

Environmental Geochemistry

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Chemistry Terms and Concepts

Terms

A [**pollutant**](#) is a substance present in greater than natural concentration as a result of human activity and having a net detrimental effect upon its environment.

The [**hydrosphere**](#) includes all water in the earth's crust.

The [**lithosphere**](#) includes the outer portion of the earth's mantle and the earth's crust in geology; however, in environmental sciences, the term is used to refer to the minerals, organic matter, water, and air which make up the surface of the solid earth, in particular the soil.

The [**atmosphere**](#) is the envelope of gases surrounding the Earth.

The **biosphere** includes all living organisms and their surrounding environment.

A **phase** is simply a homogenous substance with uniform composition and properties, e.g., the atmosphere, sea water, a mineral grain. The concept of a phase becomes less clear on a microscopic scale near phase boundaries, because there is always a variation in composition near phase interfaces.

A **solution** is generally a liquid phase composed predominantly of one component, the solvent (e.g., water) and less abundant components, the solutes (e.g., dissolved salts). A solution can also be a solid or a gas phase, e.g., a solid solution (e.g., halite, the solvent, with minor impurities such as sodium bromide, a solute) or a mixture of gas components (e.g., the atmosphere). The term **fluid** can refer to either a liquid or gas phase.

Anions - negatively charged ions or complexes in aqueous solutions. An anion forms by reduction through acceptance of electrons. The major anions and their charges are OH^- , Br^- , Cl^- , F^- , HCO_3^- , HS^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} .

Cations - positively charged ions or complexes in aqueous solutions. A cation forms by oxidation through donation of electrons. The major cations and their charges are H^+ , K^+ , Na^+ , Ca^{2+} , Fe^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} . The important class of pollutants known as heavy metals generally exist in solution as cations.

Complexes - molecules that can be anions, cations, or neutral in charge. For example, SiO_2 combines with $2\text{H}_2\text{O}$ in aqueous solution as a neutral aqueous molecule in the form of H_4SiO_4 . Another example is $\text{Al}(\text{OH})_4^-$, a negatively charged complex consisting of an Al^{3+} cation and $4(\text{OH})^-$ anions joined together.

Electrical Balance - In a solution, the charges contributed by the cations have to balance those contributed by the anions. Elemental analyses are frequently done which list the concentrations of the major components without determining if they exist in solution by themselves or as part of different complexes. For example, an analysis will only determine total Na concentration and not the proportion that actually exists in solution as Na^+ , NaCl^0 , NaHCO_3^0 , NaCO_3^- , etc. However, the overall electrical balance can still be estimated by summing the electrical charges in the elemental analyses using the dominant charge for each of the elemental components. For example all of the sodium is given a +1, all of the chloride is given a -1, all of the sulfate is given a -2, etc. The overall electrical balance gives an idea of the accuracy of the solution analyses. Without sophisticated corrections, errors in the computed electrical balance will arise for elements existing in solution with multiple oxidation states, e.g., Fe^{2+} and Fe^{3+} or with different complexes of hydrogen ions, e.g., HS^- and H_2S . The former produces an error because only the total of an element is generally measured and you would need to know the fraction in each oxidation state for the correct electrical balance. The latter produces an error because the pH, not total H^+ , is measured and most of the H^+ is not included in the electrical balance except indirectly in the aqueous complexes. For example, you would need to know if most of the inorganic carbon is CO_3^{2-} or HCO_3^- to account for it in the electrical balance. In general these are minor errors but to be precise, a computer program

can partition elements into different oxidation states and into different concentrations of complexes with hydrogen species for an accurate computation of electrical balance.

Always do a simple hand computation of the electrical balance of analyses from commercial laboratories. A poor electrical balance often means that the data should be disregarded. A perfect electrical balance means that one of the components was determined from the electrical balance and not by analysis. This is often the case for either Na^+ or Cl^- .

Concentration Units

In solutions, the fundamental concentration unit is the **mole fraction** X_i ; in which for j components, the i th mole fraction is

$$X_i = n_i / (n_1 + n_2 + \dots n_j),$$

where the number of moles n of a component is equal to the mass of the component divided by its molecular weight. **Note that a substance composed of only one substance will have a mole fraction of unity for that substance.** In an aqueous solution, the mole fraction of water, the solvent, is always near unity. In solids that are nearly pure phases, e.g., limestone, the mole fraction of the dominant component, e.g., calcite, will be near unity. In general, only the solutes (minor components) in a liquid solution and gas components in a gas phase will have mole fractions that are significantly different from unity.

Other more commonly used concentration units for the solutes are given below:

per cent, **parts per hundred**

ppt, **parts per thousand**

ppm, **parts per million**

ppb, **parts per billion**

ppt, **parts per trillion**

These units are often assumed to be in terms of mass (weight) unless otherwise stated. Note that one mg/kg is one ppm where a mg is 1/1000th of a gram and kg is 1000 grams. Similarly, one $\mu\text{g/g}$ is also one ppm where a μg is 1/1,000,000th of a gram. One $\mu\text{g/kg}$ is a ppb.

Because one liter of water weighs approximately one kg, mg/liter units of solution are nearly equal to ppm units. The precise equivalence is obtained by dividing by the density p :

$$\text{ppm}_i = [\text{mg}_i/\text{liter}]/p$$

where the solution density is in grams/cm^3 . Older texts will substitute specific gravity for density in the above equation. The specific gravity is the ratio of the solution density to that of the density of pure water at 4°C. Since the density of pure water at 4°C is 1 gram/cm^3 , the specific gravity is equal to the solution density when expressed in metric units of g/cm^3 .

Note that a ml (1/1,000th of a liter) is equal to a cm^3 . The units of ppt and ppm are commonly used for the concentrations of solutes in aqueous solutions such as sea water. Trace components are represented in the ppb and ppt range.

The units of g/cm^3 are used in diffusion. This unit is nearly equivalent to weight fraction for an aqueous solution since one cm^3 of water approximates one gram.

Other concentrations units are described in terms of the number of moles of a components.

The **molarity** of i , M_i , is the moles of component i per liter (1000 cm^3 or 1000 ml) of solution.

The **formality** of i, f_i , is the moles of component i per kg of solution.

The **molality** of i, m_i , is the moles of component i per kg of solvent (e.g., water). Molality is used only in aqueous solutions. In making thermodynamic calculations, the units used are molality for all aqueous components.

The **equivalents** of i, e_i , is generally the moles of charge of i in molarity, formality, or molality units. If the equivalents refer to a particular reaction, then it refers to the equivalents of charge needed for the reaction to be completed in terms of molarity, formality, or molality units./P>

Multiplication of the above mole concentration units by one thousand will convert them to milli units, e.g., mM_i, mf_i, mm_i, and me_i.

Note that molarity is defined in terms of volume, a liter of solution. Any concentration unit involving volume will change with temperature and pressure, because volume is a function of those parameters. For this reason, geochemists prefer not to use molarity units in aqueous solutions; however, chemists prefer molarity units.

To convert from ppm to formality units

$f_i = \text{ppm}_i / (1000 \text{ Mw}_i)$ where Mw_i is the molecular weight of i.

To convert from ppm to molality units

$$m_i = [\text{ppm}_i / (1000 \text{ Mw}_i)] [1 / (1 - \text{tds} / 1,000,000)]$$

where tds is the total dissolved solids in ppm in the solution.

To convert from ppm to molarity units

$$M_i = [\text{ppm}_i / (1000 M_{w_i})] \rho$$

The concentration units are not absolute amounts of a component in the solution but are relative amounts, having been normalized to the total mass or volume of the solution or solvent. Hence, changing the amount of a solution does not change the concentration of any of the components. Concentration units, as well as temperature T and pressure P, are intensive parameters that do not depend upon the total mass of a solution. Volume is an example of an extensive parameter, one that depends upon the total mass of the solution.

Unit Conversion Exercise

Use the formulas given above with the seawater composition given below (Pytkowicz and Kester, 1971, for sea water of 19000 ppt chlorinity) in a spreadsheet program such as Excel to convert from ppm to mg/l to mmolality and mmolarity. For the density of seawater use 1.025 g/ml. Check to see if the electrical balance in mequivalents is zero.

Cl ⁻	18,971	ppm
Na ⁺	10,565	ppm
SO ₄ ²⁻	2,660	ppm
Mg ²⁺	1,269	ppm
Ca ²⁺	404.2	ppm
K ⁺	391.4	ppm
HCO ₃ ⁻	142.3	ppm
Br ⁻	65.99	ppm
B(OH) ₃	26.1	ppm
Sr ²⁺	7.79	ppm
F ⁻	1.3	ppm
Li ⁺	0.19 ppm	

Mass Balance Exercise

A scientist looks at a sample of sea water in limestone and predicts that 100 mg of calcite are dissolving per liter of sea water and that 50 mg of dolomite formed in the process. Sea

water has an expected Ca, Mg, and HCO_3 concentration of 412, 1210, and 146 mg/l, respectively, as total concentrations. What are the concentrations of Ca, Mg, and HCO_3 in the altered sea water that are consistent with the scientist's prediction.

Dissolution of 100 mg/l of calcite releases $(40.08/100.09)100$ mg/l or 40 mg/l of Ca and $(60.01/100.09)100$ mg or 60 mg of CO_3 . Precipitation of 50 mg/l of dolomite removes $(40.08/184.41)50$ mg or 10.9 mg Ca, $(24.312/184.41)50$ mg or 6.6 mg Mg, and $(120.018/184.41)50$ mg or 32.5 mg CO_3 . Overall, there is a net release of Ca of 29.1 mg/l, a decrease of Mg of 6.6 mg/l, and a net increase of CO_3 of 27.5 mg/l. Expressed as HCO_3 , the latter is a net increase of 28 mg. Hence, the expected Ca concentration is 441 mg/l, the expected Mg concentration is 1,203 mg/l, and the expected HCO_3 concentration is 174 mg/l.

Conservative Mixing Relations

If two endmember solutions I and II are mixed, the conserved (unreactive) concentrations of component a and component b in the mixture can be expressed as a function of the solution fraction of I, f_I by

$$\text{ppm}_{a,\text{mix}} = \text{ppm}_{a,I}f_I + \text{ppm}_{a,II}(1-f_I)$$

$$\text{and } \text{ppm}_{b,\text{mix}} = \text{ppm}_{b,I}f_I + \text{ppm}_{b,II}(1-f_I)$$

Combining the two equations yields to eliminate f

$$\text{ppm}_{a,\text{mix}} = (m1)\text{ppm}_{b,\text{mix}} + m2$$

$$\text{where } m1 = (\text{ppm}_{a,I} - \text{ppm}_{a,II})/(\text{ppm}_{b,I} - \text{ppm}_{b,II})$$

$$\text{and } m2 = -(\text{ppm}_{a,I} - \text{ppm}_{a,II})/(\text{ppm}_{b,I} - \text{ppm}_{b,II})\text{ppm}_{b,II} + \text{ppm}_{a,II}$$

and m_1 and m_2 are the slope and intercept of a straight line in which $\text{ppm}_{a,\text{mix}}$ is plotted versus $\text{ppm}_{b,\text{mix}}$.

Note that a straight line is also obtained if the ratio of the components concentrations is plotted versus the concentration reciprocal of the component in the denominator.

$$\text{ppm}_{a,\text{mix}}/\text{ppm}_{b,\text{mix}} = m_2/\text{ppm}_{b,\text{mix}} + m_1$$

where the slope is now m_2 and the intercept is m_1 .

An isotopic ratio such as $^{87}\text{Sr}/^{86}\text{Sr}$ should be plotted versus the reciprocal of the concentration of ^{86}Sr to obtain a straight mixing line. Because the percentage of Sr in a solution (endmembers and mixture) that is ^{86}Sr is essentially constant, the following approximation is often used.

$$\text{ppm } ^{86}\text{Sr}_{\text{mix}} = (m_3) \text{ ppm}_{\text{Sr},\text{mix}} \text{ where } m_3 \text{ is a constant.}$$

The constant m_3 becomes part of the slope and a straight line plot is obtained if the isotopic ratio versus the reciprocal of the total element concentration, i.e.,

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{mix}} = (m_2/m_3)/(\text{ppm}_{\text{Sr},\text{mix}}) + m_1$$

In Louisiana, pollution sometimes involves saline contamination of ground-waters that are used for irrigation. The saline contamination is often high sodium and chloride concentrations on the order of that found in sea water, approximately 10 to 30 ppt. These salinities can result from mixing dilute ground waters having a salinity of about 1 ppt with brines having concentrations of 100 ppt or more, e.g., oil field brines leaking up well bores. Determining which brines are the pollution sources is used to determine responsibility for cleanup.

Conservative-mixing of unreactive components can be used to pinpoint the brine compositions that are the source of the pollution. Because mass, not volume, is conserved in mixing, the data should be in units such as ppm (mass basis) or molality, not mg/liter. As shown above, the concentrations of two conserved components, plotted versus each other, fall on a straight line if they are the result of mixing. The concentrations in the polluted waters can be used to fit a linear line which can then be extrapolated to brine salinities. Then real brine compositions can be tested against the extrapolated brine composition to determine if they could be the pollution source. Conserved aqueous components in mixing are usually Na, Cl, Br, I, and certain isotopic ratios. However, as discussed above, isotopic ratios of an element have to be plotted versus the reciprocal of the total concentration of the element to produce a straight mixing line. An example of an application of the above procedure to determine the salinity source polluting fresh water is given by Stoessell (1997, Ground Water, 35, 409-417).

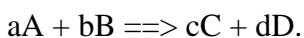
For example plots of Cl versus Br in ppm of the contaminated waters can be used to derive a linear mixing line which can then be extrapolated to brine compositions. Isotopic ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ can also be plotted versus the reciprocal of total Sr in ppm to produce a linear mixing line which can be used to extrapolate to brine compositions. Also, it is always best to plot in linear space rather than log space because the actual fit of the data to a best-fit line is much easier to judge. Researchers have always used log-log plots when they want their data to look better than it really is. Another trick used by some researchers is to fit a best-fit linear line to two sets of clustered data: one in the polluted waters and one from actual brine samples that they hope to prove are the source of the pollution. The data will fit to a straight line with a correlation coefficient close to unity, because the data is clustered at two separated salinities.

Chemical Equilibrium

Definition of the Equilibrium Constant of a Reaction

The equilibrium constant **K** for a reaction can be compared with the reaction quotient **Q** of the activities (thermodynamic concentration units) of reaction components to test if the reaction is at equilibrium. The equilibrium constant is related to the mass-action expression described below.

The generalized chemical reaction below has reactants on the left being transformed into products on the right,



The absolute values of the reaction coefficients for A, B, C, and D are a, b, c, and d, respectively. The reaction coefficient of a reactant is negative because the reactant is being destroyed and the reaction coefficient for a product is positive because the product is being produced. The components can be in different phases, e.g., carbon dioxide in the atmosphere can be reacting with calcium carbonate in limestone and with sea water, or all within the same phase, e.g., H^+ reacting with CO_3^{2-} to form HCO_3^- in ground water. If all the reaction components are within the same phase, a good assumption is that the reaction is at equilibrium. Notable exceptions are reactions involving redox (oxidation and reduction) reactions in aqueous solution which are generally not in equilibrium.

The reaction rate can be increased by increasing the activities (concentrations) of the reactants. Once equilibrium is reached, the reaction can be reversed by increasing the activities (concentrations) of the components on the right side of the reaction, driving the reaction to the left. This reversal would make the components on the right side, the reactants, and those on the left side, the products.

The **mass-action expression** or **law at equilibrium** is

$$\mathbf{K} = \mathbf{Q} = (a_{\text{C}})^c (a_{\text{D}})^d (a_{\text{A}})^{-a} (a_{\text{B}})^{-b}$$

Frequently, the law is written in log units because the activities are often very small numbers.

$$\log \mathbf{K} = \log \mathbf{Q} = c \log a_{\text{C}} + d \log a_{\text{D}} - a \log a_{\text{A}} - b \log a_{\text{B}} = \log [(a_{\text{C}})^c (a_{\text{D}})^d] / [(a_{\text{A}})^a (a_{\text{B}})^b]$$

where **K** is the equilibrium constant for the reaction as written with the reactants on the left and the products on the right. The product of terms on the right and left sides of the equation is called the **reaction quotient Q** and is only equal to **K** at equilibrium. Hence, measuring **Q** at equilibrium is one way to determine **K**; however, **K** can also be predicted from thermodynamics. **In Q, each term is raised to the power of its reaction coefficient which are positive for reactants and negative for reactants.** a_i is the activity which is the product of the concentration c_i and a proportionality coefficient called the activity coefficient. Although c_i is measured experimentally, the activity coefficient has to be computed. **Note that chemists use the pK, which is the negative log of K, i.e., -log K.**

If Q is less than K (or $\log Q/K < 0$), the reaction is moving from left to right. If Q equals K (or $\log Q/K = 0$), the reaction is at equilibrium. If Q is greater than K (or $\log Q/K > 0$) than the reaction is going from right to left, and the reaction is moving in the reverse direction from written.

For determining the direction of the reaction, it doesn't matter if the reaction was actually reversed from the way it was written. For example if $Q > K$, the reaction is moving right to left. If we reverse the reaction as written so the right side becomes the left side and vice versa, we also have to change the values of Q and K . Their new values are the reciprocals of their old values. The new values would give $Q < K$, predicting the reaction moving from left to right, consistent with reversing the way the reaction was written.

K is predicted from thermodynamics or measured experimentally. The value of K depends upon the conventions used to define the activities of the components. These conventions are based on the definition of the standard state chemical potential of each component (see below) in which the activity relates the actual state of a component to its standard state. K varies with pressure P and/or temperature T if the standard states of the components in the reaction move with P and/or T . In geochemistry, K varies with pressure P and temperature T for all reactions except those involving only gas components. The K for reactions involving only gas components varies with temperature but not pressure because the standard states for gas components are always held at 1 bar P . As shown in thermodynamics, if the effect of a variable such as pressure isn't included in the standard state of a component it is included in its activity. See the definition of activity below for gas components for use in the reaction quotients.

In thermodynamics, K is computed using the following relations based on the definition of the ΔG_r , the Gibbs Free Energy change, in a Reaction:

$$\Delta G_r = \Delta G_r^0 + 2.303 RT \log Q \text{ where } \Delta G_r^0 = \sum n_i \mu_i^0 \text{ and } \log Q = \sum n_i \log a_i$$

where ΔG_r^0 is the standard state change in Gibbs Free Energy of the reaction at the P and T of interest. n_i and μ_i^0 are the reaction coefficient (positive for a product and negative for a reactant) and the molar standard state Gibbs Free Energy (also called the standard state chemical potential) for the i th reaction component. μ_i^0 values are tabulated in reference books at 25°C and 1 bar pressure. R and T are the gas constant and absolute temperature (at 25°C and 1 bar $R = 1.9872 \text{ cal/mol}^\circ \text{K}$ and 298.15°K at 25°C). Although not covered in this course, various algorithms exist for calculating the standard state chemical potential values at different pressures and temperatures for use in computing equilibrium constants. This is covered in Geology 4659, Geochemical Thermodynamics.

At Equilibrium, $\Delta G_r = 0$; hence, $\log K = - \sum n_i \mu_i^0 / (2.303 RT)$ which is the relation used to compute **K** if **Q** cannot be measured at equilibrium.

The values of μ_i^0 correspond to the energy a component has as a result of bond energies, heat content, and spatial location of the atoms on a lattice. These values are from experimental measurements of energy changes in reactions in which the component is formed from the elements. By convention, the μ_i^0 of each element in its stable form at 25°C and 1 bar is set to zero. This allows the change in free energy at 25°C and 1 bar in the reaction forming the component from the elements to be assigned to the component. In aqueous solutions, two additional conventions are needed, setting μ_i^0 for H^+ and for e^- to zero at 25°C and 1 bar. The use of these conventions is justified because we always are calculating the equilibrium constant from a free energy change across a reaction which is mass balanced, allowing the effect of the conventions to cancel out. These conventions and how to use them are covered in Geology 4659, Geochemical Thermodynamics.

From the above relations we can write by substitution: $\Delta G_r = 2.303 RT \log (Q/K)$ which is zero at equilibrium when **Q = K**.

The expression **log (Q/K)** is often called the saturation index and is negative if the reaction goes to the right and positive if the reaction goes to the left.

Note the simple form of the mass-action law. The expression **Q** contains the **product** (not the sum) **of the activities** of the components taking part in the reaction. **Each activity is raised to the power represented by its reaction coefficient**. This coefficient is positive for products (because the reactants are being produced) and negative for reactants (because the reactants are being destroyed).

$$Q = \prod (a_i^{n_i})$$

The mass-action law is important if the **K** for a reaction is known. By computing **Q** and comparing it with **K**, the reaction can be tested to determine if equilibrium exists. If **Q** is not equal to **K** then there is no equilibrium. However, all reactions proceed in the direction of equilibrium, so the future reaction path can be predicted.

Whenever reactions are added together to form a new reaction, the equilibrium constant K for the new reaction is simply the product of the individual equilibrium constants of the reactions. In log space, the log of the equilibrium constant for the addition of reactions is simply the sum of the logs of the equilibrium constants for the individual reactions.

Subtracting a reaction means reversing the right and left sides of a reaction and then adding the reversed reaction to another reaction. If a new reaction is formed from subtracting one reaction from another reaction, the equilibrium constant of the new reaction is simply the quotient of the two reactions in which the denominator contains equilibrium constant of the reaction that is being subtracted. In log space, the log of the equilibrium constant for the first reaction minus the log

equilibrium constant for the reaction being subtracted is the log of the equilibrium constant of the new reaction.

Definition of Activity of a Species and/or Component

The definitions given below are the common ones used in geochemistry. Whenever, an equilibrium constant is used to evaluate if equilibrium exists, the user must use the activity definitions that are consistent with the conventions used to define the equilibrium constant. Any equilibrium constant given in the literature should list those conventions. Unfortunately, different conventions are sometimes used by chemists, geochemists, and chemical engineers, generating confusion if the conventions are not listed.

For an aqueous component in a solution, $a_i = m_i \gamma_i$ where m_i is the molality of the i th component and γ_i (gamma) is the activity coefficient discussed later.

For a solid component in a solid phase or a liquid component in a non-aqueous solution, $a_i = X_i \lambda_i$ where X_i is the mole fraction of the i th component in the phase and λ_i (lambda) is the activity coefficient discussed later.

For a gas component in a gas phase, $a_i = X_i \chi_i P$ where X_i is the mole fraction of the i th component in the gas phase, χ_i (chi) is the activity coefficient discussed later, and P is the total gas pressure. Remember that K will not vary with pressure for a reaction involving only gaseous components. The reason is that pressure is already included in the activity expression of all the components.

Chemists generally use the same conventions as geochemists and the same activity definitions, with one exception. Their K values do not vary with pressure for liquids and solids. The result is that pressure variation is included in activity coefficient computations in these phases.

Definition of the Activity Coefficient of a Species and/or Component

The activity coefficients γ_i , λ_i , and χ_i each relate the activity to a concentration unit. In thermodynamics, the activity coefficient corresponds to a measure of the interactions of the i th component with other components in the phase. The activity coefficient with the concentration unit in the activity term allows for a correction to the Gibbs free energy of the component from what it would be in its standard state. The standard state is the pure substance for a solid and for liquids, a pure 1 bar ideal gas (obeys ideal gas law) for a gas component, and an infinitely dilute-behaving solution for dissolved aqueous components. The activity coefficient is one when the component is behaving as though it is in its standard state (in which there are no interactions with other components). In general the activity coefficient of the solvent component making up a nearly pure phase, e.g., water in an aqueous solution or a mineral that is nearly pure can be regarded as having unit

activity coefficients. However, the activity coefficients of dissolved ionic salts are rarely one.

The activity coefficient of a charged aqueous component is generally calculated by a modified Debye-Hückel expression. For components in solids, gas phases, other non-aqueous solutions, various empirical and semi-theoretical expressions are used. The actual calculation of activity coefficients usually represents the biggest error in using mass-action laws. Examples of activity-coefficient expressions will be given in class. The Debye-Hückel equation and its modifications for use in higher ionic strength solutions are:

$$\log \gamma_i = -Az_i^2 I^{1/2} \text{ for very dilute solutions, } I < 10^{-2.3}$$

$$\log \gamma_i = -Az_i^2 I^{1/2} / (1 + Ba_i^0 I^{1/2}) \text{ for } I < 10^{-1}$$

$$\log \gamma_i = -Az_i^2 I^{1/2} / (1 + Ba_i^0 I^{1/2}) + m_i C \text{ for } I < 1$$

and the modification known as the Davies Equation which is generally written as

$$\log \gamma_i = -Az_i^2 [I^{1/2} / (1 + I^{1/2}) - 0.3I]$$

where A and B are solvent (water) parameters which vary with pressure and temperature and have values of 0.5101 and 0.3285×10^8 , respectively, at 25°C and 1 bar. C and a_i^0 are fit parameters for the *i*th component and z_i is its charge. In general, a_i^0 ranges from 2×10^{-8} to 8×10^{-8} and depends upon the size of the *i*th ion. **I** is the ionic strength of the **total aqueous solution** which can be defined as

$$I = 0.5(m_j z_j^2 + m_{j+1} z_{j+1}^2 + \dots \text{ for all aqueous species}).$$

When a salt is dissolved in water, the concentrations can refer to the stoichiometric concentrations resulting from dissolution or the true concentrations which take into account new species or complexes formed between ions in solution. If **I** is computed using the stoichiometric or total molalities of each component, then **I** is called a stoichiometric ionic strength. If **I** is computed using the true or "free" molalities of all species (including complexes) in solution, then **I** is called a true ionic strength.

The importance of the distinction is that the ionic strength is used to compute activity coefficients of aqueous species. If we use the true molality of a species such as Ca^{2+} in solution, then we use the true ionic strength (based on all true molalities) to compute the "free" activity coefficient. On the other hand, if we use the stoichiometric molality of Ca^{2+} , then we use the stoichiometric ionic strength (based on all stoichiometric molalities) to compute the stoichiometric activity coefficient. The resulting activity of Ca^{2+} must be the same following either convention, hence the stoichiometric activity coefficient is always less than the "free" activity coefficient.

For use in the Debye-Hückel equation, use the "TOTAL" ionic strength computed for the entire solution using all dissolved salts. A common mistake among students is to use only the ionic strength contribution of a component in the Debye-Hückel equations in computing its activity coefficient.

If a solid is composed predominantly of one component, that component can usually be assumed to have an activity coefficient of unity, leading to an activity of unity because the mole fraction is near unity. Similarly, water in an aqueous solution can usually be assumed to have an activity coefficient of unity and an activity of unity if the solution is not a brine. In reality, for calculating osmotic pressures and other parameters, the activity coefficient of water cannot be assumed to be unity. However, for use in the mass-action law, the activities of nearly pure solids and water in aqueous solutions (not brines) are often set equal to unity.

For a noncharged species, e.g., SiO_2 or H_4SiO_4 , CH_4 _{aq} the aqueous activity coefficient can often be computed from a **linear relationship with the solution ionic strength**:

$$\log \gamma_i = k_i I$$

where k_i can be thought of as a salting-out coefficient due to the fact that the solubility of a neutral species frequently decreases with increasing ionic strength I . The solubility decrease is related to the decrease in free water molecules caused by the hydration of the dissolved salts. This decrease in solubility is input in the mass-action law by the increase in activity caused by the increase in γ_i .

Stoessell (1982, *Geochim. Cosmochim. Acta*, 46, 1327-1332) measured the activity coefficient of methane in various single salt solutions at 25°C, showing the above equation represented the methane activity coefficient but with a different salting-out constant for each different type of salt solution, e.g., NaCl versus CaCl_2 solutions.

Definition of pH

The pH is defined as the $-\log a_{\text{H}^+}$ in an aqueous solution where the a_{H^+} refers to the free (uncomplexed) H^+ ion. In field samples, the **pH** must be measured immediately, before gas exchange takes place with the atmosphere. The temperature of the sample at the time of **pH** measurement would be recorded, so the **pH** can be back-computed for the temperature of the *in situ* sample.

The definition of **pH** relates to our concept of acids and bases in aqueous solutions. An acidic solution has a higher concentration of hydrogen ions H^+ than of OH^- ions. These two ions are related through the disassociation reaction with water H_2O .

$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$ where $K_{\text{H}_2\text{O}} = a_{\text{H}^+} a_{\text{OH}^-} / a_{\text{H}_2\text{O}}$ is the mass-action law.

At 25°C and 1 bar (near atmospheric pressure), K_{H_2O} is 10^{-14} .

The activity of water in most aqueous solutions (except brines) can be assumed to be unity, leading to

$$10^{-14} = a_{H^+} a_{OH^-} \text{ for the mass-action law.}$$

From the mass-action law, in a neutral solution the H^+ and OH^- activities must each be 10^{-7} . This neutral solution is neither acid nor basic and has a **pH** of 7 ($-\log a_{H^+} = 7$). Acidic solutions have a **pH** lower than 7 and basic solutions have a **pH** greater than 7.

The pH can be measured with a glass electrode or calculated from any mass-action expression for a reaction at equilibrium which involves the hydrogen ion. All non-oxidation-reduction reactions involving only aqueous components can generally be assumed to be at equilibrium. For example, the reaction between inorganic carbon species in an aqueous solution

$HCO_3^- = CO_3^{2-} + H^+$ can be used to compute the **pH**. The mass action law is

$$K_{HCO_3(-)} = a_{CO_3(2-)} a_{H^+} / a_{HCO_3(-)}.$$

where **pH** = $-\log a_{H^+} = -\log K_{HCO_3(-)} + \log a_{CO_3(2-)} + \log a_{HCO_3(-)}$.

The activities can be computed by measuring the concentrations of CO_3^{2-} then be computed using the $K_{HCO_3(-)}$ value.

Definition of pe and Eh

The pe is defined as the $-\log a_{e^-}$ where a_{e^-} represents an aqueous electron activity in solution. In reality, free aqueous electrons do not exist in a solution; however, we can still use the concept. The **pe** is a measure of how oxidizing or reducing a solution can be. An oxidizing solution can be considered to have a deficiency in aqueous electrons, promoting the giving up of electrons to the solutions by ions being oxidized. A reducing solution can be considered to have an excess of aqueous electrons, promoting the acceptance of electrons by ions being reduced. Hence an oxidizing solution has a low a_{e^-} (positive **pe**) and a reducing solution has a high a_{e^-} (negative **pe**).

pe can be calculated from the activities of reaction components in any "half cell" oxidation-reduction reaction. The term "half-cell reaction" implies that the electrons released or consumed are not cancelled out in the overall reaction. A major problem is the general lack of equilibrium in oxidation-reduction (redox) reactions, combined with the necessity of accurate measurements of ion concentrations in different oxidation states. The latter is particular difficult, because exposure to the atmospheric oxygen during sampling and measurement will change the elemental proportions in different oxidation states.

An example of oxidation and reduction in an aqueous solution is the oxidation of ferrous iron with molecular oxygen.



The reaction is actually the sum of two half-cell reactions. Either one of the half-cell reactions can be used to compute **pe**. For example, the oxidation half-cell reaction, involving the oxidation of aqueous iron, (becomes more positive), is

$\text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}^-$ where $K_{\text{ox}} = a_{\text{Fe}^{3+}}a_{\text{e}^-}/a_{\text{Fe}^{2+}}$ is the mass-action law. In terms of this expression, $\log K_{\text{ox}} = \log a_{\text{Fe}^{3+}} + \log a_{\text{e}^-} - \log a_{\text{Fe}^{2+}}$ or **pe** = - log a_{e^-} = - log K_{ox} + log $a_{\text{Fe}^{3+}}$ - log $a_{\text{Fe}^{2+}}$

The reduction half-cell reaction involves the reduction of aqueous oxygen (becomes more negative).

$0.25\text{O}_2 + \text{e}^- + \text{H}^+ = 0.5\text{H}_2\text{O}$, and **pe** could also be computed using the mass-action law for this reaction.

Note that the **K** value in the mass-action law is for a particular reaction, hence **K** will have a different value for the oxidation half-cell reaction (for Fe) then for the reduction half-cell reaction (for O₂); however, the **pe** calculated from each half-cell reaction should be identical.

The pe calculation from half-cell reactions assumes equilibrium for the overall oxidation-reduction reaction, because the K values hold only for equilibrium.

Frequently, the calculated **pe** values are different using different half-cell reactions. There are many oxidation-reduction reactions occurring in a solution, and **pe** values computed from the different half-cell reactions of the various oxidation-reduction reactions may not agree for the same solution, indicating a lack of equilibrium. Hence, the calculated **pe** values are often difficult to apply to the solution!

A different approach is to use an inert platinum electrode to measure the half-cell voltage of the aqueous solution relative to the oxidation of 0.5H₂ to H⁺ in the standard hydrogen electrode **SHE**. The standard hydrogen electrode consists of hydrogen gas being bubbled under a pressure of 1 bar through an HCl aqueous solution in which H⁺ has unit activity. By convention, the voltage of **SHE** is set to zero, so the measured cell voltage (at zero current flow) is assigned to the aqueous solution connected through it by the salt bridge. The measured cell voltage is called the **Eh**. The platinum electrode contributes no voltage but is simply a conductor for the flow of electrons. In practice, the **SHE** half cell is too hard to maintain for making measurements. Instead, the cell voltage is measured across an external circuit between the platinum electrode in the sample solution and a reference electrode, connected by a salt bridge to the solution. The **Eh_{ref}** of the reference electrode relative to oxidation in SHE has to be added to the measured voltage EMF to compute **Eh** for the solution. **Eh_{ref}** is 0.2444 volts at 25°C and 1 bar for the saturated (4.16 M KCl)

calomel electrode, corresponding to the reduction of $0.5\text{Hg}_2\text{Cl}_2$ to $\text{Hg}^0 + \text{Cl}^-$, relative to oxidation in the standard hydrogen electrode. The saturated Ag-AgCl reference electrode has a voltage of 0.1986 volts (199 mv) for the reduction of AgCl to Ag(s) + Cl^- at 25°C and 1 bar.

$$E_h = \text{EMF}_{\text{measured}} + E_{h_{\text{ref}}}$$

By thermodynamic convention, the voltage corresponding to **SHE** is zero and the electron activity in **SHE** is unity. When these conventions are combined with other conventions used in the half-cell reactions, the **E_h** can be shown to be related to the **pe** by the following relationship.

$$pe = (F/(2.303RT))E_h$$

where **F** is the Faraday constant (96,485 J/V/mole), **R** is the gas constant (8.314 J/mole) and **T** is the temperature in degrees Kelvin (298.15°K = 25°C).

However, measuring the **E_h** with a platinum electrode is not always accurate, because the surface of the electrode can be poisoned upon contact with the solution, or the redox reactions are not equilibrium so the measured value doesn't correspond to the actual **E_h**. If the solution contains the Fe redox couple (e.g., Fe^{2+} and Fe^{3+} , or the Mn redox couple or significant HS^- , then the solution generally gives a reliable **E_h** reading. In particular, the presence of HS^- always results in a negative **E_h** and is a good indicator for anaerobic conditions, e.g., low dissolved O_2 .

Reactions between Phases

In general, any reaction taking place completely within a phase can be considered to be at equilibrium. The major exceptions are the oxidation-redox reactions discussed above within an aqueous solution. Reactions taking place wholly within a phase are usually at equilibrium because the reaction takes place rapidly.

Reactions taking place between phases can usually not be assumed to be at equilibrium. Exceptions are the generally fast reactions involving exchange of gaseous components from a gas phase to an aqueous phase or the adsorption and desorption of components between an aqueous solution and a solid surface. For example, the transfer of CO_2 between the atmosphere and the surface ocean waters or the exchange of cations between clay interlayers and ground water usually reach equilibrium.

The importance of reactions being at equilibrium is the advantage of being able to use the mass-action law to predict equilibrium concentrations. However, even if reactions are not at equilibrium, we can generally test them to see how close they are to equilibrium and evaluate what changes in component concentrations are to be expected. The mass-action laws are extremely useful because all reactions will tend towards equilibrium if given enough time.

Solubility of a Component in a Phase

The saturation of one component in a phase represents an equilibrium between the component in two different phases. For example, the saturation of silver chloride AgCl in water represents an equilibrium of solid AgCl with the aqueous solution. The reaction can be written as

$\text{AgCl} = \text{Ag}^+ + \text{Cl}^-$ where the ions are in solution and the compound is a separate solid phase. The mass-action law is

$K_{\text{AgCl}} = a_{\text{Ag}^+} a_{\text{Cl}^-} / a_{\text{AgCl}}$ where the activity of the solid AgCl can be assumed to be unity if the solid AgCl is essentially a pure AgCl phase with only minor impurities. At 25°C and 1 bar, K_{AgCl} equals $10^{-9.74}$. Thus,

$$10^{-9.74} = a_{\text{Ag}^+} a_{\text{Cl}^-}$$

Assuming activity coefficients of unity for Ag^+ and Cl^- , AgCl would dissolve in pure water until each of the ions had a molality of $10^{-4.87}$, a close approximation of zero concentration. AgCl is very insoluble. The precipitation of AgCl can be used to measure aqueous Cl^- in solution.

1st Example Problem Using Calcite Solubility

What is the 25°C and 1 bar calcite solubility and pH in water in equilibrium with the atmosphere with a mole fraction of CO_2 of $10^{-3.5}$. The aqueous species are listed below in solution. The μ_i° values at 25°C and 1 bar are listed below.

Component	μ_i° in cal/mol
Ca^{2+}	-132,300 cal/mol
CaCO_3°	-258,470
CaHCO_3^+	-274,330
HCO_3^-	-140,260
CO_3^{2-}	-126,170
H_2CO_3	-148,940
H_2O	- 56,687
OH^-	- 37,594
H^+	0
CO_2 gas	- 94,254
CaCO_3 calcite	-269,800

Procedure to do the Problem

Write the reactions for the complexes and the solubilities of calcite and CO_2 in terms of the following components: H^+ , HCO_3^- , Ca^{2+} , and H_2O . Write out the corresponding mass-action equations for the reactions. Write an electrical solution balance.

The electrical solution balance equation can be simplified by substitution of the mass action equations so that only the molality of H^+ is a variable plus the activity coefficients of the various components. Initially assume the activity coefficients are one. Solve for the molality of H^+ by trial and error on a spreadsheet. Then calculate component molalities from the mass-action expressions with this molality. Use these to calculate an ionic strength and calculate activity coefficients for the components with the Davies equation. Again solve for the molality of H^+ in the electrical neutrality expression, using the new activity coefficients. Then recalculate the molalities from the mass action equations and repeat the process if there is any significant change in the molalities. The solubility of calcite is equal to the molality of $\text{Ca}^{2+} + \text{CaHCO}_3^+ + \text{CaCO}_3^0$.

2nd Example Problem Using Anhydrite Dissolution

Dissolve 0.001 moles of CaSO_4 in 1 kg of water containing 0.001 moles of anhydrite, CaCl_2 . Several important species are listed below with their μ_i^0 at 25°C and 1 bar. Cl^- does not form complexes significantly so its molality will remain at 0.002. Calculate the true molalities of the species listed below. Use the Davies equation below for aqueous activity coefficients of charged species.

$\log \gamma_i = -Az_i^2 \mathbf{I}^{1/2} / (1 + \mathbf{I}^{1/2}) + 0.3\mathbf{I}$ where \mathbf{I} is the true ionic strength. At 25°C and 1 bar, $A = 0.5085$. Assume neutral species have an activity coefficient of 1.

Component μ_i^0 in cal/mol

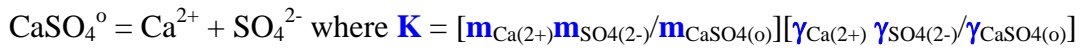
Ca^{2+} **-132,300 cal/mole**

SO_4^{2-} **-177,750**

CaSO_4^0 **-310,270**

Calculate the equilibrium constant for the formation of CaSO_4^0 in the reaction below using the relation

$\log \mathbf{K} = -\Delta G_r / 2.303R\mathbf{T}$ where $R = 1.987 \text{ cal}^\circ\text{K/mol}$ and $\mathbf{T} = 298.15^\circ\text{K}$:



$\log K$ is found to equal 0.16 or $K = 1.45$.

Procedure to do the Problem

The procedure uses two mass balance equations for the total number of moles of aqueous Ca and aqueous sulfate:

$$n_{\text{Ca}} = 0.002 = \mathbf{m}_{\text{Ca}(2+)} + \mathbf{m}_{\text{CaSO}_4(o)}$$

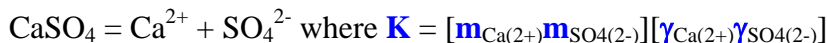
$$n_{\text{SO}_4} = 0.001 = \mathbf{m}_{\text{SO}_4(2-)} + \mathbf{m}_{\text{CaSO}_4(o)}$$

Initially neglect CaSO_4° , i.e., use the stoichiometric (total) Ca and SO_4 molalities to calculate the ionic strength and then calculate γ_i , the activity coefficients for Ca^{2+} and SO_4^{2-} . Use these stoichiometric activity coefficients together with the stoichiometric molalities in the above equilibrium quotient to calculate $\mathbf{m}_{\text{CaSO}_4(o)}$ and then use the mass balance equations to calculate $\mathbf{m}_{\text{Ca}(2+)}$ and $\mathbf{m}_{\text{SO}_4(2-)}$. If the molalities differ significantly from the previous step then repeat the procedure until they agree without significant difference. When repeating the procedure use the new ionic strength with the new molalities to recalculate the activity coefficients.

Third Example Problem Using Anhydrite Solubility

This is the same problem as before but now we want to dissolve CaSO_4 (anhydrite) until it is at equilibrium with the solution. We want to know the solubility of anhydrite in this solution.

The only additional information needed is the anhydrite equilibrium reaction. We assume anhydrite is pure so its activity is one.

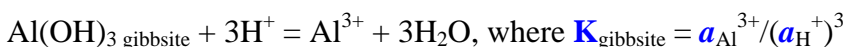


and μ_i° of anhydrite, CaSO_4 , is -315930 cal/mol, so $K = 0.000049008$.

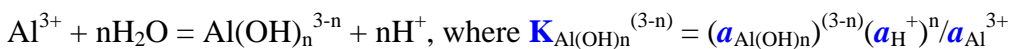
In this case we can solve directly for $\mathbf{m}_{\text{Ca}(2+)}$ in the above reaction quotient because $\mathbf{m}_{\text{Ca}(2+)} = \mathbf{m}_{\text{SO}_4(2-)} + 0.001$. We use the stoichiometric molalities to calculate the stoichiometric ionic strength and then the activity coefficients. We substitute for $\mathbf{m}_{\text{Ca}(2+)}$ in the reaction quotient which produces a quadratic equation and solve for $\mathbf{m}_{\text{SO}_4(2-)}$. We then use the new molalities to calculate $\mathbf{m}_{\text{CaSO}_4(o)}$ and a new "true" ionic strength and calculate "true or free" activity coefficients. The process is repeated, solving again for $\mathbf{m}_{\text{SO}_4(2-)}$. The new molalities are compared with the old molalities to see if they have changed significantly. If so, the calculation is repeated. The major error in this process is that the Davis equation is not accurate at high ionic strengths (above 1) and the true solubility is much less because of a large increase in activity coefficients at high ionic strengths.

Fourth Example Problem Using Aluminum Solubility at 25°C and One Bar

Aluminum solubility is usually controlled in soils by gibbsite precipitation ($\text{Al}(\text{OH})_3$). The precipitation reaction is written as



where the activities of water and the pure solid gibbsite can be assumed to be unity (one). The solubility of aluminum is limited by the maximum value that the activity of Al^{3+} can have in the above equation, such that the ratio of $a_{\text{Al}^{3+}} / a_{\text{H}^+}^3$ remains below K_{gibbsite} . With increasing activity of Al^{3+} , eventually gibbsite will precipitate. However, aluminum also form aqueous complexes with hydroxides and maintains equilibrium with these complexes, e.g.,



If the activity of Al^{3+} increases, more $\text{Al}(\text{OH})_n^{3-n}$ forms, helping to keep the activity of Al^{3+} below the solubility of gibbsite. Determine the solubility of gibbsite in (sum of the molality of aqueous Al species) as a function of **pH** (8 **pH** values: 3, 4, 5, 6, 7, 8, 9, 10). Use the following standard state Gibbs free energies of formation at 25°C and 1 bar to calculate the equilibrium constants and use the Davis Equation to calculate activity coefficients. The OH^- data is given so its concentration can be calculated to help compute the ionic strength of the solution for use in the Davis Equation. Note that R equals 1.9872 cal/mol K at 25°C (298.15°K).

Component	μ_i° in cal/mol
Al^{3+}	-116,551
$\text{Al}(\text{OH})^{2+}$	-166,477
$\text{Al}(\text{OH})_2^+$	-215,511
$\text{Al}(\text{OH})_3^0$	-263,050
$\text{Al}(\text{OH})_4^-$	-312,094
H_2O	-56,678
H^+	0
OH^-	-37,572
$\text{Al}(\text{OH})_3 \text{ gibbsite}$	-276,018

To do this problem you simply calculate the activity of Al^{3+} in equilibrium with gibbsite at each **pH** value and then use the the equilibrium reactions linking $\text{Al}(\text{OH})_n^{3-n}$ with Al^{3+} to calculate the activities of each $\text{Al}(\text{OH})_n^{3-n}$ species. The sum of all the molalities of all these Al species would be the solubility of gibbsite at each **pH** point. However, at this stage, you have only calculated the sum of the activities. By assuming the activity

coefficients are one, each activity becomes a molality and can be used to calculate an ionic strength. This ionic strength can be used to compute the activity coefficients of each of the species and they can be inserted into the activity expression to calculate molalities of each of the species. The molalities of the aluminum species can then be summed to get the solubility of gibbsite.

Gas Solubility

The solubility of inert gases can be predicted using equilibrium between the gas phase, e.g., the atmosphere, and the aqueous solution. The term inert implies that other reactions such as hydrolysis (as in the case of dissolved CO_2) are not taking place.

The mass-action expression for a gas component G in equilibrium with both a gas phase and an aqueous solution is

$$G_{\text{gas}} = G_{\text{aq}}, \text{ where } K_G = a_{G \text{ aq}} / a_{G \text{ gas}} = (m_G \gamma_G)_{\text{aq}} / (X_G \chi_G P)_{\text{gas}}$$

or $m_{G \text{ aq}} = X_G P (K_G \chi_{G \text{ gas}} / \gamma_{G \text{ aq}})$ or expressed in terms of the Henry's law constant k_H and the partial pressure of the gas component of the gas phase $X_G P$ $m_{G \text{ aq}} = X_G P (k_H)$ Hence, $k_H = (K_G \chi_{G \text{ gas}} / \gamma_{G \text{ aq}})$

Note that k_H is only a constant if the activity coefficient ratio of the component between the gas phase and the aqueous solution is constant. Henry's law constants have been measured for a large number of gases in equilibrium with the atmosphere with different aqueous solutions. These constants can be used to predict the solubility of various inert gases in natural waters in equilibrium with the atmosphere. If a gas hydrolyses into other components, e.g., CO_2 , then the solubility is only that of the unhydrolyzed component and does not include HCO_3^- or CO_3^{2-} .

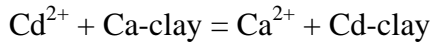
An example of the use of Henry's Law constant can be made with the aqueous solubility of O_2 in contact with the atmosphere. k_H in units of mol atm/l is 1.28×10^{-3} . This is a value measured for dry air in which the mole fraction of O_2 is 0.2095 (also the volume fraction). Water vapor in saturated air has a mole fraction of 0.0313 so to correct the mole fraction of O_2 , multiply P by $(1 - 0.0313)$. Note that k_H values are almost always reported in molarity and atmosphere units, rather than in molality and bar units.

$$M_{\text{O}_2} = X_G (k_H) = 0.2095(1 - 0.0313)(1 \text{ atm})(0.00128 \text{ mol atm/l}) = 0.00026.$$

Exchange Reactions

Cation Exchange

The exchange of an aqueous component in solution with a component on the surface of a solid is a common reaction between clays and an aqueous solution as well as colloids and an aqueous solution. For example, the exchange of aqueous cadmium with calcium on the surface of a clay can be written as



where the mass-action law becomes

$$\mathbf{K} = a_{\text{Ca}(2+)} a_{\text{Cd-clay}} / a_{\text{Cd}(2+)} a_{\text{Ca-clay}}$$

and $a_{i\text{-clay}} = X_{i\text{-clay}} \lambda_{i\text{-clay}}$ where $X_{i\text{-clay}}$ is the mole fraction of i on the exchange sites, e.g.,

$$X_{\text{Cd-clay}} = m_{\text{Cd on clay}} / (\text{moles}_{\text{Ca on clay}} + \text{moles}_{\text{Cd on clay}})$$

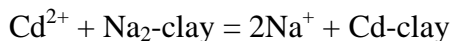
However, if the exchange involved cations of different charge, $X_{i\text{-clay}}$ has been used as either the charge fraction or mole fraction of the exchange ion (as shown below). $\lambda_{i\text{-clay}}$ is the activity coefficient of i on the exchange sites. There is no way to compute or measure $\lambda_{i\text{-clay}}$ independently of $a_{i\text{-clay}}$.

The ratio of the solution activities is usually called a partition coefficient $\mathbf{K_p}$, e.g.,

$$\mathbf{K_p} = a_{\text{Ca}(2+)} / a_{\text{Cd}(2+)} = \mathbf{K} a_{\text{Ca-clay}} / a_{\text{Cd-clay}}$$

In the literature, these partition coefficients can be defined in many different ways. For example, they may be defined in terms of concentration ratios rather than activity ratios, so the activity coefficients would be removed from the activities. They are sometimes defined for the direct exchange reaction of the component with itself on the solid. The important point is never use a partition or distribution coefficient without knowing how it is defined. The same is true of equilibrium constants.

If the reaction involved the exchange of a monovalent with a divalent cation, the reaction may be written with the **Gapon convention**, e.g.,



$$\text{and the mass-action law becomes } \mathbf{K} = (a_{\text{Na}(+)})^2 a_{\text{Cd-clay}} / [a_{\text{Cd}(2+)} a_{\text{Na}(2)\text{-clay}}]$$

where the mole fractions of Na_2clay and Cd-clay are identical to the charge fractions of Cd^{2+} and Na^+ on the exchange sites, e.g.,

$$\text{charge fraction of Na on clay} = \text{moles}_{\text{Na on clay}} / (\text{moles}_{\text{Na on clay}} + 2 \text{ moles}_{\text{Cd on clay}})$$

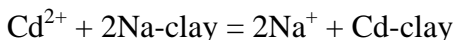
$$= 2 \text{ moles}_{\text{Na}(2)\text{-clay}} / (2 \text{ moles}_{\text{Na}(2)\text{-clay}} + 2 \text{ moles}_{\text{Cd-clay}}) = \text{mole fraction of Na}_2\text{-clay}$$

The power exchange function used in geochemistry is a modification of the above equilibrium constant and has a power exchange constant, $\mathbf{K_{p.e.}}$.

$$\mathbf{K_{p.e.}} = [(a_{\text{Na}(+)})^2 / a_{\text{Cd}(2+)}] [X_{\text{Cd-clay}} / X_{\text{Na}(2)\text{-clay}}]^n$$

where n is a exponent to fit the data. Note that there are no activity coefficient terms for Na₂-clay and Cd-clay in the expression so the constant is not a true constant but has to contain those terms which will vary with the clay composition.

An alternative procedure to the **Gapon convention** is to write the exchange reaction between the monovalent and bivalent cations as



and the mass-action law becomes $\mathbf{K} = (a_{\text{Na}^+})^2 a_{\text{Cd-clay}} / [a_{\text{Cd}^{2+}} (a_{\text{Na-clay}})^2]$

where the **Vanselow convention** uses mole fractions and the **Gaines-Thomas convention** uses charge fractions, respectively, of Cd²⁺ and Na⁺. This produces confusion because the charge fractions are not equal to the mole fractions. Your instructor believes the **Gapon Convention** is the thermodynamically consistent way of handling heterovalent cation exchange (Stoessell, 1998, Clays and Clay Minerals, 46, 215-218).

Isotherms

Three exchange algorithms called isotherms are commonly used in which a component M exchanges with itself on sites on a solid: Distribution, Freundlich, and Langmuir. All of these neglect explicit inclusion of the competition by other components for the sites on the solid. The reaction can be written as follows:

$$\text{M} = \text{M}_{\text{solid}} \text{ where } \mathbf{K} = a_{\text{M solid}} / a_{\text{M}} = [\text{X}_{\text{M solid}} / m_{\text{M}}] [\lambda_{\text{M solid}} / \gamma_{\text{M}}]$$

The first bracketed ratio can be measured experimentally and is a modified Distribution coefficient which is often used for prediction in other solutions. However, this ratio will be a function of the solution composition, so it cannot be generally considered a constant.

In practice, the isotherms are written with units for M of mg/kg of solid called S_M and mg/liter of solution called C_M. **K_D**, the Distribution coefficient is defined as:

$$\mathbf{K_D} = S_M / C_M$$

Note that the concentration of M cannot increase without changing the ratio which would change the value of **K_D**. Hence, the implication is that there are an unlimited number of sites available for M to sorb on in order to prevent the ratio from increasing.

The Freundlich (isotherm) algorithm is a modification of the Distribution algorithm.

$$\mathbf{K_F} = S_M / (C_M)^n$$

where **K_F** is the Freundlich coefficient and n lies between a range of 0.7 and 1.1. If n is one, the expression reduces to the Distribution algorithm.

Other times, experimental data can be fitted to the Langmuir adsorption algorithm (Langmuir isotherm) which has a maximum value of S_M called S_{\max} incorporated as a parameter into the algorithm.

$S_M = S_{\max} K_L C_M / (K_L C_M + 1)$ where K_L is the Langmuir coefficient.

In general, in modeling contaminant flow, either simple Distribution, Freundlich, or Langmuir isotherms are used. Experimental data are used to pick which of the best three equations fit the data.

Test the ability of the different isotherms to fit sorption data. Use a modified Power Exchange Function to predict the data and then fit it to the Distribution, Freundlich, and Langmuir Isotherms.

The modified Power Exchange Function for this reaction: $2\text{Na}^+ + \text{Zn-Clay} = \text{Zn}^{2+} + \text{Na}_2\text{-Clay}$, is $K_{pe} = [M_{\text{Zn}}^{2+} / (M_{\text{Na}}^+)^2] [X_{\text{Na}_2\text{-Clay}} / (X_{\text{Zn-Clay}})]^n$ where the modification is to use molarities instead of aqueous activities. Note n is a fit parameter and the X symbols refer to mole fractions or charge fractions on the clay exchange sites. Because of the use of the Gapon convention, the mole fractions are equal to the charge fractions.

Use values of K_{pe} and n of 0.32 and 0.80, respectively, and assume the clay has 100 meq/liter of exchange sites per kg of clay. Assume a constant equilibrium molarity of 0.001 for Na and 10 different equilibrium Zn molarities of 1×10^{-7} , 2×10^{-7} , 3×10^{-7} , ..., 1×10^{-6} . Calculate the equilibrium $X_{\text{Na}_2\text{-Clay}} / (X_{\text{Zn-Clay}})$ for each solution composition of 0.001 M Na paired with one of the Zn molarities. Express this data as mg of Zn/kg of clay and mg of Zn/liter of solution. You will have to make use of the total of 100 meq/kg of exchange sites on the clay. Plot the data and then fit it to the 3 isotherms and comment on the fits.

Determine the phosphate solution isotherms on bauxite at different ionic strengths in 0.1, 0.01, 0.001 M NaCl

Equilibrate different concentrations of NaH_2PO_4 in 25 ml of a NaCl solution containing 0.1 grams of bauxite of a given size. Put the bottles on a shaker overnight to equilibrate. Use 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, and 6.4 mM NaH_2PO_4 solutions in a matrix of either 0.1 M, 0.055 M, and 0.01 M NaCl - so 7 bottles per ionic strength. Each student should do one of the NaCl solutions, i.e., pick one of the above concentrations. Measure the PO_4 concentrations on the liquid ion chromatograph and plot the data as mM PO_4 in solution versus mM PO_4 absorbed per cm^2 of bauxite. Note that the density of bauxite is about 2.4 g/cm^3 , and you have to assume a cube of a particular size and calculate the total surface area for your 0.1 gram of sample. Fit your data to a Langmuir or Freundlich isotherm. Compare your results to determine the effect of ionic strength.

Determine phosphate, sulfate, and nitrate pH sorption curves in 0.01 M NaCl containing 0.1 grams of bauxite.

Each student can do one of the anions. Place 0.50 grams of bauxite in 200 ml of 0.01 M NaCl and 0.00005 M of the sodium salt of the anion, e.g., either Na₂SO₄, NaH₂PO₄, or NaNO₃. Let sit overnight to come to equilibrium. In the titration, add enough acid to lower the starting pH to about 4, let equilibrate for 10 minutes and take a 2 ml sample and filter it. Try not to remove any of the bauxite. Record how many ml of acid were added, how many ml of solution were removed and the equilibrated pH. Add base to raise the pH a half pH unit, let equilibrate for 10 minutes and take another 2 ml sample and filter it. Again try not to remove any of the bauxite. Record the equilibrated pH, the ml of base added, and the ml of sample taken. Repeat the process to bring the pH to about 10. Analyze your solutions on the liquid ion chromatograph and compute the amount of sorption on the solids from the concentration left in solution. You will have to correct for the volume changes due to addition of acid and for the volume changes due to removal of sample. Plot the amount of anion sorbed as a function of pH.

Retardation of Pollutant Partition Concentration Front

The retardation of a concentration front of a pollutant B can be computed using a mass balance across the concentration front. This method uses a flushing factor equal to the mass needed to advance the concentration front one pore volume divided by the difference in mass per pore volume of the pollutant between that in upstream pore fluid and in the downstream pore fluid.

The concentration front moves downstream by replacing downstream ground water with the upstream ground water and the downstream mass of pollutant on sediment sites with those in equilibrium with the upstream ground water. If the pollutant is absent downstream, the retardation of the front R_f is equal to the mass of pollutant (per pore volume) on the upstream solids plus in the upstream ground water divided by the amount of pollutant (per pore volume) in the upstream ground water.

The retardation factor of the front is written below in equation form, using the ratio of ρ/τ , the ratio of the dry sediment density to the sediment porosity fraction, to normalize to one pore volume. The equation is simply a statement of the mass constraints governing the movement of the front. The retardation factor is the factor by which the ground water velocity should be divided to get the velocity of the concentration front.

$$R_f = [(C_{B,upstream} - C_{B,downstream}) + (S_{B,upstream} - S_{B,downstream})] (\rho/\tau) / (C_{B,upstream} - C_{B,downstream})$$

or $R_f = 1 + (S_{B,upstream} - S_{B,downstream}) (\rho/\tau) / (C_{B,upstream} - C_{B,downstream})$.

If the Distribution Coefficient holds, substitution into the above equation yields: $R_f = 1 + K_D(\rho/\tau)$

The latter is the well known retardation factor presented in hydrology texts. It is almost always derived from the advection and sorption partial differential equation with dispersion set to zero. That equation, which describes the movement of a dissolved component and is used in numerical modeling, is based on the continuity equation which is a statement of the conservation of mass over a finite volume element. As will be shown later, the partial differential approach is important in that the retardation of a particular composition can be determined if the appropriate algorithm describing sorption is known. However, since that algorithm is never known accurately in the field, the second equation above gives a very accurate calculation of the retardation factor, as recently shown by Stoessell (1999, Ground Water, 37, 701-705) in a comparison of retardation factors from published column experiments versus those predicted by the equation.

Example problem in calculating a ground water velocity based on a retardation front and then calculating the amount left after flushing the polluted area.

A sandstone has a porosity fraction of 0.25, and a density of 2.5 g/ml (equal to 2.5 kg/l). In ten years a pollution front containing zinc has moved 0.5 meters downstream (from a point source of zinc) through the sandstone. Upstream of the front, the ground water has 5 mg/l of zinc in solution and 49.5 mg/kg of zinc on the sandstone. Downstream of the front there is no zinc in ground water and no zinc on the sandstone. What is the velocity in m/y of the ground water in the sandstone?

In the above question, the pollution point source is removed and unpolluted ground water now enters the 0.5 m of zinc-containing sandstone and flows through it. After 1 year what is the average concentration of sorbed zinc in mg/kg of sandstone, within the 0.5 m block of sandstone? There are two different approaches to answering this question. One way of answering this question requires the ground-water velocity and the other procedure doesn't.

Octanol Partition Coefficient

The "so-called" octanol partition coefficient K_{ow} gives the equilibrium distribution of the solute between equal volumes of an octanol solution and an aqueous fluid, measured at a particular temperature and pressure. The octanol solution is often used to simulate any nonpolar solvent, e.g., gasoline. Hence, K_{ow} is used as the partition coefficient K_{pc} for doing partitioning calculations of a component between water and any organic phase.

$$K_{ow} = X_{oc}/X_{aq} \text{ where } X_{oc} + X_{aq} = 1.$$

The X fractions refer to the actual solute fraction of the total moles of solute in both phases, not their mole fractions within the two fluids. Because equal volumes were used, the mole fraction ratio equals the concentration ratio in units of mass per unit volume. For example, consider the exchange of n moles of benzene between equal volumes of octanol and water.

$K_{ow} = \{n_{\text{benzene in octanol}} / [n_{\text{benzene in octanol}} + n_{\text{benzene in water}}]\} / \{n_{\text{benzene in water}} / [n_{\text{benzene in octanol}} + n_{\text{benzene in water}}]\} = n_{\text{benzene in octanol}} / n_{\text{benzene in water}} = [n_{\text{benzene in octanol}} / \text{liter of octanol}] / [n_{\text{benzene in water}} / \text{liter of water}] = \text{ratio of benzene concentrations (molarities) in octanol to water.}$

Note that K_{ow} is equal to an apparent thermodynamic equilibrium constant for a chemical reaction passing a component between the two phases in which the constant contains the thermodynamic equilibrium constant and the ratio of activity coefficient terms. The concentration units in this apparent thermodynamic equilibrium constant are in terms of molarity/liter.

As an example in the use of this constant, suppose there was a leak of 1000 gallons of gasoline, containing 100 moles of benzene, into a ground-water aquifer. If the gasoline came into contact with 10,000 gallons of water, describe the partitioning of benzene between the two phases. K_{ow} for benzene is 2. Assume the same value holds for partitioning benzene between gasoline and water.

The mass balance is $n_{\text{moles benzene in gasoline}} + n_{\text{moles benzene in water}} = 100$,

and $K_{pc} = 2 = [n_{\text{moles benzene in gasoline}} / 1,000 \text{ gallons}] / [n_{\text{moles benzene in water}} / 10,000 \text{ gallons}]$.

With these two relations, we can solve for the two unknowns: $n_{\text{moles benzene in gasoline}}$ and $n_{\text{moles benzene in water}}$.

Partition Coefficient Exercise

10 moles of xylene are within 1000 liters of an organic solvent forming a liquid pool in contact with ground water in the subsurface. The partition coefficient of xylene between the organic fluid and water is 75. The partition coefficient is the concentration (moles/l) ratio of xylene in the organic fluid to that in water.

There are two scenarios. What will be the concentration of xylene in the organic fluid if 10,000 liters of ground water equilibrate with the organic solvent? What would be the final concentration of xylene in the organic fluid if instead of 10,000 liters equilibrating at once, 10 successive 1,000 liters of ground water equilibrated with the organic fluid and then moved on, leaving the organic fluid behind?

The conservation of mass equation is: $n_{\text{total xylene}} = [n_{\text{xylene in org. sol.}} + n_{\text{xylene in water}}]$

and the partition coefficient function is: $K_{pc} = 75 = [n_{\text{xylene in org. sol.}} / \text{liters}_{\text{org. sol.}}] / [n_{\text{xylene in water}} / \text{liters}_{\text{water}}]$

By substitution into the conservation of mass equation: $n_{\text{total xylene}} = n_{\text{xylene org. sol.}} [1 + (\text{liters}_{\text{water}} / \text{liters}_{\text{org. sol.}}) 1/75]$

For the first situation: $10 = n_{\text{xylene in org. sol.}}[1 + 0.1333]$ Hence, $n_{\text{xylene in org. sol.}} = 8.824$ moles

For the second situation, the xylene concentration is solved for a 1000 liter equilibration with water and a new total moles of xylene computed from that remaining in the 1000 liter organic solvent. The calculation is then repeated 9 more times.

The equation becomes: $n_{\text{total xylene}} = n_{\text{xylene in org. sol.}}(1.01333)$. The initial step has $n_{\text{total xylene}} = 10$. Hence, $n_{\text{xylene in org. sol.}} = 9.868$ moles which is then used in the next iteration as $n_{\text{total xylene}}$

iteration - total moles of xylene - moles of xylene in org. sol.

1	10	9.868
2	9.868	9.738
3	9.738	9.610
4	9.610	9.484
5	9.484	9.359
6	9.359	9.236
7	9.236	9.114
8	9.114	8.994
9	8.994	8.876
10	8.876	8.760

Addition of Decay to Partition Coefficient Exercise

In nature, a pollutant such as xylene is eaten by bacteria. Bacterial decay usually follows first order kinetics in which

$$\ln N_{\text{Xy}}/N_{\text{Xy}}^0 = -k(t-t^0)$$

where N_{Xy} is the moles of xylene at time t in days and k is the decay constant. Assume the half life of xylene is 90 days and the partitioning of 10 moles of xylene in the above exercise between 1000 liters of organic solvent and 1000 liters of ground water takes place over a 36 day time span. How much xylene is left in the organic phase after 360 days (about one year) in which ten 1000 liter equilibrations will have occurred.

Organic Chemistry Review

Organic compounds contain carbon atoms. Isomers are compounds having the same formulas but different structures.

Hydrocarbons

Hydrocarbons are organic compounds containing carbon and hydrogen atoms. Each carbon atom has four electrons in the outer s and p orbitals, and can be used to make **four bonds** which can be in different combinations of single, double, and triple bonds. For the atoms being bonded, a single bond involves 2 electrons; a double bond, 4 electrons; and a triple bond, 6 electrons. Each hydrogen atom has only one electron to donate to make one bond. In the absence of radicals or carbonium ions, all four bonds of C are utilized in organic compounds, leading to 4 single bonds, or 2 single bonds and a double bond, or 1 single bond and a triple bond, or 2 double bonds.

Aliphatic Hydrocarbons

The **alkanes, alkenes, and alkynes** exist as straight chains and as branching chains with attachments. They do not form rings.

alkanes C_nH_{2n+2}
(paraffins)

only C-C bonds

methane CH_4

ethane C_2H_6

propane C_3H_8

butane C_4H_{10}

pentane C_5H_{12}

hexane C_6H_{14}

heptane C_7H_{16}

octane C_8H_{18}

nonane C_9H_{20}

decane $C_{10}H_{22}$

alkenes C_nH_{2n}
(olefins)

one C=C bond

ethene (ethylene) C_2H_4

propene (propylene) C_3H_6

butene (butylene) C_4H_8

pentene C_5H_{10}

hexene C_6H_{12}

heptene C_7H_{14}

octene C_8H_{16}

nonene C_9H_{18}

decene $C_{10}H_{20}$

alkynes C_nH_{2n-2}

one $C\equiv C$ bond

acetylene C_2H_2

propyne C_3H_4

butyne C_4H_6

pentyne C_5H_8

heptyne C_7H_{12}

octyne C_8H_{14}

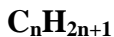
nonyne C_9H_{16}

decyne $C_{10}H_{18}$

Note that a **diene** has two C=C bonds with a general formula of C_nH_{2n-2} similar to that of an alkyne.

Loss of a H atom leads to the formation of **radicals which have an unshared electron**, making them very reactive. **Radicals do not carry a charge**, i.e., they are not ions.

alkyl radical



methyl CH_3

ethyl C_2H_5

propyl C_3H_7

butyl C_4H_9

allyl radical



Cyclic Aliphatic (Alicyclic) Hydrocarbons

These include **cycloalkanes** and **cycloalkenes**, formed into rings from the chains of alkanes and alkenes. The rings differ from the aromatic hydrocarbon rings which have a resonance nature, such that the structure oscillates between two isomers. An example of a cyclic aliphatic hydrocarbon is cyclohexane (C_6H_{12}) which can be considered to have formed from hexane (C_6H_{14}) by removing the two end hydrogens and joining the two end carbons together.

Aromatic Hydrocarbons (Arenes or Aryl Hydrocarbons)

Aromatic hydrocarbons form from derivatives of benzene rings C_6H_6 in which various radicals are attached to benzene rings through replacement of the hydrogens. Other aromatic compounds do not contain a benzene ring; however, they have similar chemical properties as benzene.

attachment of a single alkyl radical

methylbenzene (CH_3) C_6H_5 (**toluene**)

ethylbenzene (C_2H_5) C_6H_5

propylbenzene (C_3H_7) C_6H_5

butylbenzene (C_4H_9) C_6H_5

attachment of a single allyl radical

styrene (C_2H_3) C_6H_5

attachment of two alkyl radicals - Note that isomers arise because of the different possible positions on the benzene ring of the two alkyl radicals.

dimethylbenzene $\text{CH}_3\text{-(C}_6\text{H}_4\text{)-CH}_3$ (**xylene**)

ethylmethylbenzene or **ethyltoluene** $\text{CH}_3\text{-(C}_6\text{H}_4\text{)-C}_2\text{H}_5$

If the benzene ring has a very complicated attachment than the benzene ring is considered the radical and named as a derivative of the attachment instead of vice versa. **The C_6H_5 benzene radical is called a phenyl.** Whenever benzene rings are attached together through an alkane, they are generally named as derivatives of alkanes.

diphenylmethane $\text{C}_6\text{H}_5\text{-(CH}_2\text{)-C}_6\text{H}_5$

diphenylethane $\text{C}_6\text{H}_5\text{-(C}_2\text{H}_4\text{)-C}_6\text{H}_5$

Organic Functional Groups Containing O and H

Different classes of organic compounds are characterized by containing a specific functional groups. Often, the functional group is derived from a hydrocarbon by substitution of a particular radical group. Some of the characteristic functional groups are given below. R and R' stand for either aliphatic or aromatic groups.

Organic Compounds Formed by Adding O (always has a double bond or two single bonds) to Organic Groups.

Note that C=O is called a carbonyl group, named after carbonic acid H_2CO_3 which has the structure of HO-(C=O)-OH .

Alcohols

have an **-OH** group attached to an aliphatic group, i.e., **R-OH**. Examples include methanol, CH_3OH ; ethanol, $\text{C}_2\text{H}_5\text{OH}$; and propanol, $\text{C}_3\text{H}_7\text{OH}$. Phenols have an OH group attached to a benzene ring (hydroxy benzenes), e.g., phenol $\text{C}_6\text{H}_5\text{OH}$. Cresols have a methyl group attached to a phenol, $\text{C}_6\text{H}_4(\text{OH})\text{CH}_3$. Creosol, the active ingredient of creosote, has a methyl group and a methoxy group attached to a phenol, $\text{C}_6\text{H}_3(\text{OH})\text{CH}_3\text{OCH}_3$.

Aldehydes

have a **H-(C=O)-** attached to an aliphatic or aromatic group or to H, i.e., **R-(C=O)-H**. Examples are formaldehyde, H(C=O)H ; acetaldehyde, $\text{CH}_3\text{(C=O)H}$. Aldehydes are closely related to ketones, described below.

Acid Anhydrides

have a **-(C=O)-O-(C=O)-** equivalent to joining two carboxylic acids (described below) in which one $(\text{C=O})\text{OH}$ group has lost the OH and the other $(\text{C=O})\text{OH}$ group has lost a H atom and the two (C=O) groups bond through the single remaining O atom, i.e., **R-**

(C=O)-O-(C=O)-R'. The anhydrides are named after the corresponding carboxylic acid, e.g., acetic anhydride $[\text{CH}_3(\text{C}=\text{O})]_2\text{O}$ for acetic acid $\text{CH}_3(\text{C}=\text{O})\text{OH}$.

Carboxylic acids

can commonly be monocarboxylic or dicarboxylic acids.

Monocarboxylic acids

have a **-(C=O)-OH** group attached to an aliphatic or aromatic group or to H, i.e., **R-(C=O)OH**. Examples are formic acid, $\text{H}(\text{C}=\text{O})\text{OH}$; acetic acid, $\text{CH}_3(\text{C}=\text{O})\text{OH}$; propionic acid, $\text{C}_2\text{H}_5(\text{C}=\text{O})\text{OH}$; butyric acid, $\text{C}_3\text{H}_7(\text{C}=\text{O})\text{OH}$; benzoic acid, $\text{C}_6\text{H}_5(\text{C}=\text{O})\text{OH}$; cyclohexanecarboxylic acid, $\text{C}_6\text{H}_{11}(\text{C}=\text{O})\text{OH}$.

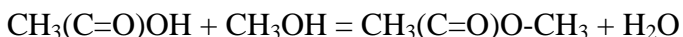
Dicarboxylic acids

have **two -(C=O)-OH** groups attached directly to each other or through an aliphatic or aromatic group, i.e., **HO(C=O)-R-(C=O)OH**. Examples are oxalic acid, $\text{HO}(\text{O}=\text{C})(\text{C}=\text{O})\text{OH}$; malonic acid, $\text{HO}(\text{O}=\text{C})\text{CH}_2(\text{C}=\text{O})\text{OH}$.

Esters

have a **-(C=O)-O-** group similar to the $-(\text{C}=\text{O})\text{OH}$ group in a carboxylic acid, except that the H has been replaced through the attachment of an aliphatic or aromatic group, i.e., **R-(C=O)O-R'**. Esters are formed by joining an alcohol with a carboxylic acid, releasing a water molecule. **Fats are esters**, generally triglycerides produced by reacting glycerol with three carboxylic acids. Esters are named after the corresponding carboxylic acid, e.g., ethyl acetate $\text{CH}_3(\text{C}=\text{O})\text{OC}_2\text{H}_5$ formed from reacting ethanol $\text{C}_2\text{H}_5\text{OH}$ with acetic acid $\text{CH}_3(\text{C}=\text{O})\text{OH}$ and releasing a water molecule.

An example of the reaction between a carboxylic acid and an alcohol to produce an ester (and releases a water molecule) is acetic acid + methanol = methyl acetate (ester) + water:



Ethers

have an **-O-** group joining two aliphatic or aromatic groups, i.e., **R-O-R'**. They are named by the two groups followed by the word *ether*. Examples are ethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$; methyl ethyl ether, $\text{CH}_3\text{OC}_2\text{H}_5$; phenyl ether, $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$. Note that only one of the groups need be named if they are identical groups. **Epoxides** are ethers in which an O is joined to two carbons that are also directly linked to each other, forming a three

member ring of two C atoms and an O atom. Epoxides are very reactive. An example is ethylene oxide, $\text{C}_2\text{H}_4\text{O}$.

Ketones

have a **$-(\text{C}=\text{O})-$** group attached to two aliphatic or aromatic groups, i.e., **$\text{R}-(\text{C}=\text{O})-\text{R}'$** . Examples are acetone, $\text{CH}_3(\text{C}=\text{O})\text{CH}_3$; methyl ethyl ketone, $\text{CH}_3(\text{C}=\text{O})\text{C}_2\text{H}_5$. See aldehydes above.

Organic Functional Groups Containing N, S, P, and Halogens

Numerous other organic compounds are formed by adding N, S, P, and halogens to organic groups.

Note that both N and P have five p and s outer shell electrons, allowing the formation of three single bonds and leaving a pair of unshared electrons. S has the same electronic configuration as O with six p and s outer shell electrons, allowing the formation of two single bonds and leaving two pairs of unshared electrons. These pairs of unshared electrons of N, P, and S allow for additional bonding, either from the direct sharing with another atom which lacks two electrons, e.g., P sharing its electron pair with S, or by partial donation of one of the electrons and then sharing the remaining electron, e.g., N, P, and S can do this with O to create a partial ionic bond. The halogens, F, Cl, Br, and I, lack one electron in their P orbitals in the outer shell and always form one bond.

Nitrogen normally has three bonds, e.g., ammonia NH_3 , and can form a positively-charged group by losing an electron through the addition of a 4th bond to a proton, e.g., ammonium, NH_4^+ . Nitrogen can also use all five electrons by forming 1 single bond (to R or OH), 1 double bond (to O), and one single bond with an ionic bond formed by donating an electron (to O).

Phosphorous usually forms three bonds but can also use the remaining pair of electrons, as a double bond with S or a mixture of 1 bond plus an ionic bond caused by donating one of the electrons to O.

Sulfur can form one bond each to two carbons (sulfide or thioether) or one bond to a carbon and one to a hydrogen (mercaptan or thiol) leaving two pairs of unshared electrons. Sulfur can also form 4 bonds as a sulfoxide, and 6 bonds as a sulfone. When S uses two electrons to bond with O, the bonding consists of sharing one electron and donating one electron to form an ionic charge. When S forms a double bond with C it shares both electrons to form a conventional C double bond.

Acid chlorides

contain the **$(\text{C}=\text{O})-\text{Cl}$** group and are similar to carboxylic acids in which the $(\text{C}=\text{O})\text{OH}$ has been replaced by $(\text{C}=\text{O})\text{Cl}$, i.e., **$\text{R}-(\text{C}=\text{O})\text{Cl}$** . They are named after the corresponding carboxylic acid, e.g., acetyl chloride $\text{CH}_3(\text{C}=\text{O})\text{Cl}$ for acetic acid $\text{CH}_3(\text{C}=\text{O})\text{OH}$.

Amides

have the $-(\text{C}=\text{O})-(\text{NH})-$ or $-(\text{C}=\text{O})-\text{NH}_2$. They are similar to carboxylic acids in which the OH group is replaced by an amine, e.g., $\text{R}-(\text{C}=\text{O})\text{NH}_2$. The amides are also named after the corresponding carboxylic acid, e.g., acetamide, $\text{CH}_3(\text{C}=\text{O})\text{NH}_2$ for acetic acid $\text{CH}_3(\text{C}=\text{O})\text{OH}$. The H atoms in NH_2 may be substituted for other organic groups. Amides link amino acids in peptide bonds to form proteins.

Amines

have a NH_2 , NH , or N attached to aliphatic or aromatic groups, i.e., $\text{R}-\text{NH}_2$. Examples are methylamine, CH_3NH_2 ; dimethylamine, $(\text{CH}_3)_2\text{NH}$; trimethyl amine, $(\text{CH}_3)_3\text{N}$; **aniline** is a benzene with an amine substituting for a H, $\text{C}_6\text{H}_5\text{NH}_2$. Amino acids contain an NH_2 group. The peptide linkage between the NH_2 on one amino acid and the $(\text{C}=\text{O})\text{OH}$ acid group on another amino acid, releases a water molecule, leaving $(\text{C}=\text{O})\text{NH}-$, an amide.

Carbamates

are derived from carbamic acid $\text{H}_2\text{N}-(\text{C}=\text{O})-\text{OH}$, losing a H from the OH group, and have the general formula of $\text{H}_2\text{N}-(\text{C}=\text{O})-\text{OR}$, e.g., $\text{NH}_2(\text{C}=\text{O})\text{OCH}_3$.

Organohalides

have halide elements, **F, Cl, Br, I** substituting for H in aliphatic or aromatic groups. Important examples are carbon tetrachloride (CCl_4), chloroform (CHCl_3), and freon (e.g., CCl_2F_2) formed from substitution of H in methane.

Nitriles

have a $-\text{C}\equiv\text{N}$ group with the nitrogen triple bond, i.e., $\text{R}-\text{C}\equiv\text{N}$. Cyanide $\text{C}\equiv\text{N}$ groups are nitriles. They hydrolyze to produce organic acids and are named after the corresponding carboxylic acid which forms by hydrolysis, e.g.,

acetonitrile $\text{CH}_3(\text{C}\equiv\text{N}) + 2\text{H}_2\text{O} = \text{acetic acid } \text{CH}_3(\text{C}=\text{O})\text{OH} + \text{NH}_3$.

Nitro compounds

have $-(\text{O}=\text{N}^+-\text{O}^-)$ attached to an aliphatic or aromatic group, i.e., $\text{R}-\text{NO}_2$. The N is sharing an electron with the R group, providing two electrons for one of the O atoms to form a double bond, providing two electrons for the second O atom in which one electron is shared and one is donated to leave the N^+ and O^- with an ionic bond, forming $\text{R}(\text{O}=\text{N}^+-\text{O}^-)$. Examples are nitromethane, CH_3NO_2 ; nitrophenol, $\text{C}_6\text{H}_4\text{OHNO}_2$; and nitroglycerin, $\text{C}_3\text{H}_5(\text{ONO}_2)_3$ which has a single bond between one O with N rather than one C with N. In nitric acid HNO_3 , an HO group replaces the R group, forming $\text{HO}(\text{O}=\text{N}^+-\text{O}^-)$.

Pyridine

compounds have **N substituting for CH in an aromatic group**, e.g., pyridine, C_5H_5N . Note that no H is attached to N in the aromatic structure because it only forms three bonds.

Sulfides

(thioethers) have **-S-** joining two aliphatic or aromatic groups, i.e., **R-S-R'**, e.g., dimethylsulfide, H_3CSCH_3 . The sulfur still has two pairs of unshared electrons.

Sulfoxides

have **-(O⁻-S⁺)-** connecting aromatic or aliphatic groups, i.e., **R-(O=S)-R'**, e.g., DMSO or dimethylsulfoxide $(CH_3)(O^--S^+)CH_3$. A sulfinic acid has the R' replaced by OH. The sulfur still has one pair of unshared electrons after providing two electrons for the bond to the oxygen.

Sulfones

have **-(O⁻-S²⁺-O⁻)-** groups attached between two hydrocarbon groups, e.g., dimethyl sulfone $CH_3SO_2CH_3$; whereas, sulfonates have $(O^--S^{2+}-O^-)O$ groups attached between hydrocarbon groups. Sulfonic acids have $(O^--S^{2+}-O^-)OH$ attached to an aromatic or aliphatic group, i.e., **R-(O⁻-S²⁺-O⁻)OH**, e.g., benzenesulfonic acid, $C_6H_5SO_2OH$. Detergents frequently have the structure of $R(O^--S^{2+}-O^-)O^-Na^+$ in which the R group is the hydrophobic end and the $(O^--S^{2+}-O^-)O^-$ is hydrophilic.

Thio and dithio acids

have **-(C=O)-SH** and **-(C=S)-SH groups**, respectively, attached to an aromatic or aliphatic group.

Thiols

(thio alcohols or mercaptans) have **-SH** attachments to an aliphatic or aromatic group, i.e., **R-SH**, e.g., methanethiol (methyl mercaptan) CH_3SH .

Synthetic Polymers

Polymers consist of long chains of molecules, made up from monomers. In the examples below, the monomers are linked together by replacing the double bonds between carbon atoms in the alkene monomers with single bonds.

polymer

polyethylene

polyvinylchloride

polypropylene

polystyrene

polyacrylonitrile

teflon

monomer

ethylene C_2H_4

chloroethylene C_2H_3Cl (vinyl chloride)

propylene $C_2H_3CH_3$

styrene $C_2H_3C_6H_5$

acrylonitrile C_2H_3CN

tetrafluoroethylene C_2F_4

Organic Matter (Proteins, Carbohydrates, and Lipids)

Proteins

Proteins are composed of linked amino acids, from a minimum of 40 to more than a 1000 amino acids. There are 22 naturally occurring amino acids, each of which contains an amino group (NH_2) and a carboxyl acid group ($C=O$)-OH bonded to CHR where R is another larger chemical group. In the simplest amino acid, glycine, R is a H atom, producing a formula of $H_2N-CH_2-(C=O)-OH$.

Amino acids are linked together by bonding between the NH_2 and the $COOH$ groups. The linkage forms a peptide bond $-(C=O)-(NH)-$ and results in the release of a water molecule.

Lipids

The most important lipids are the triglycerides, which form fats and oils and are esters. Fats are usually solid at room temperature; whereas, oils are liquid. Fats are generally from animals and oils are from plants; however, fish oils are a notable exception. A triglyceride molecule is made from one molecule of glycerol $[CH_2OH][CHOH][CH_2OH]$ linked to three carboxylic acids, $3R(C=O)OH$, where each R group represents a chain of carbon atoms. The linkage releases three water molecules, producing a triglyceride formula of $[CH_2R(C=O)O][CHR(C=O)O][CH_2R(C=O)O]$. The carboxylic acids may be the same or different in the lipid molecule. Variations in carboxylic acids produce different lipids.

Carbohydrates

The general formula often used for carbohydrates is CH_2O which is the reduced formula of a monosaccharide molecule which has 2 to 7 carbons. The simplest carbohydrates are monosaccharide molecules, e.g., glucose $C_6H_{12}O_6$. **They are alcohols and aldehydes or ketones.** The monosaccharide molecule glucose has a OH alcohol group linked to each C atom, with the exception of one end C atom which forms an aldehyde group $-(C=O)H$, e.g. for glucose $(HO)CH_2[HC(OH)]_4(C=O)H$. More complex carbohydrates result from linking monosaccharide molecules together through the release of water to form disaccharides and polysaccharides. Linkages are between the $(C=O)$

group on one monosaccharide and one of the OH groups on the other monosaccharide and are accompanied by the loss of one H and one OH group to form H₂O.

Water

Water Properties

The source of water in the hydrosphere is the result of degassing from the earth's interior through volcanic emissions over geologic time.

Hydrologic Cycle

- 1) atmospheric water vapor
- 2) transfer of atmospheric water to the land surface by rain, sleet, snow, hail
- 3) return of water vapor to the atmosphere by evaporation, transpiration, sublimation
- 4) surface water stored on land as streams, lakes, and glaciers, moving towards the oceans.
- 5) ground water stored underground, moving towards the oceans
- 6) oceans serve as the storage reservoir for most water
- 7) water trapped in the pores of sediments until released by erosion

In the continental U.S., the average precipitation is 76 cm/yr (30 in/yr). 53 cm/yr (21 in/yr) is returned by evaporation and transpiration. Of the remaining 23 cm/yr (9 in/yr), we use one third or 8 cm/yr (3 in/yr). Water use in this country amounts to 8% municipal, 46% industry, and 46% agriculture.

Water is an excellent solvent for ionic and polar (having a separation of charge) compounds due to its high dielectric constant and polar nature. Non-polar organic molecules are not very soluble in water; however, water provides the transport of nutrients and waste products for organisms.

Water's high surface tension results in the formation of drops in the presence of the atmosphere. The high surface tension reflects the low stability (high energy) of the interface between water and the atmosphere. Water tends to form shapes with a minimum surface area exposed to the atmosphere. This governs the shape of water particles in aerated soils as well as causing partially-wet sand grains to stick together.

Water is transparent to visible and ultraviolet wavelength which allows for photosynthesis in surface waters. With increasing depths, the red end of the spectrum

(long wavelengths) is filtered out, leaving the bluish colors. Underwater pictures taken below 50 feet show no red colors without artificial light.

Maximum density of waters occurs above its freezing point (4°C) at one atmosphere pressure. Ice floats because it is less dense than liquid water. Because ice floats on top of a lake, it insulates the water below, generally preventing lakes from freezing solid, protecting lake organisms.

In lakes, mixing often occurs in the spring and fall when surface waters have equal or greater density than deep waters. During the summer, lake waters increase in density with increasing depth, because the water temperature decreases. The warm surface layer (**epilimnion**) floats upon the cold bottom layer (**hypolimnion**), separated by the **thermocline** where the water temperature decreases rapidly with depth. In the fall, as surface waters cool, their density increases to the point that their density is equal or greater than the deep waters, producing mixing. In winter, surface waters colder than 4°C are less dense than the warmer, underlying waters. In spring, as the surface waters warm to 4°C, they become more dense than the underlying water, producing mixing.

Water has a high heat capacity (takes a lot of heat transfer to change its temperature), a high heat of evaporation (takes a lot of heat to evaporate water), and a high heat of fusion (takes a lot of heat to melt ice). These properties help to stabilize the temperature of water and allow it to act as a heat sink in controlling the surface temperature of the earth.

Lake Classification and Explanation of Wetlands, Reservoirs, and Estuaries

Oligotrophic lakes - deep, clear, nutrient deficient, lacking much biological activity, e.g., Lake Superior.

Mesotrophic lakes - intermediate between oligotrophic and eutrophic lakes, e.g., Lake Pontchartrain.

Eutrophic lakes - turbid, excess nutrients, much biological activity, characterized by swings in dissolved O₂ and pH due to algae photosynthesis and respiration, e.g., fresh-water lakes in swamp and marsh areas of south Louisiana.

Dystrophic lakes - shallow, clogged with plant life, low pH (due to respiration), colored water (due to organic compounds), fresh-water ponds and ditches in swamp and marsh areas of south Louisiana.

Wetlands - generally shallow flooded areas such as swamps and marshes; however, the U.S. Army Corps defines wetlands to include all areas with sufficient water-saturation of soil pores (wetland hydrology) to produce hydric soils and have a majority of hydric plants. (Hydric is a term which means wetlands). The precise amount of water saturation is a matter of dispute for the wetland hydrology. The Corps' definition in this area

includes most of the pine savannah of southern Louisiana and certainly almost all of Orleans and Jefferson Parishes that hasn't been previously filled in.

Reservoirs - Reservoirs have impounded water which allows suspended sediment to settle. They may hold the water for an appreciable time (storage reservoirs) or allow for more rapid flow-through (run-of-the-river reservoirs). Reservoirs generally have lower organic matter concentrations, less turbidity (due to lack of mixing), and less hardness (lower Ca and Mg content) due to precipitation of Ca and Mg minerals. However, the oxygen content is lowered because of decrease in mixing, pollutants accumulate, the bottom of the reservoir is no longer cleaned by scour from moving water, and photosynthetic algae growth is increased as the sediment falls out of suspension. As organic material accumulates at the reservoir bottom, oxygen is used up in bacterial decay processes and not replenished by mixing. Reducing conditions at the bottom promote the formation of undesirable components that are soluble under reducing conditions: hydrogen sulfide, ferrous iron, manganese.

Estuaries - drowned stream valleys where sea water mixes with fresh water, e.g., Barataria Bay. Estuaries have often been carved by rivers during times of lower sea level, e.g., an Ice Age. Note that a fiord is an estuary that was originally carved by a glacier during a time of lower sea level.

Aquatic Organisms

algae - single-cell and simple multi-cell plant-like organisms with simple sex organs, found in water and in wetlands. Note that algae undergo photosynthesis in the presence of light, giving off oxygen (raising the **pe**), using up CO₂ (raising the **pH**). However, in the dark, algae (like other plants) utilize oxygen in their metabolism (lowering the **pe**), giving off CO₂ (lowering the **pH**). Photosynthetic bacteria (cyanobacteria) are sometimes included in algae. Algae also include the dinoflagellates (in corals) and phytoplankton such as diatoms and calcareous nannoplankton. Algae can produce spores for reproduction that can remain inactive until favorable conditions exist.

autotrophs - organisms using solar energy to build organic matter (plant-like)

bacteria - single-cell (prokaryote) organisms that can be autotrophic or heterotrophic. Blue-green bacteria are autotrophic because they undergo photosynthesis. These are the cyanobacteria (algae) which produce stromatolites from algal mats. Other bacteria are aerobic heterotrophic, using oxygen to break organic matter down to carbon dioxide. Still other anaerobic bacteria reduce sulfur in sulfate as an energy source (*Desulfovibrio* genus). Aerobic bacteria (*Thiobacillus* genus) obtain energy by oxidizing hydrogen sulfide in their metabolism. Photosynthetic purple and green bacteria oxidize S²⁻ by reducing inorg. C to produce CH₂O. Strictly aerobic bacteria and strictly anaerobic bacteria are called **obligates**, and bacteria which can survive under aerobic and anaerobic conditions are **facultates**. Atmospheric environments in which the O₂ content is < 1% of the normal atmospheric value are anaerobic. Water compositions in which the dissolved

oxygen (DO) content is less than 1 ppm are anaerobic. The normal aerobic content is about 10 ppm.

Bacteria range from 0.3 to 50 μm in size. They can exist at temperatures from 0 to 80°C, and can be divided into bacteria with optima temperature below 20° (psychrophilic bacteria), 20 to 45°C (mesophilic bacteria), and above 45°C (thermophilic bacteria). Bacteria will grow exponentially with time until a limiting factor is encountered, e.g., presence of toxic material, depletion of essential nutrient, etc. The exponential growth is defined by

$$N = N_0 e^{kt}$$

where N is the population at time t, N_0 is the population at time t_0 and k is the growth rate constant. The value of k in the growth equation is based on first order kinetics, as in radioactive decay, with the difference that the change in time represents an increase rather than a decrease. Bacteria can produce spores for reproduction that can remain inactive until favorable conditions exist.

biota - living organisms (autotrophs and heterotrophs)

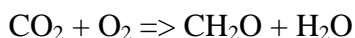
Fungi are heterotrophs or reducers and range from single-cell yeasts to multi-cellular toadstools. They are commonly filamentous and can secrete the enzyme cellulase to breakdown cellulose outside the fungal cells. Fungi can produce spores for reproduction that can remain inactive until favorable conditions exist.

Eutrophication - low-dissolved oxygen content (DO) in waters. Eutrophication forms from decay of organic matter in waters having high productivity. For example, waters adjacent to farmlands often become eutrophic in the spring, after collecting the runoff of nutrient-rich waters from fertilized fields. High nutrient content produces high productivity, followed by high biochemical oxygen demand (**BOD**) in the subsequent decay of the organic matter, lowering the **DO** content in waters.

heterotrophs - organisms using chemical energy to build organic matter (animal-like), including herbivores (plant eaters), omnivores (plant & animal eaters) and carnivores (animal eaters)

nutrients - nitrogen, phosphorous, (sometimes silicon and potassium) used in addition to carbon, hydrogen, and oxygen to build organic tissue. Plant growth can be limited by the amount of a nutrient present, either nitrogen or phosphorous. Fertilizers contain nutrients.

photosynthesis is the reaction utilizing solar energy, nutrients, water, and carbon dioxide to produce oxygen and organic tissue. In water, photosynthesis requires dissolved carbon dioxide. The general reaction is



productivity - ability of an H₂O body to produce living organisms

Respiration is the reaction utilizing chemical energy through a transformation such as oxygen reduction during the oxidation of organic matter to release energy and produce carbon dioxide and water. Respiration is the reverse of the above photosynthesis reaction and is used by bacteria in decay processes. In water, respiration requires dissolved oxygen which is present in only small amounts. Hence, decay processes can rapidly remove oxygen faster than it can be replenished from diffusion across the atmosphere-water surface, making anaerobic conditions.

Viruses cannot grow by themselves and are 1/20th to 1/30th the size of bacterial cells. We know little of their survival in natural waters.

Colloidal Particles, Flocculation and Coagulation

These are particles in suspension in solution and range in size from 0.001 μm to 1 μm . Their size range corresponds to that range of the wavelength of visible light, resulting in light-scattering ability. The particles are frequently stable because they are hydrated with water molecules which prevents the particles from aggregating or they have a surface charge which repels them. The surface charge is usually negative around a pH of 7.

The particles can be divided into three groups: hydrophilic, hydrophobic, and association.

Hydrophilic Colloids

These include bacteria and macromolecules such as proteins and synthetic polymers that have strong interactions with water through functional groups such as $-\text{CO}_2^-$ and $-\text{NH}_3^+$. These particles can be stable even without a surface charge (which would repel the particles to keep them from aggregating).

Hydrophobic Colloids

These particles interact less with water than the hydrophilic colloids. Their suspensions are stable because the charged surfaces repel each other. Examples include clays, Fe and Mn oxides, petroleum droplets. Under **pH** conditions of natural waters (6 to 9), most particles have negatively-charged surfaces. The solution layer nearest the surface has oppositely-charged ions (counter ions). The solid surface plus this adjacent solution layer are called the double layer. The surface charge can be neutralized by surface sorption of H^+ ions through the lowering of the pH or by shrinkage of the double layer through the addition of dissolved salts, resulting in coagulation to form aggregates that precipitate. The former is a technique used in the laboratory to induce coagulation and the latter occurs in estuaries when river water mixes with sea water. That is why sea water is clear, and river water is full of suspended sediment.

Association Colloids

These particles consist of aggregates of organic molecules and ions to form micelles, e.g., soap such as sodium stearate $[(\text{CH}_2)_{16}\text{CH}_2\text{CO}_2\text{Na}^+]$ and detergents. One end of the molecule or ion has a hydrophilic end which is hydrated with water molecules. The other end is organophilic and is unhydrated and tends to associate with other organophilic ends forming a micelle. An organic particle will be surrounded by the organophilic ends in a micelle.

Surface Charge Effects

The surface charge on a colloid can be due to sorption and desorption of H^+ and other ions, e.g., Fe and Mn oxides, or from ion replacement in the interior of the lattice, e.g., clays. In any solution, there will be a **pH** at which the surface charge is zero. This **pH** is called the zero point of charge (**ZPC**). If the only ions being sorbed and desorbed are H^+ , this **pH** is called the isoelectric point. At **pH** values above the ZPC, the surface will be negatively charged. Most particle surfaces are negatively charged in the **pH** range of natural waters.

The sorption and desorption of H^+ ions is tied in with the hydration of the surface. The absorbed water molecules may release or gain H^+ ions. Other ions, including ligands, may displace water molecules and attached directly to the surface. Anions, such as the phosphate ion (PO_4^{3-}), can be sorbed onto negatively-charged surfaces by the removal of hydroxides (OH^-).

Coagulation and Flocculation

Coagulation occurs with the neutralization of the surface charge, usually induced by the addition of dissolved salts, resulting in aggregation and precipitation.

Flocculation occurs when bridging compounds of polyelectrolytes and nonionic polymers form between colloidal particles. Polyelectrolytes are polymers that high formula weight that normally contain ionizable functional groups. The polyelectrolytes can be negatively charged, e.g., anionic polyelectrolytes (polyacrylate, $(\text{CH}_2)-(\text{CH}_2)-\text{CO}_2^-$) or positively charged, e.g., cationic polyelectrolytes (polyethyleneimine, $-(\text{CH}_2)-(\text{CH}_2)-\text{NH}_3^+$). An example of an uncharged nonionic polymer is polyvinyl alcohol ($\text{C}_2\text{H}_3\text{OH}$). The anionic polyelectrolyte is more effective in the presence of low metal concentrations, where the positively charged metals form a bridge to the negatively charged surfaces of the colloid and the polyelectrolyte.

Dissolved Oxygen and Carbon Dioxide

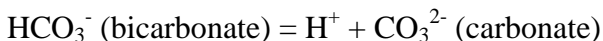
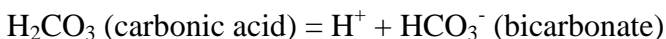
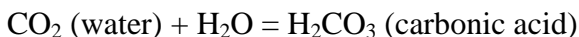
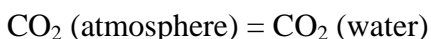
Dissolved oxygen (DO) and carbon dioxide concentrations are related to their solubilities in equilibrium with the atmosphere. In general, the solubility of gases is greater with decreasing temperatures, increasing pressures, and decreasing dissolved salt content. Lower temperatures reduce the thermal energy of gas molecules,

reducing their ability to leave the water. Higher external pressures prevent the escape of a gas molecule back to the atmosphere. Lower dissolved salt content frees up more water molecules to dissolve gas molecules, because dissolved salts bind water molecules (salting-out effect).

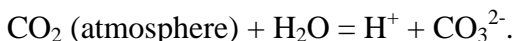
Aquatic photosynthetic organisms can add oxygen and remove carbon dioxide (driving up pH) while decay processes will remove oxygen and add carbon dioxide (lowering pH). Carbon dioxide has a much higher solubility than oxygen in water. The solubility of carbon dioxide increases as the pH rises due to the formation of HCO_3^- and CO_3^{2-} species. Surface waters, in contact with the atmosphere, can dissolve more atmospheric CO_2 if their pH rises. The pH of the water has no direct effect on the solubility of oxygen.

Dissolved carbon dioxide is frequently called inorganic carbon. It does not include carbon in organic molecules, such as carbohydrates.

The important reactions involving dissolved carbon dioxide are listed below. The first reaction involves two phases and can usually be assumed to be at equilibrium for surface waters. The remaining three reactions are at equilibrium within any aqueous phase.



Addition of all four reactions gives:



As the pH is raised, the H^+ concentration decreases, driving the reaction from left to right. For this reason, an aqueous solution with a high pH will absorb CO_2 from the atmosphere, lowering the pH, in an attempt to reach equilibrium with the atmosphere. The opposite is true at low pH values.

Excess carbon dioxide is usually present in ground waters due to CO_2 from bacterial decay processes. Ground water almost always has a higher dissolved CO_2 content (and a lower pH) than would occur through equilibrium with the atmosphere. For this reason, groundwater will release CO_2 when exposed to the atmosphere, e.g., as in a cave. The above reaction goes from right to left, raising the pH, in an attempt to reach equilibrium with the atmosphere.

Alkalinity, Acidity, and Hardness

Alkalinity is the capacity of water to neutralize H^+ ions and acidity is the capacity of water to neutralize OH^- ions. Most ground waters are basic, possessing alkalinity but no acidity. Acidity is rarely measured on water samples, except for low-pH, e.g., acid mine drainage, polluted samples.

The dominant cations in hard waters are calcium and magnesium; whereas, the dominant cations in soft waters are sodium and potassium. Hard waters with high alkalinities will have the capacity to precipitate calcium and magnesium hydroxides and calcium carbonates. The precipitate in coffee pots of calcium and magnesium hydroxides, is an example of precipitation in hard water. Soft waters will not precipitate salts upon standing, because sodium and potassium hydroxides and carbonates are very soluble. Soft waters usually have a lower pH than hard waters and tend to leach heavy metals from pipes making them more dangerous for drinking; however, they tend to lather easily and much more pleasant for showering than hard waters.

In practice, alkalinity is measured by recording the amount and strength of acid added until the solution pH is lowered to a particular value, e.g., 4.5 for inorganic carbon alkalinity. Below a pH of 4.5 all inorganic carbon is in the form of H_2CO_3 cannot accept more H^+ ions. Acidity is measured by recording the amount and strength of base added until the solution pH is raised to a particular value, usually a pH of 8.3. **Alkalinity and acidity are not affected by exchange of gases which change the solution pH, because gas exchange contains self-cancelling effects in the calculation of alkalinity and acidity.** However, precipitation and dissolution reactions will change alkalinity and acidity. Alkalinities on field samples are usually measured in the field on filtered samples.

Important Alkalinity Reactions in Natural Waters:

Inorganic Carbon: $CO_3^{2-} + 2H^+ = H_2CO_3$ and $HCO_3^- + H^+ = H_2CO_3$

Below a pH of 8.3, carbonate (CO_3^{2-}) is nearly absent. This pH is near the phenolphthalein end point which is pink in color above 8.2 pH. Below a pH of 4.5, bicarbonate (HCO_3^-) is nearly absent which is near the pH 4.3 end point of methyl orange. Below a pH of 4.5, all the inorganic carbon is in the form of dissolved CO_2 and carbonic acid H_2CO_3 , in which they are both called $H_2CO_3^*$. Without a pH meter, inorganic carbon alkalinity is often determined by titrating acid to the methyl orange end point. However, other H^+ neutralizing species may contribute to the alkalinity such as HS.

Water: $OH^- + H^+ = H_2O$

Hydrogen Sulfide: $HS^- + H^+ = H_2S$

Acetate: $CH_3COO^- + H^+ = CH_3COOH$

Alkalinity in meq/l is computed from the following formula in which the acid normality is in meq/l. To convert alkalinity to mg HCO_3^- /liter, multiply by the gram molecular weight of HCO_3^- . To convert alkalinity to mg CaCO_3 /liter, multiply by 1/2 the gram molecular weight of CaCO_3 .

$$\text{Alkalinity} = (\text{ml of acid added})(\text{normality of acid})/(\text{ml of sample})$$

The pH used as the final end-point in an alkalinity titration is the pH corresponding to the point where all species capable of accepting H^+ ion have been neutralized. In practice, this pH is easily found by recording the change in pH with a change in addition of acid. These end-points have rapid changes in pH with addition of acid and plot as an inflection point on a pH (y axis) versus mls of acid added (x axis). There may be more than one pH end-point for an alkalinity titration, e.g., inorganic carbon has two end points; 8.3 and 4.5. Organic acids generally have a lower pH end point than 4.5; whereas, hydrogen sulfide has a higher pH endpoint. In a mixture of different H^+ accepting groups, the end points are difficult to interpret. Below the final end point, a plot of pH versus ml of acid added will show by the continuous slope that the pH is changing only by the addition of H^+ ions without any neutralization of basic species.

Effects of Gas Exchange on Alkalinity

Gas exchange of the sample with the atmosphere that results in the loss of species such as HCO_3^- or HS^- can be written as:



The hydrogen ions used-up in forming the gases are from the solution. The solution is losing equivalent numbers of both hydrogen ions and species capable of accepting hydrogen ions. Hence, the solution pH will change but not the alkalinity.

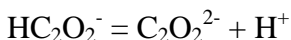
Alkalinity exercise to predict inflection points in which oxalate and bioxalate are titrated.

Listed below are the 25°C and 1 bar standard state Gibbs free energies of formation of different oxalate species. Assume the pH inflection points of an alkalinity titration occur when a species concentration has decreased to 1% of the total oxalic acid species concentration. What are the inflection points for titrating the alkalinity of a solution containing oxalic acid.

Component	cal/mol
H^+	0
$\text{C}_2\text{O}_4^{2-}$	-161,100
HC_2O_4^-	-166,907
$\text{H}_2\text{C}_2\text{O}_4^0$	-168,640

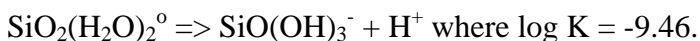
Use $R = 1.98716 \text{ cal/}^\circ\text{K/mol}$, $T = 298.15^\circ\text{K}$, $\log K = -G_r/(2.303RT)$

Procedure: Assume activities equal molalities for the oxalate species and find the pH for a ratio of 0.01 of the more protonated species to the less protonated species. The two necessary reactions are given below but you should be able to write out these reactions yourself.



Amphoteric Hydrated Cations (Metals) and Neutral Species

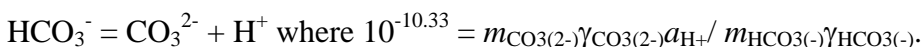
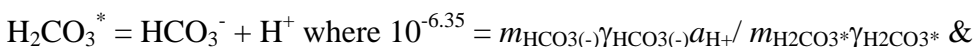
Cations and neutral species hydrated with water molecules can often donate H^+ , acting as an acid at high pH values. At low pH values, hydrated species can accept H^+ ions, acting as a base. For example, SiO_2 in solution actually exists as $\text{SiO}_2 \cdot 2\text{H}_2\text{O}^0$ or as it is sometimes written, H_4SiO_4^0 . At pH values above 9, it loses a H^+ to become H_3SiO_4^- and below a pH of 9, it gains back a H^+ to become H_4SiO_4^0



Cations which have several different hydrated forms in solution, will switch as a function of the solution **pH**. The result, as shown later, is that such cations are often much soluble in acidic and basic solutions than in neutral solutions.

Inorganic Carbon Species in Water

There are four species of inorganic carbon in water: CO_3^{2-} , HCO_3^- , H_2CO_3 , and CO_2 . Because of the difficulty in distinguishing between dissolved CO_2 and H_2CO_3 in measurements, the sum of the concentrations of these two species are treated together as H_2CO_3^* . We can calculate how the activities of the three species will vary with **pH** by using the equilibrium constants for the two reactions relating the three species.



where $10^{-6.35}$ and $10^{-10.33}$ are the equilibrium constants for the two reactions at 25°C and 1 bar. The conservation of mass for inorganic carbon is

$$m_{\text{inorg. C}} = m_{\text{H}_2\text{CO}_3^*} + m_{\text{HCO}_3(-)} + m_{\text{CO}_3(2-)}$$

As a first approximation, assume the activity coefficients are unity. Then by substitution for $m_{\text{H}_2\text{CO}_3^*}$ and $m_{\text{CO}_3(2-)}$ into the conservation of mass equation and solving for $m_{\text{HCO}_3^-}$ gives

$$m_{\text{HCO}_3(-)} = m_{\text{inorg. C}} / (a_{\text{H}^+} / 10^{-6.35} + 1 + 10^{-10.33} / a_{\text{H}^+})$$

Similar equations can be derived for $m_{\text{H}_2\text{CO}_3^*}$ and $m_{\text{CO}_3(2-)}$, allowing computation of the relative molal concentrations of each species as a function of pH and the actual molalities if $m_{\text{inorg. C}}$ is known. The classic exercise is to calculate the inorganic carbon fraction of each of the three inorganic carbon species as a function of pH.

At 25°C and 1 bar, the pH of an aqueous solution can only be lowered to about 4.5 by dissolving excess carbon dioxide, e.g., from respiration of organisms. Degassing carbon dioxide from a solution will raise the pH, e.g., from photosynthesis. Carbon dioxide is more soluble at high pH values than at low pH values. Calcite and other carbonate minerals will generally dissolve at low pH values and tend to precipitate at high pH values. Hence, if a ground-water sample, containing excess CO_2 from respiration, is allowed to degas CO_2 to the atmosphere, CaCO_3 may precipitate.

If an aqueous solution is in equilibrium with solid calcite at 25°C and one bar, a new equation links the molalities of H_2CO_3^* , CO_3^{2-} , and HCO_3^- with the pH and the molality of Ca^{2+} .

$$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-} \text{ where } 10^{-8.30} = m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} m_{\text{CO}_3(2-)} \gamma_{\text{CO}_3(2-)}$$

where the activity of CaCO_3 is not in the equation because it is unity for a pure solid substance. The solubility equation could also have been written as

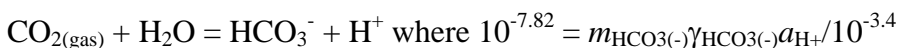
$$\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^- \text{ where } 10^{2.03} = m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} m_{\text{HCO}_3(-)} \gamma_{\text{HCO}_3(-)} / a_{\text{H}^+}$$

Both equations hold at equilibrium with calcite because HCO_3^- and CO_3^{2-} are in equilibrium with each other. Similarly, the calcite solubility equation could have been written to H_2CO_3^* .

The equilibrium constant for the above reaction, $10^{2.03}$ is equal to $10^{-8.30} / 10^{-10.33}$ because the reaction is equivalent to subtracting the HCO_3^- & CO_3^{2-} reaction with an equilibrium constant of $10^{-10.33}$ from the above calcite solubility reaction with an equilibrium constant of $10^{-8.30}$. If the two reactions had been added together to form a new reaction, the new equilibrium constant would have been the product of the two equilibrium constants. **The equilibrium constant for any new reaction can be computed from known equilibrium constants for reactions which can be added or subtracted to form the new reaction.** The only problem is that the equilibrium constants for those reactions may not be known.

If the solution is in equilibrium with the atmosphere at 25°C and 1 bar, then an additional equation can be written which constrains the amount of dissolved inorganic carbon in

water. The partial pressure of CO_2 is $10^{-3.4}$ in the atmosphere which is equal to the product of the mole fraction times atmospheric pressure ($X_{\text{CO}_2}P_{\text{ATM}}$). This is the activity of CO_2 in the atmosphere if the activity coefficient is one.



where the activity of water is not in the equation because it is assumed to be unity, and the activity of CO_2 in the atmosphere is about $10^{-3.4}$. As in the case for equilibrium with calcite, the equilibrium with CO_2 gas could also have been written to H_2CO_3^* or CO_3^{2-} .

We can calculate how much carbon dioxide will dissolve in distilled water with the above equation. The activity coefficient of any dissolved species is near unity in nearly pure water, so $\text{HCO}_3(-)$ and H^+ can be set to unity. Distilled water has a pH of 7 which means that all the inorganic carbon will be in the form of HCO_3^- . Each CO_2 molecule will produce one H^+ ion and one HCO_3^- ion. The H^+ ions produced by water disassociation are insignificant and can be ignored. Therefore, the concentration of HCO_3^- should be equal to the activity of H^+ ions. Thus,

$$10^{-11.22} = m_{\text{HCO}_3(-)}a_{\text{H}^+} \text{ and } m_{\text{HCO}_3(-)} = a_{\text{H}^+}, \text{ gives } m_{\text{HCO}_3(-)} = a_{\text{H}^+} = 10^{-5.61}.$$

So the pH would be 5.6 and the molality of dissolved inorganic carbon should be about $10^{-5.6}$. This is the reason that both rain water and laboratory-distilled water, equilibrated with the atmosphere, are slightly acidic.

Speciation, Complexation (Chelation), and Metal Solubility

The speciation in an aqueous solution involves the existing species and their concentrations. The species include many complexes in which various component species are bound together to form new species that can be charged or neutral. The bonding can be electrostatic; however, the bonding is more often covalent due to the sharing of electrons. In the absence of oxidation and reduction, complexes can always be assumed to be in equilibrium with the component species that unite to form them. For example, HCO_3^- is a complex of H^+ and CO_3^{2-} . **The concentration of any complex can be predicted using the equilibrium constant for the reaction forming the complex and the concentrations of the component species in the reaction.** In practice, computer programs are used to compute the speciation within an aqueous solution. The total concentrations of the fundamental components, e.g., Na^+ , Cl^- , etc, are input and the computer solves for the concentrations of all the different species using a series of mass-action equations (one for each complex) and their equilibrium constants plus a mass-balance equation for each fundamental component.

The negative (and sometimes neutral) component species in a complex is commonly called a ligand. Ligands bond to metals by donating or sharing electrons. A ligand with only one bonding site is a unidentate ligand. A ligand with more than one site for bonding is called a chelating agent. The more bonding sites on a ligand, the stronger are the complexes formed by the ligand with a metal. In general, most metals in natural waters

are complexed with ligands rather than existing as free species. This is particularly true of the contaminant metal ions which exist in trace concentrations and are usually in complexes. These complexes control the mobility of metals and determine if the metals precipitate out of solution. By complexing the metal, the solubility of the metal is increased, allowing it to move in ground water rather than precipitating out.

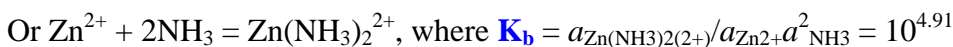
The metal component species in a complex is commonly positively charged. The coordination number of the metal is the number of ligands that are complexed to it. Each ligand donates electrons to fill an orbital on the metal ion. Polynuclear complexes contain two or more metal ions joined through bridging ligands, frequently OH^- .

In general, different metals will compete for the same ligands to form complexes. The mass-action law predicts that the metals with larger concentrations have a greater chance of forming a complex, so most of the ligands will be complexed to the most abundant metals. However, some ligands form much more stable complexes with certain metals, as reflected in their equilibrium constants, increasing the probability of complexing with those metals. For example, Na^+ is commonly the most abundant metal in solution; however, it forms weak complexes. In general, Na^+ and K^+ are less likely to form significant concentrations of complexes than other metals such as Ca^{2+} and Mg^{2+} .

Equilibrium constants for the bonding of more than one ligand to a metal can be written in two ways: as stepwise equilibrium constants or as overall equilibrium constants. For example, in water



where K_1 and K_2 are stepwise formation constants.



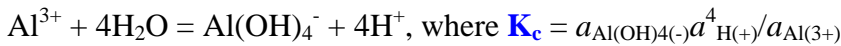
and K_b is the overall equilibrium constant for the addition of the two reactions. Note that $K_b = K_1K_2$

Some of the important ligands are OH^- , F^- , HCO_3^- , CO_3^{2-} , PO_4^{3-} , NH_3 , CN^- , HS^- , amino acids (NH_2RCOO^-), carboxylates (acetate, oxalate, citrate etc), pyrophosphate ($\text{P}_2\text{O}_7^{4-}$) and resulting chains of linear polyphosphates containing $(\text{P}_n\text{O}_{3n+1})^{(n+2)-}$, and synthetic compounds such as ethylenediamine-tetraacetate (EDTA), nitrilotriacetate (NTA, $\text{N}(\text{CH}_2\text{CO}_2)_3$). The humic substances are degradable-resistant organic materials and can be divided into humin, humic acid, and fulvic acid. Some humic substances can be extracted in a solution with a strong base. If this solution is acidified, the organic material which precipitates is called **humic acid**, and **fulvic acid** is the organic material that remains in solution. The non-extractable plant residue, left behind in the initial extraction with the strong base, is called **humin**.

The increase in solubility of a metal by complexation can be illustrated by aluminum which forms the Al^{3+} species in solution together with numerous complexes, involving inorganic and organic ligands. Aluminum solubility is controlled by gibbsite precipitation ($\text{Al}(\text{OH})_3$). The precipitation reaction is written as



where the activities of water and the pure solid gibbsite have been assumed to be unity. The solubility of aluminum is limited by the maximum value that the activity of Al^{3+} can have in the above equation, such that the ratio of $a_{\text{H}^+}^3 / a_{\text{Al}^{3+}}$ remains below K_s . With increasing activity of Al^{3+} , eventually gibbsite will precipitate. However, aluminum also form aqueous complexes with hydroxides and maintains equilibrium with these complexes, e.g.,



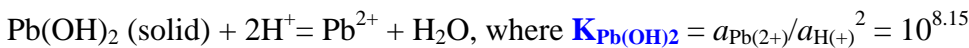
If the activity of Al^{3+} increases, more $\text{Al}(\text{OH})_4^-$ forms to maintain the reaction quotient equal to K_c , helping to keep the activity of Al^{3+} below the solubility of gibbsite.

For many metals that pollute the environment, their oxides are so insoluble that their concentrations in aqueous solutions would approximate zero in the absence of complexes. Predicting the solubilities of these metals in aqueous solutions, involves computing the concentrations of the important complexes in the solution.

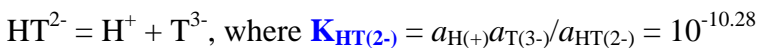
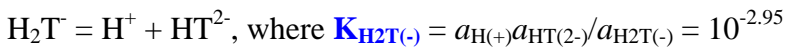
Lead Example, Assuming $a_{\text{H}_2\text{O}} = 1$, and $a_{\text{solid}} = 1$

Assume one kg of water in equilibrium with solid $\text{Pb}(\text{OH})_2$ is contaminated by the addition of 10^{-6} molal Nitrilotriacetic Acid, $\text{N}(\text{CH}_2(\text{C}=\text{O})\text{OH})_3$ and represented by H_3T . What concentrations of lead will be present in the solution at pH values of 4, 6, 8, and 10.

The mass-action law representing equilibrium between solid $\text{Pb}(\text{OH})_2$ and the aqueous solution is



The mass-action laws representing equilibrium between H_3T , H_2T^- , HT^{2-} , and T^{3-} in aqueous solution are:



Pb will be complexed by T to form PbT^- . The mass-action law is

$\text{Pb}^{2+} + \text{T}^{3-} = \text{PbT}^-$, where $\mathbf{K_{PbT(-)}} = a_{\text{PbT(-)}}/(a_{\text{Pb(2+)}}a_{\text{T(3-)}}) = 10^{11.39}$

The total concentration of lead in solution, $m_{\text{Pb aq.}} = m_{\text{Pb(2+)}} + m_{\text{PbT(-)}}$,

where $m_{\text{Pb2+}} = a_{\text{H(+)}}^2 \mathbf{K_{Pb(OH)2}}$ (from the solubility of Pb(OH)_2) and $m_{\text{PbT-}}$ can be solved from the known total molality for all T-bearing species, $m_{\text{T aq.}}$, if we assume activity coefficients are unity except for H^+ .

$$m_{\text{T aq.}} = 10^{-6} = [m_{\text{H3T}} + m_{\text{H2T(-)}} + m_{\text{HT(2-)}} + m_{\text{T(3-)}} + m_{\text{PbT(-)}}] = \\ [(m_{\text{H3T}}/m_{\text{PbT(-)}} + m_{\text{H2T(-)}}/m_{\text{PbT(-)}} + m_{\text{HT(2-)}}/m_{\text{PbT(-)}} + m_{\text{T(3-)}}/m_{\text{PbT(-)}} + 1] \\ m_{\text{PbT(-)}} \text{ or } m_{\text{PbT-}} = 10^{-6}/[(m_{\text{H3T}}/m_{\text{PbT(-)}} + m_{\text{H2T(-)}}/m_{\text{PbT(-)}} + m_{\text{HT(2-)}}/m_{\text{PbT(-)}} + m_{\text{T(3-)}}/m_{\text{PbT(-)}} + 1]$$

where $m_{\text{T(3-)}}/m_{\text{PbT(-)}} = 1/m_{\text{Pb(2+)}} \mathbf{K_{PBT(-)}} = 1/[(a_{\text{H+}}^2 \mathbf{K_{Pb(OH)2}}) \mathbf{K_{PbT(-)}}]$ and

$$m_{\text{HT(2-)}}/m_{\text{PbT(-)}} = m_{\text{T(3-)}}/m_{\text{PbT(-)}} [a_{\text{H+}}/\mathbf{K_{HT(2-)}}] = [1/[(a_{\text{H+}}^2 \mathbf{K_{Pb(OH)2}}) \mathbf{K_{PbT(-)}}]] [a_{\text{H+}}/\mathbf{K_{HT(2-)}}]$$

etc, for $m_{\text{H2T(-)}}/m_{\text{PbT(-)}}$ and $m_{\text{H3T}}/m_{\text{PbT(-)}}$.

What if there was a question as to which solid was maintaining equilibrium with lead? It will always be the solid giving the lowest lead solubility. For example, PbCO_3 will control lead solubility rather than Pb(OH)_2 , if the $m_{\text{CO3(2-)}}$ is high enough that the amount of Pb^{2+} in equilibrium with PbCO_3 is less than in equilibrium with Pb(OH)_2 .

If the solution is in equilibrium with the atmosphere which has a partial pressure for CO_2 of $10^{-3.5}$, the relevant equation is between the solid PbCO_3 and atmospheric CO_2 .

$$2\text{H}^+ + \text{PbCO}_3 \text{ solid} = \text{Pb}^{2+} + \text{CO}_2 \text{ gas} + \text{H}_2\text{O} \text{ where } \mathbf{K_{PbCO3}} = a_{\text{Pb(2+)}}a_{\text{CO2(gas)}}/a_{\text{H(+)}}^2 = 10^{5.33}.$$

Therefore, $a_{\text{Pb(2+)}} = \mathbf{K_{PbCO3}}/a_{\text{H(+)}}^2/a_{\text{CO2(gas)}}$.

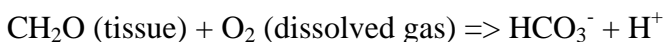
So for the above example of the solubility of Pb in the water solution, if a given concentration of inorganic carbon was present, say 10^{-2} , than $m_{\text{Pb2+}}$ would have to be computed at a particular pH using equilibrium with Pb(OH)_2 and with PbCO_3 , and the one with the lowest solubility is the solid maintaining equilibrium. The \mathbf{K} for that equilibrium would then be used in the expression for $m_{\text{PbT(-)}}$ in the total concentration of all species containing T.

The problem is more complicated if we assume non-equilibrium with respect to the atmosphere and if more Pb complexes are included, e.g., Pb(OH)^+ and Pb(OH)_3^- .

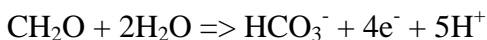
Oxidation-Reduction (Redox) Reactions

Oxidation-reduction reactions involve the transfer of electrons. Components lose electrons when oxidized (become more positively charged), and components gain electrons when reduced, (become more negatively charged). As previously discussed, aqueous environments having components present in their reduced form have a negative pe or Eh environment; whereas, aqueous environments having components present in their oxidized form have a positive pe or Eh environment. Oxidizing environments generally have O₂ and are called aerobic; whereas, reducing environments lack O₂ (less than 1 ppm in aqueous solution) and are called anaerobic. pe is the negative log of the activity of aqueous electrons and Eh can be computed from the pe (Eh = 2.303 RT pe F = 16.90 pe). Because redox reactions often involve the transfer of H⁺ ions, changes in pe and pH are related. Just as with pH in which a low pH means a high activity of H⁺ ions, a low (negative) pe or Eh means a high activity of aqueous electrons.

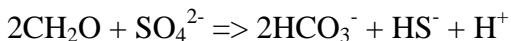
Respiration in animals involves the oxidation of carbon in tissue and the simultaneous reduction of oxygen. In an aqueous environment, respiration becomes



The overall reactions can be written as the sum of two half-cell reactions with the same number of electrons in the reactants and products.

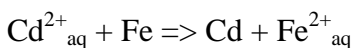


In the absence of oxygen, other components serve to accept electrons and be reduced. There is a sequence in which bacteria switch from using O₂ in respiration to NO₃⁻, to Fe³⁺, and Mn⁴⁺, to SO₄²⁻. After oxygen is used up, the N⁵⁺ in nitrate is reduced to N⁰ during denitrification; then the Fe³⁺ and Mn⁴⁺ in ferric and manganese minerals are reduced to Fe²⁺ and Mn²⁺; and finally the S⁶⁺ in sulfate is reduced to sulfide S²⁻. In each case, the reduction is accompanied by the oxidation of carbon tissue, e.g.,



Oxidation and reduction reactions are important in controlling metal mobility and the stability of various organic contaminants that can be destabilized by oxidation.

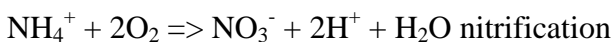
For example, metallic cadmium (Cd) will precipitate out when aqueous Cd²⁺ comes in contact with metallic iron (Fe). Cd is reduced and Fe is oxidized.



Iron in the ferrous state (Fe²⁺) is generally soluble (in the absence of aqueous sulfide); however, iron in the ferric state (Fe³⁺) is generally insoluble. So if the oxidation of Fe

goes only to Fe^{2+} , in the above example, soluble Cd^{2+} has been replaced by soluble Fe^{2+} . Iron in the Fe^{3+} state will generally precipitate out as $\text{Fe}(\text{OH})_3$ or iron hydroxides.

Nitrogen can be in the form of nitrate (NO_3^-) or (less commonly) ammonia (NH_3) to be used by plants in making tissue. In general, N^{3-} in ammonia (NH_3) or ammonium (NH_4^+), from decaying plants, is oxidized to N^{5+} in nitrate, e.g., nitrification before being taken in by plants. The plant tissue uses nitrogen in amines so the plant reduces nitrate to ammonia.



pe can be calculated for any solution using measured solution concentrations of the oxidized and reduced components and other activities such as the pH. A half reaction is written between the reduced and oxidized components in which aqueous electrons appear in either the products or reactants. For example, the half reaction for the oxidation of N in the nitrification reaction can be written:



In log units, the log K can be written as follows:

$$\log K = \log a_{\text{NO}_3(-)} + 8\log a_{\text{e}(-)} + 10 \log a_{\text{H}(+)} - \log a_{\text{NH}_4(+)} - 3\log a_{\text{H}_2\text{O}}.$$

If we assume $a_{\text{H}_2\text{O}} = 1$ (because the aqueous solution is dominantly H_2O) and substitute in the definitions for **pH** and **pe**, we have

$$\log K = \log (a_{\text{NO}_3(-)}/a_{\text{NH}_4(+)} - 8\text{pe} - 10\text{pH}$$

Assuming the **K** of the half reaction is known (from thermodynamics) then solution data can be used to compute **pe**.

pe and **pH** diagrams are frequently used to represent the stability fields of components involved in redox reactions. The y axis is used for **pe** and the x axis is used for **pH**. The approximate stability boundaries of water under surface conditions are plotted on the diagram using the mass-action expressions for the following reactions at an activity of 1 for H_2 and 1 for O_2 gases (meaning their partial pressures are about 1) and assuming unit activity for water (H_2O):



$$K = 1 = a_{\text{H}_2}/[a_{\text{H}(+)}^2 a_{\text{e}(-)}^2] \text{ or (in log space)}$$

$$0 = \text{pH} + \text{pe} \text{ for minimum pe of water stability;}$$

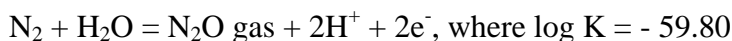
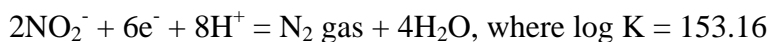
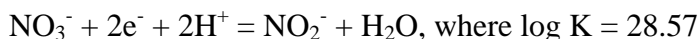
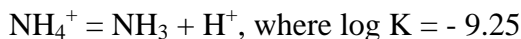
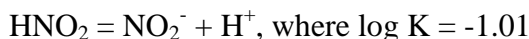
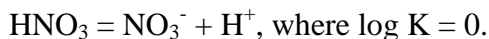


$$K = 10^{(20.78)/4} = a_{\text{H}_2\text{O}}^2 / [a_{\text{O}_2} a_{\text{H}^{(+)}}^4 a_{\text{e}^{(-)}}^4] \text{ or (in log space)}$$

$20.78 = \text{pH} + \text{pe}$ for maximum **pe** of water stability.

Remember that the activity of a gas is computed from $a_i = X_i \chi_i P$. An activity of unity will occur when a gas component exerts a pressure of 1 atm and behaves ideally (doesn't interact with other gas components). Gases are nearly ideal at low pressures, so unity activity can be approximated by single-component gas phases at 1 atm pressure. The **K** values for the reactions above are for 25°C and 1 atm pressure.

A **pe** and **pH** diagram can be constructed for the nitrogen system containing aqueous HNO_3 , NO_3^- , HNO_2 , NO_2^- , N_2 , NH_4^+ , and NH_3 in the presence of water and N_2 and N_2O in a gas phase at 25°C and 1 bar. Reactions linking the species together along with their log **K** values are given below. We will do this diagram in class.



A **pe** and **pH** diagram can also be constructed for the sulfur system containing aqueous H_2S , HS^- , HSO_4^- , SO_4^{2-} , and solid sulfur (S) in the presence of water.

The following reactions define the stabilities of these components. Set the activity of solid S to one, implying that it is a pure solid. Stability boundaries between aqueous components occur at equal activities. Assume activity coefficients of aqueous species are unity except for H^+ ions and aqueous e^- .



$$\text{or } 41.0 = 10\mathbf{pH} + 8\mathbf{pe} \text{ when } m_{\text{H}_2\text{S}} = m_{\text{SO}_4^{2-}}$$



$$5) \text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- = \text{HS}^- + 4\text{H}_2\text{O}, \log K_5 = 34.0 = \log[m_{\text{HS}(-)}/m_{\text{SO}_4(2-)}] + 9\text{pH} + 8\text{pe}$$

$$\text{or } 34.0 = 9\text{pH} + 8\text{pe} \text{ when } m_{\text{HS}(-)} = m_{\text{SO}_4(2-)}$$

$$6) \text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+, \log K_6 = -2.0 = \log[m_{\text{SO}_4(2-)} / m_{\text{HSO}_4(-)}] - \text{pH}$$

$$\text{or } 2. = \text{pH} \text{ when } m_{\text{HSO}_4(-)} = m_{\text{SO}_4(2-)}$$

$$7) \text{H}_2\text{S} = \text{H}^+ + \text{HS}^-, \log K_7 = -7.0 = \log[m_{\text{H}_2\text{S}} / m_{\text{HS}(-)}] - \text{pH}$$

$$\text{or } 7.00 = \text{pH} \text{ when } m_{\text{H}_2\text{S}} = m_{\text{HS}(-)}$$

$$8) \text{HS}^- = \text{S}^{2-} + \text{H}^+, \log K_8 = -12.92 = \log[m_{\text{S}(2-)} / m_{\text{HS}(-)}] - \text{pH}$$

$$\text{or } 12.92 = \text{pH} \text{ when } m_{\text{S}(2-)} = m_{\text{HS}(-)}$$

Reactions 2, 5, 6, 7 and 8 can be plotted as lines on a pe and pH diagram, as can the stability boundaries of water. This is done in each case by assuming two pH values and calculating the corresponding pe values for each reaction. This gives two points that define a straight line. Draw the lines on the diagram. Where lines intersect there will be metastable extensions of stability boundaries which have to be eliminated (as will be discussed in class). Reactions 1, 3, and 4 contain other variables besides pH and pe and must be handled with a conservation of mass equation, similar to that done with in the organic carbon problem.

The conservation of mass equation for total aqueous sulfur is

$$m_{\text{S aq.}} = m_{\text{HSO}_4^-} + m_{\text{SO}_4(2-)} + m_{\text{H}_2\text{S}} + m_{\text{HS}^-} + m_{\text{S}(2-)}$$

Assume a total molality $m_{\text{S aq.}}$ of 0.01 and substitute from the mass-action expressions that link the species to solve for $m_{\text{SO}_4(2-)}$ in the first mass-action expression and do the same $m_{\text{H}_2\text{S}}$ and $m_{\text{HSO}_4(-)}$ with the expressions for reactions 3 and 4. In each of these mass-action expressions, the mass conservation equation for the aqueous component will be written in terms of pe and pH. The boundary lines plotted on pe and pH diagram will be curves for these three boundaries.

For example, an expression for $m_{\text{HSO}_4(-)}$ can be written to use in equation (4) by using the mass balance equation and several of the mass-law equations.

$$\begin{aligned} m_{\text{HSO}_4(-)} &= m_{\text{S aq.}} / [1 + m_{\text{SO}_4(2-)} / m_{\text{HSO}_4(-)} + m_{\text{H}_2\text{S}} / m_{\text{HSO}_4(-)} + m_{\text{HS}^-} / m_{\text{HSO}_4(-)} + m_{\text{S}(2-)} / m_{\text{HSO}_4(-)}] \\ &= m_{\text{S aq.}} / [1 + m_{\text{SO}_4(2-)} / m_{\text{HSO}_4(-)} + (m_{\text{H}_2\text{S}} / m_{\text{SO}_4(2-)})(m_{\text{SO}_4(2-)} / m_{\text{HSO}_4(-)}) + \\ &\quad (m_{\text{HS}^-} / m_{\text{SO}_4(2-)})(m_{\text{SO}_4(2-)} / m_{\text{HSO}_4(-)}) + (m_{\text{S}(2-)} / m_{\text{SO}_4(2-)})(m_{\text{SO}_4(2-)} / m_{\text{HSO}_4(-)})] \\ &= m_{\text{S aq.}} / [1 + 10^{-2} / a_{\text{H}(+)} + (10^{41} a_{\text{H}(+)}^{10} a_{\text{e}(-)}^8)(10^{-2} / a_{\text{H}(+)}) + (10^{34} a_{\text{H}(+)}^9 a_{\text{e}(-)}^8)(10^{-2} / a_{\text{H}(+)}) + \dots] \end{aligned}$$

Plot the nine boundaries plus the two for the stability of water on a pe-pH diagram. Parts of the boundary lines will be metastable and should be erased. These metastable boundaries are recognized by one or both of the components being metastable in that region of the diagram.

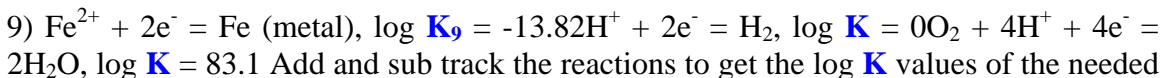
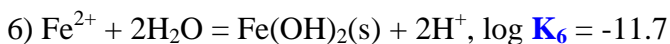
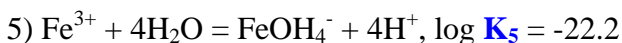
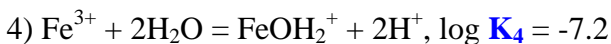
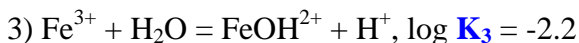
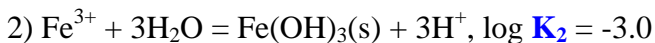
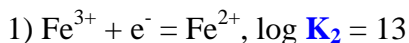
Short Cut

To obtain the boundaries between S and H₂S, SO₄²⁻, and HSO₄⁻, assume that their molalities are equal to total aqueous sulfur in the specific pH and pe regions where they are the dominant species. That way, there is no need to substitute the conservation of mass equation back into the mass-action expressions.

Homework Problem

Plot on a **pe** and **pH** diagram, at 25°C and 1 bar, the stability fields in the FeO, Fe₂O₃, H₂O, CO₂ system considering the aqueous species Fe³⁺, FeOH²⁺, Fe(OH)₂⁺, Fe(OH)₄⁻, Fe²⁺, FeOH⁺, the amorphous iron hydroxides Fe(OH)₃, Fe(OH)₂, the iron carbonate (siderite) FeCO₃ and the iron metal Fe. Plot from -20 to +20 for pe on the y axis and from 0 to 15 for pH on the x axis. Overlay the stability field of water in which the log a_{O2} and log a_{H2} are zero at the high and low pe values, respectively, and assume the log a_{CO2} is at its atmospheric value of 10^{-3.5} bars. Assume activity coefficients are one. Assume that the total molality of the aqueous Fe species is 10⁻⁵. Use the short-cut procedure described above for the S system.

Use the log **K** information given below. Note that unless otherwise stated, all species are aqueous.



reactions. Show your work. Comment on what the diagram tells you about the solubility of iron and the forms that it exists in within aqueous solution.

Discussion of homework

pe-pH diagram

The pe and pH diagram was done at 25°C and 1 bar in the FeO, Fe₂O₃, H₂O, CO₂ system with the constraints that the sum of the aqueous iron species was limited to 10⁻⁵, the activities of H₂O and solids were 1, total activity of gaseous CO₂ was 10^{-3.5}, and aqueous activity coefficients were 1. Four solids [(Fe(OH)₃, Fe(OH)₂, FeCO₃ (siderite) and Fe metal] were considered in the diagram. Six aqueous species were considered: Fe³⁺, Fe(OH)²⁺, Fe(OH)₂⁺, Fe(OH)₄⁻, Fe²⁺, and Fe(OH)⁺.

Procedure

Initially, the pe-pH fields of the different aqueous species were mapped to determine the areas where their concentrations could be set equal to 10⁻⁵. The reactions were written between the different iron solids (minerals) that were balanced on iron so that aqueous iron did not enter the reactions. Reactions involving FeCO₃ used 10^{-3.5} for the activity of gaseous CO₂. The reaction between FeCO₃ and Fe(OH)₂ showed that at this level of CO₂, siderite was stable over Fe(OH)₂. After drawing the boundaries between the phases, then solution boundaries were drawn with the dominant aqueous iron species activity set to 10⁻⁵. Metastable boundaries were eliminated when the aqueous iron species used in the reaction produced a boundary in which it wasn't the dominant iron species.

Results

The boundary between an iron mineral and the aqueous solution occurs at equilibrium with a total aqueous iron molality of 10⁻⁵. An increase in aqueous iron would expand the mineral field at the expenses of the solution field. Within the stability field of each iron mineral, the total equilibrium iron molality is less than 10⁻⁵, i.e., the iron mineral controls the amount of iron in solution, and can immobilize iron in the solid phase.

The solution phase with 10⁻⁵ total molality of iron is at low pH and very high pH (above 4). In general, iron minerals limit aqueous iron over a solution pH range that increases going from 8 to 14 to 3 to 14 as the pe rises from low pe to high pe. Increasing the amount of CO₂ would increase this pH range at low pe because the siderite field would expand into the solution field. An increase of CO₂ would be expected in ground water due to bacteria respiration in soils. Note that metallic iron has no stability field within the general stability field of water, corresponding to the general observation that iron is unstable and rusts if exposed to the atmosphere.

It would be interesting to use aqueous equilibrium with the iron minerals to contour total aqueous iron in the stability fields of the minerals but you will be doing this with your Minteq exercise.

Take Home Test Problem

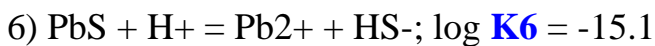
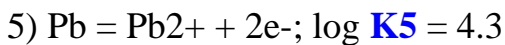
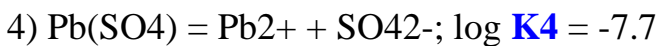
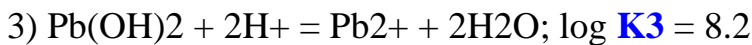
The problem is similar to the iron problem described above except that inorganic carbon is not controlled by equilibrium with the atmosphere and metal sulfides have been added as a possibility.

Plot on a **pe** and **pH** diagram, at 25°C and 1 bar, **the mineral and aqueous stability fields** in the Pb & PbO, SO₃ & H₂S, CO₂, and H₂O, system considering the aqueous species Pb²⁺, PbOH⁺, H₂CO₃⁰, HCO₃⁻, CO₃²⁻, HSO₄⁻, SO₄²⁻, H₂S⁰, HS⁻, and S²⁻. Consider the following Pb solids: Pb (metal), Pb(OH)₂, PbCO₃ (cerussite), PbS (galena), and PbSO₄ (anglesite). Plot from -20 to +20 for pe on the y axis and from 0 to 15 for pH on the x axis. Overlay the stability field of water in which the log *a*_{O₂} and log *a*_{H₂} are zero at the high and low pe boundaries, respectively. The total amount in moles (in solution and in the solids) per kilogram of water is 0.002 for inorganic carbon, 0.0005 for S as sulfate plus sulfide, and 0.00001 for lead. Assume the activity coefficients are one.

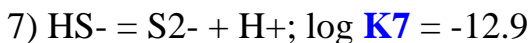
Contour the total aqueous concentration of lead (Pb²⁺ + Pb(OH)⁺) on the diagram and **comment on what the diagram says about the mobility of lead in ground water**. Note that a total sulfur concentration of 0.002 molal units is about 200 mg/l which is higher than normal by about a factor of 4 but the total inorganic carbon concentration is about average.

Use the following information.

Aqueous Pb species

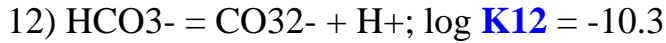
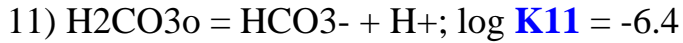


Sulfide and sulfate aqueous species

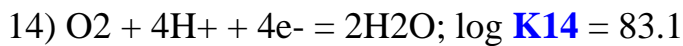
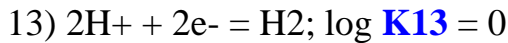




Inorganic carbon aqueous species



Water stability boundaries



OK Class - I just finished it (midnight on 12/11/02).

First - I changed the total aqueous sulfur concentration (when no solids are present) to 0.0005. I already made the change above in the problem description. Second, Check the minerals: PbS, PbSO₄, and PbCO₃ to see there is enough aqueous sulfide, aqueous sulfate, and aqueous carbonate to precipitate them; i.e., use the log K and 0.00001 for the lead concentration in the dissolution of each mineral to see if the computed equilibrium concentrations of aqueous sulfide, aqueous sulfate, and aqueous carbonate are less than the total concentrations given for sulfur and inorganic carbon. Ignore any mineral that cannot be precipitated. Third, Do the problem in steps. Begin with the two aqueous lead species and the Pb(OH)₂ mineral and derive the stability boundaries. Then add inorganic carbon to the system to see if PbCO₃ is present. If so, modify the previous stability boundaries and insert the phase. Then add aqueous sulfur to the system to see if PbS and/or PbSO₄ is/are present. If so, then modify the previous stability boundaries to insert these phases. Then try to contour the total aqueous lead over the mineral stability fields. If the addition of aqueous sulfur is too tough then stop with the addition of inorganic carbon and contour the aqueous lead concentrations for those mineral stability fields for partial credit.

Good Luck Dudes!

Pollutant Retardation

As previously shown the retardation factor for the downstream movement of the concentration front of contaminant A can be predicted using a mass balance across the front.

$$(\text{moles of } A_{\text{solution}} + A_{\text{rock}}) / \text{moles of } A_{\text{solution}} = [1 + \text{moles of } A_{\text{in rock}} / \text{moles of } A_{\text{solution}}]$$

The **velocity** of contaminant A, v_A , becomes $v_A = v_{\text{fluid}} / [1 + \text{moles } A_{\text{in rock}} / \text{moles } A_{\text{in solution}}]$

in which the denominator is usually called the **retardation factor** R_f .

If the source maintains a constant concentration of the contaminant, then the velocity is often approximately that of the center of the concentration front moving downstream. Typically the center is at a concentration of 50% of the source concentration because dispersion and diffusion will produce a concentration front over a finite distance in which the 50% concentration is at the center of the front. Cation exchange can skew the concentration front so that the center is no longer at 50% concentration. If the Distribution Coefficient applies,

$$\text{The moles of } A_{\text{in rock}} / \text{moles of } A_{\text{in solution}} = (KD_{\text{CES}} \text{ kg rock } \rho_{\text{rock}}) / (\tau_{\text{rock}} a)$$

where **KD**, the Distribution coefficient is a Freundlich constant with unit exponent with units of charge fraction of cation exchange sites/moles of A per liter of solution. $CE_{\text{Skg rock}}$ is the equivalents of cation exchange sites per kg of rock. ρ_{rock} is the density of the dry rock (kg rock/liter rock), τ_{rock} is the porosity fraction of the rock (liter fluid/liter rock), and a is the charge valence of A.

If **KD*** has units of mole fraction of cation exchange sites/moles of A per kg of water then divide by ρ_{fluid} , the density of the fluid, times $[1 - (\text{tds}/106)]$, i.e.,

$$\text{The moles of } A_{\text{in rock}} / \text{moles of } A_{\text{in solution}} = (KD^* CE_{\text{Skg rock}} \rho_{\text{rock}}) / (\tau_{\text{rock}} \rho_{\text{fluid}} a [1 - (\text{tds}/106)])$$

One Dimension Mass Transport of a metal Bb^+ or a neutral organic molecule B

The one dimensional partial differential equation describing contaminant movement with sorption, decay, and reaction terms is:

$$[\partial MBb^+ / \partial t]_x = D[\partial^2 MBb^+ / \partial x^2]_t - v_x [\partial MBb^+ / \partial x]_t - CE_{\text{Crock}} \rho_{\text{rock}} / (\tau_{\text{rock}} b) [\partial X_B / \partial t]_x, \text{sorption}$$

$$+ [\partial MBb^+ / \partial t]_x, \text{decay} + \varpi_{i,B} [\partial n_i / \partial t]_x, \text{reaction}$$

where M_{Bb+} is the molarity in moles per liter of solution, t is the time in sec, D is the combined diffusion and dispersion coefficient in cm^2/sec , x is the distance in cm, v_x is the x velocity in cm/sec , CEC is the exchange capacity in equivalents/kg of rock, ρ_{rock} is the rock density in kg/liter , τ_{rock} is the rock porosity fraction, b is the absolute value of the charge, X_B is the charge fraction of B on the exchange sites, $\omega_{i,B}$ is the reaction coefficient for B_{b+} in the i th chemical reaction in which n_i moles of a substance is precipitated or dissolved per liter of solution. If a substance is precipitated, $\omega_{i,B}$ is negative and positive if a substance dissolves.

If instead of a dissolved ion, B is a neutral organic molecule which is being sorbed on and off surfaces and undergoing decay then

$$\begin{aligned} \left[\frac{\delta M_B}{\delta t} \right]_x = & D \left[\frac{\delta^2 M_B}{\delta x^2} \right]_t - v_x \left[\frac{\delta M_B}{\delta x} \right]_t - N_{\text{rock}} \rho_{\text{rock}} / (\tau_{\text{rock}}) \left[\frac{\delta X_B}{\delta t} \right]_x, \text{ sorption} \\ & + \left[\frac{\delta M_B}{\delta t} \right]_x, \text{ decay} + \omega_{i,B} \left[\frac{\delta n_i}{\delta t} \right]_x, \text{ reaction} \end{aligned}$$

where N_{rock} is the moles of sites per kilogram of sediment and X_B is the mole fraction of B on the sites.

If radioactive decay B_{b+} or bacterial decay is removing B from the aqueous solution, then

$$\left[\frac{\delta M_{Bb+}}{\delta t} \right]_{x, \text{decay}} = -M_{Bb+} k_{\text{decay}}$$

where k is a first-order rate constant. This expression can be substituted into the above equations for the decay term. If B is a neutral organic molecule, simply remove the $b+$ superscript.

If sorption can be described by a distribution coefficient , then

$$KD = X_B / M_{Bb+}, \text{ so that } \left[\frac{\delta X_B}{\delta t} \right]_x = KD \left[\frac{\delta M_{Bb+}}{\delta t} \right]_x$$

and can be substituted into the above equations in the sorption term. The retardation factor is defined by collecting all the $\delta M_{Bb+} / \delta t$ terms. The retardation becomes

$$[1 + KD CEC \rho_{\text{rock}} / (\tau_{\text{rock}} b)]$$

The reciprocal of this factor can be multiplied by the ground-water velocity to give an estimate of the velocity of B_{b+} in aqueous solution. The estimate depends on B_{b+} not undergoing any decay or precipitation-dissolution reactions and that its only interaction with the sediment can be described by **KD**. This retardation factor been shown to be simply the ratio of the total amount of B_{b+} in the sediment plus solution to the amount in solution. Use of **KD** assumes this mass ratio remains constant, resulting in a constant retardation factor from the linear Distribution algorithm.

Note that the distribution coefficient is usually defined in the soil literature as

$KD\# = WB/MBb+$, where $WB = XBCEC(MWB)/b$

in which MWB is the molecular weight of B. The difference is just a constant factor between KD and $KD\#$. If B is a neutral organic molecule than $WB = XBNsed(MWB)$.

If sorption can be described by a Freundlich-type expression, then

$KF = XB/(MBb+)^n$ where n is a fit parameter,

so that $[\delta XB/\delta t]_x = nKF(MBb+)^{n-1} [\delta MBb+/\delta t]_x$ and can be

Substitute into one of the above equations for sorption term. Can you define the retardation factor using the Freundlich-type expression? Note that it is not constant and the Freundlich algorithm is referred to in the literature as a non-linear algorithm.

As was the case of the distribution coefficient, the general Freundlich coefficient is usually defined as

$KF\# = WB/(MBb+)^n$, where $WB = XBCEC(MWB)/b$

in which MWB is the molecular weight of B. The difference is just a constant factor between KF and $KF\#$. If B is a neutral organic molecule than $WB = XBNsed(MWB)$

If sorption can be described by a Langmuir-type expression, then

$XB = aMBb+/(1 + cMBb+)$.

The first constant "a" represents the maximum site occupancy for B and the second constant "b" is the Langmuir Coefficient. What is $[\delta XB/\delta t]_x$ for a Langmuir-type expression, and what is the corresponding retardation factor? Again, as was the case of the distribution coefficient, the general Langmuir-type expression is usually defined as

$WB = a*MBb+/(1 + cMBb+)$ where $WB = XBCEC(MWB)/b$

in which MWB is the molecular weight of B. The difference is just a constant factor between a and a*. If B is a neutral organic molecule than $WB = XBNsed(MWB)$

V) If sorption is described by exchange between two cations $Aa+$ and $Bb+$ using a power-exchange function, then

$Kex = (MBb+)/(MAa+)[XA/XB]^n$

where n is an integer which varies between 0.8 and 2 and a and b are integers (reaction coefficients in the cation-exchange reaction) obtained by dividing a and b , respectively, by their largest common integer factor j . For example, if a and b are both 2 then j is 2 and a and b are both 1. What is the retardation factor based on this power-exchange function?

Numerical Modeling of the Partial Differential Equation for Mass Transport

The simplest way of solving the partial differential equation for mass transport would be to use finite difference approximations of the partial derivatives at points along the x axis. One simple implicit representation of the partial derivatives at location j along the x axis for time k is

$$[\delta MBb+/\delta t]j = [MBb+[j,k] - MBb+[j,k-1]]/t$$

$$[\delta MBb+/\delta x]k = [MBb+[j+1,k] - MBb+[j-1,k]]/2x$$

$$[\delta^2 MBb+/\delta x^2]k = \{ [MBb+[j+1,k] - MBb+[j,k]]/x \} - \{ [MBb+[j,k] - MBb+[j-1,k]]/x \}/x$$

Substitution of these relations into the mass transport equation for a sequence of points can yield a tridiagonal matrix of linear equations which can be solved for MBb+ at each j point for time k. The procedure is then repeated with an increase in time. Boundary conditions need to be specified such as at j = 0, MBb+ is constant for all time k which means that the source concentration remains constant. At some large value of j, i.e., j = 1000, [MBb+/x]k = 0 which eliminates mass transport of Bb+ at j = 1000. Initial conditions could be MBb+ = 0 for all j > 0. t and x need to be set at values such as 105 sec and 1 cm, respectively, with vx set to 3 times 10⁻⁶ cm/sec (95 cm/year). You might have to experiment with t and x values if the concentrations are unstable in the numerical approximation.

Note that I said the above procedure can yield a tridiagonal matrix of linear equations. This would be the case if a simple distribution coefficient described the sorption and simple first order kinetics described decay. Anything more complicated will lead to a set of nonlinear equations which would have to be linearized (probably with a Newton-Raphson procedure) before solving them.

Potential Homework Problem

A) Using EXCEL, follow a concentration wavefront moving downstream in which benzene absorbs onto organics in an aquifer. The organic molecule has a Kd of 2 and is not undergoing any decay or other chemical reactions. The Kd value is an estimate based on multiplying a Koc value of 100 by an organic weight fraction of 0.02. Koc is a measured soil absorption coefficient which relates absorption to organic carbon present per unit volume of ground water. We will discuss this in class.

Do not consider dispersion. The groundwater velocity is 1 cm/day. The source concentration is 0.0005 moles/liter. Nsites, the moles of sites per kilogram of sediment, is 0.2. sed, the sediment density, is 2.65 kg/liter, and sed, the porosity fraction, is 0.25. Equilibrate at one cm intervals, a pore volume moving downstream from the source through a distance of 20 cm. Because the ground-water velocity is 1 cm/day, each cm corresponds to the distance a pore volume moves in one day. Do this sequentially for a total of 40 pore volumes.

The essential relationships are $K_d = X_B/M_B$,

The mass balance equation for benzene is

Total Moles of B = $M_{B,upstream} + (N_{sitespsed}/\tau_{sed})X_{B,previous\ time\ step}$

= $M_{B,new} + (N_{sitespsed}/\tau_{sed})X_{B,new} = X_{B,new}(1/K_d + N_{sitespsed}/\tau_{sed})$

B) Repeat the above problem with decay of benzene sorbed onto the sites. Assume the benzene in solution is not undergoing bacterial decay. Basically, we are assuming that the bacteria are active on the solid substrate but not in the solution.

Use a first-order decay constant corresponding to a half life of 14 days, i.e., $k_{decay} = -(\ln 0.5)/(604,800\ sec)$ and $\ln [(X_B\ after\ decay)/(X_B\ before\ decay)] = -k_{decay}(\text{time in sec})$.

To do this problem, in each step you need to remove the amount of sorbed benzene which has decayed over the preceding 24 hours, prior to equilibrating the new arriving pore volume with the remaining sorbed benzene. The essential relationship is

$\ln[(N_{sitespsed}/\tau_{sed})X_{B,previous\ time\ step\ after\ decay}/(N_{sitespsed}/\tau_{sed})X_{B,previous\ time\ step}]$

= $-k_{decay}(86,400\ sec)$ or

$X_{B,previous\ time\ step\ after\ decay} = \exp(-k_{decay}86,400)X_{B,previous\ time\ step}$

which replaces $X_{B,previous\ time\ step}$ in the mass balance expression in the previous problem.

C) The final part is to add decay to the amount in solution. Use a first order rate constant corresponding to a half life of 28 days, i.e., decay is slower in solution than on the sediment. In each step, you will need to subtract out the aqueous benzene moving in from upstream that has been lost to decay just as you had to subtract out the sorbed benzene that was lost to decay in the preceding problem.

For the 3 scenarios above, plot the aqueous concentrations as a function of distance from the source after 20 days and after 40 days.

For example, after 20 days, the 20th pore volume entering the column is occupying the 1st cm of the column, the 19th pore volume that entered the column occupies the second cm, and so forth to the end of the column where the 1st pore volume that entered the column occupies the 20th cm. Plot the corresponding concentrations using the midpoint of each cm for the average concentration within each cm of column. Plot this on a linear, not log scale, to delineate the location of the concentration wavefront.

On a separate sheet, briefly outline the computational procedure for each scenario and attach the corresponding spreadsheet data. What conclusions can you draw from the exercise?

Computing the retardation of a concentration front moving downstream.

1) Lead is being released into ground water from a pile of discarded lead batteries. The polluted ground water near the batteries has an aqueous concentration of 1 mg/l. Sediment in contact with this ground water has a sediment lead concentration of 33 mg/kg of dry sediment. The adjacent sediment has a porosity of 30 percent and a dry density of 1.6 mg/cm³. The unpolluted downstream lead concentrations are 20 micrograms/liter and 0.659 mg/kg dry sediment. What will be the retardation factor of lead as it moves away from the discarded lead batteries. What are the Freundlich parameters that describe the sorption.

$$R = 1 + [(S_{\text{upstream}} - S_{\text{downstream}})_{\text{sediment}}] / (C_{\text{upstream}} - C_{\text{downstream}})_{\text{sediment}}$$

$$R = 1 + \{[(33 - 0.659)\text{mg/kg}] [(1.6 \text{ g/cm}^3)(\text{kg}/1000 \text{ g}) (1000 \text{ cm}^3/\text{l})]\} / [(1 - 0.02)\text{mg/l} (0.3)] = 177$$

Freundlich isotherm $K_f = S/C^n$ can be rewritten as $\log K_f = \log S - n \log C$

There are 2 unknowns and we have two points to apply the equation:

Upstream, $S = 33 \text{ mg/kg}$ and $C = 1 \text{ mg/l}$ and downstream, $S = 0.659 \text{ mg/l}$ and $C = 0.02 \text{ mg/l}$

$$\log K_f = \log 33 - n \log 1 = \log 33 \text{ or } K_f = 33$$

$$\text{and } \log K_f = \log 0.659 - n \log (0.02) = -0.181 - n \log (0.02)$$

$$\text{or } 1.51 = -0.181 - n (1.699) \text{ or } n = 0.995$$

The fact that n is so close to one means that we could predict the retardation based on a linear distribution function, assuming $K_f = K_d$, i.e., $R = 1 + K_d / \epsilon = 1 + 33(1.6)/0.3 = 177$.

Another example of lead retardation using Minteqa2.

Anglesite (PbSO_4) has precipitated in soil beneath a pile of broken automobile batteries. Ground water moving through the soil has a pH of 7 and contains 0.0002 molal each of Na, K, Ca, Mg, and 0.00000001 molal each of Pb and SO_4 and 0.0004 molal each of CO_3 and Cl. The ground water then reacts with the anglesite, changing its pH, possibly precipitating hydrocerrusite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$], releasing lead to the solution in the process which then moves downstream. Use MINTEQA2 to model this reaction.

The released aqueous lead is retarded by sorption on the soil. Lead sorption on this soil obeys the following Langmuir sorption isotherm $S_{\text{soil}} = [(30)(1.5)S_{\text{aq}} / (1 + 1.5 S_{\text{aq}})]$ for concentration units in mg/l for S_{aq} and mg/g for S_{soil} . The dry soil density is 2 g/ml with 30% porosity. What is the retardation of the lead moving downstream in the ground water? Summarize your work and explain how you came up with your answer. Include a copy of your input files for MINTEQA2 and the resulting equilibrium distributions.

The solution is run first at a pH of 7 to obtain the total hydrogen ion molal concentration in solution. This is 0.0004703 molal. The solution is then reacted with anglesite, allowing hydrocerrussite to precipitate. The resulting lead concentration is 0.0001286 molal at a pH of 5.89. The conversion to mg/l is

$$\text{mg/l of Pb} = \text{ppm of Pb} \left(\frac{1000 \text{ Mwi}}{\text{Mwi}} \right) = 26.64 \text{ mg Pb/l}$$

This is the upstream concentration in the retardation computation. The unpolluted lead concentration is the downstream concentration which was 0.00000001 molal or 0.0020719 mg Pb/l.

The retardation of the lead cannot be computed accurately using a constant distribution coefficient because the nonlinear partitioning follows the Langmuir isotherm. The retardation is computed from the equation given to you in class that you used on your midterm.

$$R = 1 + (\text{Supstream} - \text{Sdownstream}) \rho_{\text{sed}} / [(\text{Cupstream} - \text{Cdownstream}) \tau_{\text{sed}}]$$

where the aqueous concentrations are in mg/l and the soil concentrations are in mg/kg. Use of the Langmuir isotherm yields

$$\text{Supstream} = 1000[(30)(1.5)26.64 / (1 + 1.5 (26.64))] = 29,270 \text{ mg/kg}$$

$$\text{Sdownstream} = 1000[(30)(1.5)0.00207 / (1 + 1.5(0.00207))] = 92.9 \text{ mg/kg}$$

$$R = 1 + [(29,279 - 92.9) \text{ mg/kg} (2 \text{ g/ml})(1000 \text{ ml/l})(1 \text{ kg}/1000 \text{ g})] / [(26.64 - 0.00207) \text{ mg/l} (0.30)] = 7,313$$

Zero Point Charge of Solids

The surface of a solid interacts with a solution by the sorption and desorption of charged species, resulting in a surface charge on the solid that is balanced by a diffuse charged layer adjacent to the surface of the solid. The ZPC point is the pH in which there is no surface charge on the solid surface.

The pH of zero surface charge on a solid can be determined by acid and base titrations in which only H^+ ions are allowed to be absorbed and desorbed off the surface. The first step is to determine the pH of a solution that the solid is to be added to. The second step is to add a given amount of the solid with a particular particle size and remeasure the pH

of the solution. By assuming the solid had zero surface charge prior to being added to the solution, the surface charge on the solid can be calculated from the change in pH of the solution. Acid and base titrations are then done in steps. After a given volume of titration solution is added, the new surface charge is calculated using the overall change in solution pH. The actual zero point charge pH is a calculated point.

If the solution titrations are done in different ionic strength solutions containing the solid, the titration curves for the different solutions will intersect at a common point when the equivalents of acid and/or base are plotted versus pH. This common point is also the calculated point of zero surface charge. The reason that they intersect at a common point is because this is the only pH at which there is no ionic potential associated with the surface of the solids (because there is no surface charge at this pH). At this common pH the solutions are independent of the solids in the solution titrations. At other pH values the ionic potential of the surface (resulting from the surface charge) together with the different ionic strength of the solutions combine to give different solution pH values.

The process is illustrated below with the equations used in calculating the surface charge from the change in pH.

Determine the Zero Point Charge of bauxite (mostly gibbsite ($\text{Al}(\text{OH})_3$) with other Al oxides).

Each student should do one of the acid-base titrations corresponding to a particular NaCl solution concentration.

In 3 beakers of 100 ml solution each containing 0.1, 0.01, or 0.001 M NaCl - measure the start pH of each solution after 10 minutes equilibration with the atmosphere (use a magnetic stirring bar). Be sure that the pH electrode was calibrated properly. From REACT, the activity coefficients of H^+ in the solutions are 0.780, 0.902, 0.965, respectively, and that of OH^- are 0.784, 0.903, and 0.965, respectively, for 0.1, 0.01, and 0.001 M NaCl. Assume the density of the solution is 1 g/ml, and note that at 25°C, the concentrations of H^+ equal $10^{-\text{pH}} / \text{activity coefficient of } \text{H}^+$ and OH^- equals $10^{(\text{pH}-14)} / \text{activity coefficient of } \text{OH}^-$. From the start pH measurements, you can calculate the total moles of H^+ and OH^- in solution.

Add 0.250 grams of bauxite (approximately 0.003205 moles of gibbsite) to each beaker, equilibrate for 30 minutes, and measure the pH. The change in solution pH is used to calculate the moles of H^+ and OH^- ions sorbed onto the solid or released from the solid. Then add 1 ml of 0.01M HCl acid to lower the pH to about 4, followed by increments 0.025 ml of 0.01M NaOH to raise the pH above 9. Always wait 10 minutes for the pH to stabilize before recording the pH and adding another increment. In each case, the change in pH between titration steps is used to determine the change in the moles of H^+ ions and OH^- ions that are sorbed or released from the solid surface.

The rationale is that the concentration change in aqueous H^+ ions is due to exchange with the solid plus addition of acid plus breakup or formation of water. Similarly, the change

in aqueous OH⁻ ions is due to exchange with the solid plus addition of base plus breakup or formation of water. Because the formation and breakup of water involve equal amounts of H⁺ and OH⁻ ions and we are including both in our calculation of surface charge, they will cancel out and we can ignore the formation and breakup of water. The initial surface charge of the dry solid is assumed to be zero. The change in surface charge, beginning with the addition of the dry solid to the solution is simply computed using these changes in H⁺ and OH⁻ concentrations.

For each step, the molar equivalent change in surface charge per gram of solid is the change in H⁺ ions in solution due to sorption minus the change in OH⁻ ions in solution due to sorption all divided by the grams of solid

$$= \{(\text{moles of solution H}^+\text{before} + \text{moles of H}^+\text{added} - \text{moles of solution H}^+\text{after}) - (\text{moles of solution OH}^-\text{before} + \text{moles of OH}^-\text{added} - \text{moles of solution OH}^-\text{after})\} / \text{grams of bauxite}$$

$$= \{[(10^{-\text{pH before}}/\gamma_{\text{H}^+}) (\text{ml solbef}) + N_{\text{acid}}(\text{ml added}) - (10^{-\text{pH after}}/\gamma_{\text{H}^+}) (\text{ml solafter})]/1000 \text{ ml} - [(10^{-(\text{pH bef.}-14)}/\gamma_{\text{OH}^-}) (\text{ml solbef.}) + N_{\text{base}}(\text{ml added}) - (10^{-(\text{pH after}-14)}/\gamma_{\text{OH}^-}) (\text{ml solafter})]/1000 \text{ ml}\} / \text{grams bauxite}$$

Plot the titration curve in surface charge of meq/g (y axis) versus pH (x axis), and the ZPC is the pH of zero surface charge.

Compare your titration curves. The curves should have a common pH for a ZPC and if plotted together, they should intersect at the ZPC. You could also simply plot the change in aqueous pH versus addition of meq of acid and base to generate a pH titration curve for each solution without computing the surface charge. The curves will still intersect at the ZPC. This is because this is the only pH point that they would share in the absence of the solid. Only at the ZPC is the solid not affecting the solution.

Classical Analyses

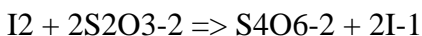
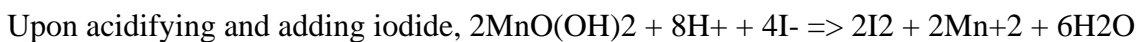
Winkler Method for Dissolved Oxygen

The analysis consists of making the solution basic, adding excess manganese cations (Mn²⁺ to precipitate as Mn(OH)₂ which absorbs dissolved oxygen as it forms a flocculant mass. The oxygen is reduced by oxidizing Mn(OH)₂ to MnO(OH)₂. After acidification, iodide is added which is oxidized to iodine by reducing the Mn⁴⁺ back to Mn²⁺. The iodine turns the solution yellow. This iodine is then titrated with thiosulfate using starch as an indicator in which the end point is from blue to colorless.

The manganese is added as a MnSO₄ solution. The hydroxide solution contains the iodide and also NaN₃ (an azide) to eliminate nitrite interference. Organic matter will not interfere if the thiosulfate titration is done immediately after iodine formation. Aqueous sulfide can reduce iodine so its presence will cause underestimation of dissolved oxygen.

However, if aqueous sulfide is present, the rotten-egg order will be noticable. Fluoride can be added to eliminate ferrous iron interference.

To reduce one mole of O_2 requires oxidation of 2 moles of Mn^{+2} to Mn^{+4} which subsequently generates 2 moles of I_2 when it is reduced. These 2 moles of I_2 require oxidation of 4 moles of $S_2O_3^{2-}$ when it is reduced.



Hence, $(M \text{ of } O_2)(\text{ml of sample}) = [M \text{ of } S_2O_3^{2-}/4](\text{ml of titrant})$,

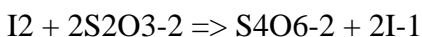
or $\text{mg/l } O_2 = (8,000)(M \text{ of } S_2O_3^{2-}) (\text{ml of titrant} / \text{ml of sample})$

Idiometric Method for Aqueous Sulfide

The analysis consists of acidifying the solution (sulfide is overestimated if not acidified), adding excess iodine, and titrating the unreacted iodine with thiosulfate. Starch is used as an indicator which turns the yellow solution to blue. The end point is from blue to colorless. (The end point is hard to see under a blue sky.)

Add HCl to acidify the solution, and then add a known (excess) amount of I_2 to oxidize S^{2-} in the sample to S while reducing the iodine to I^- . Oxidizing one mole of S^{2-} requires reducing one mole of I_2 . The remaining I_2 is then reduced by titration with $S_2O_3^{2-}$ which is oxidized to $S_4O_6^{2-}$. One mole of I_2 is reduced by oxidizing 2 moles of $S_2O_3^{2-}$.

$S^{2-} + I_2 \Rightarrow S + 2I^-$, followed by the thiosulfate titration:



Hence, $M \text{ of } S^{2-} = (M \text{ of } I_2 / \text{ml of sample}) (\text{ml of } I_2 \text{ used to oxidize } S^{2-})$.

In terms of thiosulfate,

$M \text{ of } S^{2-} = [M \text{ of } S_2O_3^{2-}/2] (\text{ml of } S_2O_3^{2-} \text{ titrate blank} - \text{ml of } S_2O_3^{2-} \text{ titrate solution}) / \text{ml sample}$.

Or, $\text{mg/l } S^{2-} = [16,032 / \text{ml sample}] [M \text{ of } S_2O_3^{2-}] (\text{ml of } S_2O_3^{2-} \text{ titrate blank} - \text{ml of } S_2O_3^{2-} \text{ titrate solution})$

EDTA Titration for Aqueous Ca and Mg

EDTA is ethylenediaminetetraacetic acid which forms strong complexes with divalent, trivalent, and tetravalent metal ions. With these cations the complex forms as one metal cation per molecule of EDTA. It does not complex strongly with monovalent alkali cations. The general procedure is to raise the sample pH to the point that metals other than Ca and Mg precipitate out and then titrate the solution using Erichrome Black T as an indicator. The endpoint color change is from wine red to blue. The concentration of Ca plus Mg is the hardness of the water sample. On a second sample the pH is raised higher to about 12 so that $\text{Mg}(\text{OH})_2$ precipitates out, leaving only Ca which is then titrated with EDTA using murexide as the indicator. The endpoint color change is from pink to reddish blue. The Ca concentration measured in this titration is subtracted from the Ca + Mg concentration measured in the first titration to obtain the Mg concentration.

The general titration equation is:

$$M_{\text{metal}} = M_{\text{EDTA}}(\text{ml of EDTA titrant})/(\text{ml of sample})$$

Clays

Clays are silicates composed of octahedral (*O*) and tetrahedral (*T*) layers with or without interlayers (*I*). The cation coordination number is 6 within the octahedral layers, 4 within the tetrahedral layers, and 12 within the interlayers.

The octahedral units in clays are $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ octahedrons which form layers of about 5 Å along the *c* axis. The tetrahedral units in clays are sheets of silica tetrahedron with a thickness of about 2 Å.

The divalent ions (Mg^{2+} , Fe^{2+}) in the octahedral layer produce trioctahedral clays, signifying occupancy of 3 out of 3 octahedral sites. The trivalent ions (Al^{3+} , Fe^{3+}) in the octahedral layers produce dioctahedral clays, signifying occupancy of 2 out of 3 octahedral sites. The difference in site occupancy occurs because two of the trivalent ions have charge equivalency to three of the divalent ions. Many clays are a mixture of dioctahedral and trioctahedral with both trivalent and divalent ions in the octahedral layers.

Clays Without a Lattice Charge

The simplest clays consist of octahedral layers as gibbsite and brucite. Gibbsite forms by weathering aluminum silicates. Brucite forms under very high pH conditions on the earth's surface or (more commonly) under hydrothermal and metamorphic conditions.

- clay - - chemical formula - - layers - - *c* spacing - - clay type -

gibbsite	$\text{Al}(\text{OH})_3$	<i>O</i>	5 Å	dioctahedral
brucite	$\text{Mg}(\text{OH})_2$	<i>O</i>	5 Å	trioctahedral

The simplest *OT* clays are kaolinite and serpentine, each consisting of 7 Å units (along the *c* axis), composed of an octahedral layer and a tetrahedral layer. Kaolinite forms under earth-surface and diagenetic conditions. Serpentine forms under hydrothermal and metamorphic conditions.

- clay -	- chemical formula -	- layers -	- <i>c</i> spacing -	- clay type -
kaolinite	(Al) ₂ (Si) ₂ O ₅ (OH) ₄	<i>OT</i>	7 Å	dioctahedral
serpentine & septachlorites	(Mg) ₃ (Si) ₂ O ₅ (OH) ₄	<i>OT</i>	7 Å	trioctahedral

An additional tetrahedral layer can be added to form pyrophyllite and talc, common hydrothermal and metamorphic minerals. They consist of 9 Å units (along the *c* axis) composed of a sandwich of a tetrahedral layer, an octahedral layer, and another tetrahedral layer.

- clay -	- chemical formula -	- layers -	- <i>c</i> spacing -	- clay type -
pyrophyllite	(Al) ₂ (Si) ₄ O ₁₀ (OH) ₂	<i>TOT</i>	9 Å	dioctahedral
talc	(Mg) ₃ (Si) ₄ O ₁₀ (OH) ₂	<i>TOT</i>	9 Å	trioctahedral

An additional octahedral layer can be added to the sandwich to form chlorite, a common diagenetic, hydrothermal, and metamorphic mineral. A chlorite consists of 14 Å units (along the *c* axis) composed of a tetrahedral unit, an octahedral layer, another tetrahedral layer and another octahedral layer. The substitution of Al³⁺ for Si⁴⁺ in the tetrahedral layer is balanced by Al³⁺ and Fe³⁺ substitution for Mg²⁺ and Fe²⁺ in the octahedral layer, so there is no structural charge. The two octahedral layers are generally thought to be different in composition, so are represented by *O* and *O'*.

- clay -	- chemical formula -	- layers -	- <i>c</i> spacing -	- clay type -
chlorite	(Mg,Fe ²⁺ ,Fe ³⁺ ,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	<i>TOTO'</i>	14 Å	trioctahedral

Chlorite is generally trioctahedral; however, substitution of two trivalent ions for three divalent ions in the octahedral layer can produce chlorites which are predominantly dioctahedral.

Clays With a Lattice Charge

Smectites are formed from pyrophyllite and talc lattices by substitution in the lattice and the addition of interlayers. Their *c* spacing is generally from 12 to 14 Å. The basic unit is the sandwich of a tetrahedral layer, octahedral layer, tetrahedral layer, followed by an interlayer. The interlayer contains cations to balance the negative lattice charge resulting from substitutions in the octahedral and tetrahedral layers. Smectites form under earth-surface conditions and during diagenesis. At higher temperatures, they are converted directly (by lattice collapse) to illite and micas or transformed to chlorites. The negative structural charge on a smectite is limited to about 0.33 eq. per formula (containing

O₁₀(OH)₂). At a larger structural charge, the lattice tends to collapse, by dehydrating the interlayer cations, to a 10 Å spacing (mica structure), and the interlayer cations become nonexchangeable.

The smectites names below are based primarily on whether the charge substitution occurs in the octahedral or tetrahedral layers and whether the clay is dioctahedral or trioctahedral. Most smectites forming under earth-surface conditions are dioctahedral. I_x in the formula refers to interlayer cations in which x is the equivalents needed to balance the negative structural lattice charge. K⁺ is never a major interlayer ion. The interlayer cations consist of Na⁺, Mg²⁺, Ca²⁺, NH₄⁺, and various metals such as Pb²⁺, Ba²⁺, and Cd²⁺. For simplicity, only the major cations in the octahedral layers have been shown in the formulas. In reality, at least minor amounts of octahedral Mg²⁺, Fe²⁺, Al³⁺, and Fe³⁺ occur in all of the smectites.

clay	- chemical formula -	- layers -	- c spacing -	- clay type -
montmorillonite	I _x (Al ₂ -xMg _x)(Si ₄)O ₁₀ (OH) ₂	TOTI	12 to 14 Å	dioctahedral
beidellite	I _x (Al ₂)(Si ₄ -xAl _x)O ₁₀ (OH) ₂	TOTI	12 to 14 Å	dioctahedral
nontronite	I _x (Fe ₂)(Si ₄ -xAl _x)O ₁₀ (OH) ₂	TOTI	12 to 14 Å	dioctahedral
saponite & vermiculite	I _x (Mg ₃)(Si ₄ -xAl _x)O ₁₀ (OH) ₂	TOTI	12 to 14 Å	trioctahedral

Note that vermiculite is not usually considered a saponite; however it is closely related in structure and composition.

Illite is similar to a dioctahedral smectite, except that the interlayer ion is primarily K⁺ and the c spacing is 10 Å. The structural charge on an illite can be more than 0.5 eq. per formula unit (O₁₀(OH)₂). The interlayer K⁺ is not exchangeable, because the unhydrated K⁺ is bound too tightly between the tetrahedral layers above and below it along the c axis. K⁺ is unhydrated because the ratio of its ionic size to charge is larger than most other ions, except for Cs⁺ (which is also unhydrated in clay interlayers). Illite forms under earth-surface (in alkaline lakes) and diagenetic (transformation from smectite) conditions and transforms to muscovite (sericite) under hydrothermal and metamorphic conditions.

clay	- chemical formula -	- layers -	- c spacing -	- clay type -
illite	K _x (Al ₂)(Si ₄ -xAl _x)O ₁₀ (OH) ₂	TOTI	10 Å	dioctahedral

Micas

The smectites and illite are closely related to the common micas of igneous rocks. They have 10Å spacing along their c axes, indicating the interlayer cations are not hydrated.

mica	- chemical formula -	- layers -	- c spacing -	- clay type -
muscovite	K (Al₂)(Si₃Al)O₁₀(OH)₂	TOTI	10 Å	dioctahedral
paragonite	Na (Al₂)(Si₃Al)O₁₀(OH)₂	TOTI	10 Å	dioctahedral
margarite	Ca₂ (Al₂)(Si₂Al₂)O₁₀(OH)₂	TOTI	10 Å	dioctahedral
phlogopite	K (Mg₃)(Si₃Al)O₁₀(OH)₂	TOTI	10 Å	trioctahedral
annite	K (Fe₃)(Si₃Al)O₁₀(OH)₂	TOTI	10 Å	trioctahedral

Clay Cation Exchange Capacity Due To Lattice Charge

Clays have a cation exchange capacity (*CEC*) due to the lattice being negatively charged by ionic substitutions, by structural defects, and by surface interactions with a solution. The *CEC* is usually given in meq/100 grams of dry weight of the clay. It is generally measured in the laboratory under constant conditions, e.g., measurement at pH 7 in a solution containing NH₄⁺ at a certain initial concentration. The *CEC* is computed from the decrease in meq of NH₄⁺ in the solution. The decrease occurs as NH₄⁺ displaces cations from the surface and interlayers of the clay. Of the major cations: Na⁺, K⁺, Ca²⁺, and Mg²⁺; only K⁺ is generally not exchangeable (due to it being unhydrated in clay interlayers). The absorption of cations onto the surface and interlayers of clays is an important sink for toxic metals. Clays are not the only soil components with a *CEC* capacity. Amorphous particles, produced in weathering and by organic decay, also absorb cations from aqueous solutions.

The theoretical cation exchange capacity in meq/100 grams for a smectite, due to its lattice charge, can be computed from its formula as

$$[(1000)I_x][100/Mw_{\text{clay}}]$$

where *Mw_{clay}* is the molecular weight of the clay in grams per mole.

Example of Cation Exchange Capacity Measurement

This is a rapid procedure which uses 60 ml of a solution containing the CuEDA₂⁺ complex to displace cations sorbed onto 0.2 grams of solid.

0.01 molar solution of Cu²⁺ diluted by the addition of 0.1 molar EDA in a 10 to 1 volume ratio to form a 0.00909 molar solution of CuEDA₂⁺. The complex is to be sorbed onto the solid; however, usually the sorption is done with a 1/6 dilution of the solution, i.e., at 0.00151517 concentration. The first step is to compute the number of moles of the complex in the sample, e.g., for a 60 ml sample the number of moles in the sample is (0.00151517)(60/1000) moles or 0.00009091 moles or 0.9091 mmoles CuEDA₂⁺.

Zero the UV VIS spectrophotometer to read zero absorbance with distilled water. Measure the absorbance of the blank molar solution, e.g., say the solution read 0.142 for the 0.00151527 molar solution. Check the linearity of the absorbance by reading the

absorbance of a solution of $\frac{1}{2}$ the concentration, e.g., check to see if it reads close to 0.071.

Measure the absorbance of the 60 ml of solution after sorption with 0.2 g of solid, e.g., say the solution now reads 0.022, so the absorbance decrease of 0.120 (from 0.142 - 0.022) would represent the concentration that was sorbed onto the solid or $(0.120/0.142)(0.00151517 = 0.00128043$ molar solution which contained $(0.001288043)(60/1000)$ or 0.00007683 moles of CuEDA2+ or 0.07683 mmoles were sorbed.

Calculate the number of millimoles of charge on CuEDA2+ sorbed onto the solid, e.g., $0.07683(2) = 0.1537$ meq.

Normalize the meq to a 100 gram sample, e.g., for a 0.2 gram sample, $0.1537(100/0.2) = 77$ meq/100 grams.

Microbial Breakdown of Organic Compounds and Oxidation of Metals

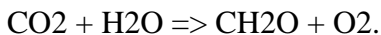
Destruction of organic matter by bacteria follows first order kinetics.

$$(C_c)_{t=0}/(C_c)_t = e^{kt}$$

where C_c is the concentration of C and k is a rate constant dependent upon the type of organic matter and the group of biota eating the substrate (organic matter). Measurement of BOD, biological oxygen demand, is done in the laboratory at 20°C in an airtight bottle for five days by measuring the decrease in O_2 concentration (1 mole of O_2 is needed to oxidize one mole of organic C).

Organic Matter Composition

Organic matter formation occurs primarily by photosynthesis by cyanobacteria, algae, and higher plants



The atomic composition of organic matter includes N, P, and minor S in the amino acids of proteins. The average compositions (excluding S) of **terrestrial organic matter** is **C882H1794O886N9P** (Deevy composition with C/N = 98) and for **marine organic matter** is **C106H263 O110N16P** (Redfield composition with C/N = 6.66). N and S are in their reduced forms (NH_3 and S^{2-}), and the P is in the oxidized orthophosphate form (PO_4^{3-}) but in chains as condensed polyphosphates.

Nitrogen must be in either the oxidized NO_3^- form or the reduced NH_3 form before plants can assimilate it. Typically, N in ammonia, produced from decaying plants, is oxidized first to NO_2^- and then to NO_3^- in the nitrification process. Some of the NO_3^- is

reduced to N_2 (denitrification process) and lost to the atmosphere. In the plant assimilation process, oxidized N is reduced and incorporated into amino acids. N in intermediate oxidation states, e.g., nitrite (NO_2^-) and N_2 cannot be assimilated by plants. N_2 has a very strong triple bond which is difficult to break. Note that NH_4^+ is the common reduced form of N under reducing conditions and is soluble in waters up to about a pH of 9. Above that pH, $NH_4^+ \Rightarrow NH_3$ and becomes volatile.

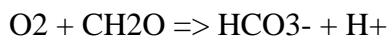
Phosphorous is assimilated in plants as PO_4^{3-} form and converted to condensed polyphosphates $(HO)_2(P=O)-O-[HO(P=O)-O-]_n(P=O)(OH)_2$, a chain of phosphates. Unlike N and like S, P concentrations in water can be controlled by mineral precipitation, e.g., $FePO_4$ (acid conditions), $AlPO_4$ (neutral pH conditions), and apatite $Ca_5(PO_4)_3(OH)$ (basic conditions). However, iron phosphate will redissolve under reducing conditions so the iron must remain in the ferric state.

Sulfur is assimilated in plants as sulfate (SO_4^{2-}) and reduced to organic sulfur So. During decay processes, S is released as S^{2-} and must be oxidized back to SO_4^{2-} before plants can assimilate it again. Iron sulfides commonly control the concentration of reduced sulfur under reducing conditions, e.g., pyrrhotite precursors (FeS), pyrite and marcasite (FeS_2).

Microbial Oxidation of Organic Matter

O₂ Reduction to Oxidize Organic Matter

Oxidation of organic matter by bacteria and fungi first occurs using oxygen. In water or a moist soil environment, **aerobic oxidation** occurs as



Some bacteria metabolize specific organic molecules, such as methane (CH_4) by *Methanomonas* bacteria



Not all of the carbon may go to CO_2 & H_2O (i.e., $HCO_3^- + H^+$). Some of the carbon may go to carbon monoxide (CO) which can then be converted to CO_2 by various soil fungi, such as *Penicillium* and *Aspergillus*.

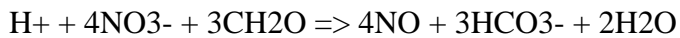
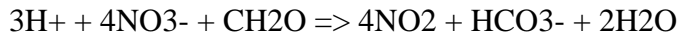
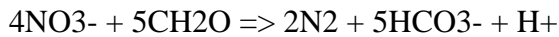


NO₃⁻ Reduction to Oxidize Organic Matter

After the oxygen is depleted, **nitrate reduction** of NO_3^- to nitrite (NO_2^-) is used by bacteria to oxidize organic tissue. In anaerobic water, the reaction becomes

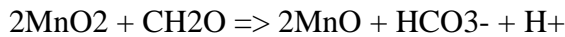


N₂, NO₂, and NO gases are produced that return fixed-nitrogen from the atmosphere back to the atmosphere. The reaction producing N₂ is much the most important and is called **denitrification**. NO₂ and NO are trace components in the atmosphere.



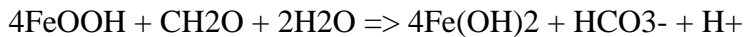
Mn⁴⁺ Reduction to Oxidize Organic Matter

During and following nitrate reduction, **Mn reduction** occurs by bacteria of Mn⁴⁺ to Mn²⁺.



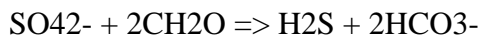
Fe³⁺ Reduction to Oxidize Organic Matter

Following the reduction of available nitrate and MnO₂, **Fe reduction** occurs by bacteria of Fe³⁺ to Fe²⁺.



SO₄²⁻ Reduction to Oxidize Organic Matter

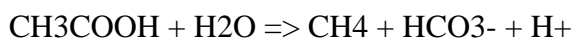
Once the nitrate, Mn⁴⁺, and Fe³⁺ ions are depleted, then **sulfate reduction** to sulfide is utilized by *Desulfovibrio* and other bacteria to oxidize tissue. Sulfate in gypsum and anhydrite and sea water are common sources of sulfur for sulfate reduction.



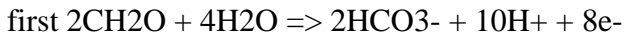
Fermentation and Methagenesis to Oxidize Organic Matter

Following sulfate depletion, **fermentation** occurs by the decarboxylation of fatty acids or the degradation of carbohydrates into methane and carbon dioxide. Fermentation reactions involve organic matter that serves as both the electron donor and receptor. **Methagenesis** refers to the reduction of inorganic carbon in carbon dioxide to methane in the presence of available electrons. Fermentation and methagenesis bacteria include the following groups: *Methanoo-bacterium*, *Methanobacillus*, *Methanococcus*, *Methanosarcina*.

The decarboxylation reaction can be written using a carboxylate acid (fatty acid) such as acetic acid.



The overall fermentation of a simple carbohydrate is shown below in which the second reaction is the methagenesis reaction.



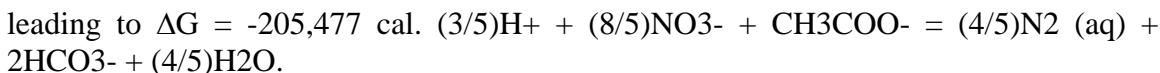
The decay reaction producing the greatest decrease in Gibb's Free Energy is favored. The change in Gibb's Free energy is calculated from

$$\Delta G = \Delta G_{\text{or}} + (2.303RT) \log Q = \sum n_i \mu_{\text{oi}} + (2.303RT) \sum n_i \log a_i$$

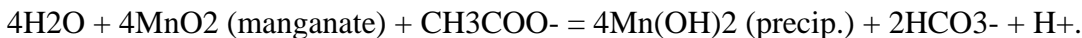
The various decay reactions can be compared using acetate as the organic carbon source at a pH of 7. The following activities were used: $\log a_{\text{HCO}_3^-} = -3$; $\log a_{\text{CH}_3\text{COO}^-} = -3$; $\log a_{\text{O}_2(\text{aq})} = -3$; $\log a_{\text{NO}_3^-} = -3$; $\log a_{\text{N}_2(\text{aq})} = -5$; $\log a_{\text{H}_2(\text{aq})} = -5$; $\log a_{\text{CH}_4(\text{aq})} = -5$; $\log a_{\text{HS}^-} = -4$; and $\log a_{\text{SO}_4^{2-}} = -3$. Standard free energies of formation at 25°C and 1 bar used were from Stumm and Morgan (1981) with the exception of $\text{N}_2(\text{aq})$ which was from Garrels and Christ (1965). For comparison sake, each reaction involves the transfer of 8 electrons.



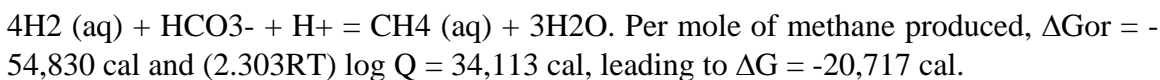
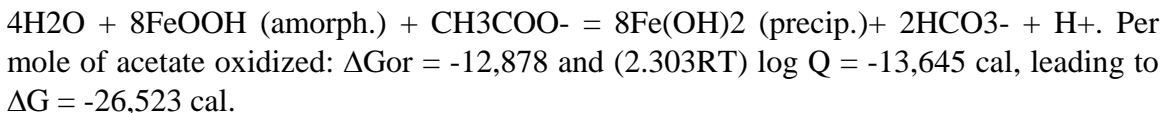
Per mole of acetate oxidized, $\Delta G_{\text{or}} = -200,019$ cal and $(2.303RT) \log Q = -5,458$ cal,



Per mole of acetate oxidized, $\Delta G_{\text{or}} = -192,600$ cal and $(2.303RT) \log Q = 2,729$ cal, leading to $\Delta G = -189,871$ cal.



Per mole of acetate oxidized: $\Delta G_{\text{or}} = -121,195$ and $(2.303RT) \log Q = -13,645$ cal, leading to $\Delta G = -134,840$ cal.



$\text{SO}_4^{2-} + \text{CH}_3\text{COO}^- = \text{HS}^- + 2\text{HCO}_3^-$. Per mole of acetate oxidized: $\Delta G_{\text{or}} = -11,364 \text{ cal}$ and $(2.303RT) \log Q = -5,458 \text{ cal}$, leading to $\Delta G = -16,822 \text{ cal}$.

$\text{H}_2\text{O} + \text{CH}_3\text{COO}^- = \text{CH}_4 (\text{aq}) + \text{HCO}_3^-$. Per mole of acetate oxidized: $\Delta G_{\text{or}} = -3,492 \text{ cal}$ and $(2.303RT) \log Q = -6,823 \text{ cal}$, leading to $\Delta G = -10,315 \text{ cal}$.

Other Microbial Reactions Involving Nitrogen

Nitrogen is involved in other microbial reactions. The N released by decay is in the form of ammonia (NH_3) and is generally be oxidized to NO_3^- before plants can utilize it. The **nitrification** process is aerobic and involves two bacterial groups: *Nitrosomas* transform NH_3 to NO_2^- and *Nitrobacter* transform NO_2^- to NO_3^- . The overall reaction is



Because these bacteria use inorganic matter to donate electrons, they are chemolithotrophic bacteria. The process occurs at a maximum rate at about a pH of 8 and the bacteria are inhibited by the presence of organic matter. The bacteria are also called chemoautotrophs, meaning they use only inorganic carbon (like plants) as their carbon source.

Nitrogen in organic matter can also be derived from the atmosphere by **nitrogen fixation**, in which N_2 is reduced to NH_3 and then subsequently oxidized to NO_3^- by nitrification. Note that nitrogen fixation must be balanced by denitrification to keep a steady state nitrogen content in the atmosphere. Nitrogen fixation can be represented by

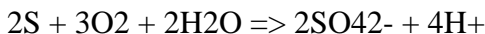
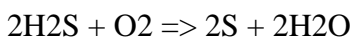


Some of the bacteria groups capable of fixing nitrogen include *Azotobacter*, some species of *Clostridium*, *Cyanobacteria* (also known as blue-green bacteria or blue-green algae), *Spirillum*, *Rhizobium*, *Actinomycetes*.

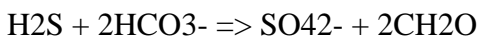
Microbial Oxidation of Sulfur, Iron, and Selenium

Microbial Oxidation of Sulfur

Some aerobic chemolithotrophic bacteria (nonfilamentous *Thiobacillus* and filamentous *Beggiator* and *Thiothris*) and anaerobic photolithotrophic (purple and green bacteria), utilize sulfide (S^{2-}), sulfur (S), and thiosulfate ($\text{S}_2\text{O}_3^{2-}$) as electron donors, as illustrated below for *Thiobacillus*.



With the anaerobic purple and green bacteria which undergo photosynthesis, the oxidation of hydrogen sulfide involves reduction of inorganic carbon in CO₂ to produce carbon molecules.



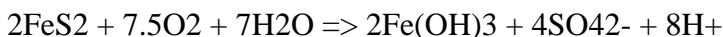
Microbial Oxidation of Iron

As with sulfur and nitrogen, iron can be utilized by chemolithotropic bacteria as electron donors. The bacterial groups include *Ferrobacillus*, *Gallionella*, and some species of *Sphaerotilus*. The reaction takes place in an aqueous environment in which ferrous (Fe²⁺) iron in a solid or iron (Fe) metal is oxidized to ferric (Fe³⁺) iron in another solid.



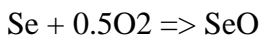
The later (overall) reaction is responsible for rusting. The bacteria set up an anaerobic environment against the metal and oxidize Fe to Fe²⁺ through the reduction of H in H₂O to form H₂. They then oxidize the Fe²⁺ to Fe³⁺ with oxygen in the aerobic environment above the metal. Etch pits form as the result of this process.

In the presence of sulfide-oxidizing bacteria, such as *Thiobacillus*, iron sulfides such as pyrite can be oxidized to iron hydroxides and sulfuric acid, producing acidic ground waters and a yellow precipitate.



Microbial Oxidation of Selenium

Elemental selenium (Se) can be oxidized by some chemolithotropic bacteria species of *Bacillus* to selenite (SeO₃²⁻).



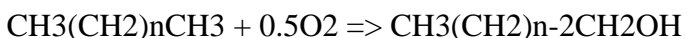
General Microbial Processes Degrading Organic Compounds

In general these process involve oxidation (adding oxygen), reduction (removing oxygen and/or adding hydrogen), and the addition of water.

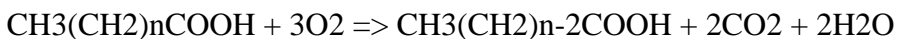
Epoxidation - Addition of an oxygen (oxidation process) to two carbons that are double-bonded to each other, i.e., an unsaturated molecule. The double bond is replaced by two single bonds from the oxygen to each carbon and a single bond connecting the two carbons. Note that the organochlorine Aldrin (C₁₂H₈Cl₆) converts to Dieldrin (C₁₂H₈Cl₆O) by this process. Unfortunately, Dieldrin is more toxic than Aldrin.

Epoxidation is often the precursor to other processes. Frequently, the oxygen will shift entirely to one of the carbons that has a hydrogen already attached to it. The oxygen and hydrogen form a hydroxide and the double bond reestablishes between the two carbon atoms. Placement of a OH group on the carbon is called **hydroxylation**.

Hydroxylation - Formation of a OH group on a carbon. As noted above, hydroxylation can follow epoxidation. In aromatic compounds, O₂ is added to two adjacent carbon atoms to form OH groups without breaking the double bond. The addition of additional O₂ can result in splitting the aromatic ring between the two adjacent carbons through the formation of COOH groups.



Organic Acid Formation - Terminal CH₃ groups on straight chain hydrocarbons are oxidized to COOH (organic acid) groups through the addition of O₂ and loss of H₂. The oxygen is usually added to the terminal carbon. Rarely, the oxygen is added to a non-terminal carbon, forming a ketone initially in the degradation process. Organic acids formed from alkanes can then be oxidized sequentially into smaller molecules, losing two of the carbons in each cycle, through the addition of O₂. Microbes active in hydrocarbon degradation through this process include *Micrococcus*, *Pseudomonas*, *Mycobacterium*, *Nocardia* bacteria and *Cunninghamella* fungi.



As mentioned above, organic acids can form by the addition of more oxygen, following hydroxylation on adjacent carbon atoms in aromatics. This process splits the aromatic ring structure.

Hydrolysis - Addition of H₂O to a molecule, generally accompanied by cleavage of the molecule into two species. At the point of cleavage, a H attaches to one species and a OH group to the other species. This is an important method of degradation with organophosphorus insecticides:

Hydrolysis is also used to degrade amino acids by bacteria and fungi, releasing ammonia (NH₃). The split of the amino acid is more complex than simple cleavage. Amino acids containing sulfur, e.g., cystine and methionine, produce both ammonia and hydrogen sulfide (H₂S) in the process. Hydrolysis of alkenes produces alcohols, a reduction process.

Dehalogenation - Loss of halide with formation of a double bond or replace halide with hydrogen. DDT (C₁₄H₉Cl₅) degrades to DDD (C₁₄H₉Cl₄); unfortunately, DDD is more toxic than DDT.

Dealkylation - Replace alkyl groups (e.g., CH₃) attached to O, N, and S with H. Microbes cannot usually pull alkyl groups off a carbon.

Reduction - The addition of hydrogen reduces aldehydes and ketones to alcohols and alkenes to alkanes. Oxygen is lost from sulfoxide reduction and hydrogen is added in disulfide reduction. Nitro reduction occurs by the loss of oxygen and the addition of hydrogen.

Waste Water Treatments

Primary Waste Water Treatment

Primary waste treatment involves removal of insoluble matter such as grit (non-biodegradable material with a high settling velocity), grease and scum (floating material) from waste water. The waste water is first screened to remove very large floating particles. Primary sedimentation removes settleable solids and skimming removes floatable solids. Settling can be aided by the addition of chemicals.

Secondary Waste Water Treatment

Secondary waste treatment involves removal of BOD (biological oxygen demand) by supplying microbes with oxygen and an environment suitable for degrading organic matter.

Septic Tanks

Waste water enters an underground tank which may or may not be aerated. Bacteria oxidize the organic matter and release the nitrogen and phosphorous as ammonium (or nitrate if the tank was aerated enough) and metaphosphate(orthophosphate in chains) and/or orthophosphate (if the tank was aerated enough).

Oxidation Lagoons

Wastewater moves through aerated lagoons to oxidized the organic matter.

Trickling Filter Process

Spray wastewater over substrate to increase contact with atmosphere.

Rotating Biological Reactors

An inert disc that is rotated slowly through waste water and through air.

Activated Sludge Process

An aerated tank is used for microbes to oxidize organic matter in waste water. The microbes increase their biomass as the waste water moves to a settling tank. Flocculation occurs of the microbe biomass and organic compounds and the resulting sludge settles in

the settling tank (secondary sedimentation). A portion of the sludge, rich in microbes, is recycled into contact with fresh waste water in the aerated tank, and the cycle repeats. The sludge can be further decomposed by fermenting bacteria, dewatered, and then incinerated or perhaps used as fertilizer if hazardous substances are not present. Heavy metals, pesticides, viruses and other dangerous microbes frequently accumulate in sludge so disposal can be a problem.

Tertiary Waste Treatment (Advanced Waste Treatment)

Drainage Fields

Conventional septic tanks discharge into an aerobic drain field in which the ammonium is oxidized to nitrate and all phosphate is converted to orthophosphate. The phosphate is sorbed onto solids or precipitated as Al, Fe, and Ca phosphates. The aerobic drain field trends into an anaerobic drain field in which the nitrate is denitrified to nitrogen gas and released to the atmosphere. Non-conventional septic tanks have an aeration system which eliminates the need for the aerobic drain field to convert ammonium to nitrate. However, an anaerobic environment in an anaerobic drain field is still needed to denitrify the nitrate. In-line anaerobic environments are being developed at UNO to denitrify nitrate using aluminum stearate as a bacteria substrate. These systems would substitute for an anaerobic drain field in urban areas where lot size limits their use and in rural areas with a high water table.

Aeration

Aeration oxidizes aqueous Fe^{2+} and Mn^{2+} to Fe^{3+} and Mn^{4+} , resulting in the formation of insoluble oxides (e.g., MnO_2) and hydroxides (e.g., FeOOH) that can be removed by settling. If organic complexing agents hold Fe and Mn in solution, stronger oxidizing agents (than O_2) can be used, e.g., chlorine (Cl_2) and potassium permanganate (KMnO_4) can be used to destroy the organic molecules. If permanganate is used as the oxidizing agent, Mn in permanganate is reduced from +7 to +4 and precipitated as MnO_2 .

Aeration also removes volatiles such as H_2S , CO_2 , CH_4 , odorous substances such as thiomethane (CH_3SH).

Water Softening

a) Add lime $\text{Ca}(\text{OH})_2$ and soda ash Na_2CO_3 , raising the pH to about 11, resulting in the overall removal of Ca, Mg, CO_3 , and HCO_3 due to precipitation of CaCO_3 and $\text{Mg}(\text{OH})_2$ in a *primary basin*. Removal of inorganic carbon reduces the alkalinity hardness, and removal of Ca and Mg removes ions that form curds with soaps. The resulting Na-rich waters are soft waters, as contrasted with Ca and Mg-rich waters which are hard waters.

Note that the precipitation of $\text{Mg}(\text{OH})_2$ requires a higher pH than the precipitation of CaCO_3 . The precipitated CaCO_3 can be recycled to lime through heating to form quicklime CaO and then hydration to $\text{Ca}(\text{OH})_2$:



Water can also be softened by using an ion-exchanger in which Ca^{2+} and Mg^{2+} are replaced by Na^+ . Excess Na^+ can be replaced by exchange with H^+ in a second ion-exchanger. Ion exchangers can be inorganic, e.g., zeolites, or organic, e.g., resins. Zeolites are aluminum-silicates that have ion-exchange sites. Ion-exchange resins are commonly used to purify water in laboratories. These organic resins can exchange cations or anions. They have exchange sites such as SO_3Na^+ , $\text{N}^+(\text{CH}_3)_3\text{OH}^-$, CO_2H^+ in which the exchange ions (in bold) can be exchanged with ions in solution. Ion exchangers can be regenerated by back-flushing concentrated solutions containing the original ions on the exchange sites. For example, in water-softeners, after all the exchange sites have been filled with Ca and Mg, they can be replaced by Na by back-flushing a NaCl-rich fluid through the ion-exchanger.

In the process of softening water with cation exchangers, the alkalinity can be lowered. Inorganic carbon species (HCO_3^- and CO_3^{2-}) can be transformed towards CO_2 by using ion exchangers that exchange H^+ ions for Ca^{2+} and Mg^{2+} . The addition of H^+ ions to the solution transforms CO_3^{2-} to HCO_3^- and HCO_3^- to H_2O and CO_2 .

Water can also be softened without removing Ca^{2+} and Mg^{2+} by complexing (chelating or sequestering) these cations so that they cannot interact with soaps or precipitate as hydroxides or carbonates. Polyphosphate salts (e.g., $\text{Na}_{n+2}(\text{PnO}_3)_{n+1}$), EDTA salts (e.g., $\text{Na}_2\text{H}_2\text{N}_2(\text{CH}_2)_2(\text{CH}_2\text{CO}_2)_4$), and NTA salts (e.g., $\text{Na}_3\text{H}(\text{CH}_2\text{CO}_2)_3$) are commonly used for this purpose.

Aqueous Ca^{2+} can also be removed by the addition of orthophosphate (PO_4^{3-}) to precipitate $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$. Remember that soaps contain phosphorous in the form polyphosphates ($\text{H}_{n+2}\text{PnO}_{2n+2}$) which can have a negative charge by losing hydrogen ions. Polyphosphates tend to complex Ca^{2+} rather than precipitate it. However, polyphosphates will hydrolysis back to orthophosphate and ultimately precipitate aqueous Ca.

Removal of Suspended Solid (Colloidal) Material

Depending upon the pH, add ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, (pH 4-11) or ferrous sulfate, copperas $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, (pH > 8.5) or aluminum sulfate, alum $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, (added at pH 5-7) which hydrolyze (and oxidize in the case of ferrous iron) to form coagulants: gelatinous $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, to settle any solid colloidal particles. These metals also formed charged hydrated molecules which exist as polymers and interact with colloidal particles, helping to coagulate them. Add activated silica (sodium silicate, $\text{Na}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$) or natural polyelectrolytes (starch and cellulose derivatives, gums) and synthetic polyelectrolytes (neutral, anionic and cationic polyelectrolytes) to stimulate

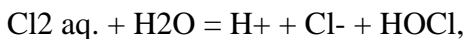
coagulation or flocculation. The settling occurs in the *secondary basin*, following carbonation. The settling may be used in combination with microstraining filtration through stainless-steel wire with pore size diameters of 60-70 microns.

Carbonation

Add CO₂ to lower pH which will solubilize any residual Ca and Mg not removed when the pH was raised. In addition, the lowered pH of the solution is between 7.5 and 8.5. The process is designed to produce waters that are approximately saturated to CaCO₃ so that it will neither precipitate or dissolve. These are called *chemically stabilized* waters, as contrasted with undersaturated waters called *aggressive* waters.

Disinfection

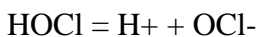
Chlorination, addition of chlorine as Cl₂ is the traditional way to kill microbes. Elemental chlorine hydrolyses in water to form hypochlorous acid.



which has a 25°C and 1 bar log K of -3.35.

$$10^{-3.35} = a_{\text{H}^+} a_{\text{Cl}^-} a_{\text{HOCl}} / a_{\text{Cl}_2}$$

Hypochlorous acid dissociates as a weak acid with a log K of -7.56. Because it dissociates as the pH is raised, it dissolves more readily at higher pH (like CO₂).



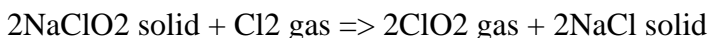
Calculations, using the above relationships, indicate elemental Cl₂ aq has a negligible concentration in waters above a pH of 3. For example, assuming unit activity coefficients, at a pH of 7 and a dissolved molality of Cl⁻ 0.001, the ratio of HOCl to Cl₂ is 106.65, and the molality of OCl⁻ is (0.28) of the molality of HOCl. Hence, The available free chlorine for killing bacteria is all in the form of HOCl and OCl⁻.

Ammonia is transformed to NH₂Cl, then to NHCl₂, and then to NCl₃ in the presence of hypochlorous acid. **See nitrogen removal.** These chloramines serve as a weak disinfectant. At the **breakpoint** when NCl₃ forms, the Cl:N ratio is large enough that some HOCl and OCl⁻ remain in solution. Additional chlorination ensures disinfection.

Chemical denitrification to produce N₂ can occur through the interactions of products such as NHCl₂ with HOCl. Hence ammonia can be totally removed by chlorination. However, chlorination of organic wastes can actually form from chlorinated hydrocarbons such as chloroform (CHCl₃) through interactions with humic substances.

Chlorine Dioxide (ClO₂) is a disinfectant that (in the absence of Cl₂) does not produce chloroform or oxidize ammonia or other nitrogen-containing compounds in water

treatment. However, this is a gas that reacts violently with organic matter and is explosive in the presence of light. For this reason it is generated on-site by reacting chlorine gas with solid sodium hypochlorite.

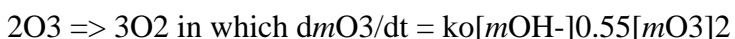


The product needs to be purified to remove any elemental chlorine. Some of its degradation products, ClO_2^- and ClO_3^- , may be hazardous.

In acidic waters, ClO_2 forms Cl^- as an oxidant: $\text{ClO}_2 + 4\text{H}^+ + 5\text{e}^- \Rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$.

In neutral waters, ClO_2 forms ClO_2^- as an oxidant: $\text{ClO}_2 + \text{e}^- \Rightarrow \text{ClO}_2^-$.

Ozone (O_3) is produced on-site by electrical discharge (20,000 volts) through air, followed by contact with water. Its aqueous solubility is low which limits its disinfective power and it decomposes spontaneously (in water) back to O_2 . The advantages are the absence of production of organochlorine compounds and its ability to destroy viruses. The rate of decomposition to O_2 follows the following empirical equation where k_o is a constant.



Ferrate iron, Fe in the 6+ state, in FeO_4^{2-}) is a strong oxidizing agent which destroys microbes and also removes heavy metals, viruses, and phosphates.

Ultraviolet light is used to disinfect waste water at the Mandeville Waste-Water Treatment Facility just prior to the final discharge of the water into adjacent natural swamps.

Additional Waste Water Treatments

Removal of Heavy Metals

Secondary waste water treatment, in the activated sludge process, floculates much of the heavy metals with the organic biomass forming the sludge.

Tertiary waste water treatment, involving the addition of lime and soda ash, removes heavy metals by precipitation of their insoluble hydroxides and carbonates, e.g., iron, manganese, copper, cadmium, mercury, lead. The process may not be complete unless aqueous sulfide is added which will precipitate metal sulfides. If organic complexing agents are holding the metals in solutions at a high pH, a strong oxidizing agent such as chlorine will destroy the organic compounds, allowing the precipitation of the metals.

Metals can also be removed by bringing the waste water in contact with activated charcoal which absorbs trace amounts of dissolved metals.

Metals can also be plated out through reduction to their elemental state as the result of oxidation of another aqueous component or a flow of electricity.

Metals can also be removed by cation exchange between the waste water and a suitable ion exchanger.

Another process, reverse osmosis, forces the waste water (under pressure) through a semi-permeable membrane, leaving charged ions behind, e.g., removing metals. The applied pressure must be greater than the osmotic pressure.

Finally, applying a direct current through a solution forces the movement of cations and anions in opposite directions. The cations move towards the negative electrode and the anions move towards the positive electrode. By setting-up semi-permeable membranes between the cathode and anode which are alternately permeable to cations and anions, aliquots of waste water can be separated into concentrated and dilute salt solutions. The process is called electrodialysis.

Distillation can be used to remove non-volatile components such as metals from water. Freezing removes most non-water molecules, especially inorganic salts.

Removal of Dissolved Organics

Dissolved organics are usually removed by adsorption onto activated carbon. Activated carbon (activated charcoal) is formed by the incomplete combustion of carbonaceous material. The carbon has enormous surface area through which adsorption can occur.

Certain synthetic polymers have strongly hydrophobic surfaces to which insoluble organic compounds (e.g., chlorinated insecticides) are attracted. Amberlite XAD-4 can remove phenols down to a tenth of a ppm in solution. These polymers can sometimes remove virtually all the nonionic organic solutes.

Phosphorus Removal

Phosphorus needs to be removed to prevent the growth of algae. Detergents are a common source of phosphorus. Phosphorus is frequently removed when the pH rises by the precipitation of hydroxyapatite ($\text{Ca}_5\text{OH}(\text{PO}_4)_3$). This can occur during secondary waste treatment (when CO_2 is not allowed to accumulate) and during the addition of soda lime and ash to soften the water in tertiary water treatment. The precipitation of hydroxyapatite requires the hydrolysis of the polyphosphates to the orthophosphate form.

Phosphate can also be removed by adsorption on activated alumina (Al_2O_3).

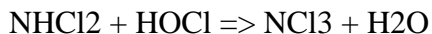
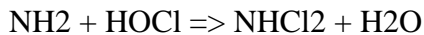
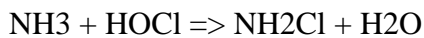
Nitrogen Removal

In the activated sludge process in secondary waste treatment, the nitrogen is usually in the form of ammonia. Ammonia can be stripped as NH_3 to the atmosphere by passing air

bubbles through wastes. However, the pH must be raised to above 11.5 to convert NH_4^+ to NH_3 , which requires the addition of lime ($\text{Ca}(\text{OH})_2$). Lime addition during water softening will raise the pH enough to form NH_3 . This would also result in precipitating phosphate as hydroxyapatite.

In the aeration step in tertiary waste treatment, ammonia is oxidized to nitrate by microbes (nitrification). However, the process requires extensive aeration (more than is usually done). The nitrate can then be reduced by bacteria to N_2 , by microbes in the presence of suitable organic matter, and returned to the atmosphere (denitrification).

The addition of chlorine in disinfection removes NH_3 and NH_4^+ through the formation of $\text{NH}_3\text{-nCl}$ in the following reactions to form N_2 by oxidation.



from which nitrogen gas can form, e.g.,



Example Problem for Mass Balance Calculations For Cleanup of Septic Tank Effluent

The discharge from home septic systems contains an average of 10 mg/l of dissolved O_2 , 20 mg/l of total nitrate (NO_3^-), and 15 mg/l of total phosphate (PO_4^{3-}). Assume a total discharge of 2000 liters per day.

The discharge flows through a container which removes the nitrate and phosphate. Carbon represents 50% by weight of cellulose. To remove the nitrate, how many grams of cellulose are needed per day for bacteria to denitrify the nitrate to nitrogen gas.

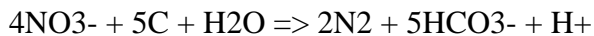
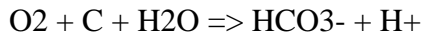
The phosphate is to be precipitated as apatite, how many grams of calcite must dissolve per day to provide the calcium for the precipitation process.

What will be the general effect on pH of the above processes? (Note that phosphate will be in the HPO_4^{2-} or H_2PO_4^- form at neutral pH values). What pH conditions would you expect apatite to precipitate most readily and why would that be a problem with calcite dissolution?

If the density of the cellulose is 0.5 g/cm³ and that of the calcite is 2.54 g/cm³, and the porosity in the container is 30%, what must be the minimum volume of the container to

totally remove the nitrate and phosphate for one year. What would be the average reaction time of the effluent in the container.

Removal of dissolved nitrate first requires removal of the dissolved oxygen because denitrification takes place only under anaerobic conditions.



C removes O₂ on a mole for mole basis and C removes NO₃⁻ at a ratio of 5 moles to 4 moles. The MW of O₂ is 31,998.8 mg/mole, that of C is 12,011 mg/mole, and that of NO₃⁻ is 62,0052 mg/mole. Hence, removal of 10 mg/l of O₂ equals 0.0003125 mol/l and requires 0.0003125 mol of C/l, and removal of 20 mg/l of NO₃⁻ equals 0.0003226 mol/l and requires 0.00040325 mol of C/l. Per liter of effluent, denitrification requires 0.0007157 mol of C/liter. At 2,000 liters per day, 1.4314 moles or 17.1925 g of C are needed per day. If cellulose is 50% by weight C then **denitrification requires 34.3851 g of cellulose per day**.

At 365 days per year, then this requires 12,550.56 grams of cellulose. At a cellulose density of 0.5 g/cm³, **the necessary cellulose volume is 25,101.12 cm³ per year**.

The removal reaction for phosphate (PO₄) is



The MW of PO₄³⁻ is 94,971.6 g/mol and for calcite is 100.0892 g/mol. Thus, 15 mg/l of PO₄³⁻ equals 0.00015794 mol/l. Because 5 calcite moles are removed for every 3 phosphate moles, 0.000263233 moles of calcite are needed per liter of effluent. At 2000 l/day, 0.5264667 moles of calcite are needed per day. Hence **phosphate removal requires 52.6936 g of calcite per day**. At 365 days/yr, 19,233 g of calcite are needed per year. Calcite has a density of 2.54 g/cm³. For phosphate removal, a volume of 7,572 cm³ of calcite are needed per year.

General pH effect - Denitrification will lower the pH and calcite transformation to apatite will raise the pH, i.e., the two processes tend to cancel each other. The reaction



implies that hydrogen ions (acid conditions) promote calcite transformation to apatite. However, apatite will precipitate most readily under high pH conditions where all of the phosphate exists as PO₄³⁻. Under these conditions, calcite is likely to be supersaturated to the solution even though it is unstable relative to apatite. There won't be a thermodynamic drive to dissolve calcite until enough apatite precipitates to move the solution to calcite undersaturation.

Use of Minteqa2 to describe the removal of phosphate.

In the above example you looked at the mass balance requirements for the removal of phosphate by precipitating it as hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. Use MINTEQA2 to thermodynamically test if calcite transform to hydroxyapatite and how effective the phosphate removal would be as a function of pH from 5 to 10. Assume the solution initially contained 0.0002 molal each of Na, K, Ca, Mg, CO_3 , Cl, and PO_4 . Discuss how effective the transformation is.

Hydroxyapatite precipitation occurred at each of the pH values, reducing the aqueous phosphate concentrations. The aqueous phosphate reduction increases with increasing pH to a pH of 9. This trend reverses going from pH 9 to 10. Above a pH of 7, essentially 100% aqueous phosphate removal has occurred.

pH	from 0.0001 to	removing
5	0.00005687	71.6%
6	0.000002748	98.6%
7	0.0000002141	99.9%
8	0.00000003592	100.%
9	0.00000001781	100.%
10	0.00000002685	100.%

Volume and reaction time - The total volume of calcite and cellulose needed for a year is shown above as $25.101 + 7.572$ liters = 32.673 liters. This volume represents 70% of the total volume if the porosity is 30%, i.e., the total volume is $32.673/0.7 = 46.676$ liters (approx. 12 gallons) for 1 year of denitrification and phosphate removal, including pore space.

The reaction time is the average time the fluid is in the barrel. $(46.676 \text{ liters})(0.3)/(2000 \text{ liters/day}) = 0.00700$ days = 10.1 min reaction time which isn't much reaction time. Note that if the container held enough solids for a 10 year period, its total volume would be 466.76 liters (approx. 123.4 gallons) and the fluid reaction time would be 101 minutes, a more reasonable reaction time.

Atmospheric Chemistry

Atmospheric Description Composition, and Stratification

Dry air in the lower atmosphere (troposphere) is composed of 78.08% N_2 , 20.95% O_2 , 0.934% argon and 0.035% CO_2 . Water vapor can range from 0.1 to 5%. The percentages are by volume and are equivalent to mole percents.

P_h , the atmospheric pressure in bars at altitude h (in cm) in the lower atmosphere, can be computed from P_0 , the atmospheric pressure at the earth's surface by

$$P_h = P_0 e^{-Mgh/RT}$$

where M is the gram weight of one mole of atmospheric particles (28.97 grams/mole), g is the earth's gravitational constant (981 cm/sec²), R is the gas constant (8.314 x 10⁷ ergs/oK/mole), and T is the absolute temperature in degrees Kelvin.

99% of the total mass of the atmosphere is within 30 km of the earth's surface; however, the atmosphere extends out about 500 km. The mean free path that an atom or molecule travels before a collision is 10⁻⁶ cm at sea level and 10⁶ cm at 500 km above the surface.

The upper levels of the atmosphere, the mesosphere and beyond are called the exosphere, because molecules and ions can escape to space. The atmosphere above the stratosphere (greater than 50 km altitude) is called the ionosphere because most of the atoms and molecules are ions. The ionization occurs in the presence of light and starts to reverse in the absence of light, resulting in the base of the ionosphere increasing in altitude at night.

Within the troposphere (within 10 to 16 km of the earth's surface) the normal situation of cold air overlying warm air creates vertical movement of air currents, as warm air rises. Mixing is rapid in the troposphere within the northern and southern hemispheres (on a time scale of 1 to 2 months); however, mixing between the hemispheres is slower (on a time scale of 1 to 2 years). **The Coriolis effect results in winds moving towards the right in the northern hemisphere and towards the left in the southern hemisphere.** In the northern hemisphere, winds rotate clockwise around a high pressure center (cold air) and counter-clockwise around a low pressure center (warm air), reversing this in the southern hemisphere. Clouds are formed of small aerosol droplets of water of 0.04 mm average diameter. **Cirrus** clouds form at great altitudes and have a feathery appearance. **Cumulus** clouds are detached masses with a flat base which have an upper "bumpy" structure. **Stratus** clouds form large sheets and give an "overcast" appearance.

Divisions of the Atmosphere

Ultraviolet light (UVC) in the 100 to 330 nm range is absorbed, raising the temperature. N₂ and O₂ disassociate.

thermosphere O >> O₂, N >> N₂

abundant ions of O₂⁺, O⁺, NO⁺

Most molecules are disassociated by the ultraviolet light. Not enough atomic O and molecular O₂ to collide to form O₃.

- 92oC **mesopause**, 85 km O = O₂ amounts

mesosphere

Ultraviolet light in the 200 to 330 nm range is absorbed; however, the temperature decreases vertically in the mesosphere because of low levels of absorbing species. Not enough atomic O and molecular O₂ to collide to form O₃. Because the mesosphere and thermosphere contain so many ions, they are called the ionosphere. The ions are created photochemically during the day. At night the lower base of the ionosphere rises as positive ions combine with free electrons.

- 20°C 50 km **stratopause**, P= 1 mbar

Temperature increases vertically in stratosphere due to heat released in the formation of ozone and as the result of O₃ absorbing ultraviolet radiation (UVB) in the 220-330 nm range.

stratosphere Contains 10 ppm O₃ at mid-level of stratosphere

Because the temperature increases vertically, there is little mixing since less dense air overlies more dense air. Water in the stratosphere comes from the reactions with CH₄.

- 56°C 10 to 16 km **tropopause**

H₂O vapor cannot escape to stratosphere because it freezes. The temperature decreases vertically because of increasing distance from the earth's surface which radiates radiation. Jet streams are winds at the tropopause, moving west to east. The troposphere thins towards the poles.

troposphere

Temperature inversions occur when a warm air mass overrides a cold air mass. Without precipitation, warm air over cold air is mechanically stable and pollutants will remain near the ground.

15°C Earth's Surface

The incoming solar radiation is in the region from 100 to 3000 nm (ultraviolet 150-400 nm [UVC 200-280 nm, UVB 280-320 nm, UVC 320-400 nm], visible 400-800 nm, near infrared 800-30,000 nm) in which the maximum intensity is at 500 nm. Half of the solar radiation is either directly reflected from the ground or clouds (produces **albedo**) or absorbed in the atmosphere and radiated back to space as **infrared radiation**. The remaining half of the solar radiation is transferred to the convecting atmosphere by contact with the earth's surface (conduction and heat released from condensation), and to both atmosphere and space by radiation.

Photochemical Reactions

The energy in a photon of radiation is equal to $h\nu$, where h is Planck's constant and ν is the frequency. As the wavelength increases, the frequency decreases because the product of the wavelength times the frequency ν is equal to the speed of light, a constant. Hence, the energy of radiation is greater at smaller wavelengths, e.g., ultraviolet wavelengths as contrasted with infrared radiation. The greater energy in ultraviolet radiation per photon, makes absorption of ultraviolet light more likely to result in chemical reactions in which electrons are lost (creating ions) or chemical bonds are broken (creating free radicals) than from absorption of infrared radiation. Absorption of infrared radiation can create higher kinetic energy which is dissipated as heat or create excited molecules or atoms which have electrons in higher energy levels than their ground state. Excited molecules or atoms dissipate energy by radiation, participation in chemical reactions, etc.

To calculate the maximum wavelength of light that can break a bond, set the change in enthalpy equal to $h\nu = hs/\lambda$ and solve for λ , where s is the speed of light and λ is the wavelength.

Absorption of photons of light energy ($h\nu$) can produce **excited atoms and molecules** denoted by $*$ in which electrons are raised to higher energy states. Excited molecules do not have to collide with another atom or molecule before reacting. They can radiate energy. Less energy is required to excite atoms or molecules than to produce ions and free radicals. O^* is the most important excited species in the atmosphere.

Ions are electrons and atoms and molecules which have lost or gained electrons. Ions are unstable but must collide with another atom, molecule, or electron before reacting. For this reason ions can be stable in the upper atmosphere. Note that ions can also be produced in the troposphere by shearing of molecules during precipitation, compression of air masses by sinking cold air, and by winds moving over hot, dry surfaces.

Free radicals denoted by o in which chemical bonds are broken to produce atoms or molecules with unshared electrons. Free radicals are unstable but must collide with another atom or molecule before reacting. For this reason free radicals are fairly stable in the upper atmosphere. Free radicals promote chain reactions with other atoms and molecules when they collide; however, collision with another radical can terminate a reaction chain. Some important free radicals in the atmosphere are:

H_3Co methyl radical

$HC(O)O$ formyl radical

$HO(O)O$ hydroxyl radical

$H_3CO(O)O$ methylperoxy radical

$HO(O)O(O)O$ hydroperoxy radical

Greenhouse Effect and the Earth's Surface Temperature

The earth radiates radiation at infrared wavelengths between 2000 to 40,000 nm with a maximum wavelength of 16,000 nm. This range of wavelengths reflects the average temperature of the earth's surface (the lower the temperature, the longer the wavelength radiated by a body). Some of the infrared light escapes to space and some is absorbed by water molecules, carbon dioxide, methane, and ozone, the major greenhouse gases. Lesser amounts are absorbed by nitrous oxide (N₂O) and the CFCs. The absorption is primarily within the troposphere. Unlike the situation for ultraviolet light, Only molecules which either have or develop a dipole (separation of + and - center of charge) during vibrations can absorb infrared light. This makes the major constituents of the earth's atmosphere, O₂ and N₂, unaffected by infrared light. After absorbing energy, greenhouse molecules radiate it in all directions, sending some of it back to the surface of the earth and raising the surface temperature.

Aerosols of sulfate and nitrate, produced by pollution, actually lower the surface temperature by reflecting solar radiation back into space. The formation of these aerosols tends to help negate the warming effects of the greenhouse gases discussed below.

As the concentration of a green house gases increases, the intensity I (amount of energy passed, not absorbed) is computed from the **Beer-Lambert law**. The law comes from the first order kinetic relationship in which the ratio of the change in intensity I (passed, not absorbed) to the change in thickness x of the absorbing layer equals a proportionality constant k times the concentration c of the absorbing species times the intensity of energy I (passed, not absorbed). For use in the atmosphere, x is the thickness of a layer of atmosphere and k is an energy sorption property of the medium (the atmosphere).

$dI/dx = -Ikc$, and after integration, from $x = 0$ to x :

$\ln(I_{\text{passing}}/I_{\text{incident}}) = -xkc$ or $I_{\text{passing}} = I_{\text{incident}} e(-xkc)$.

Hence, $I_{\text{absorbed}}/I_{\text{incident}} = (I_{\text{incident}} - I_{\text{passing}})/I_{\text{incident}} = 1 - e(-xkc)$.

where I_{passing} is the amount of energy not absorbed and I_{incident} is the amount of energy prior to absorption. Note, that the actual amount of absorption by a particular gas species does not double with a doubling of its concentration and that some of the absorbed energy will be reradiated away from Earth into space.

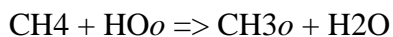
Please note that in discussing concentrations of gases in the atmosphere using %, ppt, ppm, or ppb, these units are per volume, not mass. But they are equivalent to mole fraction times the appropriate constant (i.e., % is times 100) because the low pressure means the ideal gas law is obeyed, correlating moles of molecules with volume.

Water is the major greenhouse gas, absorbing at the two ends of the infrared spectrum, between 5,500 and 7,500 nm and at wavelengths greater than 16,000 nm. Water vapor accounts for two-thirds of the absorption of infrared energy. The H₂O absorption effect is

responsible for the decrease in temperature over deserts during the night when the heat can be radiated back to space more easily in the presence of dry air. As global warming increases, atmosphere-water equilibrium will put more water vapor in the atmosphere, increasing the absorption of water vapor; however, clouds will also be increased, resulting in more direct reflection of solar heat into space. Certainly, more hygroscopic aerosols will form, and they will reflect more solar heat as well as absorb more infrared energy.

Carbon dioxide is the second most important greenhouse gas, absorbing between 12,000 and 16,300 nm, and accounting for one-fourth of the absorption of infrared energy. CO₂ is produced in oxidation reactions in engines, wood burning, making of cement, and organic respiration in animals, bacteria, and plants. CO₂ is removed from the atmosphere by plant photosynthesis (fixed carbon), organic and inorganic precipitation of carbonates from aqueous solution, and by dissolving it into the oceans which form a large reservoir to store CO₂. Unfortunately, an amount equivalent to the CO₂ removed in making plant tissue is usually returned yearly by decay processes, and ocean mixing is slow between the upper layer (above the thermocline) and the much larger, deeper ocean. Carbon dioxide concentrations in the troposphere are higher in the winter than in the summer when plants undergo more photosynthesis. The fluctuation is about 7 ppm yearly. On the average, CO₂ concentrations have increased from 315 to 340 ppm between 1958 and 1985. Prior to the industrial revolution, there was about 280 ppm in the atmosphere. The average residence time for a CO₂ molecule is over a century before being destroyed.

Methane is the third most important greenhouse gas, absorbing at around 7,700 nm, and producing one-twelfth of the absorption of infrared energy. Methane is produced by anaerobic decomposition of organic matter in wetlands, landfills, and rice paddies; escape of methane from natural gas deposits; ruminant (grazing animals); and partial oxidation in biomass burning. Enormous amounts of methane are stored in permafrost areas and as gas hydrates on the deep sea floor. Global warming could release this methane adding significantly to global warming. Methane is 27 times more efficient than carbon dioxide in absorbing infrared energy; however, the total concentration of methane is only about 1.7 ppm (1980s) in the troposphere. The concentration was 0.75 ppm before the industrial revolution. The dominant sink for methane in the troposphere is the production of the methyl radical by reacting with the hydroxyl radical. The atmospheric residence time is about 10 years for a CH₄ molecule before being destroyed.



Nitrous oxide (N₂O) is a minor greenhouse gas which absorbs at 8,600 and 7,800 nm, the latter being nearly the same absorption wavelength as methane. Nitrous oxide is biologically produced in soils during nitrification (from NH₃ to NO₃⁻) and denitrification (from NO₃⁻ to N₂). The gas forms as an intermediate step and sometimes escapes to the atmosphere before the process is completed. There are no sinks for the gas in the troposphere and it doesn't break apart photochemically until it reaches the stratosphere. N₂O is 270 times as effective as CO₂ in absorbing infrared energy; however, the current concentrations of N₂O in the troposphere are only 0.31 ppm, an increase of only 9%

since the beginning of the industrial revolution. N₂O has an average residence time of more than a century in the atmosphere.

Ozone is the fourth most important greenhouse gas, absorbing between 9,000 and 10,000 nm. Ozone is unstable in the troposphere, being reactive in oxidation reactions and undergoing photochemical decomposition, and is present in only trace concentrations, 0.03 ppm in the troposphere. It is produced by the breakup of NO₂ in the presence of UVA light.

$\text{NO}_2 + h\nu \Rightarrow \text{NO} + \text{O}$, followed by $\text{O} + \text{O}_2 \Rightarrow \text{O}_3$.

Ozone is destroyed in the troposphere by reactions with organics, peroxy radicals such as -OO₂, and reactions with NO.

$\text{NO} + \text{O}_3 \Rightarrow \text{NO}_2 + \text{O}_2$.

Industrial activity has increased the ozone concentration in the troposphere but decreased it in the stratosphere, contributing both to a colder stratosphere and to a warmer troposphere.

CFCs (chloro fluoro carbons) are trace greenhouse gases which are very effective absorbers of infrared energy in the range of 8,000 to 13,000 nm. They are 10,000 to 20,000 times as effective at absorbing infrared energy as CO₂ but are present in concentrations of only 0.0002 to 0.0005 ppm in the troposphere. Because they cause ozone destruction in the stratosphere, their heating effect in the troposphere cancels out with their cooling effect in the stratosphere. CFCs are being replaced with substitutes that are less efficient absorbers of infrared energy but they are still greenhouse gases.

Prediction of the Earth's surface temperature in the absence of the atmosphere

The surface temperature of the earth can be predicted in the absence of the greenhouse gases from the Stefan-Boltzmann law. The law assumes the earth's surface acts as a black body, radiating an equal amount of heat outward, equivalent to the solar heat received.

$I = kT^4$ where k is the universal constant (Stefan-Boltzmann constant) equal to $13.60 \times 10^{-13} \text{ cal}/(\text{cm}^2\text{K}^4\text{sec})$. T is the temperature in degrees Kelvin ($0^\circ\text{C} = 273.15\text{K}$), and I is the average solar energy received from the sun ($0.007994 \text{ cal}/\text{cm}^2/\text{sec}$). Solving for T gives 277K or 4°C which is less than the average temperature of 15°C . Other values that I've seen are -15°C for using the Stefan-Boltzmann law. The above value for I assumed $0.032 \text{ cal}/\text{cm}^2/\text{sec}$ perpendicular to the incoming rays and decreased that by 75% to account for 50% darkness and 0.50 ratio of surface area of a circle to that of half a sphere.

Greenhouse Gas Homework Problem

In 1992, the CO₂ and CH₄ concentrations in the troposphere were 356 and 1.74 ppm, respectively. They absorb infrared radiation at 15 and 7.7 μm, respectively, absorbing 77 and 60%, respectively, of the outgoing solar radiation intensity at those wavelengths. Use the Beer-Lambert law to calculate the xk parameter for each gas in the atmosphere. What would the concentrations have to increase in order to absorb 90% of the incoming solar intensity at those wavelengths? When will this be if CO₂ and CH₄ are increasing at a yearly rate of 0.4% and 0.6%, respectively. How can we distinguish CO₂ produced from decay of present-day plant and animal tissue versus CO₂ produced from burning fossil fuels.

The Beer Lambert law is $I_{\text{absorbed}}/I_{\text{incident}} = (I_{\text{incident}} - I_{\text{passing}})/I_{\text{incident}} = 1 - e(-xkc)$.

For a c of 356 ppm CO₂ $0.77 = 1 - \exp(-356xk)$ or $0.23 = \exp(-356xk)$. Hence $xk = 0.00413$ for CO₂. If the amount absorbed is 90% then $0.9 = 1 - \exp(-0.00413c)$ or $0.1 = \exp(-0.00413c)$. Hence $c = 558$ ppm CO₂ for 90% absorption.

If CO₂ is increasing at a rate of 0.4% per year, then to go from 356 ppm to 558 ppm, $558 = 356(1+0.004)^n$ where n is the number of years. This is the same formula used for compounded interest on an annual basis. Hence, $558/356 = 1.004^n$ or $\ln(1.5674) = n \ln(1.004)$ or $n = 113$ years.

For a c of 1.74 ppm CH₄ $0.60 = 1 - \exp(-1.74xk)$ or $0.40 = \exp(-1.74xk)$. Hence $xk = 0.526604$ for CH₄. If the amount absorbed is 90% then $0.9 = 1 - \exp(-0.526604c)$ or $0.1 = \exp(-0.526604c)$. Hence $c = 4.37$ ppm CH₄ for 90% absorption.

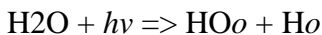
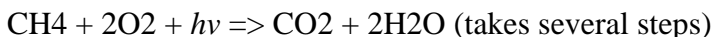
If CH₄ is increasing at a rate of 0.6% per year, then to go from 1.74 ppm to 4.37 ppm. $4.37 = 1.74(1+0.006)^n$ where n is the number of years. Hence, $4.37/1.74 = 1.006^n$ or $\ln(2.51149) = n \ln(1.006)$ or $n = 154$ yrs.

CO₂ from fossil fuels is characterized by depletion in 14C.

Stratosphere Chemistry Including Ozone Depletion

Stratospheric HO₂ Radical

The HO₂ radical is produced in the stratosphere from the photochemical breakup (photolysis) of water which was produced from CH₄ moving up from the troposphere.



The radical can also be produced directly from the reaction of CH₄ with excited atomic O, produced from O₃ destruction by absorption of UVC and UVB radiation.

$O_3 + h\nu \Rightarrow O^* + O_2$ followed by $O^* + CH_4 \Rightarrow HO\cdot + CH_3\cdot$ and the radical is destroyed and regenerated in the destruction of O₃.

$O_3 + HO\cdot \Rightarrow O_2 + HOO\cdot$ followed by $HOO\cdot + O \Rightarrow HO\cdot + O_2$

Stratospheric O₂ and O

Above the troposphere, absorption of ultraviolet light breakups molecular oxygen. O₂ filters out UV light (UVC) of 120 to 220 nm in this process.

$O_2 + h\nu \Rightarrow O + O$

The reaction occurs more in the upper stratosphere than in the lower stratosphere because of the decrease in UV radiation of 120-220 nm as the troposphere is approached.

Stratospheric O₃

Ozone (O₃) is produced by reactions between molecular oxygen and atomic oxygen, in the presence of another molecule to serve as a catalyst. As the troposphere is approached the amount of O₃ formed is decreased because of the decrease in atomic O. Within the stratosphere, O₃ concentrations increase going towards the poles because stratospheric winds blow towards the poles.

$O_2 + O \Rightarrow O_3$

O₃ is unstable and is responsible for removing 100% of UV radiation (UVC and UVB) in the range of 220-290 nm and 80% from 290 to 320 nm.

$O_3 + h\nu \Rightarrow O^* + O_2 \Rightarrow O + O_2$

The heat released in the reaction is responsible for some warming of the stratosphere. Rarely, ozone is removed by reacting directly with atomic O.

$O_3 + O \Rightarrow 2O_2$

As a result of regenerating chain reactions, HO· and NO· serve to remove most of the ozone in the higher and middle stratosphere, respectively. Cl and Br also can destroy ozone in regenerating chain reactions. All of these species remove an O from ozone and can regenerate themselves by reacting with an atomic O to release O₂. Because atomic O is rare near the troposphere boundary, the regeneration doesn't work well in the lower stratosphere.

$O_3 + HO\cdot \Rightarrow O_2 + HOO\cdot$ followed by $HOO\cdot + O \Rightarrow HO\cdot + O_2$

$\text{O}_3 + \text{NO}_o \Rightarrow \text{NO}_2_o + \text{O}_2$ followed by $\text{NO}_2_o + \text{O} \Rightarrow \text{NO}_o + \text{O}_2$

$\text{O}_3 + \text{Cl}_o \Rightarrow \text{ClO}_o + \text{O}_2$ followed by $\text{ClO}_o + \text{O} \Rightarrow \text{Cl}_o + \text{O}_2$

$\text{O}_3 + \text{Br}_o \Rightarrow \text{BrO}_o + \text{O}_2$ followed by $\text{BrO}_o + \text{O} \Rightarrow \text{Br}_o + \text{O}_2$

Near the troposphere boundary, the regenerating chain reaction with Cl_o and HO_o can operate without atomic O.

For example, regeneration of HO_o can occur by $\text{O}_3 + \text{HOO}_o \Rightarrow 2\text{O}_2 + \text{HO}_o$

And consequently most ozone in the lower stratosphere is actually destroyed by this reaction: $2\text{O}_3 \Rightarrow 3\text{O}_2$

Cl_o can be temporarily stored in an inactive form as HCl . Cl_o and NO_o are also temporarily stored in inactive forms as ClONO_2 as a combination of ClO_o and NO_2_o . In addition, NO_o is stored in an inactive form as HNO_3 containing NO_2_o and HO_o . The formation of HCl , ClONO_2 , and HNO_3 acts as a storage for most of the stratospheric Cl_o and much of the NO_o and HO_o , preventing the total destruction of O_3 . ClO_o , NO_2_o and HO_o are subsequently released when ClONO_2 and HNO_3 disassociate and Cl_o is released when HCl reacts with HO_o . The "so-called" Antarctica ozone hole is due to the release of active forms of Cl_o from inactive compounds in the polar spring. The hole is closed when nitric acid is decomposed to release large amounts of NO_2_o which ties up ClO_o in ClONO_2 .

$\text{O}_3 + \text{Cl}_o \Rightarrow \text{ClO}_o + \text{O}_2$ followed by $\text{ClO}_o + \text{NO}_2_o \rightleftharpoons \text{ClONO}_2$

$\text{Cl}_o + \text{CH}_4 \Rightarrow \text{HCl} + \text{CH}_3_o$ and $\text{HO}_o + \text{NO}_2_o \rightleftharpoons \text{HNO}_3$

In the polar winter, the polar stratospheric clouds (PSCs) form within the lower stratosphere over Antarctica as a result of the temperature dropping below 80oC producing a vortex which isolates the air. The clouds form from hydrated nitric acid ice particles which hold inactive Cl_2 and HOCl on their surfaces until released in the polar spring.

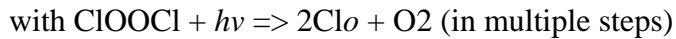
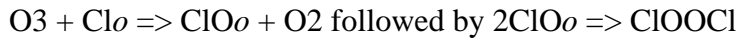
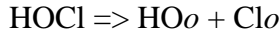
$\text{HCl}_{\text{solid}} + \text{ClONO}_2 \text{ gas} \Rightarrow \text{Cl}_2 \text{ gas} + \text{HNO}_3 \text{ solid}$

$\text{H}_2\text{O}_{\text{solid}} + \text{ClONO}_2 \text{ gas} \Rightarrow \text{HOCl}_{\text{gas}} + \text{HNO}_3 \text{ solid}$

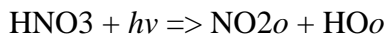
Note that during the polar winter, gravity pulls some of the clouds into the troposphere, removing some of the ozone-destroying chemicals from the stratosphere.

Sunlight in the polar spring converts Cl_2 and HOCl to Cl_o in large amounts, causing the formation of the ozone hole. The regeneration process lacks atomic O and uses ClO_o .

$\text{Cl}_2 + h\nu = 2\text{Cl}_o$



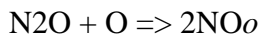
Clo is not rendered inactive by the formation of ClONO₂ until the ice crystals melt (destroying the clouds and the vortex) at the end of the polar spring, releasing nitric acid that decomposes to form NO₂o. Other sources of NO₂o move into the area once the vortex is destroyed.



Clo is eventually removed as HCl diffusing back into the troposphere where it is washed out by rain to the earth's surface. Similarly, NO₂o and HOo move back into the troposphere as HNO₃ and are washed out of the atmosphere by rain.

Stratospheric NO_x compounds

NO_o is produced by N₂O moving up from the troposphere where it is produced by denitrification reactions and by the breakup of the N₂ molecules..

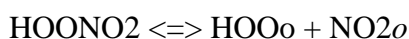
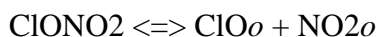


and by the high temperature combustion of fuels in the troposphere, e.g., $\text{N}_2 + \text{O}_2 \Rightarrow 2\text{NOo}$.

NO_o is transformed to NO₂o by destruction of O₃ and then regenerated by reacting with atomic O.



Much of the NO_x compounds, in the presence of Clo and Bro, end up being stored as NO₂o in inactive compounds such as ClONO₂ and BrONO₂. In the presence of HOo, NO₂o is stored as nitric acid HNO₃. In addition, in the lower stratosphere HOONO₂ may act as a temporary storage for NO₂o. These compounds can disassociate in sunlight, releasing NO₂o.

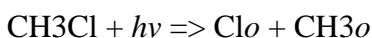


Eventually, NO_x compounds, in the form of nitric acid, diffuse into the troposphere, forming particulates or being dissolved into water and fall to the earth's surface.

Stratospheric Cl and Br compounds

Chlorinated compounds which make it up into the stratosphere, are disassociated by the UV light, releasing Cl and Br as radicals Cl[•] and Br[•]. The presence of H atoms in the compounds promote destruction in the troposphere, preventing most of such compounds from reaching the stratosphere. Note that F is inactive as HF in the stratosphere and does not destroy ozone.

Methyl chloride is one of the natural chlorinated compounds which sometimes reach the stratosphere and then breakup.



Most of the Cl is anthropogenic due to the release of CFCs (chlorofluorocarbons such as freon CF₂Cl₂) which are so stable that they rarely break up until reaching the stratosphere. These are being replaced with the HCFCs (hydrofluorocarbons such as the CHF₂Cl replacement for freon) which are less stable due to the H atom. These will be replaced by HFCs (hydrofluorocarbons) which have no chlorine. Fluorine does not destroy ozone in a chain reaction because HF forms and does not disassociate to release F[•].

Anthropogenic Br is from halon compounds, the BFCs and BCFCs (bromofluorocarbons and bromochlorofluorocarbons such as CF₃Br and CF₂BrCl) used in fighting fires. Methylbromide CH₃Br is used as a soil fumigate and can reach the stratosphere.

Once Cl[•] and Br[•] are released, they can enter into regenerating chain reactions to destroy O₃, e.g.,



Cl[•] is removed temporarily by storing it as HCl and as ClO[•] in ClONO₂, preventing the total destruction of O₃. Cl[•] is subsequently released (as ClO[•]) when ClONO₂ disassociates and when HCl reacts with HO[•]; however, most of the Cl[•] is stored in these two compounds in the stratosphere.

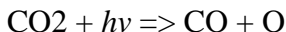


Br reacts as Cl does in the above reactions; but, there is far less Br than Cl in the stratosphere. In addition, a smaller percentage of Br is tied up in inactive forms such as HBr. Br is actually more efficient in destroying ozone than Cl. Eventually, Br and Cl

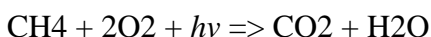
diffuse into the troposphere as HBr and HCl and they dissolve in water and are returned to the surface of the earth as precipitation.

Stratospheric CO₂, CO and H₂O

In the upper atmosphere, CO₂ should transform to CO.



Water does not pass easily above the troposphere because it freezes in the tropopause. Most of the water in the upper atmosphere is produced by photochemical oxidation of methane.



Ozone Homework Problem

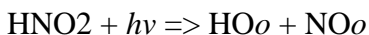
1) Ozone requires 105 kJ/mole to break it into an diatomic molecule and a monatomic atom. What is the maximum wavelength of light that can cause ozone to break up, if hc (Planck's constant times the speed of light) is 119,627 kJ/mol? Diatomic oxygen has a bond energy of 295 kJ/mol. What is the maximum wavelength of light that can break up diatomic oxygen to break up. How does this explain the general lack of these reactions in the earth's troposphere.

2) Ozone in the troposphere and stratosphere varies from about 250 to 350 to 450 Dobson units going from the tropics to the mid latitudes to the polar latitudes (neglecting ozone holes in the stratosphere over the poles). Use an average value of about 350 Dobson units. (A Dobson unit is the amount of ozone in a 1 μm layer of pure ozone at 1 atmosphere pressure and 0°C.) Within the UVB radiation bandwidth, atmospheric ozone only removes 80% of the critical radiation (for skin cancer) between 290 and 320 nm. The ozone concentration is thought to be decreasing at an annual rate of 0.5%. At this rate, what will be the increase in radiation between 290 and 320 nm at the earth's surface in 25 years?

Troposphere Chemistry Including Acid Rain and Smog Formation

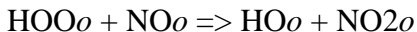
Tropospheric HO₂ Radical

During the formation of smog, the HO₂ radical is produced in the troposphere by reacting with organic matter and by decomposition of nitrous acid HNO₂ during daylight.

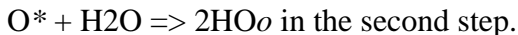
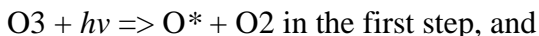


Note, that this reaction goes in reverse during the night and results in storing NO as HNO₂ in areas with lots of automobile emissions. The HO₂ is released during the early morning light in the first step of smog formation.

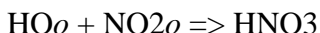
The HO₂ radical is also produced in the transformation of NO₂ to NO through reaction with the hydroperoxy radical HOO₂.



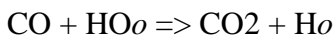
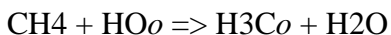
In the unpolluted troposphere, HO₂ is produced by the photolysis of ozone (O₃) with UVB radiation that passes through the stratosphere.



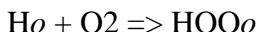
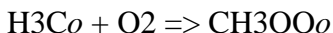
The HO₂ radical can be removed from the troposphere by removing NO₂ as nitric acid, HNO₃. This is the final removal mechanism for NO_x compounds in the atmosphere. They subsequently are dissolved in water or form particulates. This reaction is a major removal mechanism for HO₂.



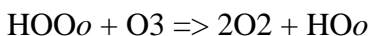
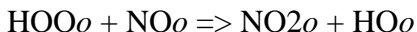
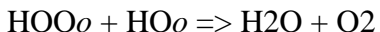
The HO₂ radical can also be (temporarily) removed from the troposphere by reaction with CH₄ and CO resulting in the formation of H₃CO and atomic H. These new species produce more free radicals.



leading to the formation of peroxy radicals



where HOO₂ can undergo chain termination reactions or regenerate HO₂ in the presence of NO and O₃.



In general, the southern hemisphere has more HO₂ because there is less CO available to destroy it. Tropical regions have more HO₂ because of the greater availability of O^{*} (formed in the presence of strong sunlight acting on ozone) to form it.

Tropospheric Oxygen

In the troposphere, oxygen is formed by photosynthesis and removed by oxidation of metals and organic molecules (respiration), e.g.,

photosynthesis: $\text{CO}_2 + \text{H}_2\text{O} \Rightarrow \text{CH}_2\text{O} + \text{O}_2$

oxidation: $4\text{FeO} + \text{O}_2 \Rightarrow 2\text{Fe}_2\text{O}_3$

respiration: $\text{CH}_4 + 2\text{O}_2 \Rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

Tropospheric CO, CO₂, and H₂O

Carbon dioxide and water are produced by organic oxidation reactions in the troposphere and removed by photosynthesis.

$\text{CH}_4 + 2\text{O}_2 \Rightarrow \text{CO}_2 + \text{H}_2\text{O}$

CO is produced as an intermediate in the oxidation of CH₄ by the HO₂ radical, by degradation of chlorophyll and other plant matter, and by combustion in the presence of a deficiency of oxygen, e.g., in forest fires, internal combustion engines, some industrial processes. CO is oxidized through reactions with HO₂ and O₂ to CO₂. CO is dangerous because it produces asphyxiation.

Tropospheric NO_x compounds and their Interactions in Forming Acid Rain and Smog (including Ozone and PAN)

Some nitrous oxide (N₂O, laughing gas) reaches the atmosphere through denitrification reactions of microbes. Most of the nitrogen entering the atmosphere is of the form of nitric oxide (NO) and is produced at high temperatures in furnaces and engines by the reaction between N₂ and O₂.

$\text{N}_2 + \text{O}_2 \Rightarrow 2\text{NO}$

In industrial processes, NO can be prevented from forming by limiting the amount of available oxygen at high temperatures. This requires two stages of combustion, in which the first stage is run at high temperatures without excess oxygen and the second stage is run with excess oxygen at a lower temperature to complete the combustion process.

The oxidation of NO to nitric acid is a major contributor to acid rain. The actual oxidation involves two steps:



although overall, the reaction is usually shown as: $2\text{NO}\cdot + \text{H}_2\text{O} + 1.5\text{O}_2 \Rightarrow 2\text{HNO}_3$

Acid rain can be neutralized rapidly if it falls on ground underlain by limestone. Otherwise, the pH of streams and lakes can fall below 5. The pH of a lake can be raised by adding lime or crushed limestone. Fish cannot reproduce at low pH levels, below 4.5 to 5. Trees can die when they are covered with acidic mist or fog but not from acid rain. The mist or fog has a lower pH, often below 3, because of less water (than in rain) to dissolve the acid in.

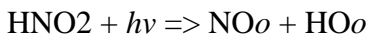
In the home $\text{NO}\cdot$ is produced by gas stoves and is subsequently oxidized to $\text{NO}_2\cdot$ by the peroxy $\cdot\text{OO}\cdot$ radicals (discussed below). The gas can build up to concentrations high enough to cause respiratory problems before escaping to the outdoors where it is finally oxidized by $\text{HO}\cdot$ to nitric acid (discussed below).

Automobile catalyst and industry scrubbing systems remove $\text{NO}\cdot$ by reduction to N_2 . Commonly, in industry scrubbing systems, nitrogen in reduced form is added as ammonia NH_3 or urea $\text{CO}(\text{NH}_2)_2$ to be oxidized as the reducing agent for the reduction of $2\text{NO}\cdot$ to N_2 . In some cases (in the absence of SO_2), methane is used as the reducing agent. In automobile catalyst, H_2 is the reducing agent. $\text{NO}\cdot$ can be reacted in the stack gas with $\text{NO}_2\cdot$ to produce N_2O_3 ($\text{NO}_2 + \text{NO} \Rightarrow \text{N}_2\text{O}_3$) which is soluble in basic solutions. This allows removing $\text{NO}\cdot$ in the same basic solution used to remove SO_2 from stack gases.

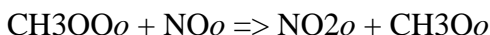
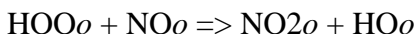
The release of $\text{NO}\cdot$ and hydrocarbons from car exhausts can result in the formation of smog. The basic sequence is as follows:

At night, $\text{N}_2 + \text{O}_2 \Rightarrow 2\text{NO}\cdot$ is produced from internal combustion in power plants and car engines, followed by $\text{NO}\cdot + \text{HO}\cdot \Rightarrow \text{HNO}_2$ which stores the $\text{NO}\cdot$ until morning.

In the morning, $\text{NO}\cdot$ is produced from rush hour traffic, together with hydrocarbons released from the engines. In addition, HNO_2 breaks down to release the stored $\text{NO}\cdot$ and the accompanying $\text{HO}\cdot$ radicals.

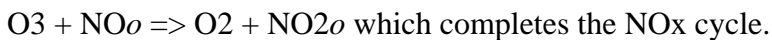
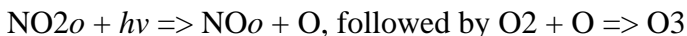
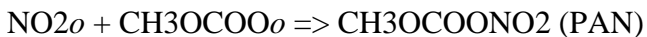


The result is that $\text{NO}\cdot$ builds up rapidly, reaching a peak between 6 and 7 AM and then decreases as $\text{NO}\cdot$ is transformed to $\text{NO}_2\cdot$ by reacting with peroxy radicals.

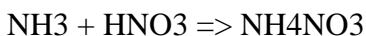
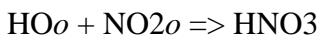


$\text{NO}_2\cdot$ builds up to a peak at about 8 AM and then decreases as it reacts with peroxy organic molecules to form compounds such as PAN (peroxyacetylnitrate). $\text{NO}_2\cdot$ also breaks down to reform $\text{NO}\cdot$, releasing atomic O which then combines with O_2 to form

ozone O₃. O₃ increases until about 12 noon when its concentration is such that it combines with NO_o to form NO_{2o} and O₂. From then on a steady state condition is reached between O₃, NO_{2o}, and NO_o. Note that O₃ is also destroyed by reacting with organics and with peroxy radicals.

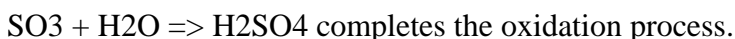


being completed. Eventually, the NO_x compounds are oxidized to nitric acid and then washed out of the troposphere as particulate matter e.g., ammonium nitrate salts, or dissolved in rain water.

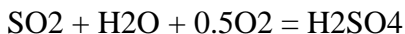


Tropospheric SO_x compounds and their Interactions in Forming Acid Rain

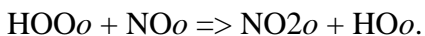
SO₂ is released in the burning of coal from power plants. In addition, H₂S and reduced sulfur in organic compounds (e.g., CH₃SH) are released from oil refineries removing sour gas and from some industrial processes. Oxidation of S compounds in the troposphere eventually leads to the formation of sulfuric acid and acid rain. The process begins with HO_o radical. Some of the problems with acid rain have already been briefly presented in the NO_x section above.



As with NO_o, the overall reaction is usually represented by

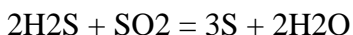


The HOO_o is returned to HO_o by reaction with NO_o to form NO_{2o}.



Scrubbing methods in industry to remove SO₂ involve dissolution in water to form sulfurous acid H₂SO₃ and precipitation as CaSO₃·0.5H₂O (calcium sulfite hemihydrate), oxidation by O₂ to SO₃ and dissolution in water to form sulfuric acid H₂SO₄ which is either captured or reacted with limestone to precipitate CaSO₄·2H₂O (gypsum). In

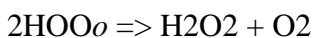
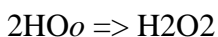
addition, SO₂ can be reduced to S by reacting it with H₂S (Claus Reaction) and the resulting S is used in industry. The H₂S for the reaction is produced from some of the SO₂ by reacting it with methane.



H₂S and S in reduced form in organic compounds can also be oxidized to S by reaction with O₂.

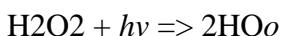
Tropospheric H₂O₂

During smog formation in the afternoon, hydrogen peroxide (H₂O₂) is produced by reactions involving either the hydroxyl radicals HO_• or the hydroperoxy radicals HOO_•.



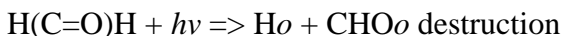
These reactions occur after NO_• has been reduced to a low level so it won't react with HOO_• to form NO₂, and NO₂ has been reduced to a low level so it won't react with HO_• to form nitric acid.

Sunlight will destroy H₂O₂ to produce the HO_• radicals. Otherwise, it will be destroyed oxidizing organic compounds.



Formaldehyde CH₂O and Other Aldehydes in the Troposphere

During smog formation, vaporized hydrocarbons react with HO_• radicals to form aldehydes of which formaldehyde is the most common. The reaction causes hydrocarbons to peak out at 8 AM and gradually decrease as the amount of aldehydes increase. The aldehydes peak out at about noon as they are photochemically decomposed into the HCO_• radical and H_• and R_• radicals, e.g., alkyl radicals during the afternoon.



Formaldehyde is also released by decomposition of synthetic materials in homes and cigarette emissions. It can collect in the home but is destroyed photochemically after mixing with the atmosphere and escaping outdoors. Formaldehyde can cause respiratory problems.

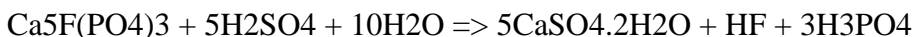
Radon in the Troposphere

The radioactive radon gases ^{222}Rn , ^{220}Rn , and ^{219}Rn are alpha emitters (helium nucleus particles) with half lives of 3.82 days, 55.6 sec, and 3.96 sec, respectively. They are part of the decay chains of ^{238}U , ^{232}Th , and ^{235}U , respectively, and are produced by the breakdown of ^{226}Ra , ^{224}Ra , and ^{223}Ra , respectively. Because of the short half lives, only ^{222}Rn can diffuse out of the near surface rock and sediment in sufficient amounts to build up high concentrations in enclosed environments such as basements of houses. The danger is not breathing radioactive radon since it is inert and would be expelled quickly before it underwent decay. The danger lies in the daughter products which are solids and would adhere to particulate matter, such as in cigarette smoke, the atmosphere. Inhaling these particles would result in them staying in the lungs and undergoing decay which would damage the lung tissue. Radon can be a problem in areas underlain by felsic igneous rocks (granite) or sediments from such rocks (arkoses).

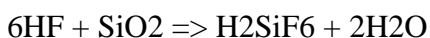
Fluorine, Chlorine and Their Gaseous Compounds in the Troposphere

Fluorine (F_2) and Hydrogen Fluoride (HF)

Fluorine gas is a strong oxidizing agent. Toxic hydrogen fluoride gas occurs naturally from volcanoes and is produced in the industrial production of phosphoric acid (H_3PO_4) by the reaction of sulfuric acid with fluorapatite $\text{Ca}_5\text{F}(\text{PO}_4)_3$.

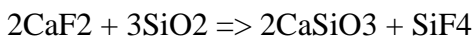


HF can be recovered by reacting the volatile HF with quartz or glass to produce water-soluble H_2SiF_6 .



Silicon Tetrafluoride (SiF_4)

Pungent SiF_4 gas is produced in mine smelting operations of silicates using fluorite (CaF_2) to produce pyroxene (CaSiO_3).



which can be recovered by reacting SiF_4 with an aqueous solution of HF to form water soluble H_2SiF_6 .

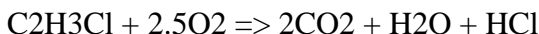
Chlorine (Cl_2) and Hydrogen Chloride (HCl)

Chlorine gas is a strong oxidizing agent that is very toxic and hydrogen chloride is a strong volatile acid. HCl occurs naturally from volcanoes and is a common industrial acid (muriatic acid) used in many processes, and Cl_2 is commonly used as a disinfectant in water treatment plants.

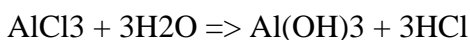
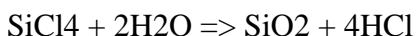
Cl₂ dissolves in water to produce HCl and hypochlorous acid (HOCl), an oxidizing agent.



Incineration of polyvinylchloride (C₂H₃Cl) produces volatile HCl.



Hydrolysis of SiCl₄ and AlCl₃ in moist air liberates volatile HCl.



Organic Molecules from Natural Sources in the Troposphere

Methane (CH₄) originates from fermenting bacteria in the soil and flatulent emissions from animals (some of your peers). Methane has a concentration of about 1.4 ppm in the troposphere where photochemical reactions of methane form ozone and carbon dioxide. In the stratosphere, photochemical oxidation of methane forms water.

Ethylene (C₂H₄) is produced by some plants and released to the atmosphere. The double carbon bond in ethylene makes it reactive with the hydroxyl radical (HO•).

Terpenes, which are composed of building blocks of 2 or more isoprene (2-methyl-1,3-butadiene) molecules, are released by many plants to the atmosphere. The double carbon bonds on the ends of the isoprene molecules may be replaced by single bonds in joining the isoprene units together in which a double bond replaces the single bond between the two center carbons.

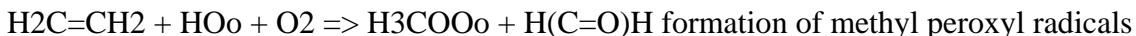
Turpentine is a mixture of terpenes which reacts with O₂ to form a peroxide that further reacts into becoming a hard resin.

Esters, (R'-O-C-R) are released by angiosperms (flowering plants), producing the fragrances associated with flowers.

Pollutant Hydrocarbons in the Troposphere

Pollutant hydrocarbons are produced from emissions from internal combustion engines and turbines, foundry operations, and petroleum refining. They consist of alkanes (C_nH_{2n+2}, with only C-C single bonds, paraffins), alkenes (C_nH_{2n}, having a single C=C double bond, olifins), dienes (C_nH_{2n-2}, having two C=C bonds), alkynes (C_nH_{2n-2}, having a single C≡C triple bond), and aromatics having benzene rings. The heavier hydrocarbons are more likely to be associated with particulate matter in the atmosphere. The alkanes are the least reactive. The presence of double and triple bonds makes a

hydrocarbon reactive. The beginning of oxidation of the hydrocarbons is initiated by reacting with the HO₂ radical, resulting in the loss of a hydrogen atom and the formation of a radical. Subsequent reactions with O₂ produce organic peroxy radicals ROO₂ with the eventual production of lower-mass hydrocarbons that are precipitated from the atmosphere with particulate matter or undergo further decomposition by reaction with sunlight and radicals.



In smog formation, the pollutant hydrocarbons build up in the morning and then decrease as they are transformed to aldehydes which peak in concentration about noon. These are subsequently destroyed by photolysis or oxidation in the afternoon by compounds such as ozone and hydrogen peroxide.

Acid Rain Homework problem

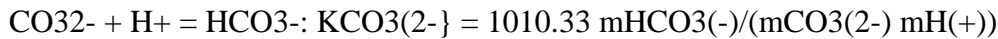
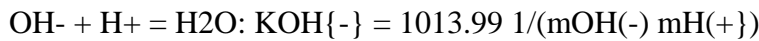
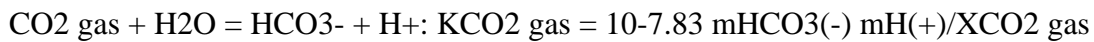
A lake has had its pH lowered to 4 as the result of acidified ground water entering the lake. Calculate the grams of CaCO₃ which need to be added at 25°C and 1 bar to raise its pH to 7 while being in equilibrium with the CO₂ in the atmosphere (CO₂ mole fraction equals 10^{-3.5}).

This is similar to the problem in which the pH is calculated for a solution in contact with the atmosphere and also in equilibrium with calcite. In this case, instead of being in equilibrium with calcite, dissolve a small amount of calcite in the solution, and calculate the resulting change in pH. By trial and error on a spread sheet you can estimate the amount needed to raise the pH to 7. Use the data below to calculate equilibrium constants. Assume activity coefficients are unity. We are not including the CaCO₃ complex because it is negligible at a pH of 7. The μ_{io} values at 25°C and 1 bar are:

Component	μ _{io} in cal/mol
Ca ²⁺	-132,300
CaHCO ₃ ⁺	-274,330
HCO ₃ ⁻	-140,260
CO ₃ ²⁻	-126,170
H ₂ CO ₃	-148,940
H ₂ O	- 56,687
OH ⁻	- 37,594
H ⁺	0
CO ₂ gas	- 94,254

Write the reactions for the complexes and CO₂ solubility so that they involve only H⁺, HCO₃⁻, Ca²⁺, and H₂O. Set activity coefficients and the activity of water to one. Using a mass balance on Ca, substitute molality of free Ca²⁺ with the total molality of Ca. Write an electrical solution balance. The equation can be simplified by substitution and by using the mass balance on Ca so that only the molality of H⁺ and the total molality of Ca are variables. Substitute 10⁻⁷ for the molality of H⁺ and solve for total molality of Ca.

From the equation, $\log K = -\Delta G_{\text{reaction}}/2.303RT$ where $R = 1.98716 \text{ cal/oK/Mole}$ and $T = 298.15\text{oK}$, we have the following reactions:



The charge balance equation is

$$2 m_{\text{Ca}^{2+}} + m_{\text{CaHCO}_3^+} + m_{\text{H}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}\{-}}$$

and the mass balance for Ca is $m_{\text{Ca}^{2+}} + m_{\text{CaHCO}_3^+} = m_{\text{tot Ca}}$

$$\text{therefore, } m_{\text{Ca}^{2+}} + m_{\text{tot Ca}} + m_{\text{H}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}\{-}}$$

where from the equilibrium reaction quotients:

$$m_{\text{HCO}_3^-} = [K_{\text{CO}_2 \text{ gas}} X_{\text{CO}_2 \text{ gas}}] / m_{\text{H}^+}; m_{\text{OH}\{-}} = 1/[K_{\text{OH}\{-}} m_{\text{H}^+}]$$

$$m_{\text{CO}_3^{2-}} = m_{\text{HCO}_3^-} / [K_{\text{CO}_3^{2-}} m_{\text{H}^+}] = [K_{\text{CO}_2 \text{ gas}} X_{\text{CO}_2 \text{ gas}}] / [K_{\text{CO}_3^{2-}} m_{\text{H}^+}^2];$$

$$m_{\text{Ca}^{2+}} = K_{\text{CaHCO}_3^+} m_{\text{CaHCO}_3^+} / m_{\text{HCO}_3^-} = K_{\text{CaHCO}_3^+} (m_{\text{tot Ca}} - m_{\text{Ca}^{2+}}) m_{\text{H}^+} / [K_{\text{CO}_2 \text{ gas}} X_{\text{CO}_2 \text{ gas}}]$$

$$= [K_{\text{CaHCO}_3^+} m_{\text{tot Ca}}] m_{\text{H}^+} / [K_{\text{CO}_2 \text{ gas}} X_{\text{CO}_2 \text{ gas}} + K_{\text{CaHCO}_3^+} m_{\text{H}^+}];$$

By substitution into the charge balance equation,

$$[K_{\text{CaHCO}_3^+} m_{\text{tot Ca}}] m_{\text{H}^+} / [K_{\text{CO}_2 \text{ gas}} X_{\text{CO}_2 \text{ gas}} + K_{\text{CaHCO}_3^+} m_{\text{H}^+}] + m_{\text{tot Ca}} + m_{\text{H}^+} =$$

$$[K_{\text{CO}_2 \text{ gas}} X_{\text{CO}_2 \text{ gas}}] / m_{\text{H}^+} + 2[K_{\text{CO}_2 \text{ gas}} X_{\text{CO}_2 \text{ gas}}] / [K_{\text{CO}_3^{2-}} m_{\text{H}^+}^2] + 1/[K_{\text{OH}\{-}} m_{\text{H}^+}]$$

Substituting in the values at a pH of 7 gives

$$10^{-1.30} m_{\text{tot Ca}} 10^{-7} / [10^{-7.83} 10^{-3.5} + 10^{-1.30} 10^{-7}] + m_{\text{tot Ca}} + 10^{-7} =$$

$$10^{-7.83} 10^{-3.5} / 10^{-7} + 2[10^{-7.83} 10^{-3.5} / 10^{10.33} 10^{-14}] + 1 / [10^{13.99} 10^{-7}]$$

$$\text{or } m_{\text{tot Ca}} 10^{-7} / [10^{-10.03} + 10^{-8.33}] + m_{\text{tot Ca}} + 10^{-7} = 10^{-4.33} + 10^{-7.36} + 10^{-6.99}$$

$$\text{or } m_{\text{tot Ca}} (20.5878) = 0.000046876 \text{ or } m_{\text{tot Ca}} = 0.000002277;$$

so adding 0.000002277 moles per liter of lake water would raise the pH to 7, using the above assumptions, e.g., unit activity coefficients.

Solid and Liquid Particulate Matter in the Troposphere

These aerosol particles are solid or liquid particles less than 100 μm in diameter. The particles grow larger by coagulation, and can be removed by several processes.

Processes to Remove Particulate Matter

Sedimentation processes removed particles by gravity in settling areas or inertial forces in centrifuges. Particles with diameter d (in cm) larger than 1 μm will settle from air with velocities v (in cm/sec) predicted from Stokes law

$$v = gd^2(pp - p_{\text{air}}) / 18\eta$$

where g is 981 cm/sec^2 (the earth's acceleration due to gravity), pp and p_{air} are the densities in g/cm^3 of the particle and air, respectively, and η is the air viscosity in poise. Particles smaller in diameter than 1 μm , will move by Brownian motion due to collisions with air molecules.

Scavenging processes remove particles by incorporating them in liquid drops. Rain is a natural scavenger. Industry uses scrubbers that inject small droplets of liquid into the flowing gases (venturi effect) to induce scavenging. The particles are sometimes ionized upstream from the scrubbers to cause attraction to water droplets having an opposite charge.

Electrostatic precipitation remove particles by charging the particles and maintaining an oppositely-charged surface for precipitation.

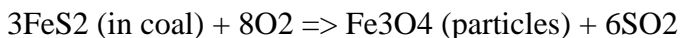
Particulate Formation by Physical Processes

Erosion, abrasion, evaporation of sea spray to form sea salts (primarily of NaCl). Release of asbestos fibers from construction material produces the curly fibers of white asbestos or chrysotile (a serpentine, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) or the short fibers of blue asbestos or

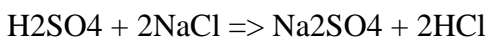
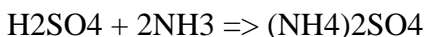
crocidolite (an amphibole). The white asbestos fibers are less dangerous than the blue asbestos fibers.

Particulate Formation by Chemical Processes

Burning fossil fuels produces **fly ash** due to inorganic matter (minerals such as pyrite and clays) in the fuel. Fly ash consists primarily of particles of oxides of iron, aluminum, calcium, silicon, and soot.



Sulfur dioxide (SO_2 produced by burning sulfur-containing coal and oil, emitted from numerous industrial processes and from internal combustion engines) is oxidized to sulfuric acid (H_2SO_4), a hygroscopic substance that attracts water molecules to form liquid droplets (acid rain). These liquid droplets are very reactive. For example, in the presence of ammonia droplets, quicklime particles, and sea salt particles, they form ammonium sulfate droplets, gypsum particles, and sodium sulfate particles, respectively.



PAH, polycyclic aromatic hydrocarbons, e.g., benzo(a)pyrene ($\text{C}_{20}\text{H}_{12}$) and chrysene ($\text{C}_{18}\text{H}_{12}$) form from burning hydrocarbons under oxygen-deficient conditions, e.g., as in engines, forest fires, cigarette smoke, barbecues. The process is called pyrosynthesis and involves dehalogenation. Cyclic aliphatics are most easily transformed into PAH compounds, followed by unsaturated hydrocarbons such as alkenes, and then by alkanes. Long chain alkanes can form PAH compounds by pyrolysis or "thermal cracking" as the chains are broken down into smaller molecules.

Important PAH compounds also include naphthalene (two fused benzene rings), benzo(a)pyrene $\text{C}_{20}\text{H}_{12}$, chrysene $\text{C}_{18}\text{H}_{12}$

Beryllium particles from metal alloys and fluorescent bulbs and inhalation causes lung disease (berylliosis).

Carbon black or soot from burning fossil fuels. Carbon black or soot has such a large surface area that many other particulates are absorbed onto the surface of the carbon particles.

Volatile methyl mercury compounds, e.g., dimethylmercury (CH₃)₂Hg and monomethylmercury CH₃Hg salts

Lead halides (chlorides and bromides), produced by burning tetraethyllead in leaded gasoline in engines in the presence of dichloroethane and dibromoethane (added to prevent lead oxides forming inside the engine).



Radioactive particles are produced from the solid decay products of radioactive gases: the noble radon gases (222Rn with t_{1/2} of 3.8 days, 220Rn with t_{1/2} of 54.5 sec which decay, respectively, to 218Po and 216Po) from radium produced as a decay product of uranium-bearing minerals, and the noble gas krypton (85Kr with t_{1/2} of 10.3 years) emitted from nuclear reactors. Coal often contains radioactive impurities which are released on burning.

Common Pollutants

Organic Compounds

Polychlorinated Dibenzo Dioxins (Dioxins), Polychlorinated Biphenyls (PCBs), and Polychlorinated Dibenzofurans (PCDFs) are the most well-known pollutants. All of these compounds bioaccumulate in fatty tissue and produce chloracne. Additional diseases are long term in development and are the subject of controversy.

Polychlorinated Dibenzo Dioxins (Dioxins)

Polychlorinated dibenzodioxins, (C₁₂H_{8-x}Cl_xO₂) e.g., TCDD (2,3,7,8-tetrachlorodibenzo dioxin) or HCDD (1,2,3,6,7,8-hexachlorodibenzo-p-dioxin), in which one to eight chlorines can be substituted for hydrogens. The structure is planar.

TCDD and HCDD, as late as the 1960s, were produced as a low-level contaminant in the manufacture of chlorophenoxy herbicides, e.g., dichloro-phenoxyacetic acid (2,4-D), trichloro-phenoxyacetic acid (2,4,5-T), trichloro-phenoxypropionic acid (2,4,5-TC or silvex). Low temperature incineration will also produce dioxins from chlorinated wastes and the burning of medical wastes has been an important source of dioxins. Dioxins also form in paper-mill processes from the reaction of chlorine used to bleach the paper with organic molecules and from burning chlorinated phenols, e.g., pentachlorophenol which is used as a wood preservative or fungicide, at temperatures between 200 and 400°C. The formation of dioxins by burning chlorinated phenols requires two phenols with Cl in the ortho positions which combine by releasing 2HCl.

High toxicity dioxins with respect to mammals have Cl in the 2,3,7,8 positions, i.e., TCDD, and Hexachlorodioxin (HCDD). Occupation by Cl of the 1, 4, 6, and 9 positions reduces toxicity. Complete chlorination produces nontoxicity. Substitution of Br for Cl results in similar toxicities. The toxicity is delayed, occurring over several weeks, and related to influences on the enzyme system.

Dioxins are difficult to biodegrade. High thermal stability results in dioxins surviving *ordinary* incineration. Very high temperatures are needed. Dioxin will decompose under ultraviolet light in the presence of organic hydrogen, by dehalogenation (replacement of chlorine with hydrogen) to produce dibenzodioxin which can be further decomposed. They have low vapor pressure and low water solubility so dioxins remain associated with solid phases. They accumulate in lipid tissue.

Polychlorinated Biphenyls (PCBs), Polybrominated Biphenyls (PBBs), and Polychlorinated Triphenyls (PCTs)

Polychlorinated Biphenyls (PCBs) and **Polybrominated Biphenyls (PBBs)** have general chemical formulas of $C_{12}H_{10-x}Cl_x$ and $C_{12}H_{10-x}Br_x$. The general structure has positions 2-6 and 2'-6' which can be occupied by H, Cl, or Br. The molecule is not planar.

These compounds have high dielectric constants and high chemical, thermal, and biological stabilities. They do not biodegrade easily and cannot be destroyed by *ordinary* incineration. PCBs were used as dielectric fluids (for coolant-insulation) in transformers and capacitors, for the impregnation of cotton and asbestos; as plasticizers, and as additives to some epoxy paints. The dielectric fluids are known as Askarel and aroclar. They contain 50 to 70% PCBs and 30-50% TCBs (trichlorobenzenes). PBBs are flame retardants and are used in fire extinguishers for airplanes and in other emergency situations. Their toxicity effects are delayed, due to enzyme inhibition, carcinogenic effects, etc.

They have low vapor pressure, and low water solubilities, leading to association with solids. They accumulate in lipid tissue. Manufacture of PCBs was discontinued in the U.S. in 1976. However, transformers are still in use that contain PCBs as dielectric fluids. Industry is trying to find a replacement for PBBs in fire extinguishers.

Biodegradation begins with anaerobic bacteria which slowly remove all but one or two chlorines on the PCBs in which the PCBs are not used as a carbon source. Instead, the Cl is used as an electron acceptor in the oxidation of organic carbon from other sources and is replaced on the PCBs by H. The H comes from the organic molecule being used as the carbon source. Aerobic bacteria then transform these residual PCBs to benzoic acid and subsequently to a chain organic acid which is easily broken down. The anaerobic portion of the overall process takes years.

PCBs can be destroyed by special incineration processes. However, furans are sometimes created in the process and furans have similar properties as dioxins.

Polychlorinated triphenyls (PCTs) have the general chemical formula of $C_{18}H_{15-x}Cl_x$ and have similar properties as PCBs.

Polychlorinated dibenzofurans (PCDFs) and Phthalate esters (PAEs)

Heating of PCBs in the presence of oxygen can produce **polychlorinated dibenzofurans (PCDFs)** which have similar properties as dioxins because they have a similar planar structure. The two chlorinated benzene molecules are linked together by a furan (five sided ring with an O that contains two double bonds in the benzene rings).

PCDFs are formed by low temperature aerobic combustion of PCBs that contain some hydrogen. The process substitutes an O for H and Cl, releasing HCl. Like dioxins, they are also formed by incinerating chlorinated wastes and from paper mill reactions involving chlorine and organic molecules. Location of chlorines in the 2,3,7, and 8 positions produce similar toxicities for PCDFs as occurs in dioxins. Because PCDFs commonly have chlorine in these positions, they may be more of an environmental threat than dioxins.

Phthalate esters are also called phthalic acid esters (PAEs) $(C_6H_{10})[-(C=O)-OR]_2$ are used as plasticizers to add to synthetic polymers to give improved flexibility, extensibility, and workability. PAEs migrate out of plastics. They have low but significant enough vapor pressures and water solubilities to migrate into the atmosphere and to move in ground water. They accumulate in the liver but degrade within 24 hours in mammals. Toxicity is low.

Soaps and Detergents

Soaps lower surface tensions of aqueous solutions by being amphiphilic with one polar end and one non-polar end. They are the salts of fatty acids. An example is sodium stearate ($NaC_{17}H_{33}O_2$) which is the sodium salt of $C_{17}H_{33}COOH$. In water, the $C_{17}H_{33}COO^-$ molecule exists as a long chain with a hydrophilic end (COO^-) and an organophilic end $C_{17}H_{33}$. The organophilic end surrounds other organic molecules, suspending them (emulsifying them) in an aqueous solution in the form of micelles. In hard water, Ca and Mg form insoluble salts with fatty acids, producing white precipitates rather than soap suds. Soaps do not produce environmental problems, because they simply precipitate out as Ca or Mg salts in sewage or other aquatic systems. Sodium soaps are solids and potassium soaps are liquids or semi-liquids.

Synthetic detergents are more soluble than soaps in water. They contain surfactants to lower the surface tension of water. These are usually the sodium salts of an organic sulfonic acid ($R-SO_3^-Na^+$). They do not form insoluble salts with Ca or Mg because of the addition of complexing agents or builders such as the polyphosphate, sodium triphosphate (STP, $Na_5P_3O_{10}$), sodium nitrilotriacetic acid (NTA, $N[CH_2(COO^-)-O^-Na^+]_3$), sodium citrate, sodium carbonate, or sodium silicate. Neither STP or NTA are used in the U.S. because of eutrophication resulting from the release of the phosphate in STP in surface waters and the potential nitrate contamination of drinking water resulting

from the slow destruction of NTA. The builders complex (tie up) Ca and Mg in solution and also make the solution slightly basic to help remove dirt from fibers.

Anionic surfactants are commonly used, e.g., primary alkyl sulfate, $\text{CH}_3-(\text{CH}_2)_n-(\text{O}=\text{S}=\text{O})-\text{O}-\text{Na}^+$. The anionic surfactant ABS (alkyl benzene sulfonate), $\text{CH}_3-(\text{CH}_2)_n-(\text{C}_6\text{H}_5)-(\text{O}=\text{S}=\text{O})-\text{O}-\text{Na}^+$, was the common surfactant in the 1960s. ABS didn't degrade easily, resulting in foam in waste waters and was replaced with LAS (alpha-benzenesulfonate), $\text{CH}_3-(\text{CH}_2)_n-[\text{HC}-(\text{C}_6\text{H}_5)-(\text{O}=\text{S}=\text{O})-\text{O}-\text{Na}^+](\text{CH}_2)_m-\text{CH}_3$, which is more biodegradable. ABS has many more tertiary carbon atoms (bonded to three other carbon atoms) which resist biodegradation.

Metals, Metalloids, Organometallic Elements, Cyanide, Nutrients and Sulfide

Some Metals (Pb, Cd, Cr), Metalloids (Hg, As), Organometallic elements (Sn), Cyanide (CN-) and Sulfide (S²⁻) in Solution

pH control

Metals are usually more water-soluble under acidic (low pH) solutions. They generally are insoluble under very basic conditions because of the formation of hydroxide, oxide, and carbonate precipitates. Aluminum is an exception being soluble under both acidic and basic conditions and insoluble at a neutral pH. The aluminum solubility at high pH is due to the formation of hydroxide complexes that increase the total aluminum in solution without increasing the activity of free (uncomplexed) aluminum. Sodium and potassium are soluble over the complete pH ranges. Silicon is not sensitive to pH except under very basic conditions when its solubility, like aluminum, is increased through the formation of hydroxide complexes.

Effect of Redox Conditions

If aqueous sulfide is present (low p_e , reducing conditions) most heavy metals (zinc, iron, manganese, lead, cadmium, arsenic, mercury, silver, copper) precipitate out as sulfide ore minerals. In the absence of aqueous sulfide, most heavy metals are soluble under reducing conditions. Under oxidizing conditions, metal hydroxides and carbonates, with the exception of uranium, will precipitate out. Uranium precipitates under reducing conditions as uraninite (UO_2) which will dissolve under oxidizing conditions. This solubility trend for uranium is responsible for the roll-front uranium deposits formed by ground water moving through an aquifer.

Chloride and Sulfate Precipitates

Silver forms an insoluble chloride precipitate. Lead and barium form insoluble sulfate precipitates.

Surface Sorption and Exchange

Surface sorption sites occur on metal oxide particles and on organic particles. These surfaces carry a positive charge at low pH conditions due to sorption of H^+ ions and a negative charge at high pH due to sorption of OH^- ions. Consequently, positively-charged metals are sorbed onto particles at high pH values and negatively-charged oxymetal complexes are sorbed onto sediments at low pH values. The crossover pH (isoelectric point) from a positive to negative surface charge occurs at different pH values for particles of different composition. The general sequence for cation preference in sorption is $Cr^{3+} > Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > NH_4^+ > Mg^{2+} > Ca^{2+} > K^+ > Na^+ > Li^+$. The general sequence for anion preference in sorption is $AsO_4^{3-} > PO_4^{3-} > CrO_4^{2-} > SO_4^{2-} > SeO_4^{2-} > NO_3^-$.

Cation exchange on clays in interlayer positions is a function of the metals undergoing exchange and the particular clay type and composition. The general order of decreasing preference in cation exchange is the same as that given above for cation sorption.

Complexes

Complexing ligands such as organic and inorganic anions, increase the solubility of metals, (e.g., EDTA, NTA) making them more mobile and able to migrate away from pollution sources.

Toxicity of Metals, Metalloids, and Organometallic Compounds

Biochemically, the metals and metalloids and those elements forming organometallic compounds are not toxic as free elements in their condensed forms. They generally pass through the body if ingested. However, Hg is toxic in its vapor form as an element and liquid mercury has a high vapor pressure. Hg^{2+} and Pb^{2+} are toxic cations which can replace one or more H atoms attached to S groups on enzymes in the body. One treatment for Hg and Pb poisoning is the administration of strong chelating compounds such as EDTA to remove the metals off the S groups in the body and then excrete the metal-chelated compound. Zn is an essential trace constituent in many enzymes and is regulated in the body by attachment to S groups on the protein metallothionein and subsequent elimination of this protein in urine. Cd^{2+} is toxic; however, because it can substitute for Zn^{2+} on S groups in the protein metallothionein, the body can eliminate it by excretion. This process protects the body against low-level Cd^{2+} exposure. As^{3+} is easily attached to the S groups on enzymes, which increases its toxicity by holding it in the body.

Hg

Hg vapor causes acute toxicological effects of the lungs, often leading to necrosis of pulmonary tissue. Methylmercury poisoning produces permanent brain injury, resulting in weakness, and progressing to paralysis. Hg can cross the placenta, producing brain damage in offspring. Methyl mercury bioaccumulates in fish in lipid tissue.

Many of the early problems related to Hg were due to Hg vapor released during ore extraction and industrial processes, e.g., roasting HgS (cinnabar) in the presence of O₂ to produce to release Hg gas (which was condensed) and SO₂ gas. Roman slaves had an average life span of 6 months in this occupation. Another bad job was to gild objects with an amalgam of Hg and Au and then to remove the Hg by heating the object which released Hg vapors. Hg was used extensively, even today, to remove Au and other metals from their ores, resulting in pollution problems, e.g., Freeport McMoran's gold mining operation in Indonesia. Hg has also been used in some pesticides. The major exposure is due to its water-soluble methylated forms which accumulate in tissue. Hg occurs in soils with a range of 0.02 to 0.41 ppm.

The common Hg mineral is cinnabar, HgS. The common forms of Hg in the environment are Hg²⁺ (mercuric, most toxic) and Hg₂²⁺ (mercurous, less toxic). HgCl₂ has been frequently used in suicides. While Hg vapor is poisonous, metallic mercury usually passes through the body with little harm. Hg is sorbed in soils at basic pH values when it is present as a cation. Hg is easily immobilized HgS in soils with trace amounts of sulfide which occur in humus. At pH values above 7, Hg(OH)₂ limits the solubility of Hg in soils and sediments but doesn't reduce it to trace constituents. Hg solubility is increased with OH and Cl complexes.

The toxic forms of Hg are usually introduced into organisms through their water-soluble methyl forms: nonvolatile CH₃Hg⁺ (methyl mercury occurring at a pH below 8) and volatile (CH₃)₂Hg (dimethyl mercury occurring at a pH above 8). These methylated forms are produced by bacteria during aerobic and anaerobic conditions. They are not considered complexes because they do not disassociate and are examples of organometallic compounds. Mercury will bioaccumulate in lipids in the food chain.

Dimethyl mercury has a high vapor pressure and will evaporate from sediments to the atmosphere. Dimethyl mercury is commonly lost from alkaline (high pH) waters. Methyl mercury is more likely to bioaccumulate than dimethyl mercury and occurs in acidic and neutral waters. The symptoms of mercury poisoning are permanent brain damage, paralysis, and loss of vision. In the absence of the methyl compounds, mercury is insoluble as a hydroxide or a sulfide.

As

The EPA maximum contaminant level MCL for arsenic in drinking water was 50 ppb in 2000 but limits as low as 10 ppb are proposed.

The common forms of As in the environment are AsO₃³⁻ (As³⁺ in arsenite as an oxyanion, most toxic) and AsO₄³⁻ (As⁵⁺ in arsenate as an oxyanion, less toxic). These forms of arsenic are rapidly excreted from the body. Arsenic exists as a negatively charged oxyanion under oxidizing conditions and is sorbed strongly on soils under acidic and neutral pH conditions. However, As³⁺ is only weakly sorbed, because under reducing conditions the neutral complex H₃AsO₃ predominates below a pH of 9, making

sorption less likely. Soils high in Ca will precipitate Ca arsenate which limits its mobility in these soils.

Environmental exposure to As is due to its extensive use in pesticides (the insecticide $\text{Pb}_3(\text{AsO}_4)_2$ and the herbicides $\text{Ca}_3(\text{AsO}_4)_2$ and Na_3AsO_3) and the paint pigment Paris Green ($\text{Cu}_3(\text{AsO}_3)_2$). The toxic forms of As in water are the neutral As^{3+} complexes: AsH_3 and $\text{As}(\text{CH}_3)_3$ which are sorbed onto S groups in enzymes. Arsenic occurs in soils with a range of 2 to 25 ppm.

Arsenic was used as a poison in the form of As_2O_3 during ancient times (toxic dose < 0.1 g). As was used extensively, even today, to remove Au and other metals from their ores, resulting in pollution problems, e.g., Freeport McMoran's gold mining operation in Indonesia.

Water-soluble methyl forms of As are generally not toxic because they are rapidly excreted, e.g., nonvolatile $\text{CH}_3\text{AsO}(\text{OH})_2$, and volatile $(\text{CH}_3)_3\text{AsO}$. One exception is trimethyl arsenic $(\text{CH}_3)_3\text{As}$ which is produced by mold living on arsenic pigments in wallpaper. This gaseous compound is easily absorbed into the body, producing "death by wallpaper." The other toxic arsenic compound is AsH_3 . Arsenic is a strong carcinogenic and is linked to lung, liver, and skin cancers in human.

Pb

Plumbism, the earliest manifestation of lead poisoning is due to the prevention of iron uptake which stops the formation of hemoglobin, leading to anemia. Severe lead poisoning, acute encephalopathy, leads to convulsions, coma, and death within 48 hours. Minimal biomagnification of lead occurs in the food chain. Lead is not methylated and hence is not absorbed in lipid tissue.

The common ore of lead is galena (PbS). Lead is commonly in the Pb^{2+} state in natural waters and the compounds that precipitate from natural waters, e.g., $\text{Pb}(\text{OH})_2$, PbCO_3 , and PbSO_4 . The organometallic compounds formed by lead involve four covalent bonds such as $\text{Pb}(\text{C}_2\text{H}_5)_4$, the synthetic compound tetraethyllead which was the lead additive in leaded gasoline.

Lead does not form methylated compounds, limiting its mobility in nonacidic water because of its insolubility as a lead hydroxide or lead carbonate. Sediments also remove lead preferentially from waters, compared to other metals, by cation exchange and sorption. Lead is more mobile in the atmosphere because tetraethyllead has a high vapor pressure and the burning of leaded gasoline (with halide additives to prevent the formation of lead oxides) produces particulates of PbCl_2 and PbBr_2 . In batteries, lead exist as Pb^{4+} in PbO_2 and Pb^{2+} in PbSO_4 . In paints, Pb_2O_3 (a mixture of lead in the +2 and +4 valence states) is used as a red pigment, and PbCrO_4 is used as a yellow pigment (schoolbus color). $\text{Pb}(\text{CO}_3)_2(\text{OH})_2$ was used as a white pigment. PbO is yellow and has been used in glazed pottery. Children tend to eat lead-contaminated soils and paint flakes because of its sweet taste. Lead was also commonly mixed with tin to make solder joints

in pipes, and the lead tends to dissolve in acidic, oxygenated waters, i.e., soft waters in pipes.

Lead has an average range in soils of 17 to 26 ppm. Lead is the most immobile of all the common heavy metals. It occurs as the Pb^{2+} form and is strongly sorbed by soils under neutral to basic conditions, being particularly attracted to sulfur groups in humus. At higher pH values, it is removed by precipitation as $Pb(OH)_2$, $PbCO_3$ and lead phosphate compounds. Under reducing conditions, precipitation as lead sulfide removes it from ground waters. In the presence of manganese oxides, it is oxidized to the extremely insoluble Pb^{4+} while reducing Mn^{4+} to Mn^{2+} . Lead does not undergo biomagnification in the food chain (also not toxic to plants) and usually enters the body through eating paint flakes or breathing lead particulates, not by drinking water. However, acidic waters (usually soft waters) can contain dangerous lead concentrations due to the leaching of lead chromate and the oxidation of lead in solder. The common symptom of lead poisoning is anemia because lead interferes with the formation of hemoglobin. High levels of lead produce permanent brain damage (especially in children) and kidney dysfunction. Over time lead will substitute for Ca in bone which acts to store the lead. Then, in old age, the lead is reactivated by the slow dissolution of bone.

Cd

The EPA drinking water standard is 10 ppb for cadmium.

Cadmium is volatile upon heating, leading to its release from zinc-mining smelters (smelting sphalerite (ZnS), due to the occurrence of cadmium with zinc in ores. Like Zn, cadmium normally occurs in the environment as Cd^{2+} . Cadmium is used as a paint pigment and in rechargeable batteries. Incineration releases the cadmium from spent batteries and pain-covered plastics, and it tends to condense on the smallest-size particles which are the most difficult to remove from smokestacks.

Cd has a range of 0.06 to 1.1 ppm in soils. It is more mobile than lead because it is weakly sorbed and is not retained by sediments through cation exchange. Unlike Hg and As, it does not form stable methylated compounds. Its solubility is limited to trace amounts in soils under reducing conditions by the precipitation of Cd sulfides. Under oxidizing conditions it is fairly soluble in acidic waters but has limited solubility in basic conditions by the precipitation of carbonates, hydroxides, and phosphates. Liming a soil will reduce the Cd uptake by plants by raising the pH which causes precipitation of Cd carbonate. Cd does some bioaccumulation in the food chain, plants and seafood and this results in our greatest exposure to cadmium. Cd toxicity is usually due to Cd substitution for Zn in enzymes. The symptoms of cadmium poisoning include severe vomiting with doses over 15 mg. A toxic dose is > 1 g. Low-level exposure, if not eliminated by the body by excretion of the protein metallothionein, results in Cd substitution for Ca in bones producing *itai itai*, a degenerate bone disease. Excess Cd is stored in the liver and kidneys.

Cr

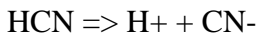
Chromium exists as Cr^{3+} and Cr^{6+} of which the toxic form Cr^{6+} only exists under a high pe (very oxidizing conditions). Cr^{6+} is part of the chromate anion (CrO_4^{2-}) which is weakly sorbed and highly mobile in the aqueous phase. At pe conditions of moderately reducing and lower and with a pH greater than 5, chromium will exist as Cr^{3+} and will either be sorbed or precipitate out as Cr_2O_3 .

Sn

Tin is not toxic in inorganic forms but is toxic to bacteria, fungi, and fish as organometallic tin compounds. Tin forms an extensive sequence of microbe-mediated methyl compounds as well as numerous environmentally-dangerous synthetic organometallic compounds, e.g., TBT (tributyl tin compounds, $(\text{C}_4\text{H}_9)_3\text{Sn-R}$,) used to coat boat hulls. Fungi are most affected by having 4 carbon atoms in unbranched chains attached to tin. These compounds get into the food chain as the result of leaching and affect fish reproduction. Mammals have the enzymatic protection of being able to break down the organometallic tin compounds rapidly.

CN-

Deadly cyanide (CN^-) exists in waters complexed to metals and as the protonated acid. HCN is a weak acid with a log K of -9.22. Volatile HCN is very toxic and has been used in executions. The metal complexes are not as toxic generally as the protonated form. CN^- bonds to ferric iron in enzymes preventing utilization of oxygen in cells.



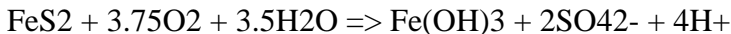
Compounds Promoting Eutrophication

Eutrophic waters are anaerobic, having a deficiency in dissolved oxygen. These waters have a high BOD (Biological Oxygen Demand) which is measured in the laboratory by the amount of oxygen utilized in a water sample over a five day period. BOD is correlated positively with TOC which is the total organic carbon in a water sample. TOC is measured directly in the laboratory. Eutrophication is frequently due to decay of excessive amounts of algae. Excess algae growth occurs when pollution provides phosphates and nitrates, as in fertilizers washed into lakes and streams. Usually, in the absence of pollution, deficiencies in these nutrients limit plant growth. The presence of certain aqueous species: nitrite (NO_2^-), sulfite (SO_3^{2-}), ammonia (NH_3), and hydrazine (N_2H_4) increase the possibility of eutrophication. They act as oxygen scavengers because they are oxidized in the presence of oxygen.

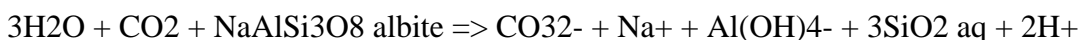
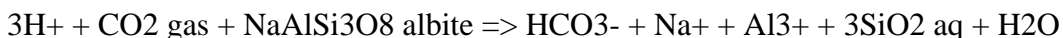
Acidic Waters, Alkaline Waters, Saline Waters

Acidic waters are associated with oxidation of sulfur and sulfides in rocks. Frequently, these sulfur-containing minerals are exposed by mining. One simple way to remove the

sulfate from the waters is to inject a soluble organic source to induce sulfate reduction which then causes the metals to precipitate out as sulfides.



Alkaline waters are common in desert regions where streams drain into closed basins. These waters contain inorganic carbon, derived from atmospheric exchange of CO_2 during weathering reactions.



The inorganic carbon concentrations increase in closed basin lakes until all aqueous calcium and magnesium are precipitated as carbonates. The waters become alkali, with high concentrations of aqueous sodium carbonate. The pH rises because of the formation of bicarbonate as the carbonate concentration increases.

Waters of high salinity occur in regions where fresh water mixes with sea water, fresh water mixes with brines in the pores of rocks, fresh water becomes concentrated by evaporation into saline brines, and fresh water dissolves evaporite deposits.

Agrichemicals

Insecticides and Narcotics

General Toxicity Effects and Physical Properties

The toxicity of insecticides is generally due to interference with the nervous system of organisms. Neurons in the nervous system contain dendrites (to receive incoming signals) and axons (to send outgoing signals). Neurons are wrapped in myelin, a lipid (fat) rich tissue. Insecticides can interfere with the electrical transfer of signals along the axons or with the chemical transfer of signals across the synapse or junction point between the end of the axon and the dendrite of another neuron.

The electrical transfer along the axons is due to the maintenance of a potential difference across the cell membrane. The interior of the axon has more K^+ and less Na^+ than outside the axon. The potential difference is maintained by a cell wall which is normally more permeable to K^+ than Na^+ . **An electrical signal passes down the axon as Na^+ is allowed to diffuse into the axon, reversing the potential difference. This potential difference is quickly reversed by the diffusion of K^+ out of the axon.** More slowly, the excess Na^+ is pumped out of the axon as K^+ diffuses back into the axon. **The**

toxicity of DDT-like organochlorine insecticides, hexachlorocyclohexane (HCH) and the pyrethroids relates to their interference with the transfer of ions across the membrane. Apparently they bind to the nerve cell membrane, keeping the membrane open to the passage of Na⁺ ions. This interference occurs in insects and also in reptiles (including birds), and amphibians for the DDT-like organochlorine insecticides and HCH.

The chemical transfer across the synapse occurs through the release of a transmitter chemical, generally the acetylcholine ($H_3C(C=O)OCH_2CH_2N^+(CH_3)_3$) or epinephrine (adrenaline) ($[(OH)_2C_6H_3]CH(OH)CH_2NH_2$). A second chemical must then be released to deactivate the transmitter. Acetylcholinesterase is released to hydrolyze acetylcholine to inactive components: acetic acid ($CH_3(C=O)OH$) and choline ($HOCH_2CH_2N^+(CH_3)_3$), and monoamine oxidase can be released to oxidize epinephrine (a slower process than the degradation of acetylcholine). The breakup of acetylcholine involves the attraction of the positively-charged (electrophilic) N atom to a negatively-charged site on acetylcholinesterase and the positively-charged (electrophilic) C atom of the carbonyl group to an OH group on acetylcholinesterase.

Organochlorine cyclodienes overstimulate the production of acetylcholine leading to a loss of nerve coordination; whereas, **organophosphorus and carbamate insecticides pirate the acetylcholinesterase, preventing the destruction of acetylcholine.** Under alkaline conditions, or due to the organism's metabolism, or in the presence of other chemicals, the acetylcholinesterase will eventually be released. In contrast to the organophosphorus and carbamates insecticides, **nicotine's toxicity is due to binding with the receptor sites of the acetylcholine**, rather than pirating the acetylcholinesterase.

Narcotics decrease the activity and sensitivity of organisms. The "indifferent" narcotics are those which are reversible and little affected in their potency by substantial changes in their structures. Indifferent narcotics include ethanol (C_2H_5OH), diethyl ether ($C_2H_5OC_2H_5$), chloroform ($CHCl_3$), carbon disulfide (CS_2), ethylene dichloride ($ClCH_2CH_2Cl$) and chloropicrin (Cl_3CNO_2). **Narcosis occurs when a narcotic reaches a threshold concentration in the lipid-rich tissue of an organism.** For a particular organism, emersion in an external fluid (liquid or gaseous solution) containing a narcotic, will produce narcosis at some characteristic activity of the narcotic in the external fluid. **Narcosis will occur at the same characteristic activity for other "indifferent narcotics", following exposure of the organism to the external fluid.** The narcosis is due to the increasing concentration of the "indifferent" narcotic in the lipid tissue of the organism. **Narcotics which are not "indifferent" will have a sensitivity factor characteristic of the narcotic for the organism.**

In discussing insecticides, the electronic structure of atoms and groups of molecules play an important part. **The atoms and groups of atoms in the large organic molecules used as insecticides, can be electrophilic (attracting electrons) or nucleophilic (repelling electrons).** The H atom in these molecules is the reference. If an atom or group of atoms is more attracted to electrons than H, the atom or group of atoms is electrophilic and vice

versa. **Negatively-charged ions are nucleophilic and positively-charged ions are electrophilic.**

Certain groups of atoms will be polar, having a positive end and a negative end, as in -NO₂ which acts as a cation because the N is the positive end and serves as the attachment point.

Polar groups of atoms are often called hydrophilic (because water is polar) and **nonpolar or apolar groups of atoms are often called lipophilic** (because lipids are apolar). **Organisms tend to excrete polar molecules (e.g., separation in the kidneys) and accumulate apolar molecules in fatty or lipid tissue.** Nerve tissue is especially rich in lipids. **Most insecticides act on nerves and accumulate in fatty nerve tissue.**

The strength of the tendency to orient a molecule in a magnetic field is the dipole moment of the molecule and directly proportional to the polarity of the molecule. The polarity can also be estimated by measuring the partition coefficient of a molecule between a polar solvent (e.g., water) and a nonpolar solvent (e.g., oil). The partition coefficient is the ratio of solubilities in the two solvents.

In general, a polar compound dissolves significantly in a polar solvent and less so in a less-polar solvent and vice versa. However, the aromaticity of an organic compound is also important. **In organic solvents of equal polarity, aromatic solutes will have higher solubilities in aromatic solvents than in non-aromatic solvents.**

The following solvents are arranged in order of decreasing polarity: salt solution > water > acetone (CH₃C(O)CH₃) > ether (C₂H₅OC₂H₅) > chloroform CHCl₃ > benzene (C₆H₆) > hexane (C₆H₁₄).

The polarity of a molecule is increased by small size, e.g., ethers, esters, and amines are water soluble if they have less than six carbon atoms. **Polarity is increased by ionization of attachment of groups of atoms**, e.g., -COO⁻, -NH₃⁺, -SO₃⁻, N⁺O₂⁻; and **by the presence of O**, e.g., OH in alcohols, O in esters, aldehydes, ethers, and ketones.

Different Insecticide Groups

Organophosphorus Insecticides

The organophosphates can be divided into six groups, containing the following groups of atoms which have attachments:

O O S phosphate -O-P-O- phosphonate -C-P-O- phosphoro -O-P-O- esters O O -thionate
O O S O phosphoro -O-P-S- phosphoro- -C-P-S phosphor -O-P-N- -thiolate O dithioate
O -amidate O

Generally there is one long sidechain attached through a single bond from a N, S, or O atom to the "right side in the diagram above" of the P atom. The toxicity of the organo-

phosphorus is not especially sensitive to the nature of the long sidechain which must detach from the phosphorous atom during the process. Two smaller side chains occur through attachments through O atoms on the left and bottom side of the P atom. The double bond attachment is to an S or an O atom. This has to be an O atom for the compound to be very toxic. In general, within organisms, the S is replaced with an O atom, i.e., arms the compound by enzymatic activity.

The organophosphate insecticides can be thought of as esters of alcohols with a phosphorus acid. They can be degraded simply by hydrolyzing them with water which removes the long attachment (turning it into an alcohol through the addition of OH) and leaving an OH or SH group attached to the P atom. The degradation proceeds most rapidly in the absence of a double bond to S. If one is present, it can be replaced through metabolic activity by a double bond to O. The O is more electrophilic than S, so it draws electrons from the P, making the P more positive, hence attracting the O atom in water. In an organism, the pirating of acetylcholinesterase takes place when there is a double bond to oxygen. Hence, the phosphorothionate and phosphorodithioates must be replaced by phosphates and phosphorothiolates before the nervous system can be attacked.

Organophosphate insecticides pirate acetylcholinesterase (E_{OH}) by releasing the long chain attached to the P atom and replacing it with deprotonated acetylcholinesterase (E_O). The process involves the release of H from a OH group on acetylcholinesterase, followed by attachment to the P atom through the O atom. The attraction between the O atom of acetylcholinesterase and the P atom of the organophosphate insecticide is increased by having an O atom already double bonded to P, making P more electrophilic. The pirating is the result of organophosphate compounds having the correct shape and size (like a key) to bond with the deprotonated acetylcholine-sterase.

Regeneration of acetylcholinesterase occurs by hydrolysis, leaving a OH group bonded to the P and an OH group completing the generation of acetylcholinesterase. The regeneration occurs rapidly under alkaline conditions. Other chemicals can free acetylcholinesterase more rapidly than OH⁻, e.g., the oximes (have a C=NOH group).

phosphorothionate example, parathion

phosphorodithioate example, malathion

phosphate esters example, paraxon

The organophosphate insecticides are easy to biodegrade (first step is hydrolysis), resulting in a half life of a few months. They have high water solubilities, thus easy to leach out of solids. They do not accumulate in lipid tissue.

Some non-aromatic forms, e.g., malathion, can be detoxified internally by mammals using enzymes to form alcohols. But, those with aromatics, e.g., parathion, are extremely poisonous to mammals. However, if a P=S is present, toxicity requires enzymatic replacement with P=O.

Organochlorine Insecticides (DDT analogues, toxaphene, cyclodienes with fused 5 member rings, and hexachlorocyclohexane [HCH] or lindane)

DDT and its Organochlorine Analogues

DDT is a chlorinated diphenyl with the structure given below. DDT and its analogues have the correct size and shape to interfere with nerve signal transmission down axons, allowing excess Na^+ to enter the axons to keep the nerves firing. These compounds are generally resistant to biodegradation and accumulate in the fatty tissue of organisms where DDT often transforms to the insecticide DDD by loss of a chlorine. The major degradation path of DDT by microbes and in metabolism leads to the formation of DDE which is resistant to biodegradation but is non-toxic to insects. Eventually DDE is transformed to a carboxyl acid which can be excreted by organisms and destroyed by microbes.

The important analogues are DDD and methoxychlor. Methoxychlor degrades more easily than DDT and does not accumulate in the food chain.

Cyclodienes

The cyclodienes are organochlorine insecticides that contain fused five member rings. The cyclodienes are more toxic to mammals than DDT and its analogues. The cause of the toxicity is different from DDT, probably being a stimulation of the production of acetylcholine, resulting in a loss of nerve coordination. Like DDT and its analogues, the cyclodienes are generally resistant to biodegradation and tend to accumulate in lipid tissue in the food chain. Their low solubilities in water and low vapor pressures make them immobile in soils.

Heptachlor has a typical structure. They are formed by reactions between chlorinated cyclodienes, e.g., hexachlorocyclopentadiene with cyclopentadiene. Common cyclodienes include chlordane, dieldrin, isodrin, and aldrin. The most important cyclodienes, e.g., endrin, have four fused 5 member rings. The cyclodiene aldrin biodegrades to dieldrin by epoxidation, but dieldrin is more poisonous than aldrin. One cyclodiene, endosulfan is degraded in the environment and does not accumulate in the food chain. Endosulfan is permitted for use in the U.S.

Hexachlorocyclohexane

HCH or lindane ($\text{C}_6\text{H}_6\text{Cl}_6$) or benzene hexachloride BHC (a misnomer since benzene is not present), is a six ring chain of carbon atoms with a single Cl attached to each C.

The toxicity of HCH is similar to DDT and its analogues but with a somewhat greater mammal toxicity. Like DDT, HCH causes a disruption in the passage of nerve signals on axons by producing a sodium-potassium imbalance. HCH may also act like the cyclodienes in causing an excessive release of acetylcholine. HCH has a higher vapor pressure than DDT and its analogues, making it more mobile. HCH also has a moderately

high water solubility (10 ppm) and does not significantly bioaccumulate in fatty tissue. Within organisms, HCH degrades through the conversion of the cyclohexane to an aromatic, together with the loss of chlorine and the addition of sulfur.

Toxaphene

C₁₀H₁₀Cl₈, a partially chlorinated camphene (C₁₀H₁₆) which is a natural terpene produced by pine trees. Toxaphene is a mixture of up to 177 different compounds. It was widely used as a replacement for DDT before being banned in 1982. Toxaphene has moderate solubility in water (3 ppm) but bioaccumulates in organic tissue (however not to the extent of DDT) and is resistant to biodegradation. I could not find any information on the cause of its toxicity to insects.

Carbamates

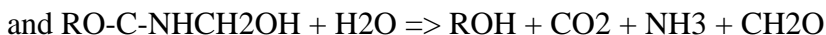
Carbamate insecticides are derivatives of carbamic acid HOC(O)NH₂, and have the general formula RO(C=O)NHR' in which R' is often CH₃ and R is a large attachment or sidechain. Aromatic carbamates usually have a benzene ring replacing one of the H atoms attached to the O atom, and thiocarbamates will have a SR atom replacing the OH atoms. Some of the aromatic carbonates will have Cl atom substitution on the benzene ring and within the R group attached to an O. The carbamates break down within a matter of weeks in the environment and do not bioaccumulate in lipid tissue. They have high water solubility, hence are easy to leach out of solids.

Carbaryl, the well-known carbamate insecticide (Sevin) which is dusted on tomatoes, has naphthalene for R.

Carbamates pirate acetylcholinesterase, as do the organophosphates. However, unlike the organophosphates, the toxicities of carbamate insecticides are sensitive to the structure of the long sidechain R group. The most toxic carbamates have a shape and size similar to that of acetylcholine with which they must compete for acetylcholinesterase.

Carbamates capture acetylcholinesterase by replacing RO (in the form of ROH) with deprotonated acetylcholinesterase EO. Through hydrolysis, acetylcholinesterase is released in its protonated form (EOH) together with HO(C=O)NHR'.

The carbamates are metabolized and detoxified by hydrolysis to form phenols (aromatic with a OH group), oximes (have a C=NOH group), or other hydroxy compounds together with methylcarbamic acid (CH₃NHCOOH) which decompose to ammonia and carbon dioxide.



Nicotinoids

Nicotine is obtained from the leaves of tobacco plants. Nicotine is toxic to all vertebrates and insects. The toxicity is due to the mimicking of acetylcholine by the nicotinium ion which carries a positive charge on the pyrrolidine nitrogen atom, thus competing for the receptors used in the passage of nerve signals between the end of axons and the dendrites of another neuron. Nicotinium is not destroyed by the acetylcholinesterase.

Pyrethroids

The natural insecticide pyrethrin is from ground-up flowers of the *genus* Chrysanthemum. Pyrethrin is composed of four esters, formed from two acids, chrysanthemic acid and pyrethric acid; and two alcohols, pyrethrolone and cinerolone. Esters, alcohols, and organic acids have the general formulas $R'-C(O)O-R$, ROH , and $RC(O)OH$, respectively. Esters containing the alcohol pyrethrolone (R includes $-CH=CH_2$) are called pyrethrin I if the acid was chrysanthemic acid (R includes CH_3) and pyrethrin II if the acid was pyrethric acid (R includes CO_2CH_3). Esters containing the alcohol cinerolone (R includes CH_3) are called cinerin I if the acid was chrysanthemic acid and cinerin II if the acid was pyrethric acid. Additional pyrethroids are synthetic. Two of these are esters of chrysanthemic acid; allethrin (formed with the alcohol allethrolone) and cyclothrin (formed with a cyclopentane analog of allethrolone). Additional compounds containing a methylenedioxyphenyl group increase the toxicity of the pyrethroids when they are applied together.

The pyrethroids cause paralysis, consistent with action on the nerves connected to the muscles. These are knock-down insecticides of high toxicity which degrade rapidly and are of minimal danger to mammals and birds. In mammals and birds, the pyrethroids are rapidly metabolized by ester cleavage, oxidation, and hydroxylation. In soils, pyrethroids are virtually immobile because of their low solubility in water; however, they degrade rapidly to carbon dioxide.

The fast action of pyrethroids on insects implies an effect on the peripheral nervous system. The causes of the toxicity of the pyrethroids are similar to those of DDT-like organochlorine compounds in interfering with the transaction of electrical impulses along axons. These insecticides keep nerves firing by delay the closing of the sodium channels that leak Na^+ across the axon cell membranes.

F) Butylamides

Fast-action natural insecticides which are not as stable as pyrethroids. These are butyldienes containing the carbonyl group ($C=O$) and NH where N is in the chain.

Herbicides

The toxicity of herbicides is often due to effects on plant photosynthesis and cellular respiration.

Photosynthesis



Photosynthesis occurs in the chloroplasts of leaf cells. In *Photochemical System II*, light energy absorption at 580 nm causes the pigment chlorophyll to move a pair of electrons to a higher energy state and donate them to an electron receptor. The electrons are subsequently replaced in the chlorophyll by removing two electrons from an oxygen in a water molecule, releasing oxygen and hydrogen ions (Hill reaction).

Photochemical System I, takes the electrons from *Photochemical System II* and through absorption of light energy in a second pigment system at 700 nm, boosts the energy of the electrons to a higher level than that achieved in *Photochemical System II*. The electrons reduce NADP^+ to NADPH which raises the energy of the NADP (nucleotide of adenine).

If NADPH is abundant or NADP^+ is not abundant, then the electrons are not used to generate NADPH. Instead, they are passed down a chain of electron receptors, releasing energy and forming a molecule of ATP (adenosine triphosphate) from the addition of P to ADP (adenosine diphosphate). ATP contains energy in its bonds that is subsequently released by cells when they need energy. This generation of ATP is called *Cyclic Electron Flow*.

The cycle then enters the *dark reaction* or *Calvin cycle*. This is the reaction in which plants manufacture food using NADPH and ATP to reduce CO_2 and water to form carbohydrates. A carbon dioxide molecule is added to a five carbon sugar molecule in the cell called ribulose diphosphate (RuDP).

The resulting 6 carbon sugar is unstable and splits into two three carbon sugars which are transformed into two molecules of PGAL (phosphoglyceraldehyde). The plant can store PGAL as glucose or starch or use PGAL as food or it may convert PGAL into fats and proteins. However, most of the PGAL (5/6th's) is changed back to RuDP to complete the cycle again.

Note that herbicides that interfere with photosynthesis, inhibit Photochemical System II.

Cellular Respiration

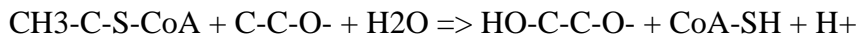
Cellular respiration takes place in non-green cells of plants, animal cells, fungi cells, and most bacteria. There are three cycles: *glycolysis*, the *Citric Acid or Krebs's cycle*, and the *electron-transport cycle*.

Glycolysis can take place under anaerobic conditions or under aerobic conditions. *The six-carbon glucose molecule is split up and changed into 2 three carbon molecules of pyruvic acid.*

In the process, 2 molecules of ATP (adenosine triphosphate) are created by adding phosphate to two molecules of ADP (adenosine diphosphate) and 2 molecules of NAD⁺ (nicotinamide adenine dinucleotide) are reduced, i.e., NAD⁺ => NADH. This is the only respiration process used by yeasts and other anaerobic organisms. In yeasts the pyruvic acid is converted to carbon dioxide and ethanol. In plants the pyruvic acid is converted to ethanol. In animals, the pyruvic acid can be converted to lactic acid which is eventually converted back to glucose in the liver and stored as glycogen. For the pathway to operate anaerobically, the NADH must be converted back to NDA⁺ utilizing energy transfer to inorganic sulfate or nitrate or to organic substances.

Under aerobic conditions, the pyruvic acid molecules oxidizes and lose one carbon in the form of CO₂. The remaining 2 carbon molecules are acetic acid and they unite with a protein enzyme called coenzyme A, or CoA, to form acetyl-CoA in which an S atom links the acetate to CoA forming a thioester.

In the *Citric Acid or Krebs cycle*, the acetyl group separates from the CoA enzyme and combines with a four carbon molecule called oxaloacetate, producing citrate and transforming NAD to NADH₂.



The citrate is oxidized, releasing two CO₂ molecules and producing oxaloacetate acid again to begin the cycle again. In this cycle, each acetyl group is used to convert 3 molecules of NAD⁺ to NADH (NADH₂?), one molecule of FAD (flavin adenine dinucleotide) to FADH₂, and the equivalent of one molecule of ADP to ATP.

In the *electron-transport cycle*, H atoms are released from NADH and NADH₂ and from the citric acid cycle. Electrons are removed from the hydrogen atoms, forming protons. The released electrons are used to reduce oxygen. Water then forms from the reduced oxygen and the protons, releasing heat. The energy released in the overall process is used to convert 34 ADP molecules to ATP molecules (oxidative phosphorylation).

Herbicides can be *total* herbicides or *selective* herbicides. *Inorganic* compounds used as *total* herbicides include copper sulfate (CuSO₄), sulfuric acid, sodium chlorate Na(ClO₃), sodium borate, and sodium arsenate (Na₃AsO₃). *Organic* compounds used as *total* herbicides include creosote (coal tar) which contain the active constituent creosol.

Selectivity depends upon several factors. *Biochemical selectivity* is due to the presence or absence of detoxifying enzymes for the herbicide within different plant groups, e.g., certain pesticides are toxic only after they have been metabolically degraded. *Morphological selectivity* is based on the surface area of leaves exposed to aerial sprays, e.g., broad-leaves versus narrow leaves. *Physiochemical selectivity* is based on low solubility in water or high cation exchange with clays, preventing deep-soil penetration to kill deep-rooted plants.

Chlorophenoxyalkane-Carboxylic Acids and Chlorinated Benzoic Acids

The chlorinated phenoxy-carboxylic acids and benzoic acids act as abnormal growth hormones, accelerating RNA production, leading to starvation as growth outstrips available nutrients. The presence of the acid group and an unsaturated ring system with an unsaturated bond next to the side chain are necessary for phytotoxicity. Chlorine atoms generally need to be attached to the 2nd and 4th carbon atoms for toxicity in the phenoxyalkane carboxylic acids. Attachment to the 3rd carbon atom can further enhance toxicity; however attachment to the 6th carbon atom can destroy toxicity. In the benzoic acids, chlorine atoms attached to the 2nd and 6th carbon atoms are essential for toxicity. A chlorine atom attached to the 3rd carbon further enhances toxicity; however, a chlorine atom attached to the 4th carbon in the benzoic acids destroys toxicity.

The most common of these herbicides are the chlorophenoxy-acetic acids: 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (2-methyl-4-chlorophenoxyacetic acid). Agent Orange (contaminated with dioxin) of Vietnam War fame is a 1:1 mixture of 2,4-D and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid):

Chlorophenoxypropionic acids are also used as herbicides with similar properties as the chlorophenoxyacetic acids, e.g., fenoprop (2,4,5-trichlorophenoxypropionic acid)

Chlorinated-phenoxyalkane carboxylic acids containing more carbon atoms than propionic acid are active herbicides if they have an odd number of methylene carbon atoms in the acid side chain. This is due to oxidative degradation in the plant, leading to the formation of 2,4-D from a starting compound with an odd number of methylene carbons on the carboxylic acid side chain. This oxidation sequence is also typical of the metabolism for carboxylic acids in mammals where it is called the *beta-oxidative degradation of fatty acids*. Because plants vary in their ability to perform the oxidative degradation, these herbicides have a biochemical selectivity factor. For example, unlike weeds, leguminous crops such as peas and clover cannot perform this oxidative degradation and are therefore immune to these herbicides.

The most common chlorinated benzoic acid pesticides are 2,3,6-TBA (2,3,6-trichlorobenzoic acid) and Dicamba (2-methoxy-3,6-dichlorobenzoic acid).

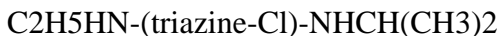
Picloram (4-amino-2-carboxy-3,5,6-trichloropyridine) is a chlorinated benzoic acid pesticide used in killing trees.

Chloroaliphatic Acids

Chlorinated aliphatic acids can be herbicidal and interfere with the metabolism of carbohydrates, lipids, and nitrogen. They are not hormonal pesticides. The chlorine atoms are necessary for toxicity, and the pesticides are degraded rapidly in the environment by hydrolysis to produce HCl and sometimes NaCl. The most active herbicides are dalapon (sodium 2,2-dichloropropionate) and TCA (trichloroacetic acid).

Triazine Herbicides

Triazines have 3 N atoms in a benzene ring, $(CH)_3N_3$. These are persistent soil herbicides which do not penetrate below 5 cm because of their low solubilities. Their toxicity is due to interference with photosynthesis, inhibiting the release of oxygen. An example is atrazine



Hydrolysis of a triazine by replacing the Cl with OH will detoxify the herbicide, a process that some plants accomplish with enzymes. This accounts for the biochemical selectivity of triazines.

D) Bipyridinium

Bipyridinium herbicides contain two pyridine rings (benzene rings, each with a nitrogen atom replacing one of the carbon atoms). Each N atom carries a + charge through the loss of an electron which allows it to form another bond outside of the benzene ring. The rings are bonded together through a single bond between one carbon on each ring. The rings must lie in the same plane to be toxic. Bipyridinium pesticides produce hydrogen peroxide (H_2O_2) during photosynthesis, which diffuses through plant membranes, destroying lipids by peroxidation. The pesticides are active only in the presence of light and oxygen and are rapidly deactivated in soils by absorption by clays in the soil. Consequently, this is a contact pesticide active only when sprayed on leaves. The two best known bipyridinium pesticides are diquat and paraquat.

Fungicides

Fungicides are active against fungi and bacteria.

Fungi may have insect-like cell walls of chitin (the basidiomycetes) or plant-like walls of cellulose (the phycomycetes). They undergo respiration like animals. Most fungi are saprophytic, externally secreting enzymes that digest dead tissue and then absorbing the digestive products. Some species are parasitic on living plants, such as rusts and smuts. Fungi grow by producing long thin filaments, hyphae, that join together to produce a spongy cottony mass, the mycelium. They perform asexual reproduction through the formation of spores and sexual reproduction through contact of different hyphae. There are three groups of fungi: the phycomycetes (containing bread molds); ascomycetes (containing yeasts, molds, mildews, truffles and morels); and basidiomycetes (containing puffballs, mushrooms, toadstools, bracket fungi, rust, and smut).

Fungicides can be active only on the plant surface (*surface* fungicides) or absorbed into the plant and active within the plant (systemic fungicides). Biodegradation of fungicides occurs within a few months up to two years for most fungicides. They are not nearly as stable as the organochlorine insecticides.

Surface fungicides are generally non-specific in toxicity, making it difficult for the fungus to develop resistance. However, *systemic* fungicides are usually site specific in toxicity, allowing resistance to develop through the mutation of a single gene. Consequently, resistance to various *systemic* fungicides has already occurred in many fungi.

Surface fungicides must penetrate the fungal spores on the surface of the plant. The spore surface is composed usually of two monolayers of lipids surrounded on either side by a layer of protein. The lipid layers require the surface fungicide to have some liposolubility to penetrate the surface of the spore. Once inside the spore, the fungicides can kill chemically by interrupting enzymatic activity such as the those used in oxidation, or physically by inhibiting cellular processes through disrupting water-oil balances. With time, weathering removes *surface* fungicides, and they are ineffective with new plant growth occurring after the fungicide application.

Inorganic Surface Fungicides

Sulfur

Sulfur interferes with redox reactions within the fungi cell because the sulfur can be reduced to sulfide. It is not the formation of hydrogen sulfide that is toxic to the cell but the process of reducing the sulfur that results in toxicity.

Metals

Metal toxicity in fungi appears related to their ability to chelate or complex with enzymes in the fungi. Metal toxicity to fungi follows the following relative sequence:

$\text{Ag} > \text{Hg} > \text{Cu} > \text{Cd} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Fe} > \text{Ca}.$

Silver (Ag), the most toxic metal, is rarely used as a fungicide. Mercury (Hg) and copper (Cu) inhibit respiratory enzymes. Cu cannot be applied as an aqueous component because of its high toxicity to plants. Instead, Cu is applied as an insoluble surface fungicide, e.g., as CuSO_4 applied to vineyards to control mildew. Hg is applied in the form of RHgX where R can be an alkyl or an aromatic (aryl) and X is an anion. The nature of the anion is not very important. Birds are adversely affected by eating seeds treated with RHgX compounds to kill fungi. Because of the high toxicity in mammals to alkyl mercury compounds, Hg fungicides are generally applied as aryl mercury compounds, e.g. phenyl mercury acetate. $(\text{C}_6\text{H}_5)_2\text{Hg} - \text{O}-\text{C}-\text{CH}_3$

Tin (Sn) is not toxic by itself to fungi; however, fungicides are formed by adding organic components to make organo-tin compounds. The relative toxicity of these compounds decreases in the following order:

$\text{R}_3\text{SnX} > \text{R}_2\text{SnX}_2 > \text{RSnX}_3$

where X is an anion and R can be an alkyl or aryl (aromatic) component. The nature of the anion is not very important. Trialkyltin compounds are more toxic to plants than triaryl tin compounds and do not degrade easily in the environment. For that reason triaryl tin compounds such as triphenyltin acetate $(C_6H_5)_3Sn - O - C - CH_3$ are more commonly used as fungicides. Degradation of the aryltin compounds in the environment occurs through the conversion to aryltin hydroxides.

While not used as a fungicide, toxic trialkyltin compounds, $(C_4H_9)_3Sn - O - Sn(C_4H_9)_3$, are used in antifouling paints. These paints inhibit the growth of algae and barnacles on ships and preserve timbers, e.g., tributyltin oxide.

Organic Surface Fungicides

Phenols

Phenols containing Cl are usually toxic to microorganisms. Most of these phenols are too toxic to plants to be used as fungicides but can be used as wood preservatives, e.g., the cresols and pentachlorophenol.

Dinitrophenols are somewhat less toxic than the chlorinated phenols and are sometimes used as fungicides. Dinocap is an example.

The toxicity of phenols results from their interference with the formation of ATP (adenosine phosphate) used as an energy source in living organisms.

Hexachlorobenzene

This compound is commonly used both as a fungicide and as the starting point for making chlorinated insecticides. It is a common pollutant, undergoing very slow biodegradation in the environment.

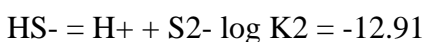
Old Homework Problems and Tests

Conservative Mixing Problem - Test if the Br and Cl concentrations in the saline irrigation waters of Angelina Plantation are due to mixing saline Wilcox or Sparta brines with fresh ground water.

In the (handout) paper by Stoessell (1997), use the Br and Cl mg/l data in Tables 2 and 5 on page 415 and Tables 1, 2, 11, and 12 on page 416. Plot the data using an x axis from 0 to 6,000 mg/l Cl and a y axis of 0 to 8 mg/l Br and derive (from a least squares fit) the equation of the straight line best fitting the data. Obtain the correlation coefficient of the fit. Then plot the line on a graph with higher concentrations of Br and Cl, 0 to 100 mg/l Br and 0 to 100,000 mg/l Cl. Plot the concentrations of Wilcox and Sparta brines from Table 6 on page 415 and the Jack Stack well in Table 1 on page 416. Draw your conclusions as to which of the saline fluids could be the brine responsible for the pollution.

Second Potential Homework Problem

Calculate and graph the molalities of H_2S , HS^- , S^{2-} as a function of pH from 0 to 14 in a salt solution containing dissolved NaCl , i.e., Na^+ and Cl^- . Plot your concentrations on the y axis in log units versus the pH values on the x axis. Assume the solution ionic strength is 0.2 and doesn't vary with a change in pH. Use 3.5×10^{-8} and 5×10^{-8} for the a_o values for HS^- and S^{2-} in the Debye-Huckel equation. Use 0.02 as the salting-out coefficient for the activity coefficient of H_2S . Assume the sum of the molalities of the three sulfide species is conserved at 0.01 molal as the pH changes. Use the following two reactions which are at equilibrium.



On the graph, note the points where equal molalities between two species occur and label the regions where each of the species is the dominant species.

Alternative Second Potential Homework Problem

Calculate and graph the individual activities of H_2S , HS^- , S^{2-} and their total activity at 25°C and 1 bar pressure as a function of pH from 0 to 14 in a solution in equilibrium with a gas phase at 1 bar pressure and containing a H_2S gas component with a mole fraction of 0.01. Plot your activities on the y axis in log units versus the pH values on the x axis. Use the following reactions which are at equilibrium. Compute the log K values using the relation:

$$G_{\text{or}} = \mu_{\text{oi}} = -2.303 RT \log K$$

where $R = 1.98726 \text{ cal/oK}$

$T = 298.15 \text{ oK}$ which is 25°C

$\mu_o \text{ cal/mol}$

$\text{H}_2\text{S}_{\text{gas}} -8,020$

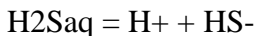
$\text{H}^+ 0$

$\text{H}_2\text{S}_{\text{aq}} -6,660$

$\text{HS}^- -2,930$

$\text{S}^{2-} -20,510$

$\text{H}_2\text{S}_{\text{gas}} = \text{H}_2\text{S}_{\text{aq}}$

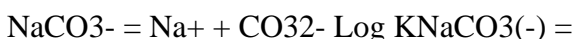
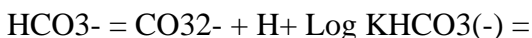
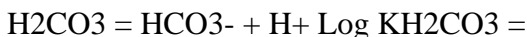
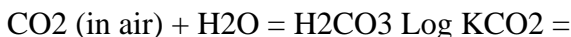


On the graph, note the points where equal activities between two aqueous sulfide species occur and label the regions where each of the species is the dominant species? If these were the only anions in solution and you did an alkalinity titration of the solution, where would the endpoints (inflection pts) be and why. Why do the activities of sulfide species increase with increasing pH?

Third Potential Homework Problem

A 0.1 molal aqueous NaCl solution is in equilibrium with the atmosphere at 25°C and 1 bar in which CO₂ has a mole fraction of 0.00035. Compute the molalities of the various inorganic carbon species.

Each class member will do this at a different pH value. Use the modified Debye Huckel equation with the parameters given in the textbook handout (pp. 128 & 130), and the salting-out coefficient of H₂CO_{3o} for all aqueous neutral species (p. 144). Assume the gas activity coefficient for CO₂ is one and that water has a mole fraction of one (with an activity coefficient of one). The aqueous inorganic carbon species in solution are H₂CO_{3o}, HCO₃⁻, CO₃²⁻, NaHCO_{3o}, NaCO₃⁻. Use the α_o parameter for HCO₃⁻ for NaHCO₃⁻. The equilibrium reactions are:



First, compute the log K values for the above reaction, using the following expression

$$\log K = -\text{Gro}/(2.303RT)$$

where R = 0.008314 KJ/oKMole and T is the absolute temperature at 25°C or 298.15oK. The Gro is the standard state change in Gibbs free energy of the reaction and is computed using the following standard state molal or molar Gibbs free energies of the components. Simply add the energies of the products and subtract the energies of the reactants, divide by 2.303RT and multiply by -1.

Components Molal or molar Gibbs free energies

Kj/mole

Na⁺ aq. -261.9

H₂O liquid -237.2

H⁺ aq. 0

CO₂ gas -394.4

H₂CO₃ aq. -623.1

HCO₃⁻ aq. -586.8

CO₃²⁻ aq. -527.8

NaHCO₃ aq. -849.7

NaCO₃⁻ aq. -792.8

Second, begin by assuming an ionic strength equal to that of a pure 0.1 molal NaCl solution, i.e., $I = 0.5[0.1(1)^2 + 0.1(1)^2]$. Use this ionic strength to calculate the activity coefficients for use in the equilibrium reaction quotients. First calculate the molality of H₂CO₃ in equilibrium with the atmosphere using the first equation. Then, use this molality in the next equation to calculate the molality of HCO₃⁻, and so on until you have calculated the molalities of all the species. For calculating molalities of NaHCO₃ and NaCO₃⁻, assume the molality of Na⁺ is 0.1.

Then using these molalities, compute a new estimate of the ionic strength of the solution using $I = 0.5\sum m_i z_i^2$. Don't forget to include 0.1 molal Cl⁻. Calculate your activity coefficients and then recalculate the molalities using these activity coefficients in the mass-action equations. For calculating molalities of NaHCO₃ and NaCO₃⁻, set the molality of Na⁺ to be 0.1 minus the molalities of NaHCO₃ and NaCO₃⁻ from the previous iteration. Repeat the procedure once more. After three iterations, the computed individual molalities should be fairly good estimates.

List the final molalities (be sure to update the Na⁺ molality based on the new molalities of NaHCO₃ and NaCO₃⁻), the activity coefficients, and the ionic strength for each of the three iterations.

What do you think of this procedure? This is how molality concentrations were done before computers were available. With a computer, you can solve for the molalities using conservation of mass for Na, H, H₂O, Cl, and aqueous inorganic C. The reaction quotients are used in these equations and you end up with a set of 6 nonlinear equations (includes one for CO₂ in the atmosphere) that are solved numerically.

4th Potential Homework Problem

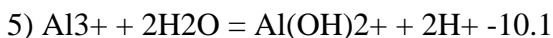
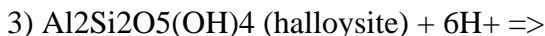
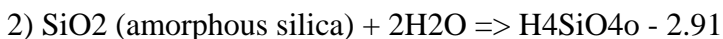
In surface weathering, the last elements to be removed in chemical weathering are Si, Fe, and Al. Si and Al are essential elements in making clays in soils. Their lack of mobility prevents rocks from totally dissolving away. Instead, the common aluminum silicate igneous minerals (e.g., feldspars) are simply replaced by aluminum silicate clays. We can plot the solubilities of these elements in equilibrium with amorphous clays. The procedure below can also be used for Fe. Generally Si solubility is controlled by amorphous silica below 100°C and by quartz at higher temperatures.

Predict the solubility of Al as a function of pH assuming equilibrium with the aqueous species Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^0$, $\text{Al}(\text{OH})_4^-$, H_4SiO_4^0 , and with amorphous silica (solid phase) together with either amorphous gibbsite or halloysite (whichever clay mineral is most stable). Assume an ionic strength of 0.3. Assume the activity coefficients and mole fractions of H_2O and the minerals are unity. Use the Davies equation (4.31) from the handout for activity coefficients of charged aqueous species. The equation lacks ion size parameters but is more accurate than the extended Debye Huckel above an ionic strength of 0.1. Use a salting-out coefficient of 0.1 for $\text{Al}(\text{OH})_3^0$.

$$\log i = -az_i^2[I^{1/2}/(1+I^{1/2}) - 0.3I].$$

Use the following reactions at 25°C and 1 bar:

Log K



Step (1) Write a reaction, balanced on Al between halloysite on one side of the reaction and amorphous gibbsite and amorphous quartz on the other side of the reaction. Determine the equilibrium constant by summing and/or subtracting reactions (1), (2), and

(3) from above to obtain the new reaction. Then use the relation that if reactions are summed, the log K values are added to obtain the log K of the new reaction and if one is, the log K value is subtracted from the other to obtain the new log K. Remember from your previous homework that

$$\log K = -\Delta G^\circ / (2.303RT)$$

Note that the new reaction has no aqueous species other than water. All the components are in their standard states. Hence the change in Gibbs free energy of the reaction is equal to the standard state Gibbs free energy of reaction which can be backcomputed from the log K above. If this is negative, the reaction goes to the right. If positive, the reaction goes to the left. If zero, the reaction is at equilibrium. Use this to determine if gibbsite or halloysite is the stable aluminum mineral phase at amorphous silica saturation.

Step (2) Write the $mAl(3+)$ in terms of the stable aluminum phase dissolving. Note that if halloysite is the stable phase than you must write halloysite dissolving to aqueous Al^{3+} and amorphous silica because the solution is in equilibrium with amorphous silica. Hence, if halloysite is used, you must combine reactions (2) and (3) to get the appropriate solubility reaction.

Step (3) Use the 4 complex reactions to write the sum of the molalities of the 5 Al species in terms of mAl^{3+} . This expression will have only two variables: $mAl(3+)$ and $aH(+)$. The former can be expressed in terms of the expression from Step 2. By combining the two expressions, the summation is only in terms of $aH(+)$. Use this combined expression to plot the summation as a function of pH.

5th Potential Homework Problem

Using the information below on the phosphate system and iron system, plot on a 25°C and 1 bar p_e and pH diagram, the stability fields of the following aqueous species: $H_3PO_4^0$, $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} , Fe^{3+} , $Fe(OH)^{2+}$, $Fe(OH)^{2+}$, $Fe(OH)^{3+}$, $Fe(OH)^{4-}$, Fe^{2+} , and $Fe(OH)^+$ and the following minerals: $FePO_4 \cdot 2H_2O$ (strengite) and $Fe_3(PO_4)_2 \cdot 8H_2O$ (vivianite). Assume the stability of both the dominant phosphate and iron species in equilibrium with one of the minerals is 10^{-6} . Assume the activity of water is 1. This diagram indicates the conditions of precipitating iron phosphates in the soil in sulfur-free environments. Because phosphate is an important nutrient, its mobility is relevant to environmental problems.

1) Use the information given in your handouts to plot the stability field boundaries of water ($a_{H_2} = 1$ and $a_{O_2} = 1$).

2) Plot the boundaries as solid lines between the aqueous phosphate species where they have equal activities. Label the stability fields with the name of the phosphate species dominant within it.

3) Plot the boundaries as dashed lines between the aqueous iron species where they have equal activities. Label the stability fields with the name of the iron species dominant within it.

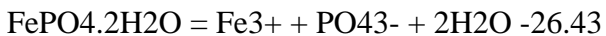
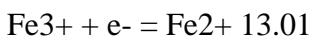
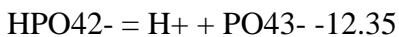
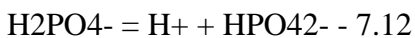
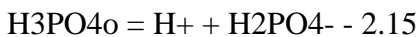
This is an overlay over the phosphate stability field in (2) above. You might color the boundaries of the iron species with one color and use another color for the boundary of the phosphate species.

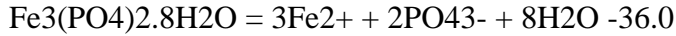
4) Plot the boundaries between the two minerals based on a reaction between them that is balanced on iron so that it is only in the solid phases. (Note that to do this you must include the half-cell reaction between ferrous-ferric iron in order to cancel both ferrous iron and ferric iron in solution.)

Plot the boundaries between each mineral and the aqueous phase by assuming an activity of 10^{-6} for the dominant iron and phosphate species. The phase boundary of a mineral with the solution will be determined by writing the reaction to the solution using the dominant species. Each region with a different set of iron and phosphate dominant species will have its own boundary with the mineral. However, the boundary lines should intersect at common point marking the transition between one set of dominant species to the next set of dominant species.

The mineral stability fields will overlay the aqueous solution fields. Hacture in the two mineral stability fields to stand out on the graph.

Reaction Log K





2 Hour Environmental Geochemistry 4658 Midterm

1) Sketch the structure of gibbsite, kaolinite, and illite.

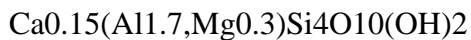
Give the Angstrom spacing of the different layers and label them as octahedral, tetrahedral, and interlayer and give a typical formula in which you label which of the cations are octahedral, tetrahedral, and Interlayer.

Gibbsite (4)

Kaolinite (4)

Illite (4)

Outline how would you compute the cation exchange capacity in equiv. per 100 gram of the smectite whose formula is given below? (2)



2) List the components used to accept electrons in the oxidation of organic matter by bacteria as a function of increasing anaerobic conditions, i.e., decreasing pe or decreasing O₂ content. (4)

aerobic => anaerobic

Under the most anaerobic conditions what reaction is used by bacteria to generate methane and CO₂. (1)

3) Give an example of each of the following organic compounds which the location of characteristic bonds or elements are shown in the formula. (11)

alcohol

organic (carboxylic) acid

ketone

ester

sulfide

amine

amide

alkene

Proteins are composed of _____

Lipids are composed of _____

Carbohydrates are composed of _____

4) Briefly outline the various nitrogen transformations in the

nitrogen cycle, i.e., the forms of nitrogen taken in by

plants, transformation within plants to make plant tissue,

transformation occurring with decay of plant tissue, and

bacterial transfers between the atmosphere. (5)

5) Sulfur and phosphorous are in what forms to be taken in by

plants, and what are their forms within plant tissue. (3)

6) Write the activity expressions for the following reaction components. (4)

aqueous species

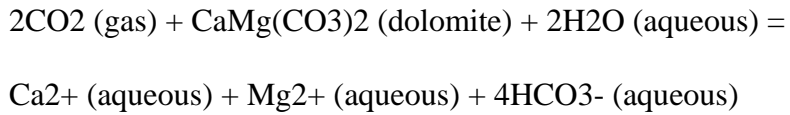
gas phase component

solid component

water

7) Write out the equilibrium constant K in terms of

concentration units and activity coefficients of the components in the reaction quotient for the following reaction. (3)



What is the new equilibrium constant if the reaction is doubled? (1)

If we subtracted another reaction with an equilibrium constant K' from the first reaction with equilibrium

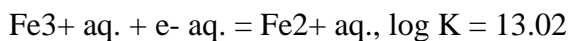
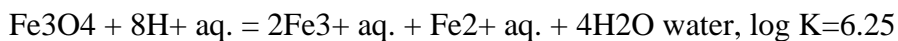
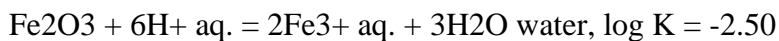
constant K , what would be the new equilibrium constant? (1)

8) What does conservative mixing of two solutions mean? (1)

9) How would you convert from ppm to molality? (2)

10) What is the equilibrium pH and pe for Fe_2O_3 (hematite) and Fe_3O_4 (magnetite) coexisting in contact with an aqueous

solution having equal activities of Fe^{2+} and Fe^{3+} ions, given the following information: (25)



State any assumptions made. Note that the equilibrium pH may not fall within the conventional pH limits of natural waters.

11) Ba^{2+} in aqueous solution is limited in solubility by the

precipitation of BaSO_4 (barite). BaCl_2 is added to a 0.01

molal solution of Na_2SO_4 until its final solution

concentration is also 0.01 molal. What is the equilibrium Ba^{2+} concentration at 25°C and 1 bar after precipitation of BaSO_4 . Use the Davis equation (given below) to include the

effect of aqueous activity coefficients expressions. Note

that the ionic strength will change with the removal of Ba^{2+} and SO_4^{2-} from solution, affecting your activity

coefficients, so you will have to iterate. (25)

BaSO_4 barite = $\text{Ba}^{2+} + \text{SO}_4^{2-}$, $\log K = -11.01$

$\log i = -Az_i^2[I^{1/2}/(1+I^{1/2}) - 0.3I^{1/2}]$ where z is the charge, I is the ionic strength and A is 0.5091.

Bonus 10 pts

Derive the retardation factor of a metal Bb^+ , assuming the distribution coefficient describes sorption.

Potential Homework Problem

Use Figure 4-5 and Table 4-2 in the handout from Colin Baird on the Greenhouse Effect and Global Warming. Assume the decreases in the earth's radiation intensity in the wavelength regions (absorption windows) marked by CO_2 , CH_4 , and O_3 in Figure 4-5 are due solely to the present-day concentrations of these components in the troposphere. Calculate the kx factor from the Beer-Lambert absorption law for each of these gas components and then plot the fraction of radiation absorbed for each of these gas components (within their absorption windows) as a function of their concentrations in the troposphere.

Use the yearly rate of increases for CO_2 and CH_4 in Table 4-2 to note when each of these constituents are expected to be absorbing 90% and 95% of the radiation in their absorption windows?

In the past, reduced levels of CO_2 and CH_4 have been postulated to have lowered the earth's surface temperature and initiated Ice Ages. From your plots, if their concentrations were half that of today, what would be the decrease in radiation absorption. Do you think this would be significant enough to start an Ice Age?

Potential Homework Problem

$\ln(I/I_0) = -(kx)C$ where I_0 is the intensity at the starting value of C . To calculate kx let C_0 be zero.

For **CO_2** , $C = 356$ ppm and the ratio of I/I_0 is about 0.25. Hence, **$k\text{CO}_2x = 0.00389/\text{ppm}$** and for $I/I_0 = 0.1$ (at 90% absorption) and 0.05 (at 95% absorption), respectively, $C = 591$ and 769 ppm.

For **CH₄**, $C = 1.74$ ppm and the ratio of I/I_0 is about 0.4. Hence, **$k_{CH_4} = 0.527/\text{ppm}$** and for $I/I_0 = 0.1$ (at 90% absorption) and 0.05 (at 95% absorption), respectively, $C = 4.37$ and 5.68 ppm.

For **O₃**, $C = 0.03$ ppm and the ratio of I/I_0 is about 0.63. Hence, **$k_{O_3} = 15.4/\text{ppm}$** and for $I/I_0 = 0.1$ (at 90% absorption) and 0.05 (at 95% absorption), respectively, $C = 0.150$ and 0.195 ppm.

If the annual rate of increase in concentration (C) with time (t) is a constant percentage of C , then this is an example of first order kinetics:

$C/t = -KC$ and after integration, $\ln(C_t/C_{t=0}) = Kt$ where K is the annual fractional increase in C .

For CO_2 with a 0.4% annual increase ($K = 0.004$), when CCO_2 has increased to from 356 to 591 ppm at 90% absorption, $t = 127$ years and when CCO_2 has increased to from 356 to 769 ppm at 95% absorption, $t = 192$ years.

For CH_4 with a 0.6% annual increase ($K = 0.006$), when CCH_4 has increased to from 1.74 to 4.37 ppm at 90% absorption, $t = 153$ years and when CCO_2 has increased to from 1.74 to 5.68 ppm at 95% absorption, $t = 197$ years.

To calculate the amount of time t needed to increase C to a new value is similar to calculating the increase in money in which it increases at an annual interest. If you didn't know how to obtain $\ln(C_t/C_{t=0}) = Kt$, then you could have done it on a spread sheet by incrementing it sequentially or by using the summation of a geometric progression. For some reason, everyone but Michelle assumed there was a annual rate increase in the absorption, instead of the concentration. This wasn't correct.

In your class notes, it was pointed out that water vapor accounts for about 2/3's of the greenhouse absorption of radiation, with the remaining gases (mainly CO_2 and CH_4) accounting for about 33%. A decrease in concentration by 50% of CO_2 would reduce its absorption from 75% to 50%. A similar decrease for CH_4 , from 60% to 37%. Overall, this is about a 35% decrease in absorption by these two gases. If both gases together account for about 30% of the present-day absorption of greenhouse gases than their absorption would be reduced to 65% of that amount, resulting in a 12% decrease in absorption of greenhouse gases. Would this be enough to initiate an Ice Age? The earth's surface temperature was about 5°C lower during an Ice Age. If the greenhouse gases results in an overall increase in the earth's surface temperature of 42°C, then a 12% decrease would be about 5°C, however, less may be needed to initiate the Ice Age.

Potential Homework Problem

Acid Mine Drainage

Using MINTEQA2, model acid-mine drainage by reacting a groundwater with pyrite (FeS_2) over a range of pe values. Plot the pH versus pe. Plot the amount of dissolution and precipitation of pyrite in a histogram versus the pe. In your write-up, explain why the pH is decreasing, in terms of the precipitation, dissolution, and formation of the various complexes.

In the problem, do not set the pH. Let the pH be computed as the result of the water-rock interaction. At the lowest pe value (-5), the program will use a total hydrogen ion concentration in order to compute a pH before equilibrating with the pyrite. From this point on, the program will use the masses of the various components at the end of the equilibration at the last pe as the input for the next pe (sweep option).

Use the following input solution composition (automatically set at 1 liter) at a pe of -5, reacting with 0.1 moles of pyrite.

H+ 0.0015

SO4²⁻ 0.0000015

HS⁻ 0.000002

CO3²⁻ 0.001

Cl⁻ 0.004

Fe²⁺ 0.000001

Fe³⁺ 0.000001

K⁺ 0.0005

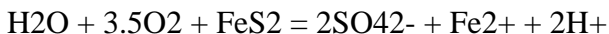
Mg²⁺ 0.0005

Ca²⁺ 0.001

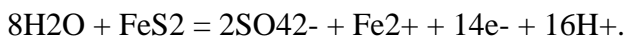
Na⁺ 0.001

Start at a pe of -5 and increment by 1 to a pe of 6. At that time total dissolution of pyrite has taken place. At a pe of 7, the program refused to converge as it tried to produce an oxygenated iron oxide. You might try to restart the sweep at a pe of 6 with an increment of 0.2 to see if you can get it to converge and precipitate such a phase. Or you could redo the sweep with lesser amounts of pyrite, i.e., 0.01 and see if it could successfully converge.

Note that it would be better to model acid mine drainage by varying the partial pressure of O₂, rather than the pe. Because MINTEQA2 varies pe by adding and removing electrons without keeping electrical balance in the solution. This doesn't cause a convergence problem because we have enough mass balance constraints plus equilibrium relations that electrical balance isn't necessary. However, it isn't reality and the result is that an overall reaction such as



becomes



The second reaction produces a lot more hydrogen ions and electrons and would lower the pe, stopping the reaction due to the buildup of electrons. However, MINTEQA2 simply removes those electrons when it holds the pe constant. In nature, the O₂ in the water would be removed rapidly, limiting the amount of pyrite dissolution, until diffusion from the atmosphere replenished the oxygen. By that time the water is no longer in contact with the pyrite and the reaction would end. For this reason, the modelling should be done with a limited amount of dissolved oxygen. MINTEQA2 has the potential for reacting O₂ in a gas phase with an aqueous solution, in equilibrium with H⁺ and H₂O through the transfer of electrons. However, I couldn't get the program to converge.

Old Final: Environmental Geochemistry Geology 4658: Write a concise page on each of the following topics.

- 1) Discuss either Ozone Depletion in the Stratosphere or Smog Generation in the troposphere
- 2) Discuss Global Warming
- 3) Discuss and Contrast the following insecticide groups: DDT analogues, Cyclodienes, Organophosphates, and Carbamates
- 4) Discuss either Disinfection Processes in Sewage Treatment or Acid Rain
- 5) Discuss Acid-Mine Drainage Processes or Soaps and Detergents

10 pt quiz on Organic Chemistry for Environmental Geochemistry

Name the following functional groups attached to hydrocarbon groups R and R'.

O O

R-C-OH R-OH R-C-O-R'

O

R-C-R' R-O-R' R-NH₂

O O

R-C-NH₂ R= N R-S-R'

O

R-S-R' R-S-R' R-SH

O

How is a polymer created from ethylene?

Sketch the structures of toluene, xylene, and phenol.

In terms of their functional groups, proteins are classified as

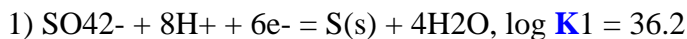
_____, fats as _____, and sugars as _____.

How do alkanes, alkenes, and alkynes differ?

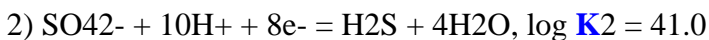
Potential Homework Problem

Construct a **pe** and **pH** diagram for the sulfur system containing aqueous H₂S, HS⁻, HSO₄⁻, SO₄²⁻, and solid sulfur (S) in the presence of water with the total aqueous activity of sulfur equal to 0.01.

The following reactions define the stabilities of these components. Set the activity of solid S to one, implying that it is a pure solid. Set the activity of water to one, implying that it is nearly pure with a mole fraction of one. Set stability boundaries between aqueous components occur at equal activities. Set stability boundaries between the aqueous solution and solid sulfur with the total aqueous sulfur activity equal to 0.01. Assume activity coefficients of aqueous species are unity except for H⁺ ions and aqueous e⁻.



$$\text{or } 36.2 = -\log m_{\text{SO}_4^{2-}} + 8\text{pH} + 6\text{pe}$$



$$\text{or } 41.0 = \log[m_{\text{H}_2\text{S}}/m_{\text{SO}_4^{2-}}] + 10\text{pH} + 8\text{pe}$$

$$3) \text{S(s)} + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{S}, \log K_3 = 4.8$$

$$\text{or } 4.8 = \log m_{\text{H}_2\text{S}} + 2\text{pH} + 2\text{pe}$$

$$4) \text{HSO}_4^- + 7\text{H}^+ + 6\text{e}^- = \text{S(s)} + 4\text{H}_2\text{O}, \log K_4 = 34.2$$

$$\text{or } 34.2 = -\log m_{\text{HSO}_4^-} + 7\text{pH} + 6\text{pe}$$

$$5) \text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- = \text{HS}^- + 4\text{H}_2\text{O}, \log K_5 = 34.0$$

$$\text{or } 34.0 = \log[m_{\text{HS}^-}/m_{\text{SO}_4^{2-}}] + 9\text{pH} + 8\text{pe}$$

$$6) \text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+, \log K_6 = -2.0$$

$$\text{or } -2. = \log[m_{\text{SO}_4^{2-}}/m_{\text{HSO}_4^-}] - \text{pH}$$

$$7) \text{H}_2\text{S} = \text{H}^+ + \text{HS}^-, \log K_7 = -7.0$$

$$\text{or } -7.00 = \log[m_{\text{H}_2\text{S}}/m_{\text{HS}^-}] - \text{pH}$$

Stability Boundaries of water, assume $a_{\text{O}_2} = 1$ and the $a_{\text{H}_2} = 1$.

$2\text{H}^+ + 2\text{e}^- = \text{H}_2$ where at 25°C and 1 bar,

$$K = 1 = a_{\text{H}_2}/[a_{\text{H}^+}^2 a_{\text{e}^-}^2] \text{ or for } a_{\text{H}_2} = 1.$$

$$0 = \text{pH} + \text{pe}$$

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$ where at 25°C and 1 bar,

$$K = 10(20.78)^4 = a_{\text{H}_2\text{O}_2}/[a_{\text{O}_2} a_{\text{H}^+}^4 a_{\text{e}^-}^4] \text{ or for } a_{\text{O}_2} = 1$$

$$20.78 = \text{pH} + \text{pe}$$

The procedure for doing this diagram is to first plot the stability boundaries of the aqueous sulfur species without the solid. This is the phase diagram for the solution without the solid phase. Then plot on this diagram the boundary lines between solid sulfur and the solution. Do this by using the reaction between the solid sulfur and each aqueous sulfur species. Plot the resulting straight line stability boundary only in the area of the phase diagram where that sulfur species is the dominant sulfur species. These stability boundaries should curve to connect across the boundary between solution areas with different dominant aqueous sulfur species. At the boundary between the dominant aqueous species, the intersection point on the curve is found using an activity of $\frac{1}{2}$ of the total aqueous sulfur activity or 0.005 because the total aqueous sulfur activity is split equally between the two aqueous sulfur species.

Old Take-Home Environmental Geochemistry Final

Use Minteqa2 in all or part of problems 1 and 2

- In a previous homework you looked at the mass balance requirements for the removal of phosphate by precipitating it as hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. Use MINTEQA2 to thermodynamically test if calcite transform to hydroxyapatite and how effective the phosphate removal would be as a function of pH from 5 to 10. Assume the solution initially contained 0.0002 molal each of Na, K, Ca, Mg, CO_3 , Cl, and PO_4 . Discuss how effective the transformation is. Include a copy of your input file for MINTEQA2 and the resulting equilibrium distributions at each of the pH values.

Hydroxyapatite precipitation occurred at each of the pH values, reducing the aqueous phosphate concentrations. The aqueous phosphate reduction increases with increasing pH to a pH of 9. This trend reverses going from pH 9 to 10. Above a pH of 7, essentially 100% aqueous phosphate removal has occurred.

at a pH Of 5 from 0.0001 to 0.00005687, removing 71.6%.

6 0.000002748, 98.6%

7 0.0000002141, 99.9%

8 0.00000003592, 100.%

9 0.00000001781, 100.%

10 0.00000002685, 100.%

- Anglesite (PbSO_4) has precipitated in soil beneath a pile of broken automobile batteries. Ground water moving through the soil has a pH of 7 and contains 0.0002 molal each of Na, K, Ca, Mg, and 0.00000001 molal each of Pb and SO_4 and 0.0004 molal each of CO_3 and Cl. The ground water then reacts with the anglesite, changing its pH, possibly precipitating hydrocerrusite $[\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]$, releasing lead to the solution in the process which then moves downstream. Use MINTEQA2 to model this reaction.

The released aqueous lead is retarded by sorption on the soil. Lead sorption on this soil obeys the following Langmuir sorption isotherm $(S_{\text{soil}}) = [(30)(1.5)S_{\text{aq}} / (1 + 1.5 S_{\text{aq}})]$ for concentration units in mg/l for S_{aq} and mg/g for S_{soil} . The dry soil density is 2 g/ml with 30% porosity. What is the retardation of the lead moving downstream in the ground water? Summarize your work and explain how you came up with your answer. Include a copy of your input files for MINTEQA2 and the resulting equilibrium distributions.

The solution is run first at a pH of 7 to obtain the total hydrogen ion molal concentration in solution. This is 0.0004703 molal. The solution is then reacted with anglesite, allowing hydrocerrusite to precipitate. The resulting lead concentration is 0.0001286 molal at a pH of 5.89. The conversion to mg/l is

$$\text{mg/l of Pb ppm of Pb mi}(1000 \text{ Mwi})] = 26.64 \text{ mg Pb/l}$$

This is the upstream concentration in the retardation computation. The unpolluted lead concentration is the downstream concentration which was 0.00000001 molal or 0.0020719 mg Pb/l.

The retardation of the lead cannot be computed accurately using a constant distribution coefficient because the nonlinear partitioning follows the Langmuir isotherm. The retardation is computed from the equation given to you in class that you used on your midterm.

$$R = 1 + \frac{(\text{Supstream} - \text{Sdownstream})\text{sediment}}{(\text{Cupstream} - \text{Cdownstream})\text{sediment}}$$

$$(\text{Cupstream} - \text{Cdownstream})\text{sediment}$$

where the aqueous concentrations are in mg/l and the soil concentrations are in mg/kg. Use of the Langmuir isotherm yields

$$\text{Supstream} = 1000[(30)(1.5)26.64/(1 + 1.5 (26.64))] = 29,270 \text{ mg/kg}$$

$$\text{Sdownstream} = 1000[(30)(1.5)0.00207/(1 + 1.5(0.00207))]= 92.9 \text{ mg/kg}$$

$$R = 1 + \frac{(29,279 - 92,9)\text{mg/kg} (2\text{g/ml})(1000\text{ml/l})(1 \text{ kg}/1000 \text{ g})}{(26.64 - 0.00207)\text{mg/l} (0.30)}$$

$$(26.64 - 0.00207)\text{mg/l} (0.30)$$

However, I gave you a density of 2 mg/ml instead of 2 g/ml leading to a retardation factor of 7.313 if you used that density.