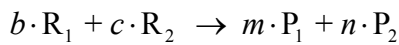# II. Basic Water Chemistry

1. Governing Concepts

- Stoichiometry (화학양론식):

- Chemical Equilibrium (화학적 평형):

- Reaction Kinetics (반응 동역학):

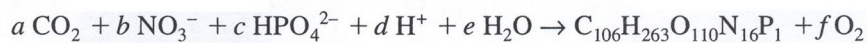### 1.1 Stoichiometry

$$b \cdot R_1 + c \cdot R_2 \rightarrow m \cdot P_1 + n \cdot P_2$$

where R_1 and R_2 = reactants,

P_1 and P_2 = products, and

b, c, m, and n = stoichiometric coefficients.

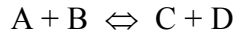**EXAMPLE 3.A.1** *Stoichiometry and Photosynthesis*

A general photosynthesis reaction may be written in the form shown below. Use the principles of stoichiometry to determine the coefficients a–f.

$$a \, CO_2 + b \, NO_3^- + c \, HPO_4^{2-} + d \, H^+ + e \, H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P_1 + f \, O_2$$

1.2 Chemical Equilibrium

- The underlying theory for chemical equilibrium is based on thermodynamics.

$$A + B \iff C + D$$

At equilibrium, the rate of "forward" reaction is identical to it of "reverse" reaction. The rate of forward reaction is expected to proportional to the rate of collisions between A and B. It means that the rate of forward reaction is directly proportional to the concentrations of A and B.

$$R_f = k_f \cdot [A] \cdot [B]$$

where R_f = rate of the forward reaction;

k_f = rate constant (vary with temperature); and

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

$$R_r = k_r \cdot [C] \cdot [D]$$

where R_r = rate of the reverse reaction;

k_r = rate constant (vary with temperature); and

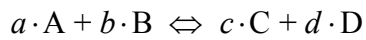[C], and [D] = concentrations of C and D.

At equilibrium,

$$R_f = R_r$$

$$k_f \cdot [A] \cdot [B] = k_r \cdot [C] \cdot [D]$$

$$\frac{[C] \cdot [D]}{[A] \cdot [B]} = \frac{k_f}{k_r} = K$$

where K = equilibrium constant of the reaction (constant at a fixed temperature)

$$a \cdot A + b \cdot B \Leftrightarrow c \cdot C + d \cdot D$$

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

EXAMPLE 3.A.3   *Water Vapor Concentration at Equilibrium*

Consider a sealed jar that is partially filled with pure liquid water and otherwise contains nitrogen gas. Assume that the temperature of the system is fixed at 293 K (20 °C). What is the steady-state molar concentration of $H_2O(g)$ in the gas phase above the liquid water?

1.3 Reaction Kinetics

-    When a system is at equilibrium?

-    How much time is needed for a system to reach equilibrium?

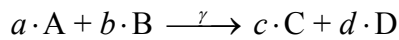-   What can we say about systems that are not at equilibrium?

$$A + B \xrightarrow{\quad 1 \quad} C$$
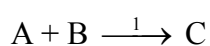
$$R_1 = -\left(\frac{d[\text{A}]}{dt}\right)_1 = -\left(\frac{d[\text{B}]}{dt}\right)_1 = \left(\frac{d[\text{C}]}{dt}\right)_1$$

where a, b, c, and d = stoichiometric coefficients;

A and B = reactants;

C = product; and

"1" = arbitrary symbol to identify the reaction.

$$a \cdot \text{A} + b \cdot \text{B} \xrightarrow{\gamma} c \cdot \text{C} + d \cdot \text{D}$$

$$R_\gamma = -\frac{1}{a}\left(\frac{d[\text{A}]}{dt}\right)_\gamma = -\frac{1}{b}\left(\frac{d[\text{B}]}{dt}\right)_\gamma = \frac{1}{c}\left(\frac{d[\text{C}]}{dt}\right)_\gamma = \frac{1}{d}\left(\frac{d[\text{D}]}{dt}\right)_\gamma$$

$$R_\gamma = k_\gamma \cdot [\text{A}]^\alpha \cdot [\text{B}]^\beta$$

where k_γ = rate constant (a function of temperature, or a function of pressure for

gaseous reactions); and

α and β = empirical coefficients.

For an elementary reaction (On the other hand, α and β must be determined experimentally)

$$R_\gamma = k_\gamma \cdot [\text{A}]^a \cdot [\text{B}]^b$$

Zero-order reaction: $R_\gamma = k_\gamma$

First-order reaction: $R_\gamma = k_\gamma \cdot [\text{A}]$ or $R_\gamma = k_\gamma \cdot [\text{B}]$

Second-order reaction: $R_\gamma = k_\gamma \cdot [\text{A}]^2$, $R_\gamma = k_\gamma \cdot [\text{B}]^2$, or $R_\gamma = k_\gamma \cdot [\text{A}] \cdot [\text{B}]$

EXAMPLE 3.A.4   *Solving a Simple Kinetic Problem*

Radon-222 is a naturally occurring radioactive gas formed by the decay of radium-226, a trace element in soil and rock. The radioactive decay of radon can be described by the elementary reaction

radon-222 → polonium-218 + alpha particle
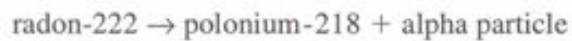
The rate constant for this reaction is $k = 2.1 \times 10^{-6}$ s^{-1}, independent of temperature. At time $t = 0$, a batch reactor is filled with air containing radon at concentration C_0. How does the radon concentration in the reactor change over time?

(Reading Assignment, 2-3 Organic Chemistry p59-62)

Waste Management Lab.-SNU

2. Phase Changes and Partitioning

2.1 Vapor Pressure

Definition:

At equilibrium condition between a species in the vapor phase and a flat surface of the pure liquid of the specimen,

$$P_i^0 = K_{vp} \quad \text{or} \quad P_i^0(T) = K_{vp}(T)$$

where P_i^o = equilibrium partial pressure of species i (dependent on temperature);

K_{vp} = an equilibrium constant (i.e., vapor pressure, dependent on temperature).

Relative Humidity: the amount of water vapor in air

$$RH = 100\% \times \frac{P_{H_2O}}{P_{H_2O}^O(T)}$$

where RH = relative humidity;

P_{H2O} = actual partial pressure of water vapor; and

P_{H2O}^0 (T) = saturation vapor pressure at given temperature.

For a mixture of single volatile liquid and nonvolatile impurities, the dilution of a liquid with nonvolatile impurities reduces the vapor pressure of the liquid because nonvolatile molecules occupy a portion of the surface, reducing the area from which evaporation takes place. Thus, higher temperature is needed than the pure liquid boils (Raoult's law).

$$P_{i,mix}^0(T) = X_i \cdot P_i^0(T)$$

where X_i = the mole fraction of the volatile component in the mixture.

2.2 Dissolution of Species in Water

Partitioning between the gas phase and water: Henry's law

$$C_w = K_{H,g} \cdot P_g \quad \text{or} \quad P_g = H_g \cdot C_w$$

where C_w = equilibrium concentration in the aqueous phase;

$K_{H,g}$ and H_g = Henry's law constant; and

P_g = equilibrium partial pressure in the gas phase.

EXAMPLE 3.B.1   *Saturation Concentration of Oxygen in Water*

Compute the equilibrium mass concentration of oxygen (O_2) in units of mg/L for water exposed to the atmosphere at sea level at a temperature of 15 °C.

EXAMPLE 3.B.2   *Partitioning of Toluene in a Closed System*

A 2 L glass jar is half filled with water and half filled with air at a temperature of 293 K. After 92 mg ($=10^{-3}$ mol) of liquid toluene is added, the jar is sealed. What is the equilibrium concentration of toluene in the water, and what is the equilibrium partial pressure of toluene in the gas phase?

Solubility of Nonaqueous-Phase Liquids

NAPL (nonaqueous-phase liquid):

Under equilibrium conditions, the quantity of the NAPL that dissolves in water depends on the species and the temperature, but not on the volume of the NAPL.

$$C_i (T) = K_{ws}(T)$$

where C_i = equilibrium concentration of NAPL compound i dissolved in water; and

K_{ws} = water solubility for the compound.

Dissolution and Precipitation of Solids

$$A_x B_y \leftrightarrow xA + yB \quad (\rightarrow: \text{dissolution, and } \leftarrow: \text{precipitation})$$
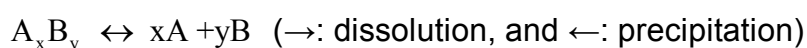
$$[A]^x \cdot [B]^y = K_{sp}(T)$$

where K_{sp} = solubility product (용해도적)

EXAMPLE 3.B.4   *Ion Concentrations from a Dissolved Solid*

Solid calcium fluoride (CaF_2) is added to pure water so that at equilibrium some solid remains undissolved. Given that the solubility product is 3×10^{-11} M^3, what is the equilibrium concentration of F$^-$ in the water?

2.3 Sorption

- Adsorption:

- Absorption:

Sometimes it is not possible to distinguish between adsorption and absorption. Then,

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the term **sorption** is used.

Sorption Isotherms

Linear: $\qquad q_e = K_{ads} \cdot C_e$

Freundlich: $\qquad q_e = K_f \cdot C_e^{1/n}$

Langmuir: $\qquad q_e = q_{max} \cdot \dfrac{b \cdot C_e}{1 + b \cdot C_e}$

where q_e = equilibrium mass of sorbed molecules per mass of sorbent; and

$\qquad C_e$ = equilibrium concentration of contaminant molecules in a fluid.

"Isotherm" means "uniform temperature". Partitioning varies with temperature.

3. Acid-Base Reactions

- Since acid-base reactions are generally very fast, pH predictions are almost always based on the assumption of equilibrium.

3.1 Acid-Base Reactions and the Hydrogen Ion

- Hydrogen ions do not exit as free H^+ species in aqueous solution. H_3O^+ is highly favored. The resulting ion may have one or more additional water molecules loosely bound to it.
- Acid and Base (donate or lose hydrogen ion or electron)

3.2 pH of Pure Water
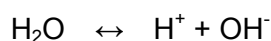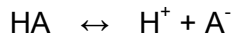
$$H_2O \quad \leftrightarrow \quad H^+ + OH^-$$

$$K' = \frac{[H^+] \cdot [OH^-]}{[H_2O]}$$

$$K'[H_2O] = [H+][OH-] = K_w = 10^{-14}$$

where K_w = equilibrium or dissolution constant for water (dependent on temperature)
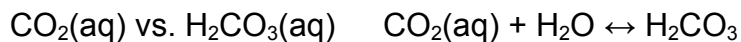
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3.3 Strong and Weak Acids

$$HA \leftrightarrow H^+ + A^-$$

$$K_A = \frac{[H^+]\cdot[A^-]}{[HA]}$$

where K_A = acid dissociation constant

pK_A are less than 1, "strong acid"

3.4 Carbonate-Bicarbonate System

$CO_2(g)$	carbon dioxide gas
$CO_2(aq)$	dissolved carbon dioxide
$H_2CO_3(aq)$	carbonic acid (a diprotic, weak acid)
$HCO_3^-(aq)$	bicarbonate ion
$CO_3^{2-}(aq)$	carbonate ion
$CaCO_3(s)$	calcium carbonate (limestone)

$CO_2(g)$ vs. $CO_2(aq)$ $[CO_2(aq)] = K_H \cdot P_{CO2}$

$CO_2(aq)$ vs. $H_2CO_3(aq)$ $CO_2(aq) + H_2O \leftrightarrow H_2CO_3$

$$\frac{[H_2CO_3]}{[CO_2(aq)]} = K_A = 10^{-2.8}$$

For engineering purposes we combine $CO_2(aq)$ and $H_2CO_3(aq)$ into one variable, $H_2CO_3^*$ because it is difficult to experimentally differentiate between $CO_2(aq)$ and H_2CO_3.

$[H_2CO_3^*] = [CO_2(aq)] + [H_2CO_3(aq)] = [CO_2(aq)] \cdot (1 + K_A) \approx [CO_2(aq)]$

$H_2CO_3^*$ vs. $HCO_3^-(aq)$ $H_2CO_3^* \leftrightarrow H^+ + HCO_3^-(aq)$

$$\frac{[H^+]\cdot[HCO_3^-]}{[H_2CO_3^*]} = K_1 = 10^{-6.3}$$

$HCO_3^-(aq)$ vs. $CO_3^{2-}(aq)$ $HCO_3^-(aq) \leftrightarrow H^+ + CO_3^{2-}(aq)$

$$\frac{[\text{H}^+]\cdot[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \text{K}_2 = 10^{-10.3}$$

$\text{CO}_3^{2-}(\text{aq})$ vs. $\text{CaCO}_3(\text{s})$ $\text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}(\text{aq})$

$$\text{K}_{\text{sp}} = [\text{Ca}^{2+}]\cdot[\text{CO}_3^{2-}(\text{aq})]$$

$$\text{C}_{\text{carbonate}} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-(\text{aq})] + [\text{CO}_3^{2-}(\text{aq})]$$

Distribution of aqueous carbonate species as a function of pH

- Figure 2-10 (p. 69), and 2-11 (p.70)

FIGURE 2–10

Plot of pC ($-$log C) versus pH for the carbonate system. ($T = 25°C$, p$K_{a1} = 6.35$, p$K_{a2} = 10.33$)
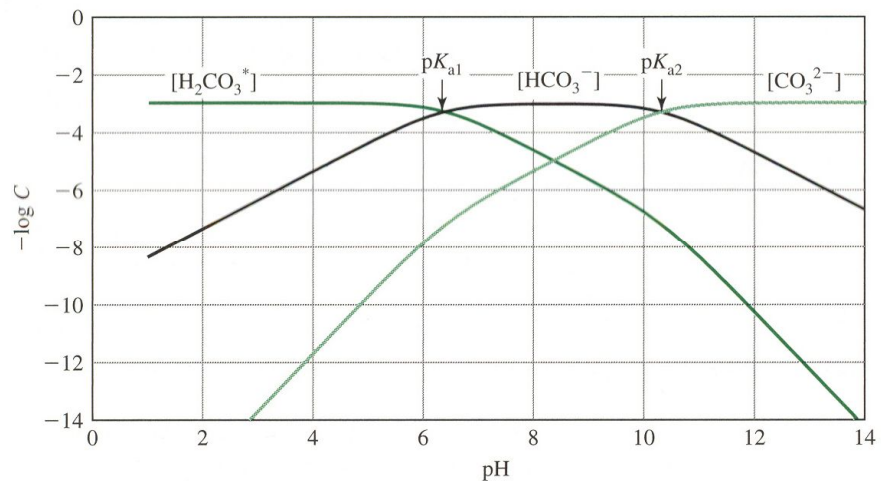
FIGURE 2–11

pC ($-$log C)–pH diagram for the carbonate system ($T = 25°C$, p$K_{a1} = 6.35$, p$K_{a2} = 10.33$; $K_H = 10^{-1.5}$ M · atm^{-1}; $P_{\text{CO}_2} = 10^{-3.5}$ atm)
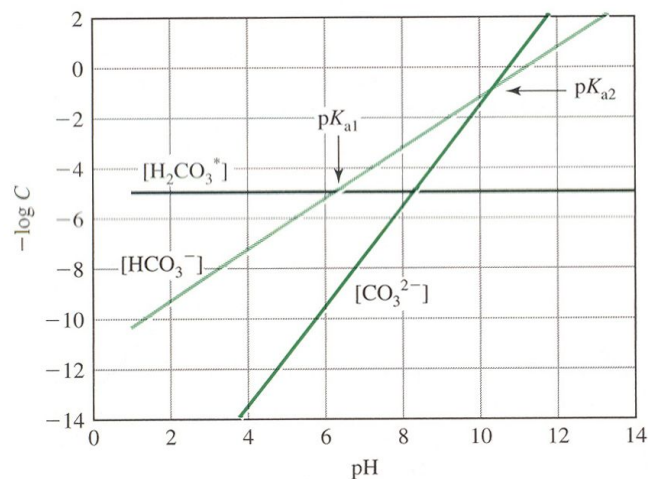
EXAMPLE 3.C.4   *pH of Pristine Rainwater*

What is the pH of rainwater in pristine environments? Assume that the temperature is 25 °C, the total air pressure is 1 atm, and the rainwater is in equilibrium with the atmosphere.

3.5 Inorganic Impurities

3.5.1 Ions in water

Table   Most prevalent ions in natural waters, along with typical molar concentrations

Ion	Seawater (M)	River water (M)
Na^+	0.47	0.23×10^{-3}
Mg^{2+}	0.053	0.15×10^{-3}
Ca^{2+}	0.010	0.33×10^{-3}
K^+	0.010	0.03×10^{-3}
Cl^-	0.55	0.16×10^{-3}
SO_4^{2-}	0.028	0.07×10^{-3}
HCO_3^-	0.0024	0.86×10^{-3}

3.5.2 Electroneutrality

$$\sum z_i \cdot C_i = 0$$

where z_i = charge per molecule on the ith ion; and

C_i = the molar concentration of the ith ionic species [M].

3.5.3 Ionic strength

$$I = \frac{1}{2} \sum_i (C_i \cdot z_i^2)$$

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where I = ionic strength

- Ionic strength of water significantly affect the activities of ionic species in water.

3.5.4 Hardness

- the sum of normalities of all multivalent cations (i.e., charge of +2 or greater)
- Hardness is often expressed in terms of the equivalent mass concentration of calcium carbonate ($CaCO_3$). For example, a hardness of 1 meq/L is the same as a hardness of 50 mg/L as $CaCO_3$.
- Soft (< 75 mg/L as $CaCO_3$), Hard (150 - 300 mg/L as $CaCO_3$), very Hard (> 300 mg/L as $CaCO_3$).

3.5.5 Alkalinity

- the capacity of water to neutralize acids

$$A = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$$

where A = alkalinity

4. Oxidation-Reduction Reactions

- Acid-base reactions: transfer of protons
- Oxidation-reduction reactions (Redox reactions):

4.1 Corrosion

A galvanic cell may occur in a water supply system when two dissimilar metals, such as iron and copper pipe, are connected. In this case, the iron will corrode.
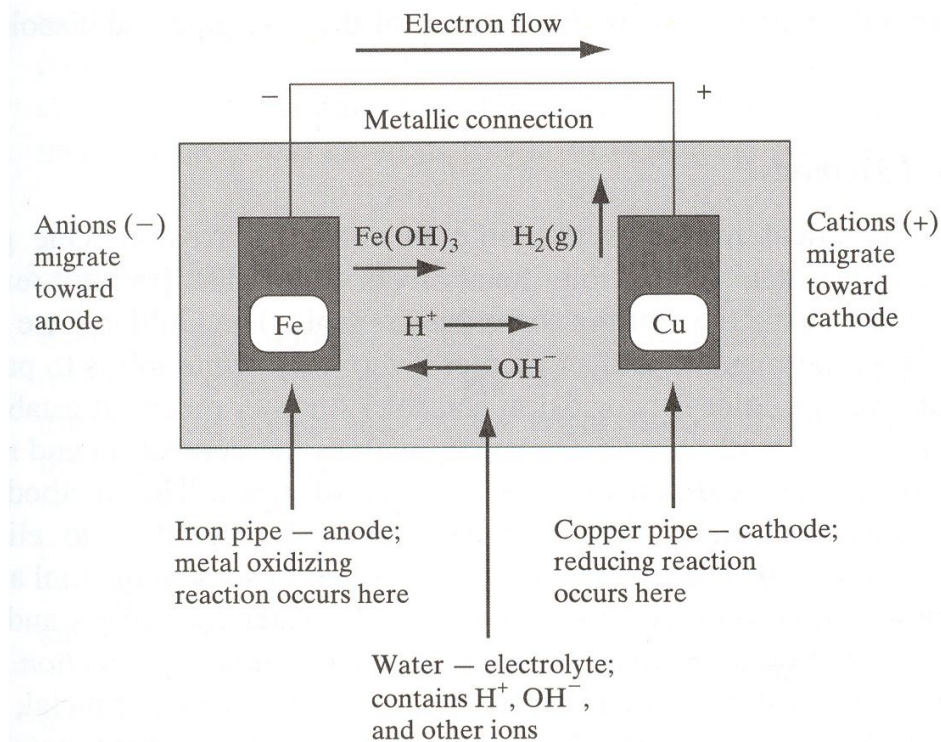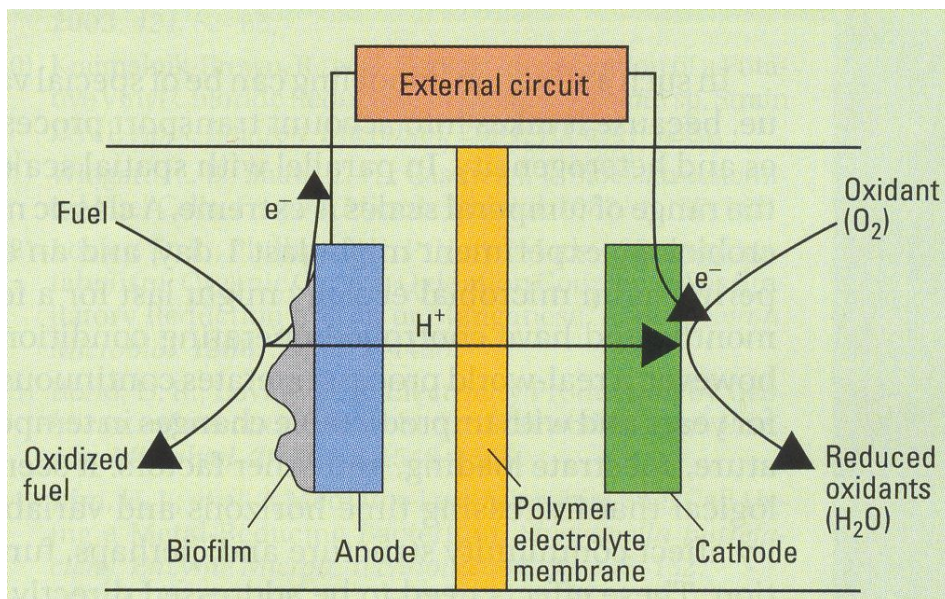

Figure 3.D.1 A galvanic cell may occur in a water supply system when two dissimilar metals, such as iron and copper pipe, are connected. In this case, the iron will corrode.

Microbial Fuel Cell

4.2 Combustion

EXAMPLE 3.D.2   *Stoichiometry and Combustion*

Lignite is burned in air at an equivalence ratio of 0.95. Assume (a) that the lignite has the chemical composition given in Table 3.D.4, (b) that the fuel nitrogen is all emitted as NO, and (c) that combustion is complete. Determine the exhaust gas composition.
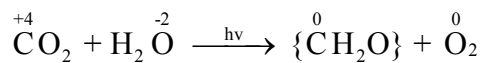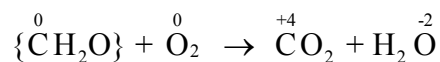

4.3 Atmospheric oxidation processes

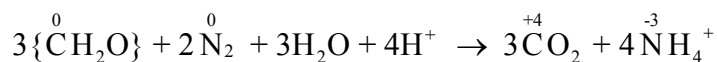Thermal reactions vs. Photolytic reactions

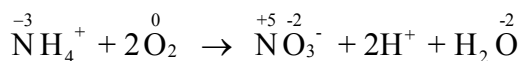## 4. 4 Microbial Reactions

Photosynthetic production of biomass

$$\overset{+4}{C}O_2 + H_2\overset{-2}{O} \xrightarrow{\ h\nu\ } \{\overset{0}{C}H_2O\} + \overset{0}{O}_2$$

Aerobic Respiration

$$\{\overset{0}{C}H_2O\} + \overset{0}{O}_2 \rightarrow \overset{+4}{C}O_2 + H_2\overset{-2}{O}$$

Nitrogen Fixation

$$3\{\overset{0}{C}H_2O\} + 2\overset{0}{N}_2 + 3H_2O + 4H^+ \rightarrow 3\overset{+4}{C}O_2 + 4\overset{-3}{N}H_4^+$$

Nitrification

$$\overset{-3}{N}H_4^+ + 2\overset{0}{O}_2 \rightarrow \overset{+5}{N}\overset{-2}{O}_3^- + 2H^+ + H_2\overset{-2}{O}$$

Nitrate Reduction (or Denitrification)

$$5\{\overset{0}{C}H_2O\} + 4\overset{+5}{N}O_3^- + 4H^+ \rightarrow 5\overset{+4}{C}O_2 + 7H_2O + 2\overset{0}{N}_2$$

Sulfate Reduction

$$2\{\overset{0}{C}H_2O\} + 2H^+ + \overset{+6}{S}O_4^{2-} \rightarrow 2\overset{+4}{C}O_2 + 2H_2O + 2H_2\overset{-2}{S}$$

Methane Formation

$$2\{\overset{0}{C}H_2O\} \rightarrow \overset{+4}{C}O_2 + \overset{-4}{C}H_4$$