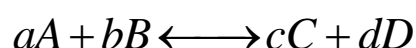$$\Delta G = \Delta G^o + RT \ln \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

where

$$\Delta G^o = \left(\sum_i \nu_i \overline{G}_i^o \right)_{products} - \left(\sum_i \nu_i \overline{G}_i^o \right)_{reac\,tan\,ts}$$

{ } = activity or active concentration

$\overline{G}_i^o$ = free energy/mole of species i at 25 °C and 1 atm

$\overline{G}_i^o$ is called the standard free energy per mole of species i.

For the reaction

$$aA + bB \longleftrightarrow cC + dD$$

The reaction quotient, Q, can be written as:

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

Or in dilute solution

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

Therefore,

$$\Delta G = \Delta G^o + RT \ln \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b} = \Delta G^o + RT \ln Q$$

When the system is at equilibrium (ΔG = 0), the value of Q is identical to that of the equilibrium constant K, we can write that

$$0 = \Delta G^{\,o} + RT \ln K$$

$$\Delta G^{\,o} = -RT \ln K$$

We obtain

$$\Delta G = -RT \ln K + RT \ln Q = RT \ln \frac{Q}{K}$$

Because the ratio of Q/K will determine the sign of ΔG for a reaction so we have another set of criteria to determine whether reactions are possible or not.

* If Q/K > 1, then the ΔG is positive and the reaction is impossible as written.

* If Q/K = 1, then the $= 0$ and the system is at equilibrium.

* If Q/K < 1, then the ΔG is negative and the reaction is spontaneous as written.

Example 1

Determine the equilibrium constant for the reaction in which liquid H_2O dissociates to H^+ and OH^- at 25 ^oC.

$$\Delta \overline{G}_f^o$$

H_2O	-56.96
H^+	0
OH^-	-37.60

ΔG^o = (1)(0) + (1)(-37.6) –(1)(-56.69) = + 19.09 kcal/mol

ΔG^o = + 19.09 = -RTlnK

K = 9.96*10^{-15} (~ 10^{-14})

Example 2

From example 1, is the reaction proceeding as written when $[H^+]$ = 10^{-6} M and $[OH^-]$ = 5*10^{-8} M?

From
$$\Delta G = \Delta G^o + RT \ln Q$$

For dilute solution, the activity coefficient approaches one, therefore

$$\Delta G = \Delta G^o + RT \ln[H^+][OH^-]$$

$$\Delta G = 19.09 + 2.3*1.98*10^{-3}(kcal/mol-K)*$$
$$298K*\log[(10^{-6})(5*10^{-8})]$$

ΔG = +1.03 kcal/mol   the reaction is not spontaneous as written

We can solve this problem alternatively using

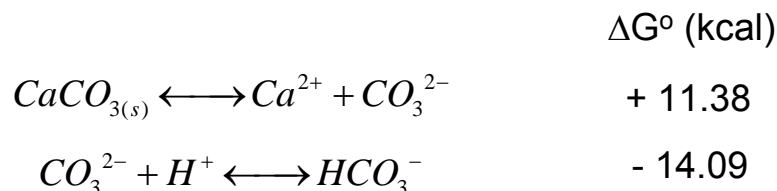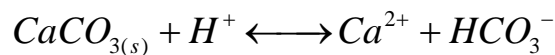$$\Delta G = RT \ln \frac{Q}{K}$$

$$Q = [H^+][OH^-] = (10^{-6})(5*10^{-8}) = 5*10^{-14}$$

$$K = 10^{-14}$$

Since Q/K > 1, ΔG must be positive. Therefore, the reaction as written is not possible.

An important property of standard free energy changes, ΔG^o, is that they are additive. For example, if in two reactions the product of one reaction serves as a reactant in the other, the ΔG^o value for the combined reactions is the sum of the ΔG^o values of the two reactions.

$$CaCO_{3(s)} + H^+ \longleftrightarrow Ca^{2+} + HCO_3^-$$

ΔG^o (kcal)

$$CaCO_{3(s)} \longleftrightarrow Ca^{2+} + CO_3^{2-}$$ + 11.38

$$CO_3^{2-} + H^+ \longleftrightarrow HCO_3^-$$ - 14.09

ΔG^o of the overall reaction is -2.71 kcal.