Chapter 2
Selected Geochemical Processes

In physical chemistry, the world is divided in two parts: the system, containing the portion of the world of particular interest, and the *surroundings*, comprising the region outside the system (Atkins and de Paula 2002). A geochemical system is an open system that may be studied within two basic frameworks:

1. *Thermodynamic system*, which is a state of equilibrium where environmental parameters, such as pressure and temperature, are imposed on the bulk composition of the system. This approach is used to predict the system stability and the impact of changing environmental conditions.
2. *Kinetic system*, wherein the pathways along the system are moving toward some state of local equilibrium, which in turn determines the rate of change along the pathway. In the context of a kinetic approach, which is relevant to geochemical processes, dissolution–precipitation, exchange-adsorption, oxidation–reduction, vaporization, and formation of new phases are discussed here.

2.1 Thermodynamics and Equilibrium

When a thermodynamic approach is used to describe geochemical phenomena in the subsurface, it is necessary to define the solids, liquids, gases, and soluble species that exist at equilibrium.

2.1.1 Enthalpy, Entropy, and the Laws of Thermodynamics

In thermodynamics, the total energy of a system is given by the sum of the total kinetic and potential energies of the molecules in the system.

The *first law of thermodynamics* is the application of the conservation of energy principle. In geochemistry, the first law considers that the change in internal

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energy ($\mathrm{d}U$) is equal to the heat added to the system ($\mathrm{d}q$) plus the work ($\mathrm{d}w$) done on the system:

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w. \tag{2.1}$$

The first law of thermodynamics applied to an adiabatic system may be expressed as the work done on a system by an adiabatic process, which is equal to the increase in its internal energy, and a function of the state of the system.

In any natural system, the system boundary is prescribed as a nonadiabatic (insulated) wall that allows the passage of heat to and from the surrounding system. The change in internal energy is not equal to the heat supplied when the system is open and free to change its volume. Under this condition, part of the energy supplied is returned to the surroundings, and the heat supplied at constant pressure is equal to the *enthalpy* (H) of the system, which is defined as

$$H = U + PV, \tag{2.2}$$

where U is the internal energy, P is the pressure, and V is its volume. Because U, P, and V are state functions, the enthalpy also is a state function.

The *second law of thermodynamics*, as formulated by Kelvin, states that “no process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work;” in other words, in any natural process involving a transfer of energy, some energy is converted irreversibly into heat that cannot be involved in further exchange. The second law of thermodynamics, therefore, is a recognition of spontaneous and nonspontaneous processes and the fact that natural processes have a sense of direction.

The second law of thermodynamics can be expressed in terms of another state function, the *entropy* (S). The thermodynamics definition considers the change in entropy $\mathrm{d}S$ that occurs as a result of a physical or chemical change and is based on the expression

$$\mathrm{d}S = \mathrm{d}q_{\mathrm{rev}}/T, \tag{2.3}$$

in which $\mathrm{d}q$ is an infinitesimal amount of heat gained by a body at temperature T in a reversible (rev) process. A reversible change in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. Because real processes are never completely reversible, the entropy is a measure of the degree in which a system has lost heat and therefore part of its capacity to do work. In general, a local decrease in entropy is possible but must be accompanied by an increase in entropy in the surrounding system. In real geochemical (open) systems, a change in entropy must be equal to (in the case of reversible change) or greater than zero:

$$\mathrm{d}S \geq \mathrm{d}q/T. \tag{2.4}$$

A *fundamental equation* combines the first and second laws of thermodynamics and, in this manner, addresses the behavior of matter. For a reversible change in a closed system of constant composition and without nonexpansion work, one can write

$$dw_{\mathrm{rev}} = -PdV. \tag{2.5}$$

Then, for a reversible change in a closed system, substitution of Eqs. (2.5) and (2.3) (written for dq_{rev}) into Eq. (2.1) yields

$$dU = TdS - PdV. \tag{2.6}$$

Equation (2.6) is called a *fundamental equation* and because dU is an exact differential, its value is independent of path. Hence, Eq. (2.6) applies to any change—reversible or irreversible—of a closed system that does no additional work (Atkins and de Paula 2002).

Given that, in the subsurface, we are dealing with an open system, the fundamental equation may be applied only when the macroscopic system is decoupled in isolated, well-defined systems. As an example, we can consider that an adiabatic "zone" of the subsurface solid phase is in contact with an aqueous solution through a rigid barrier, surrounded by an insulating wall.

Gibbs free energy (G) is probably the most frequently used quantity in thermodynamics; it measures spontaneity of a reaction or energy available to do work in a system. Free energy is a state function because it is defined formally only in terms of the state functions enthalpy and entropy and the state variable temperature. The Gibbs free energy is defined as

$$G = H - TS. \tag{2.7}$$

At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs free energy. Some reactions are spontaneous because they give off energy in the form of heat ($\Delta H < 0$). Other reactions are spontaneous because they lead to an increase in the disorder of the system ($\Delta S > 0$). Calculations of ΔH and ΔS can be used to probe the driving force behind a particular reaction.

2.1.2 Equilibrium

A system is in equilibrium when all acting influences are canceled by others, resulting in a stable, balanced, or unchanging system in relation to its surroundings. In the subsurface, equilibrium can be defined in terms of thermal, chemical, or mechanical equilibrium. Usually, in the subsurface, changes occur slowly over geological time scales, so that a state of equilibrium is never reached. However, in the subsurface, when mainly anthropogenic-induced effects are involved, various changes do occur over "observable" time scales, ranging from seconds to years. Under these conditions, an *apparent equilibrium* may be reached. The concept of equilibrium in subsurface systems is discussed in classical books of geochemistry, soil science, or aquatic chemistry (e.g., Stumm and Morgan 1995; Sposito 1981), and the reader is directed to such sources for ample information on this topic.

In a closed system when temperature and pressure are constant, the sum of chemical potentials of all components is fixed; in contrast, in an open system, the chemical potential of all components is influenced by both the thermodynamic parameters of the phases and various parameters outside the system. The main relationship among phases, components, and physical conditions is given by the phase rule.

The *phase rule* states that when equilibrium conditions are sustained, a minimum number of intensive properties of the (subsurface) system can be used to calculate its remaining properties. An *intensive property* is a property that is independent of the amount of substance in the domain. Examples of intensive properties include temperature (T), pressure (P), density (ρ), and chemical potential (μ), which is a relative measure of the potential energy of a chemical compound. The phase rule specifies the minimum number of intensive properties that must be determined to obtain a comprehensive thermodynamic depiction of a system.

A *phase* is defined as a state of matter that is uniform throughout in terms of its chemical composition and physical state; in other words, a phase may be considered a pure substance or a mixture of pure substances wherein intensive properties do not vary with position. Accordingly, a gaseous mixture is a single phase, and a mixture of completely miscible liquids yields a single liquid phase; in contrast, a mixture of several solids remains as a system with multiple solid phases. A phase rule, therefore, states that, if a limited number of macroscopic properties are known, it is possible to predict additional properties.

A system is *homogeneous* when the intensive properties are not a function of position, while a system is *heterogeneous* when the composition of a given mixture varies as a function of position. For example, the subsurface liquid phase usually comprises an aqueous solution incorporating a number of solutes; in contaminated subsurface environments, nonaqueous phase liquids also may be present. The air phase of the subsurface includes gases with various partial pressures, and the solid phases comprise a mixture of minerals and organic compounds.

A *phase diagram* describes how a system reacts to changing conditions of pressure and temperature and consists of a field in which only one phase is stable, separated by boundary curves along which a combination of phases coexist in equilibrium.

2.1.3 Solubility, Chemical Potential, and Ion Activities

The chemical potential of species i, μ_i, is expressed in terms of the Gibbs free energy added to a system at constant T and P, as well as relative to the mole fraction of each added increment of i. When adding an incremental number of molecules of i, free energy is introduced in the form of internal energies of i as well as by the interaction of i with other molecules in the system. As i increases, the composition of the mixture changes and consequently μ_i changes as a function of the amount in moles (n) of i:

$$\mu_i = \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_{j\neq 1}}. \tag{2.8}$$

Because $\mu_i = G_i = H_i - TS_i$, the chemical potential can be used to assess the tendency of components i to be transferred to another system or transformed within a system; in other words, matter flows spontaneously from a region of high chemical potential to a region of low chemical potential, just as mass flows from a position of high gravitational potential to a position of low gravitational potential. The chemical potential, therefore, can be used to determine whether or not a system is in equilibrium: at equilibrium, the chemical potential of each substance is the same in all phases appearing in the system.

An *ideal solution* can be defined as a solution in which the chemical potential of each species is given by the expression

$$\mu_i = \mu_i^0(P,T) + RT\ln x_i, \tag{2.9}$$

where R is the gas constant (=0.001987 kcal/mol/K), T is the temperature, and x_i is the mole fraction of species i. The chemical potential of a pure species i, $\mu_i^0(P,T)$, is a measure of the activity of compound i in its standard state, that is, pure organic liquid at the same pressure (P) and temperature (T). The term $\mu_i^0(P,T)$ is referred to as the *standard state chemical potential*. From Eq. (2.9), it is seen that the chemical potential of a species in an ideal solution is lower than the chemical potential of the pure component.

Usually, only very dilute solutions can be considered ideal. In most aqueous solutions, ions are stabilized because they are solvated by water molecules. As the ionic strength is increased, ions interact with each other. Thus, when calculating the chemical potential of species i, a term that takes into account the deviation from ideal conditions is added. This term is called an *excess term* and can be either positive or negative. The term usually is written as $RT \ln \gamma_i$, where γ_i is the activity coefficient of component i. The complete expression for the chemical potential of species i then becomes

$$\mu_i = \mu_i^0(P,T) + RT\ln x_i + RT\ln\gamma_i = \mu_i^0(P,T) + RT\ln(x_i\gamma_i). \tag{2.10}$$

As mentioned previously, in this expression, $\mu_i^0(P,T)$ is the chemical potential of a pure species i. For a pure species i, $x_i = 1$, and consequently, from Eq. (2.10), $\gamma_i = 1$, too.

The expression $x_i\gamma_i$ is referred to as the *activity* of the species, a_i, and is a measure of how active a compound is in a given state compared to its standard state (e.g., the pure liquid at the same T and P).

For aqueous solutions of salts, $\mu_i^0(P,T)$ represents the chemical potential of pure ions. This chemical potential cannot be measured experimentally. Instead of using this hypothetical standard state, the activity coefficients of ions often are normalized by introducing the "asymmetrical activity coefficient," γ_i^* defined as

$$\gamma_i^* = \frac{\gamma_i}{\gamma_i^\infty}, \tag{2.11}$$

where γ_i^∞ is the activity coefficient of species i at infinite dilution. If the chemical potential of species i is expressed in terms of γ_i^*, we obtain the expression

$$\begin{aligned} \mu_i = \mu_i^0 + RT\ln(x_i\gamma_i^*\gamma_i^\infty) &= \mu_i^0 + RT\ln\gamma_i^\infty + RT\ln(x_i\gamma_i^*) \\ &= \mu_i^* + RT\ln(x_i\gamma_i^*). \end{aligned} \tag{2.12}$$

The standard state chemical potential, $\mu_i^* = \mu_i^0 + RT\ln\gamma_i^\infty$, has the advantage that it can be measured experimentally.

In the *molality concentration scale*, the molality m_i of solute i is the amount of solute i per kg of solvent. If the solvent is water (subscript w), the following relation between mole fraction and molality of solute i can be derived:

$$m_i = \frac{n_i}{n_\mathrm{w}M_\mathrm{w}} \Rightarrow n_i = m_i n_\mathrm{w} M_\mathrm{w} \tag{2.13}$$

$$x_i = \frac{n_i}{\sum\limits_{\mathrm{ions}} n_i + n_\mathrm{w}} = \frac{m_i n_\mathrm{w} M_\mathrm{w}}{\sum\limits_{\mathrm{ions}} n_i + n_\mathrm{w}} = m_i M_\mathrm{w} x_\mathrm{w} \tag{2.14}$$

where n is the number of moles and M_w is the molecular mass of water (kg/mol). Using this relation, the chemical potential of ion i can be expressed as a function of the molality and the molal activity coefficient γ_i^∇:

$$\begin{aligned} \mu_i = \mu_i^0 + RT\ln\left(m_i M_\mathrm{w} x_\mathrm{w}\gamma_i^*\gamma_i^\infty\right) &= \mu_i^0 + RT\ln\left(m_\mathrm{w} m^0\gamma_i^\infty\right) + RT\ln\left(\frac{m_i}{m^0}\gamma_i^* x_\mathrm{w}\right) \\ &= \mu_i^\nabla + RT\ln\left(\frac{m_i}{m^0}\gamma_i^\nabla\right) \end{aligned} \tag{2.15}$$

where the term $m^0 = 1$ mol/kg has been included to make the expression dimensionless. The standard state chemical potential is $\mu_i^\nabla = \mu_i^0 + RT\ln M_\mathrm{w}\mathrm{m}^0\gamma_i^\infty$ when the molality concentration scale is used. The molal activity coefficient is related to the asymmetrical mole fraction activity coefficient by $\gamma_i^\nabla = \gamma_i^* x_\mathrm{w}$, where x_w is the mole fraction of water.

2.1.4 Kinetic Considerations and Reaction Rate Laws

Thermodynamic considerations provide a basic approach for predicting what may or may not happen in a given system. On a practical level, large and growing numbers of chemical species are contained in thermodynamic databases. Given the increasing ease of data retrieval and extrapolation and the availability of free energy minimization algorithms, this information is accessible and useful, allowing application of thermodynamics to a wide variety of geochemical systems.

Despite this usefulness, thermodynamic considerations have limitations, and these most often are apparent in environmental systems at lower temperatures, in biological systems, and in the description of reactions at phase boundaries. Thermodynamics applies to chemical processes among large numbers (i.e., Avogadro's number) of molecules and deals with overall reactions among a set of chemical species. Strictly speaking, equilibrium thermodynamics provide no information about how a chemical system reached its current state.

The earth's subsurface is not at complete thermodynamic equilibrium, but parts of the system and many species are observed to be at local equilibrium or, at least, at a "dynamic" steady state. For example, the release of a toxic contaminant into a groundwater reservoir can be viewed as a perturbation of the local equilibrium, and we can ask questions such as, What reactions will occur? How long will they take? and Over what spatial scale will they occur? Addressing these questions leads to a need to identify actual chemical species and reaction processes and consider both the thermodynamics and kinetics of reactions.

For any chemical reaction, whether inorganic or organic, we must choose which kinetic species to include in the elementary reactions that make up the overall process; ideally, molecular or chemical information is available to guide this choice. In general, for an elementary (irreversible) reaction among species A and B, to give species C and D, in relative amounts a, b, c, and d, respectively,

$$aA + bB \rightarrow cC + dD, \tag{2.16}$$

the rate of the reaction is

$$\text{Rate} = -\frac{1}{a}\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{1}{c}\frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{1}{d}\frac{\mathrm{d}[D]}{\mathrm{d}t} = k[A]^a[B]^b, \tag{2.17}$$

where [ ] denotes concentration, $a + b$ is the order of the reaction, and the coefficient k is the rate constant for the reaction.

In a *first-order reaction*, the rate-determining step involves a transformation where one reactant reacts to give one product, that is, $A \rightarrow B$. In first-order reactions, there is an exponential decrease in the reactant concentration, so that at any given time, the transformation rate is dependent on the corresponding concentration of the reactant at the same time. This can be expressed in the following way:

$$\text{Rate} = \frac{\mathrm{d}[A]}{\mathrm{d}t} = -k[A], \tag{2.18}$$

$$[A]_t = [A]_0 \mathrm{e}^{-kt}, \tag{2.19}$$

where here k is the first-order rate constant with dimension [time^{-1}] and the subscripts t and 0 denote time and initial time, respectively. Plotting $\ln[A]_t/[A]_0$

against time yields a linear relation with a slope equal to –k that intersects the origin.

In *second-order reactions*, the rate-determining step involves a transformation where two reactants interact to give one product. The simplest case of such a reaction is $2A \rightarrow B$, and in such a case, we can write

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k[A]^2, \tag{2.20}$$

$$[A]_t = \frac{[A]_0}{1 + kt[A]_0}, \tag{2.21}$$

where here k is the second-order rate constant with dimensions [mol^{-1} volume time^{-1}]. As a consequence, the decay period depends on the initial concentration $[A]_0$. This result has implications for environmental pollutants that decompose by second-order reactions; in such cases, pollutants may persist for longer times at low concentrations, compared to first-order reactions, because decay times become longer as the concentration decreases.

When the reaction rate is not dependent on the reactant concentration, the reaction is *zero order*:

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = k. \tag{2.22}$$

In nature, the reaction rate depends on the reactant concentration. However, practically speaking, when a reactant exists at a very high concentration, it is essentially unchanged due to the reaction, and the reaction is called *pseudo-zero order*.

In geochemistry, interest is focused on *open systems*, in which mass is added or removed over observable time periods. A simple example of such a case is that of steady fluid flow in a system, with constant inflow of species A. Then, for constant recharge of species A at concentration $[A]_0$ (and discharge at concentration A), at rate k^*, with loss A in reaction with species B (recall Eq. 2.16), we have

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k[A] + k^*[A]_0 - k^*[A] \tag{2.23}$$

so that

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k[A] + k^*([A]_0 - [A]) = -(k + k^*)[A] + k^*[A]_0. \tag{2.24}$$

The solution of this first-order differential equation is

$$[A] = \frac{k^* + k\mathrm{e}^{-(k+k^*)t}}{k^* + k}[A]_0. \tag{2.25}$$

When $k^* \ll k$, that is, the recharge is very slow, we return to a simple first-order reaction. When the recharge is very fast, compared to the reaction rate, that is, when $k^* \gg k$, then $[A] \cong [A]_0$ and the concentration of A remains constant in the system during the period of observation.

Many reactions use the *Arrhenius parameter*; for example, plotting ln k against $1/T$ gives a linear relationship that can be written in the form

$$\ln k = \ln A - \frac{Ea}{RT}, \tag{2.26}$$

where Ea is the activation energy, and ln A corresponds to the interception point when $1/T = 0$; A is called the *pre-exponential factor* or *frequency factor*. The higher the Ea, the stronger the dependence of the rate constant on temperature. The *activation energy Ea* is the minimum kinetic energy that reactants must have to form a product. The pre-exponential factor is a measure of the rate at which transformation of a reactant to products occurs, irrespective of their energy.

An excellent example combining thermodynamics, kinetics, and equilibrium considerations was presented by O'Day (1999), who considered the precipitation reaction of solid lead carbonate, in the form of the mineral cerussite ($PbCO_{3(s)}$) according to the reaction

$$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_{3(s)}. \tag{2.27}$$

The equilibrium constant is governed by a function of temperature and pressure and can be expressed using the standard state equilibrium constant (K_{eq}) and the change in standard free energy of the reaction:

$$K_{eq} = \frac{a_{PbCO_{3(s)}}}{a_{Pb^{2+}} a_{CO_3{}^{2-}}} \tag{2.28}$$

$$\Delta G_r^0 = -RT \ln K_{eq}, \tag{2.29}$$

where a is the activity of each species, and ΔG_t^0 denotes the change in free energy of a reaction at standard state. By convention, the activities of chemically pure solids are set equal to 1. The description of cerussite precipitation given by Eq. (2.27) is an example of a thermodynamic equilibrium. However, when examining the reaction system at the molecular level, before equilibrium is achieved, the reaction is much more complicated. For example, aqueous species take part in pH-dependent reactions that determine the form of carbon in solution and thus affect the precipitation of cerussite:

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \tag{2.30}$$

$$H_2CO_3 \rightleftharpoons HCO_3^- \tag{2.31}$$

$$H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}. \tag{2.32}$$

Thus, at the molecular level, the reactions that actually take place and their associated chemical pathways can be completely different from the cerussite precipitation scheme presented in Eq. (2.27).

In addition to a number of solution species and a solid, species adsorbed to and desorbed from the surface can be included and described using elementary reactions. As discussed previously, to determine the reaction order, rate-determining steps, or other kinetic parameters, one must choose the kinetic species to be included in the elementary reactions that make up the overall process. Ideally, molecular or chemical information is available to guide this choice. Therefore, the set of kinetic species for any overall chemical reaction is generally larger (and usually more complicated) than the set of equilibrium species. The only constraints on overall reactions are that they proceed in the same direction as ΔG_r^0 and that the overall reaction rate approaches zero at equilibrium. This connection between the rate of an overall reaction and the driving force supplied by thermodynamics can be expressed by including a free energy term in a rate equation.

The change in free energy of a reaction not at equilibrium (ΔG_r) is given by

$$\Delta G_r = RT \ln \frac{Q}{KE}, \tag{2.33}$$

where R, T, and K_{eq} have the same meaning as in Eq. (2.29) and Q is the measured ion activity product for the reaction. By comparing the activity product of a species observed in the system with the expected concentration product at equilibrium (K_{eq}), the ratio Q/K_{eq} provides a measure of how far from equilibrium the reaction is and in which direction it is going (note that $Q = K_{eq}$, and therefore $\Delta G_r = 0$, at equilibrium). In general, rate equations derived from experiments have many terms that account explicitly for variables such as concentrations of species in solution, pH, ionic strength, possible catalytic or inhibitory effects, and different forms of expression for $f(\Delta G_r)$. Rate expressions should be able to account for the difference in reaction rate far from and close to equilibrium. However, it cannot be assumed that the reaction mechanism is the same for both dissolution and precipitation. In the context of environmental systems, the first, and sometimes the most difficult, task is determining the species and stoichiometry of reactions that govern the fate of the elements of interest, then deciding whether they can be treated as equilibrium reactions for the time scale of interest. Reactions that occur at surfaces and the molecular species involved are inherently difficult to characterize because their concentrations usually are lower than those of bulk species and they often are transitory.

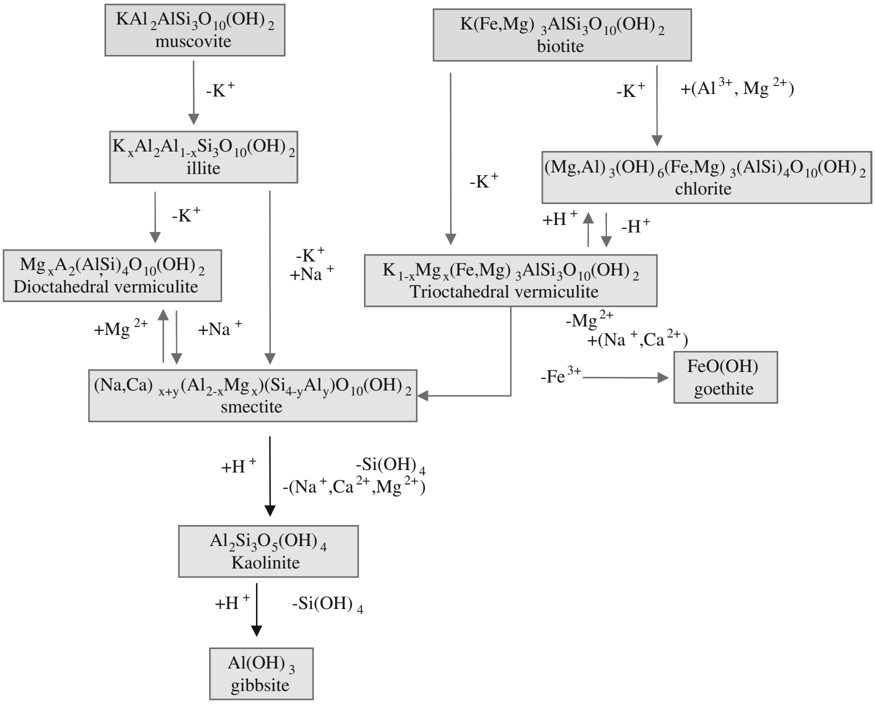

Fig. 2.1 Possible chemical weathering pathways of muscovite and biotite

2.2 Weathering

Weathering of subsurface solid phases occurs as a result of their direct interaction with liquid phases, which may also in turn be affected by the gaseous environment. Examples of weathering processes include reactions that convert primary minerals such as quartz and clays into metal oxides and metal hydroxides.

The major chemical weathering agent in the subsurface is water, which can act as either a weak acid or a base. Oxygen can oxidize organic hydrocarbons and a variety of metals that include Fe^{2+} and S^{2-}. Carbon dioxide can be transformed to function as an inorganic acid (e.g., HCO_3^-) or as an organic acid (e.g., HCOOH), and the conjugate bases are often strong ligands that complex metals.

A possible chemical weathering process of two primary minerals, muscovite and biotite, and their various mineral products is presented in Fig. 2.1.

2.2.1 *Dissolution and Precipitation*

Dissolution and precipitation in the subsurface are controlled by the properties of the solid phases, by the chemistry of infiltrating water, by the presence of a gas phase, and by environmental conditions (e.g., temperature, pressure, microbiological activity). Rainwater, for example, may affect mineral dissolution paths differently than groundwater, due to different solution chemistry. When water comes in contact with a solid surface, a simultaneous process of weathering and dissolution may occur under favorable conditions. Dissolution of a mineral continues until equilibrium concentrations are reached in the solution (between solid and liquid phases) or until all the minerals are consumed.

The initial compositions of both the infiltrating water and the solid materials may change due to their interaction, which in turn may affect the solubility and the pathway of processes with time. When a particular component of the dissolved solution reaches a concentration greater than its solubility, a precipitation process occurs. Table 2.1 includes the solubility of selected sedimentary minerals in pure water at 25 °C and total pressure of 1 bar, as well as their dissolution reactions. All of the minerals listed in Table 2.1 dissolve, so that the products of the mineral dissolution reactions are dissolved species. Figure 2.2 shows the example of gypsum precipitation with its increasing concentration in an NaCl aqueous solution.

The presence of organic ligands in the infiltrating water phase may cause the complexation of some minerals, leading to an increase in their solubility. For example, oxalate anions enhance the solubility of ZnO in the range of pH = 6–8, and EDTA (ethylenediamine tetraacetic acid) dissolves hydrous ferric oxide up to a pH = 9 (Stumm and Morgan 1995). Fulvic acids in the soil layer may act as chelating agents, contributing to an increase in solubility of the minerals and, as a consequence, enhancing their mobility. Laboratory experiments performed by Bennett et al. (1988) showed that organic acids can greatly enhance the dissolution process, especially where reactions take place in an open, flow-through (non-equilibrium) system.

Carbon dioxide has a dominant effect on the dissolution of carbonate minerals, such as calcite and dolomite (Table 2.1). If a carbonate mineral dissolves in water that is equilibrated with a constant source of CO_2, then the concentration of dissolved carbonic acid remains constant and high. However, when calcite dissolution is accompanied by consumption of carbonic acid and a continuous source of CO_2 is not maintained, the reaction proceeds further to achieve equilibrium.

The subsurface generally is an open system. The presence of CO_2 and other gases in the atmosphere affects the partial pressure of gas constituents in the subsurface. For example, carbonate mineral dissolution in a system open to atmospheric CO_2 does not achieve equilibrium. However, higher local subsurface CO_2 concentrations can originate from biological activity and other oxidation processes.

The rate of chemical weathering of minerals in the subsurface depends on a number of factors, including mineralogy, temperature, flow rate, surface area, the presence of ligands and CO_2, and H^+ concentrations in the subsurface water (Stumm et al. 1985). Figure 2.3 shows the rate-limiting steps in mineral dissolution consisting of (a) transport of solute away from the dissolved crystal or

Table 2.1 Dissociation reactions and solubility of selected minerals that dissolve congruently in water (Freeze and Cherry 1979)

Mineral	Dissociation reaction	Solubility at pH = 7 (mg/L or g/m^3)
Gibbsite	$Al_2O_3 \cdot 2H_2O + H_2O = 2A1_3^+ + 6OH^-$	0.001
Quartz	$SiO_2 + 2H_2O = Si(OH)_4$	12
Hydroxylapatite	$Ca_5OH(PO_4)_3 = 5Ca^{2+} + 3PO_4{}^{3-} + OH^-$	30
Amorphous silica	$SiO_2 + 2H_2O = Si(OH)_4$	120
Fluorite	$CaF_2 = Ca^{2+} + 2F^-$	160
Dolomite	$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3{}^{2-}$	90–480
Calcite	$CaCO_3 = Ca^{2+} + CO_3{}^{2-}$	100–500
Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4{}^{2-} + 2H_2O$	2100
Sylvite	$KCl = K^+ + Cl^-$	264,000
Epsomite	$MgSO_47H_2O = Mg^{2+} + SO_4{}^{2-} + 7H_2O$	267,000
Mirabillite	$Na_2SO_4 \cdot 10H_2O = 2Na^+ + SO_4{}^{2-} + 10H_2O$	280,000
Halite	$NaCl = Na^+ + Cl^-$	360,000

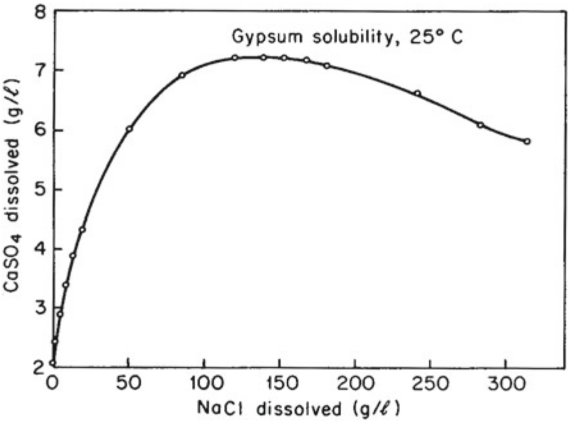

Fig. 2.2 Solubility of gypsum in aqueous solutions with an increasing NaCl content (Shternina 1960)

transport-controlled kinetics, (b) surface reaction-controlled kinetics where ions or molecules are detached from the crystal surface, and (c) a combination of transport and surface reaction-controlled kinetics.

Based on the results of Berner (1978, 1983), Sparks (1988) showed that in transport-controlled kinetics, the dissolution ions are detached very rapidly and accumulate to form a saturated solution adjacent to the surface. In surface reaction-controlled kinetics, ion detachments are slow, and ion accumulation at the crystal surface is equivalent to the surrounding solution concentration. The third type of rate-limiting mechanism for dissolution of minerals occurs when the surface detachment is fast, and the surface concentration is greater than the solution concentration.

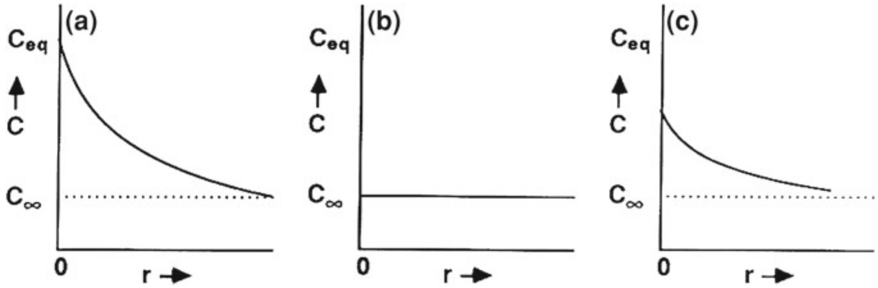

Fig. 2.3 Rate-limiting steps in mineral dissolution: **a** transport-controlled, **b** surface reaction-controlled, and **c** mixed transport and surface reaction control. Concentration (C) versus distance (r) from a crystal surface for three rate-controlling processes, where C_{eq} is the saturation concentration and C_∞ is the concentration in an infinitely diluted solution. Reprinted from Sparks (1988). Copyright 2005 with permission of Elsevier

2.2.2 Redox Processes

Redox processes in the subsurface involve the transfer of electrons among the constituents of aqueous, gaseous, and solid phases. As a result, changes in the oxidation state of the reactants and products occur. *Oxidation* is the half reaction where electrons are lost or removed from a species, while *reduction* is the half reaction where electrons are gained or added to a species. Accordingly, in a redox reaction, an oxidation agent (or oxidant) is an electron acceptor, and a reducing agent (or reductant) is an electron donor.

All oxidation reactions are coupled to reduction reactions. In many cases, redox reactions can also involve or be affected by changes in the surrounding environment, such as changes in the pH or temperature (i.e., endothermic or exothermic reactions). Many elements in the subsurface can exist in various oxidation states; some examples include elements like carbon, nitrogen, oxygen, sulfur, iron, cobalt, vanadium, and nickel.

The great importance of redox reactions and redox potentials in biogeochemical processes and their effect on the subsurface system is well established. In general, the redox potential pE (or Eh) and pH are considered the principal variables controlling geochemical reactions in geological and aquatic environments; many of the processes that are discussed in the next chapters involve redox reactions. The redox potential, Eh, is also commonly given as pE, the measure of electron activity analogous to pH. By convention, half reactions are written in terms of reduction; for example,

$$aA + bB + e^- \rightleftharpoons cC + dD. \tag{2.34}$$

In aqueous solutions, the general form of a redox reaction equation is given as

$$mA_{\mathrm{ox}} + nH^{+} + ne^{-} \rightleftharpoons pA_{\mathrm{red}} + s\mathrm{H_2O_{(1)}} \tag{2.35}$$

where A is a chemical species in any phase and ox and red denote oxidized and reduced states, respectively. The parameters m, n, p, and s represent stoichiometric coefficients, and H^{+} and e^{-} refer to protons and electrons, respectively, in aqueous solution. The equilibrium constant that corresponds to the half reaction in Eq. (2.35) is

$$K_{\mathrm{eq}} = \frac{[A_{\mathrm{red}}]^{p}[\mathrm{H_2O}]^{s}}{[A_{\mathrm{ox}}]^{m}[\mathrm{H}^{+}]^{n}[e^{-}]^{n}}. \tag{2.36}$$

An example of such a reaction is the reduction of iron,

$$\mathrm{Fe(OH)_{3(s)}} + 3\mathrm{H}^{+} + \mathrm{e}^{-} \rightleftharpoons \mathrm{Fe}^{2+} + 3\mathrm{H_2O_{(1)}} \tag{2.37}$$

with $\log K_{\mathrm{eq}} = 15.87$.

The voltage of the general reaction presented in Eq. (2.34) is given by the Nernst equation:

$$\mathrm{Eh(volts)} = \mathrm{E}^{\circ} + \frac{RT}{nF} \ln \frac{[A]^{a}[B]^{b}}{[C]^{c}[D]^{d}} \tag{2.38}$$

where R is the gas constant (=0.001987 kcal/mol/K), T is the temperature (in °K), F is the Faraday constant (23.061 kcal/mol/volt). Using 2.303 $\log_{10}$ instead of ln, then we obtain the term (2.303 RT/F), which is called the *Nernst factor*. This factor is equal to 0.05916 volts at 25 °C, so that Eq. (2.38) becomes

$$\mathrm{Eh(volts)} = \mathrm{E}^{\circ} + \frac{0.05916}{n} \log \frac{[A]^{a}[B]^{b}}{[C]^{c}[D]^{d}} \tag{2.39}$$

In a redox reaction, the energy released in a reaction due to movement of charged particles gives rise to a potential difference. The maximum potential difference is called the *electromotive force* (EMF), E, and the maximum electric work, W, is the product of charge q in Coulombs (C), and the potential ΔE in volts or EMF:

$$W = q\Delta E. \tag{2.40}$$

Note that the EMF (or ΔE) is determined by the nature of the reactants and electrolytes, not by the size of the system or amounts of material in it. The change in Gibbs free energy, ΔG, is the negative value of maximum electric work,

$$\Delta G = -W = -q\Delta E. \tag{2.41}$$

A redox reaction equation requires well-defined amounts of reactants and products. The number (n) of electrons in such a reaction equation is related to the amount of charge transferred when the reaction is completed. Because each mole of electron has a charge of 96,485 coulombs (known as the Faraday constant, F), $q = nF$, so that

$$\Delta G = -nF\Delta E. \tag{2.42}$$

The free electron activity, pE, which indicates the redox intensity in a system, is defined as

$$\mathrm{pE} = -\log[e^-] \tag{2.43}$$

Based on the pE value, redox environments are classified as follows: (a) pE > 7 indicates an oxic environment (b) at pE values between 2 and 7, the environment is considered suboxic, and (c) pE < 2 indicates an environment considered anoxic. The occurrence of redox reactions in the subsurface environment is limited by the decomposition and reduction of water:

- The upper bound is defined by the decomposition of water

$$\begin{gathered} {}^{1}\!/_{2}\mathrm{H_2O} \leftrightarrow {}^{1}\!/_{4}\mathrm{O_2(g)} + \mathrm{H^+} + e^- \\ K_{eq} = -20.78, \mathrm{E}^\circ = 1.22\mathrm{V} \\ (\mathrm{P_{O_2}} = 0.21\ \mathrm{atm}, \mathrm{E}^\circ = 1.22\mathrm{V}[\mathrm{H_2O}] \approx 1) \\ \mathrm{pE} = -\log e^- = \log K_{\mathrm{eq}} - \mathrm{pH} + {}^{1}\!/_{4}\log[\mathrm{O_2}] \\ \mathrm{Eh(volts)} = \mathrm{E}^\circ + 0.059\log\frac{[\mathrm{O_2}]^{0.25}[\mathrm{H^+}]}{[\mathrm{H_2O}]} \\ \mathrm{pE} = 20.61 - \mathrm{pH}; \quad \mathrm{Eh} = 1.22 - 0.059\ \mathrm{pH} \end{gathered}$$

- The lower bound is defined by the reduction in water:

$$\begin{gathered} 2\mathrm{H_2O} + 2e^- \leftrightarrow \mathrm{H_2} + 2\mathrm{OH^-}\ \text{or}\ \mathrm{H^+} + e^- = {}^{1}\!/_{2}\mathrm{H_2} \\ (\mathrm{P_{H_2}} = 1\ \mathrm{atm},\ \mathrm{E}^\circ = 0.0\,\mathrm{V}\ \text{by definition}) \\ \mathrm{pE} = -\log[e^-] = \log\ \mathrm{K_{eq}} - \mathrm{pH} + {}^{1}\!/_{2}\log[\mathrm{H_2}] \\ \mathrm{Eh(volts)} = \mathrm{E}^\circ + 0.059\log\frac{[\mathrm{H_2}]^{0.5}}{[\mathrm{H^+}]} \\ \mathrm{pE} = -\mathrm{pH};\ \mathrm{Eh} = -0.059\,\mathrm{pH} \end{gathered}$$

Redox diagrams are used to express the stability of dissolved species and minerals. An example diagram is presented in Fig. 2.4, where the redox potentials of various types of aqueous systems are shown as a function of pH. It can be seen that at acidic pH, a mine water system has a very high oxidation potential (Eh > 500 mv). In contrast, groundwater at natural to basic pH shows a reduction capability as low as −500 mv and even lower. As mentioned previously, redox reactions are affected by the environmental conditions prevailing in the system and thus the presence of acid functional groups (e.g., humic acids) on porous material interfaces, for example, can affect redox activity in the subsurface.

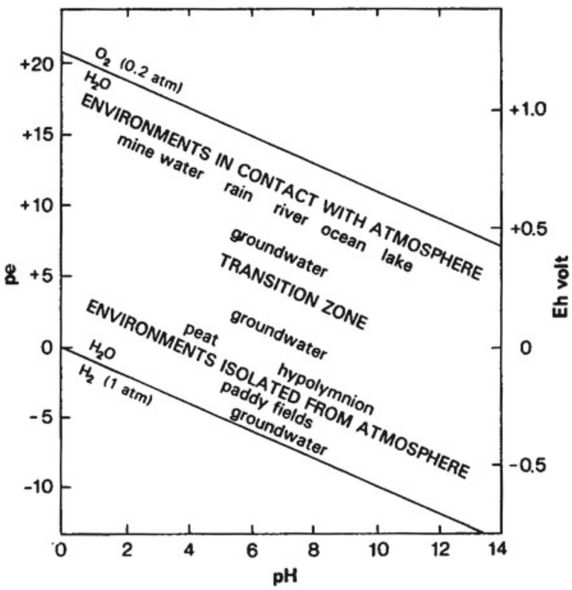

Fig. 2.4 The stability of water and the ranges of pE and pH conditions in natural environments (Appelo and Postma 1993)

In many cases, redox reactions that are favorable from a thermodynamic point of view may not actually take place: Sometimes, the activation energy barriers for such reactions are too high to allow fast transformation, according to the preferred thermodynamic considerations. For example, the complete oxidation of any organic molecule to carbon dioxide and water is thermodynamically favorable. However, such oxidation is not favorable kinetically, which implies that organic molecules—including all forms of living species—are not oxidized immediately; this fact explains the ability to sustain life. The reason for this difference between kinetic and thermodynamic considerations, for redox reactions, is partly because redox reactions are relatively slow compared to other reactions and partly due to the fact that in many cases, reactions are poorly coupled because of slow species diffusion from one microenvironment to another. Therefore, many redox reactions are dependent on catalytic processes.

2.3 Adsorption

Adsorption is the net accumulation of matter on the solid phase at the interface with an aqueous solution or gaseous phase. In this process, the solid surface is the *adsorbent* and the matter that accumulates is the *adsorbate*. *Adsorption* also may be defined as the excess concentration of a chemical at the subsurface solid interface compared to that in the bulk solution, or the gaseous phase, regardless of the nature of the interface region or the interaction between the adsorbate and the solid surface that causes the excess. Surface adsorption is due to interactions between electrical charges, or nonionized functional groups, on mineral and organic constituents.

Adsorption removes a compound from the bulk phase and thus affects its behavior in the subsurface environment. Due to some hysteresis effects, sometimes reflected in formation of bound residues, the release of compounds from the solid phase to the liquid or gaseous phase does not always reach the amount of adsorbate retained on solid surfaces.

When measured adsorption data are plotted against the concentration value of the adsorbate at equilibrium, the resulting graph is called an *adsorption isotherm*. The mathematical description of isotherms invariably involves adsorption models described by Langmuir, Freundlich, or Brauner, Emmet and Teller (known as the BET model). Discussion of these models is given in Part III, as conditions relevant to chemical-subsurface interactions are examined.

2.3.1 Adsorption of Charged Ionic Compounds

Adsorption of charged ionic compounds on the surface of a solid phase is subject to a combination of chemical binding forces and electric fields. The solid phase has a net charge that, in contact with liquid or gaseous phases, is faced by one or more layers of counter- or co-ions having a net charge equal to and separated from the surface charge. Electrical neutrality on the colloidal surface requires that an equal amount of charge of the opposite sign must accumulate in the liquid phase near the charged surface. For a negatively charged surface, this means that positively charged cations are electrostatically attracted to the charged surface. Anions are repelled by such a surface with diffusion forces acting in an opposite direction, such that there is a deficit of anions near the surface. The overall pattern, known as a *diffuse double layer* (DDL), is described by the Gouy–Chapman theory (see Sect. 5.4). This theory assumes that the exchangeable cations exist as point charges, the colloid surfaces are planar and infinite in extent, and the surface charge is distributed uniformly over the entire colloid surface. Stern (1924) and Grahame (1947) refined this theory, showing that the counter-ions are unlikely to approach the surface more closely than the ionic radii of anions and the hydrated radii of cations. Detailed, critical presentations of diffuse double-layer theory applied to earth materials can be found in Sposito (1981, 1989), Sparks (1988), and Bolt et al. (1991).

Cation exchange and selectivity are processes involving the cationic concentration in solution, the cation dimensions, and the configuration of the exchange sites. For cationic molecules, the retention properties follow the relation

$$\frac{A_{\mathrm{aq}}}{B_{\mathrm{aq}}} = K_k \frac{A_{\mathrm{ads}}}{B_{\mathrm{ads}}}, \tag{2.44}$$

where K_k is a selectivity coefficient that expresses the inequality of the activity ratios of the cationic molecules, A and B, in solution (aq) and adsorbed (ads). Kerr (1928) was the first to propose this equation, and K_k is therefore called the *Kerr coefficient*.

When cations of differing charge are involved, the exchange equation (Eq. 2.44) is modified. Gapon (1933) proposed that in the case of an exchange between mono- and bivalent cations, the expression should be

$$\left(\frac{M^{+}}{M^{2+}}\right)_{\text{ads}} = K_G \left(\frac{M^{+}}{\left(\frac{M^{2+}}{2}\right)^{1/2}}\right)_{\text{aq}}, \tag{2.45}$$

where the solute concentration is measured in terms of activity and the adsorption is measured in terms of equivalents, M denotes metal ion, and K_G is the Gapon coefficient.

The exchange properties of negatively charged surfaces do not affect different cations that have the same valence. This is due to differences in size and polarization among the cations themselves, the structural characteristics of the surfaces, and the differences in the surface charge distribution. The preference of the minerals in the subsurface for monovalent cations decreases according to the order Cs > Rb > K > NH_4 > Na > Li, which is known as the *lyotropic series*. In this case, a greater attraction of the surfaces for less-hydrated cations may be observed. This mechanism is relevant to minerals having isomorphic substitution in the tetrahedral sheet of the layer (recall Sect. 1.1) and is less evident in the case of divalent alkaline earth cations and trivalent cations. In the case of organomineral complexes, the pattern of cation selectivity is modified considerably (Greenland and Hayes 1981).

The selectivity of the exchange between two cations is specific to saline subsurface systems, described by the sodium adsorption ratio (SAR). Based on Na^{+} content in soil solutions, the US Salinity Laboratory (US Salinity Laboratory 1954) derived the equation

$$\mathrm{SAR} = \frac{[\mathrm{Na}^{+}]}{\sqrt{\frac{[\mathrm{Ca}^{2+}]+[\mathrm{Mg}^{2+}]}{2}}} \tag{2.46}$$

where the solution concentration is in μmol/L.

Metal cation adsorption processes include exchange, Coulombic, and site-specific adsorption. Heavy metal cations exhibit exchange reactions with negatively charged surfaces of clay minerals. Cationic adsorption is affected by the pH and in an acid environment ($pH < 5.5$), and some heavy metals do not compete with Ca^{2+} (a ubiquitous constituent in the subsurface) for mineral adsorption sites. At a higher pH, heavy metal adsorption increases abruptly and becomes irreversible.

Negative adsorption occurs when a charged solid surface faces an ion in an aqueous suspension and the ion is repelled from the surface by Coulomb forces. The Coulomb repulsion produces a region in the aqueous solution that is depleted of the anion and an equivalent region far from the surface that is relatively enriched. Sposito (1984) characterized this macroscopic phenomenon through the definition of the relative surface excess of an anion in a suspension, by

$$\Gamma_i^{(\mathrm{w})} = \frac{n_i - M_{\mathrm{w}} m_i}{S} \tag{2.47}$$

where n_i is total moles of ion i in the suspension per unit mass of solid, M_{w} is the molecular mass of water in the suspension per unit mass of solid, m_i is the molality of ion i in the supernatant solution, and S is the specific surface area of the suspended solid. This $\Gamma_i^{(\mathrm{w})}$ is the excess moles of ion (per unit area of suspended solid) relative to an aqueous solution containing M_{w} kilograms of water and the ion of molality, m_i.

If an anion approaches a charged surface, it is subject to attraction by positively charged surface sites on the surface or repulsion by negatively charged ones. Because clay materials in the subsurface normally are negatively charged, anions tend to be repelled from mineral surfaces. Negative adsorption of anions is affected by the anion charge, concentration, pH, the presence of other anions, and the nature and charge of the surface.

2.3.2 Adsorption of Nonionic Compounds

Adsorption of nonionic compounds on subsurface solid phases is subject to a series of mechanisms such as protonation, water bridging, cation bridging, ligand exchange, hydrogen bonding, and van der Waals interactions. Hasset and Banwart (1989) consider that the sorption of nonpolar organics by soils is due to enthalpy-related and entropy-related adsorption forces.

Enthalpy-related adsorption forces include the following processes:

1. Hydrogen bonding, which refers to the electrostatic interaction between a hydrogen atom covalently bound to one electronegative atom and to another electronegative atom or group of atoms in a molecule. The hydrogen atom may be regarded as a bridge between electronegative atoms. In general, this bonding is conceptualized as a dipole phenomenon, where the hydrogen bond exhibits an asymmetrical distribution of the first electron of the H atom induced by various electronegative atoms.
2. Ligand exchange processes, involving replacement of one or more ligands by the adsorbing species and, in some cases, can be considered a condensation reaction.
3. Protonation mechanisms, including a Coulomb electrostatic force resulting from charged surfaces. Due to the surface acidity, solutes having proton-selective organic functional groups can be adsorbed through a protonation reaction.
4. Pi (π) bonds, occurring as a result of overlapping of π orbitals when they are perpendicular to aromatic rings.

5. London–van der Waals forces, which are multipole interactions produced by correlation between fluctuation-induced multipole moments in two nearly uncharged polar molecules. These forces also include dispersion forces that arise from the correlation between the movement of electrons in one molecule and those of neighboring molecules. The van der Waals dispersion interaction between two molecules is generally very weak, but when many groups of atoms in a polymeric structure act simultaneously, the van der Waals components are additive.
6. Chemisorption, denoting the situation when an actual chemical bond is formed between the molecules and surface atoms.
7. Atoms that are rearranged, forming new compounds at the demand of the unsatisfied valences of the surface atoms.

Entropy-related adsorption, known as *hydrophobic sorption*, involves the partitioning of nonpolar organics from a polar aqueous phase onto hydrophobic surfaces, where they are retained by dispersion forces. The major feature of hydrophobic sorption is the weak interaction between the solute and the solvent. The entropy change is due largely to the destruction of the cavity occupied by the solute in the solvent and the destruction of the structured water shell surrounding the solvated organic.

2.3.3 Kinetic Considerations

A perspective based on kinetics leads to a better understanding of the adsorption mechanism of both ionic and nonionic compounds. Boyd et al. (1947) stated that the ion exchange process is diffusion controlled and the reaction rate is limited by mass transfer phenomena that are either film diffusion (FD) or particle diffusion (PD) controlled. Sparks (1988) and Pignatello (1989) provide a comprehensive overview on this topic.

In the case of subsurface cation exchange, charge compensation cations are held in the solid phase within crystals in interlayer positions, structural holes, or surface cleavages and faults of the crystals as well as on the external surfaces of clay minerals. Cations held on external surfaces are immediately accessible to the aqueous phase. On reaching this phase, they move by diffusion to regions of smaller concentration, the diffusion being affected by the tortuosity of the porous medium. An additional restriction affecting the rate of exchange is given by the fact that the arrival rate of incoming cations to the exchange sites is much slower than the release rate of the outgoing cations. The characteristic period of ion exchange in the subsurface ranges from a few seconds to days, being due to various constituents of the solid phase and the properties of the adsorbate.

In the case of nonionic compounds, the driving forces for adsorption consist of entropy changes and weak enthalpic (bonding) forces. The sorption of these compounds is characterized by an initial rapid rate followed by a much slower approach to an apparent equilibrium. The faster rate is associated with diffusion on the surface, while slower reactions have been related to particle diffusion into micropores.

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