# CHAPTER 3: SOLUTIONS AND THERMODYNAMICS OF MULTICOMPONENT SYSTEMS

## 3.1 INTRODUCTION

In the previous chapter, we introduced thermodynamic tools that allow us to predict the equilibrium mineral assemblage under a given set of conditions. For example, having specified temperature, we were able to determine the pressure at which the assemblage anorthite+forsterite is in equilibrium with the assemblage diopside+spinel+enstatite. In that reaction the minerals had unique and invariant compositions. In the Earth, things are not quite so simple: these minerals are present as solid solutions*, with substitutions of Fe for Mg, Na for Ca, and Cr and $Fe^{3+}$ for Al, among others. Indeed, most natural substances are solutions; that is, their compositions vary. Water, which is certainly the most interesting substance at the surface of the Earth and perhaps the most important, inevitably has a variety of substances dissolved in it. These dissolved substances are themselves often of primary geochemical interest. More to the point, they affect the chemical behavior of water. For example, the freezing temperature of an aqueous NaCl solution is lower than that of pure water. You may have taken advantage of this phenomenon by spreading salt to de-ice sidewalks and roads, or adding salt to ice to make ice cream.

In a similar way, the equilibrium temperature and pressure of the plagioclase+olivine ⇄ clinopyroxene+spinel+orthopyroxene reaction depends on the composition of these minerals. To deal with this compositional dependence, we need to develop some additional thermodynamic tools, which is the objective of this chapter. This may seem burdensome at first: if it were not for the variable composition of substances, we would already know most of the thermodynamics we need. However, as we will see in Chapter 4, we can use this compositional dependence to advantage in reconstructing conditions under which a mineral assemblage or a hydrothermal fluid formed.

A final "difficulty" is that the valance state of many elements may vary. Iron, for example, may change from its $Fe^{2+}$ state to $Fe^{3+}$ when an igneous rock weathers. The two forms of iron have very different chemical properties; for example $Fe^{2+}$ is considerably more soluble in water than is $Fe^{3+}$. Another example of this kind of reaction is photosynthesis, the process by which $CO_2$ is converted to organic carbon. These kinds of reactions are called "oxidation–reduction", or "redox" reactions. The energy your brain uses to process the information you are now reading comes from oxidation of organic carbon — carbon originally reduced by photosynthesis in plants. To fully specify the state of a system, we must specify its "redox" state. We treat redox reactions in the final section of this chapter.

Though Chapter 4 will add a few more tools to our geochemical toolbox, and treat a number of advanced topics in thermodynamics, it is designed to be optional. With completion of this chapter, you will have a sufficient thermodynamic background to deal with a wide range of phenomena in the Earth, and most of the topics in the remainder of this book.

## 3.2 PHASE EQUILIBRIA

### 3.2.1 SOME DEFINITIONS

#### 3.2.1.1 PHASE

Phases are real substances that are homogeneous, physically distinct, and (in principle) mechanically separable. For example, the phases in a rock are the minerals present. Amorphous substances are also phases, so glass or opal would be phases. The sugar that won't dissolve in your ice tea is a distinct phase from the tea, but the dissolved sugar is not. *Phase* is not synonymous with *compound*. Phases

*The naturally occurring minerals of varying composition are referred to as plagioclase rather than anorthite, olivine rather than forsterite, clinopyroxene rather than diopside, and orthopyroxene rather than enstatite.

need not be chemically distinct: a glass of ice water has two distinct phases: water and ice. Many solid compounds can exist as more than one phase. Nor need they be compositionally unique: plagioclase, clinopyroxene, olivine, etc., are all phases even though their composition can vary. Thus a fossil in which the aragonite ($CaCO_3$) is partially retrograded into calcite (also $CaCO_3$) consists of 2 phases. Systems, and reactions occurring within them, consisting of a single phase are referred to as *homogenous*; those systems consisting of multiple phases, and the reactions occurring within them, are referred to as *heterogeneous*.

### 3.2.1.2 Species

*Species* is somewhat more difficult to define than either *phase* or *component*. A species is a chemical entity, generally an element or compound (which may or may not be ionized). The term is most useful in the context of gases and liquids. A single liquid phase, such as an aqueous solution, may contain a number of species. For example, $H_2O$, $H_2CO_3$, $HCO_3^-$, $CO_3^{2+}$, $H^+$, and $OH^-$ are all species commonly present in natural waters. The term species is generally reserved for an entity that actually exists, such as a molecule, ion, or solid on a microscopic scale. This is not necessarily the case with components, as we shall see. The term species is less useful for solids, although it is sometimes applied to the pure end-members of solid solutions and to pure minerals.

### 3.2.1.3 Component

In contrast to a species, a *component* need not be a real chemical entity, rather it is simply an algebraic term in a chemical reaction. The *minimum number of components** of a system is rigidly defined as *the minimum number of independently variable entities necessary to describe the composition of each and every phase of a system.* Unlike species and phases, components may be defined in any convenient manner: what the components of your system are and how many there are depend on your interest and on the level of complexity you will be dealing with. Consider our aragonite-calcite fossil. If the only reaction occurring in our system (the fossil) is the transformation of aragonite to calcite, one component, $CaCO_3$, is adequate to describe the composition of both phases. If, however, we are also interested in the precipitation of calcium carbonate from water, we might have to consider $CaCO_3$ as consisting of 2 components: $Ca^{2+}$ and $CO_3^2$ .

There is a rule to determine the minimum number of components in a system once you decide what your interest in the system is; the hard part is often determining your interest. The rule is:

$$c = n - r \qquad 3.1$$

where *n is the number of species*, and *r is the number of independent chemical reactions possible between these species*. Essentially, this equation simply states that if a chemical species can be expressed as the algebraic sum of other components, we need not include that species among out minimum set of components. Let's try the rule on the species we listed above for water. We have 6 species: $H_2O$, $H_2CO_3$, $HCO_3^-$, $CO_3^{2+}$, $H^+$, and $OH^-$. We can write 3 reactions relating them:

$$HCO_3^- = H^+ + CO_3^{2-}$$
$$H_2CO_3 = H^+ + HCO_3^-$$
$$H_2O = H^+ + OH^-$$

Equation 3.1 tells us we need 3 = 6 – 3 components to describe this system: $CO_3^{2+}$, $H^+$, and $OH^-$. Put another way, we see that carbonic acid, bicarbonate, and water can all be expressed as algebraic sums the hydrogen, hydroxyl, and carbonate ions, so they need not be among our minimum set of components.

In igneous and metamorphic petrology, components are often the major oxides (though we may often chose to consider only a subset of these). On the other hand, if we were concerned with the isotopic

*Caution: some books use the term *number of components* as synonymous with *minimum number of components*.

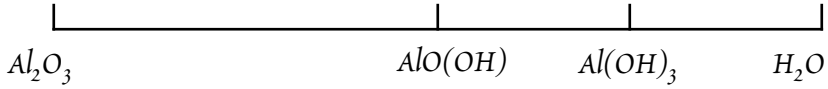


Figure 3.1. Graphical Representation of the System $Al_2O_3$-$H_2O$.

equilibration of minerals with a hydrothermal fluid, $^{18}O$ would be considered as a different component than $^{16}O$.

Perhaps the most straightforward way of determining the number of components is a graphical approach. If all phases can be represented on a one-dimensional diagram (that is, a straight line representing composition), we are dealing with a two component system. For example, consider the hydration of $Al_2O_3$ (corundum) to form boehmite (AlO(OH)) or gibbsite $Al(OH)_3$. Such a system would contain 4 phases (corundum, boehmite, gibbsite, water), but is nevertheless a two component system because all phases may be represented in one-dimension of composition space, as is shown in Figure 3.1. Because there are two polymorphs of gibbsite, one of boehmite, and two other possible phases of water, there are 9 phases possible phases in this two-component system. Clearly, a system may have many more phases than components.

Similarly, if a system may be represented in 2 dimensions, it is a three-component system. Figure 3.2 is a ternary diagram illustrating the system $Al_2O_3$–$H_2O$–$SiO_2$. The graphical representation approach reaches it practical limit in a four component system because of the difficulty of representing more than 3 dimensions on paper. A four component system is a quaternary one, and can be represented with a three-dimensional quaternary diagram.

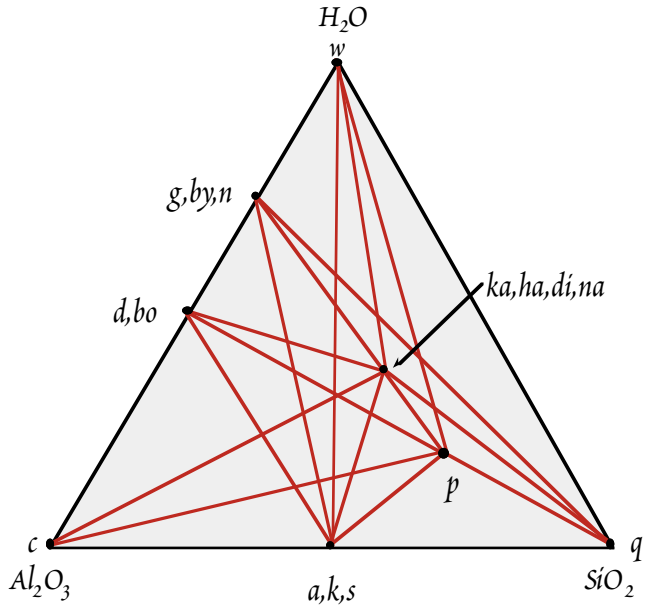


Figure 3.2. Phase diagram for the system $Al_2O_3$–$H_2O$–$SiO_2$. The lines are called *joins* because they join phases. In addition to the end-members, or components, phases represented are *g*: gibbsite, *by*: bayerite, *n*: norstrandite (all polymorphs of $Al(OH)_3$), *d*: diaspore, *bo*: boehmite (polymorphs of AlO(OH)), *a*: andalusite, *k*: kyanite, *s*: sillimanite (all polymorphs of $Al_2SiO_5$), *ka*: kaolinite, *ha*: halloysite, *di*: dickite, *na*: nacrite (all polymorphs of $Al_2Si_2O_5(OH)_4$), and *p*: pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). There are also 6 polymorphs of quartz (coesite, stishovite, tridymite, cristobalite, α-quartz, and β-quartz).

It is important to understand that a component may or may not have chemical reality. For example in the exchange reaction:

$$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+$$

we could alternatively define the *exchange operator* $KNa_{-1}$ (where $Na_{-1}$ is -1 mol of Na ion) and write the equation as:

$$NaAlSi_3O_8 + KNa_{-1} = KAlSi_3O_8$$

In addition, we can also write the reaction:

$$K - Na = KNa_{-1}$$

Here we have 4 species and 2 reactions and thus a minimum of only 2 components. You can see that *a component is merely an algebraic term.*

There is generally some freedom in choosing components. For example, in the ternary (i.e., 3 component) system $SiO_2$ – $Mg_2SiO_4$ – $MgCaSi_2O_6$, we could choose our components to be quartz, diopside, and forsterite, or we could choose them to be $SiO_2$, MgO, and CaO. Either way, we are dealing with a ternary

system (which contains $MgSiO_3$ as well as the three other phases).

#### 3.2.1.4 Degrees of Freedom

The number of degrees of freedom in a system is equal to the sum of the number of independent *intensive* variables (generally T & P) and independent concentrations (or activities or chemical potentials) of components in phases that must be fixed to define uniquely the state of the system. A system that has no degrees of freedom (i.e., is uniquely fixed) is said to be invariant, one that has one degree of freedom is univariant, etc. Thus in an univariant system, for example, we need specify only the value of one variable, for example, temperature or the concentration of one component in one phase, and the value of pressure and all other concentrations are then fixed, i.e., they can be calculated (assuming the system is at equilibrium).

### 3.2.2 The Gibbs Phase Rule

The Gibbs‡ Phase Rule is a rule for determining the *degrees of freedom*, or *variance*, of a system *at equilibrium*. The rule is:

$$\boxed{f = \mathbf{c} - \phi + \mathbf{2}} \qquad 3.2$$

where $f$ is the degrees of freedom, $c$ is the number of components, and $\phi$ is the number of phases. The mathematical analogy is that the degrees of freedom are equal to the number of variables less the number of equations relating those variables. For example, in a system consisting of just $H_2O$, if two phases of coexist, for example, water and steam, then the system in univariant. Three phases coexist at the triple point of water, so the system is said to be invariant, and T and P are uniquely fixed: there is only one temperature and one pressure at which the three phases of water can coexist (273.15 K and 0.006 bar). If only one phase is present, for example just liquid water, then we need to specify 2 variables to describe completely the system. It doesn't matter which two we pick. We could specify molar volume and temperature and from that we could deduce pressure. Alternatively, we could specify pressure and temperature. There is only 1 possible value for the molar volume if temperature and pressure are fixed. It is important to remember this applies to intensive parameters. To know volume, an extensive parameter, we would have to fix one additional extensive variable (such as mass or number of moles). And again, we emphasize that all this applies only to systems at equilibrium.

Now consider the hydration of corundum to form gibbsite. There are 3 phases, but there need be only two components. If these 3 phases (water, corundum, gibbsite) are at equilibrium, we have only 1 degree of freedom, i.e., if we know the temperature at which these 3 phases are in equilibrium, the pressure is also fixed.

Rearranging equation 3.2, we also can determine the *maximum* number of phases that can coexist at equilibrium in any system. The degrees of freedom cannot be less than zero, so for an invariant, one component system, a maximum of three phases can coexist at equilibrium. In a univariant one-component system, only 2 phases can coexist. Thus sillimanite and kyanite can coexist over a range of temperatures, as can kyanite and andalusite. But the three phases of $Al_2SiO_5$ coexist only at one unique temperature and pressure.

Let's consider the example of the three-component system $Al_2O_3$–$H_2O$–$SiO_2$ in Figure 3.2. Although many phases are possible in this system, for any given composition of the system only three phases can coexist at equilibrium over a range of temperature and pressure. Four phases, e.g., a, k, s and p, can coexist only along a one-dimensional line or curve in P-T space. Such points are called univariant lines (or curves). Five phases can coexist at invariant points at which both temperature and pressure are uniquely fixed. Turning this around, if we found a metamorphic rock whose composition fell within

‡ J. Williard Gibbs (1839-1903) is viewed by many as the father of thermodynamics. He received the first doctorate in engineering granted in the U. S., from Yale in 1858. He was Professor of Mathematical Physics at Yale from 1871 until his death. He also helped to found statistical mechanics. The importance of his work was not widely recognized by his American colleagues, though it was in Europe, until well after his death.

the $Al_2O_3$–$H_2O$–$SiO_2$ system, and if the rock contained 5 phases, it would be possible to determine uniquely the temperature and pressure at which the rock equilibrated.

### 3.2.3 The Clapeyron Equation

A common problem in geochemistry is to know how a phase boundary varies in P-T space, e.g., how a melting temperature will vary with pressure. At a phase boundary, two phases must be in equilibrium, i.e., $\Delta G$ must be 0 for the reaction Phase 1 ⇄ Phase 2. The phase boundary therefore describes the condition:

$$d(\Delta G_r) = \Delta V_r dP - \Delta S_r dT = 0.$$

Thus the slope of a phase boundary on a temperature-pressure diagram is:

$$\boxed{\frac{dT}{dP} = \frac{\Delta V_r}{\Delta S_r}} \qquad 3.3$$

where $\Delta V_r$ and $\Delta S_r$ are the volume and entropy changes associated with the reaction. Equation 3.3 is known as the *Clausius-Clapeyron Equation*, or simply the *Clapeyron Equation*. Because $\Delta V_r$ and $\Delta S_r$ are functions of temperature and pressure, this, of course, is only an instantaneous slope. For many reactions, however, particularly those involving only solids, the temperature and pressure dependencies of $\Delta V_r$ and $\Delta S_r$ will be small and the Clapeyron slope will be relatively constant over a large T and P range.

Because $\Delta S = \Delta H/T$, the Clapeyron equation may be equivalently written as:

$$\frac{dT}{dP} = \frac{T\Delta V_r}{\Delta H_r} \qquad 3.4$$

Slopes of phase boundaries in P-T space are generally positive, implying that the phases with the largest volumes also generally have the largest entropies (for reasons that become clear from a statistical mechanical treatment). This is particularly true of solid-liquid phase boundaries, although there is one very important exception: water. How do we determine the pressure and temperature dependence of $\Delta V_r$ and why is $\Delta V_r$ relatively T and P independent in solids?

We should emphasize that application of the Clapeyron equation is not limited to reactions between two phases in a one-component system, but may be applied to any univariant reaction.

## 3.3 Solutions

*Solutions are defined as homogeneous phases produced by dissolving one or more substances in another substance.* In geochemistry we are often confronted by solutions: as gases, liquids, and solids. Free energy depends not only on T and P, but also on composition. In thermodynamics it is generally most convenient to express compositions in terms of mole fractions, $X_i$, the number of moles of *i* divided by the total moles in the substance (moles are weight divided by atomic or molecular weight). The sum of all the $X_i$ must, of course, total to 1.

Solutions are distinct from purely mechanical mixtures. For example, salad dressing (oil and vinegar) is not a solution. Similarly, we can grind anorthite ($CaAl_2Si_2O_8$) and albite ($NaAlSi_3O_8$) crystals into a fine powder and mix them, but the result is not a plagioclase solid solution. The Gibbs Free Energy of mechanical mixtures is simply the sum of the free energy of the components. If, however, we heated the anorthite-albite mixture to a sufficiently high temperature that the kinetic barriers were overcome, there would be a reordering of atoms and the creation of a true solution. Because this reordering is a spontaneous chemical reaction, there must be a decrease in the Gibbs Free Energy associated with it. This solution would be stable at 1 atm and 25°C. Thus we can conclude that the solution has a lower Gibbs Free Energy than the mechanical mixture. On the other hand, vinegar will never dissolve in oil at 1 atm and 25°C because the Gibbs Free Energy of that solution is greater than that of the mechanical mixture.

### EXAMPLE 3.1: THE GRAPHITE-DIAMOND TRANSITION

At 25°C the graphite-diamond transition occurs at 1600 MPa (megapascals, 1 MPa =10 b). Using the standard state (298 K, 0.1 MPa) data below, predict the pressure at which the transformation occurs when temperature is 1000°C.

| | Graphite | Diamond |
|---|---|---|
| $\alpha$ ($K^{-1}$) | $1.05\times10^{-05}$ | $7.50\times10^{-06}$ |
| $\beta$ ($MPa^{-1}$) | $3.08\times10^{-05}$ | $2.27\times10^{-06}$ |
| S° (J/K-mol) | 5.74 | 2.38 |
| V ($cm^3$/mol) | 5.2982 | 3.417 |

*Answer:* We can use the Clapeyron equation to determine the slope of the phase boundary. Then, assuming that $\Delta S$ and $\Delta V$ are independent of temperature, we can extraplate this slope to 1000° C to find the pressure of the phase transition at that temperature.

First, we calculate the volumes of graphite and diamond at 1600 MPa as (equ. 2.139):

$$V = V°(1 - \beta\Delta P) \qquad 3.5$$

where $\Delta P$ is the difference between the pressure of interest (1600 MPa in this case) and the reference pressure (0.1 MPa). Doing so, we find the molar volumes to be 5.037 for graphite and 3.405 for diamond, so $\Delta V_r$ is –1.6325 cc/mol. The next step will be to calculate $\Delta S$ at 1600 MPa. The pressure dependence of entropy is given by equation 2.143: $\partial S/\partial P)_T = -\alpha V$. Thus to determine the effect of pressure we integrate:

$$S_P = S° + \int_{Pref}^{P_1} \left(\frac{\partial S}{\partial P}\right)_T dP = S° + \int_{Pref}^{P_1} -\alpha V \, dP \qquad 3.6$$

(We use $S_p$ to indicate the entropy at the pressure of interest and S° the entropy at the reference pressure.) We need to express V as a function of pressure, so we substitute 3.5 into 3.6:

$$\begin{aligned} S_P &= S° + \int_{Pref}^{P_1} -\alpha V°(1 - \beta P)dP \\ &= S° - \alpha V°\left[\Delta P - \frac{\beta}{2}(P_1^2 - P_{ref}^2)\right] \end{aligned} \qquad 3.7$$

The reference pressure, $P_{ref}$, is negligible compared to $P_1$ (0.1 MPa vs 1600 PMa), so that this simplifies to:

$$S_P = S° - \alpha V°\left[\Delta P - \frac{\beta}{2}P_1^2\right]$$

For graphite, $S_p$ is 5.66 J/K-mol, for diamond, it is 2.34 J/K-mol, so $\Delta S_r$ at 1600 MPa is -3.32 $J\text{-}K^{-1}\text{-}mol^{-1}$.

The Clapeyron slope is therefore:

$$\frac{\Delta S}{\Delta V} = \frac{-3.322}{-1.63} = 2.035 \text{ } JK^{-1}cm^{-3}$$

One distinct advantage of the SI units is that $cm^3 = J/MPa$, so the above units are equivalent to K/MPa. From this, the pressure of the phase change at 1000° C can be calculated as:

$$P_{1000} = P_{298} + \Delta T \times \frac{\Delta S}{\Delta V}$$

$$= 1600 + 975 \times 2.035 = 3584 \text{ MI}$$

The Clapeyron slope we calculated (solid line) is compared with the experimentally determined phase boundary in Figure 3.3. Our calculated phase boundary is linear whereas the experimental one is not. The curved nature of the observed phase boundary indicates $\Delta V$ and $\Delta S$ are pressure and temperature dependent. This is indeed the case, particularly for graphite. A more accurate estimate of the volume change requires $\beta$ be expressed as a function of pressure.

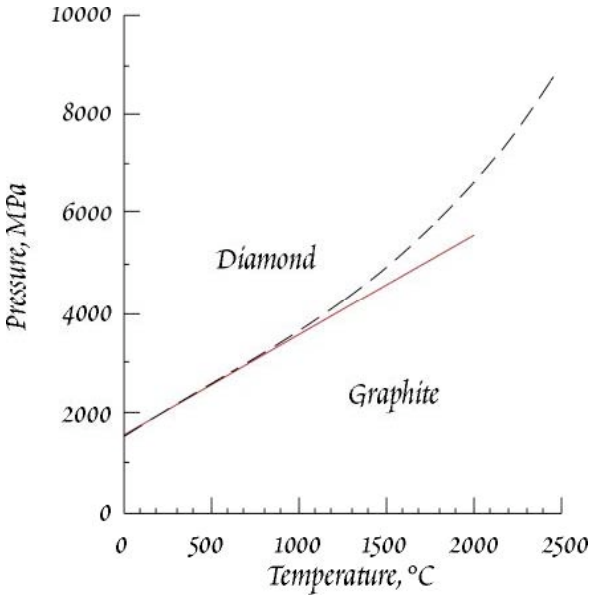



Figure 3.3. Comparison of the graphite-diamond phase boundary calculated from thermodynamic data and the Clapeyron slope (solid line) with the experimentally observed phase boundary (dashed line).

### 3.3.1 RAOULT'S LAW

Working with solutions of ethylene bromide and propylene bromide, Raoult[¶] noticed that the vapor pressures of the components in a solution were proportional to the mole fractions of those components:

$$\boxed{P_i = X_i P_i^o} \qquad 3.8$$

where $P_i$ is the vapor pressure of component *i* above the solution, $X_i$ is the mole fraction of *i* in solution, and $P_i^o$ is the vapor pressure of pure *i* under standard conditions. Assuming the partial pressures are additive and the sum of all the partial pressures is equal to the total gas pressure ($\Sigma P_i = P_{total}$):

$$\boxed{P_i = X_i\, P_{total}} \qquad 3.9$$

Thus partial pressures are proportional to their mole fractions. *This is the definition of the* ***partial pressure*** *of the* $i^{th}$ *gas in a mixture.*

Raoult's Law holds only for *ideal solutions,* i.e., substances where there are no intermolecular forces. It also holds to a good approximation where the forces between like molecules are the same as between different molecules. The two components Raoult was working with were very similar chemically, so that this condition held and the solution was nearly ideal. As you might guess, not all solutions are ideal. Fig. 3.4 shows the variations of partial pressures above a mixture of water and dioxane. Significant deviations from Raoult's Law are the rule except where $X_i$ approaches 1.

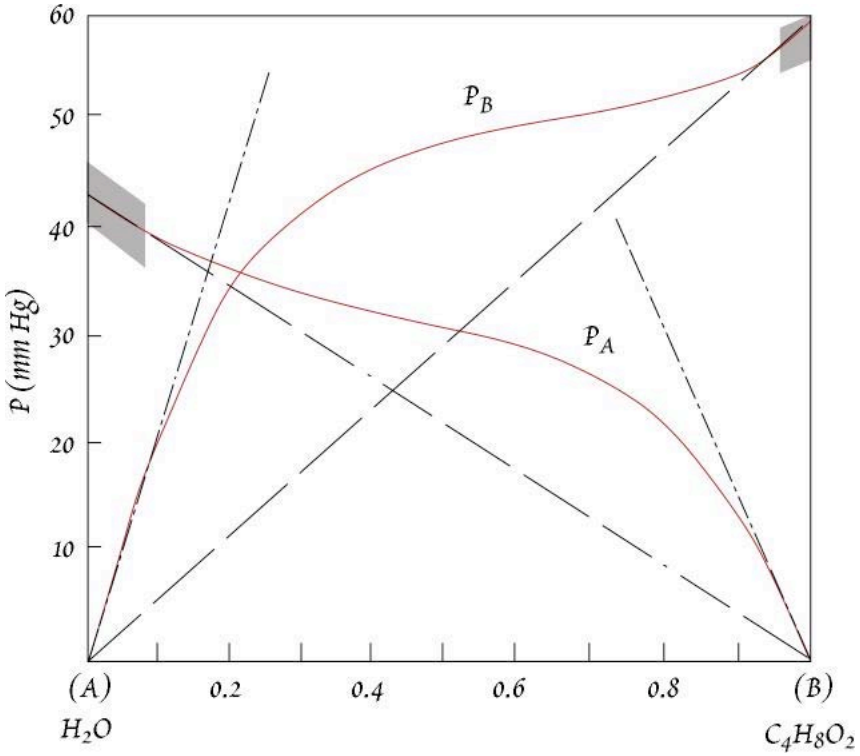



Figure 3.4. Vapor pressure of water and dioxane in a water-dioxane mixture showing deviations from ideal mixing. Shaded areas are areas where Raoult's Law (dashed lines). Henry's Law slopes are shown as dot-dashed lines. After Nordstrom and Munoz (1986).

[¶] Francois Marie Raoult (1830-1901), French chemist.

### 3.3.2 HENRY'S LAW

Another useful approximation occurs when $X_i$ approaches 0. In this case, the partial pressures are not equal to the mole fraction times the vapor pressure of the pure substance, but they do vary linearly with $X_i$. This behavior follows Henry's Law£, which is:

$$\boxed{P_i = hX_i \quad for\ X_i << 1} \qquad 3.10$$

where *h* is known as the Henry's Law constant.

## 3.4 CHEMICAL POTENTIAL

### 3.4.1 PARTIAL MOLAR QUANTITIES

Free energy and other thermodynamic properties are dependent on composition. We need a way of expressing this dependence. For any extensive property of the system, such as volume, entropy, energy, or free energy, we can define a *partial molar value*, which expresses how that property will depend on changes in amount of one component. For example, we can define partial molar volume of component *i* in phase $\phi$ as:

$$v_i^{\phi} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j,j\neq i}} \qquad \text{such that} \qquad V = \sum_i n_i v_i \qquad 3.11$$

(we will use small letters to denote partial molar quantities; the superscript refers to the phase and the subscript refers to the component). The English interpretation of equation 3.11 is that *the partial molar volume of component* i *in phase* $\phi$ *tells us how the volume of phase* $\phi$ *will vary with an infinitesimal addition of component* i, *if all other variables are held constant.* For example, the partial molar volume of Na in an aqueous solution such as seawater would tell us how the volume of that solution would change for an infinitesimal addition of Na. In this case *i* would refer to the Na component and $\phi$ would refer to the aqueous solution phase. In Table 2.2, we see that the molar volumes of the albite and anorthite end-members of the plagioclase solid solution are different. We could define $v_{Ab}^{Pl}$ as the partial molar volume of albite in plagioclase, which would tell us how the volume of plagioclase would vary for an infinitesimal addition of albite. (In this example, we have chosen our component as albite rather than Na. While we could have chosen Na, the choice of albite simplifies matters because the replacement of Na with Ca is accompanied by the replacement of Si by Al.)

The second expression in 3.11 says that the volume of a phase is the sum of the partial molar volumes of the components times the number of moles of each component present. Thus the volume of plagioclase would be sum of the partial molar volumes of the albite and anorthite components weighted by the number of moles of each.

Another example might be a solution of water and ethanol. The variation of the partial molar volumes of water and ethanol in a binary solution is illustrated in Figure 3.5. This system illustrates very clearly why the qualification "for an infinitesimal addition" is always added: the value of a partial molar quantity of a component may vary with the amount of that component present.

Equation 3.11 can be generalized to all partial molar quantities and also expresses an important property of partial molar quantities: *an extensive variable of a system or phase is the sum of it's partial molar quantities for each component in the system*. In our example above, this means that the volume of plagioclase is the sum of the partial molar volume of the albite and anorthite components.

Generally, we find it more convenient to convert extensive properties to intensive properties by dividing by the total number of moles in the system, $\Sigma n$. Dividing both sides of equation 3.11 by $\Sigma n$ we have:

$$\bar{V} = \sum_i X_i v_i \qquad 3.12$$

£ named for English chemist William Henry (1775-1836), who formulated it.

This equation says that the molar volume of a substance is the sum of the partial molar volumes of its components times their mole fractions. *For a pure phase, the partial molar volume equals the molar volume since X=1.*

### 3.4.2 Definition of Chemical Potential and Relationship to Gibbs Free Energy

We define $\mu$ as the *chemical potential*, which is simply the partial molar Gibbs Free Energy:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j,j\neq i}} \qquad 3.13$$

The chemical potential thus tells us how the Gibbs Free Energy will vary with the number of moles, $n_i$, of component *i* holding temperature, pressure, and the number of moles of all other components constant. We said that the Gibbs Free Energy of a system is a measure of the capacity of the system to do chemical work. Thus the chemical potential of component *i* is the amount by which this capacity to do chemical work is changed for an infinitesimal addition of component *i* at constant temperature and pressure. In a NiCd battery (common rechargeable batteries) for example, the chemical potential of Ni in the battery (our system) is a measure of the capacity of the battery to provide electrical energy per mole of additional Ni for an infinitesimal addition.

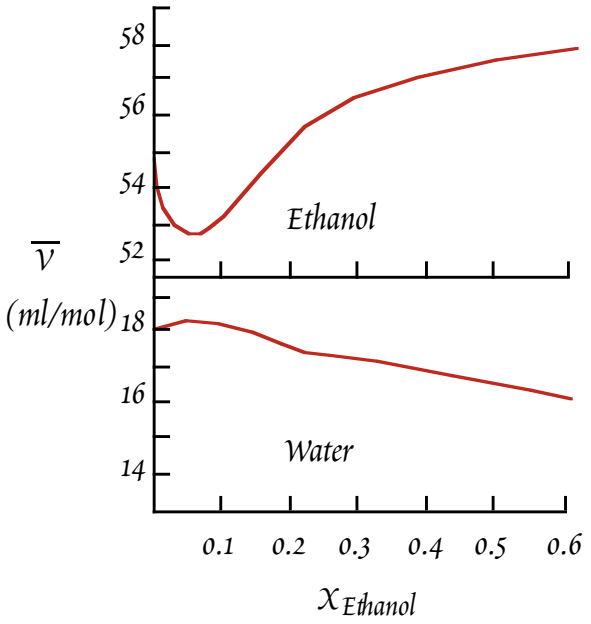



Figure 3.5. Variation of the partial molar volumes of water and ethanol as a function of the mole fraction of ethanol in a binary solution. This figure also illustrates the behavior of a very non-ideal solution.

The total Gibbs Free Energy of a system will depend upon composition as well as on temperature and pressure. The equations we introduced for Gibbs Free Energy in Chapter 2 fully describe the Gibbs Free Energy only for single components systems or systems containing only pure phases. The Gibbs Free Energy change of a phase of variable composition is fully expressed as:

$$dG = VdP - SdT + \sum_i \mu_i dn_i \qquad 3.14$$

### 3.4.3 Properties of the Chemical Potential

We now want to consider two important properties of the chemical potential. To illustrate these properties, consider a simple two-phase system in which an infinitesimal amount of component *i* is transferred from phase $\beta$ to phase $\alpha$, under conditions where T, P, and the amount of other components is held constant in each phase. One example of such a reaction would be the transfer of Pb from a hydrothermal solution to a sulfide mineral phase. The chemical potential expresses the change in Gibbs Free Energy under these conditions:

$$dG = dG^{\alpha} + dG^{\beta} = \mu_i^{\alpha} dn_i^{\alpha} + \mu_i^{\beta} dn_i^{\beta} \qquad 3.15$$

since we are holding everything else constant, what is gained by $\alpha$must be lost by $\beta$, so $-dn_i^{\alpha} = dn_i^{\beta}$ and:

$$dG = \left(\mu_i^{\alpha} - \mu_i^{\beta}\right) dn_i \qquad 3.16$$

At equilibrium, dG = 0, and therefore $\mu_i^{\alpha} = \mu_i^{\beta}$ 3.17

Equation 3.17 reflects a very general and very important relationship, namely:

**In a system at equilibrium, the chemical potential of every component in a phase is equal to the chemical potential of that component in every other phase in which that component is present.**

Equilibrium is the state toward which systems will naturally transform. The Gibbs Free Energy is the chemical energy available to fuel these transformations. *We can regard differences in chemical potentials as the forces driving transfer of components between phases*. In this sense, the chemical potential is similar to other forms of potential energy, such as gravitational or electromagnetic. Physical systems spontaneously transform so as to minimize potential energy. Thus for example, water on the surface of the Earth will move to a point where it's gravitational potential energy is minimized, i.e., downhill. Just as gravitational potential energy drives this motion, the chemical potential drives chemical reactions, and just as water will come to rest when gravitational energy is minimized, chemical reactions will cease when chemical potential is minimized. So in our example above, the spontaneous transfer of Pb between a hydrothermal solution and a sulfide phase will occur until the chemical potentials of Pb in the solution and in the sulfide are equal. At this point, there is no further energy available to drive the transfer.

We defined the chemical potential in terms of the Gibbs Free Energy. However, in his original work, Gibbs based the chemical potential on the internal energy of the system. As it turns out, however, the quantities are the same:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j,j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j,j\neq i}} \qquad 3.18$$

It can be further shown (but we won't) that:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j,j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j,j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j,j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j,j\neq i}}$$

### 3.4.4 The Gibbs-Duhem Relation

Since $\mu$ is the partial molar Gibbs Free Energy, the Gibbs Free Energy of a system is the sum of the chemical potentials of each component:

$$G = \sum_i n_i \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j,j\neq i}} = \sum_i n_i \mu_i \qquad 3.19$$

The differential form of this equation (which we get simply by applying the chain rule) is:

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \qquad 3.20$$

Equating this with equation 3.14, we obtain:

$$\sum_i n_i d\mu_i + \sum_i \mu_i dn_i = VdP - SdT + \sum_i \mu_i dn_i \qquad 3.21$$

Rearranging, we obtain the *Gibbs-Duhem Relation*:

$$\boxed{VdP - SdT - \sum_i n_i d\mu_i = 0} \qquad 3.22$$

The Gibbs-Duhem Equation describes the relationship between simultaneous changes in pressure, temperature and composition in a single-phase system. In a closed system at equilibrium, net changes in chemical potential will occur only as a result of changes in temperature or pressure. *At constant temperature and pressure*, there can be no net change in chemical potential at equilibrium:

$$\boxed{\sum_i n_i d\mu_i = 0} \qquad 3.23$$

*This equation further tells us that the chemical potentials do not vary independently, but change in a related way.* In a closed system, only one chemical potential can vary independently. For example, consider a two component system. Then we have $n_1 d\mu_1 + n_2 d\mu_2 = 0$ and $d\mu_2 = -(n_1/n_2)d\mu_1$. If a given variation in composition produces a change in $\mu_1$ then there is a concomitant change in $\mu_2$.

For multi-phase systems, we can write a version of the Gibbs-Duhem relation for each phase in the system. For such systems, the Gibbs-Duhem relation allows us to reduce the number of independently variable components in each phase by one. We will return to this point later in the chapter.

We can now state an additional property of chemical potential:

**In spontaneous processes, components or species are distributed between phases so as to minimize the chemical potential of all components.**

This allows us to make one more characterization of equilibrium: *equilibrium is point where the chemical potential of all components is minimized*.

### 3.4.5 Derivation of the Phase Rule

Another significant aspect of the Gibbs-Duhem Equation is that the phase rule can be derived from it. We begin by recalling that the variance of a system (the number of variables that must be fixed or independently determined to determine the rest) is equal to the number of variables less the number of equations relating them. In a multicomponent single-phase system, consisting of $c$ components, there are $c$ +2 unknowns required to describe the equilibrium state of the system: T, P, $\mu_1$, $\mu_2$, ...$\mu_c$. But in a system of $\phi$ phases at equilibrium, we can write $\phi$ versions of equation 3.23, which reduces the independent variables by $\phi$. Thus the number of independent variables that must be specified to describe a system of $c$ components and $\phi$ phases is:

$$f = c + 2 - \phi$$

which is the Gibbs phase rule.

Specification of $f$ variables will completely describe the system, at least with the qualification that in thermodynamics we are normally uninterested in the size of the system, that is, in extensive properties such as mass, volume, etc. (though we are interested in their intensive equivalents) and outside forces or fields such as gravity, electric or magnetic fields, etc. Nevertheless, the size of the system is described as well, provided only that one of the $f$ variables is extensive.

## 3.5 Ideal Solutions

Having placed another tool, the chemical potential, in our thermodynamic toolbox, we are ready to continue our consideration of solutions. We will begin with *ideal solutions*, which, like ideal gases, are fictions that avoid some of the complications of real substances. For an ideal solution, we make an assumption similar to one of those made for an ideal gas, namely that there were no forces between molecules. In the case of ideal solutions, which may be gases, liquids, or solids, we can relax this assumption somewhat and require only that *the interactions between different kinds of molecules in an ideal solution are the same as those between the same kinds of molecules*.

### 3.5.1 Chemical Potential in Ideal Solutions

How does chemical potential vary in an ideal solution? Consider the vapor pressure of a gas. The derivative of G with respect to pressure at constant temperature is volume:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Written in terms of partial molar quantities:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = v$$

If the gas is ideal, then: $$\left(\frac{\partial \mu}{\partial P}\right)_{T,ideal} = \frac{RT}{P} \quad 3.24$$

and if we integrate from P° to P we obtain:

$$\mu^P - \mu^{P^o} = RT \ln \frac{P}{P^o} \quad 3.25$$

where $\mu^{P^\circ}$ is the chemical potential of the pure gas at the reference (standard state) pressure $P^\circ$. This is the standard-state chemical potential and is written as $\mu^\circ$. If we let $P^\circ$ be the vapor pressure of pure $i$ and $P$ be the vapor pressure of $i$ in an ideal solution, then we may substitute X for P/P° into Raoult's Law (Equation 3.8) and to obtain the following:

$$\boxed{\mu_{i,ideal} = \mu_i^o + RT \ln X_i} \quad 3.26$$

This equation describes the relationship between the chemical potential of component $i$ and its mole fraction in an ideal solution.

### 3.5.2 Volume, Enthalpy, Entropy, and Free Energy Changes in Ideal Solutions

We will be able to generalize a form of this equation to non-ideal cases a bit later. Let's first consider some other properties of ideal mixtures. For real solutions, any extensive thermodynamic property such as volume can be considered to be the sum of the volume of the components plus a volume change due to mixing:

$$\overline{V} = \sum_i X_i \overline{V}_i + \Delta V_{mixing} \quad 3.27$$

The first term on the right reflects the volume resulting from mechanical mixing of the various components. The second term reflects volume changes associated with solution. For example, if we mixed 100 ml of ethanol and 100 ml of water (Figure 3.5), the volume of the resulting solution would be 193 ml. Here, the value of the first term on the right would be 200 ml, the value of the second term would be -7 ml. We can write similar equations for enthalpy, etc. But the volume change and enthalpy change due to mixing are both 0 in the ideal case. This is true because both volume and enthalpy changes of mixing arise from intermolecular forces, and, by definition, such intermolecular forces are absent in the ideal case. Thus:

$$\Delta V_{ideal\ mixing} = 0$$

therefore: $$\overline{V}_{ideal} = \sum_i X_i v_i = \sum_i X_i \overline{V}_i$$

and $$\Delta H_{ideal\ mixing} = 0$$

and therefore: $$\overline{H}_{ideal} = \sum_i X_i h_i = \sum_i X_i \overline{H}_i$$

This, however, is not true of entropy. You can imagine why: if we mix two substances on an atomic level, the number of possible arrangements of our system increases even if they are ideal substances. The entropy of ideal mixing is (compare equation 2.110):

$$\Delta \overline{S}_{ideal\ mixing} = -R \sum_i X_i \ln X_i \quad 3.28$$

$$\overline{S}_{ideal\ solution} = \sum_i X_i \overline{S}_i - R \sum_i X_i \ln X_i \quad 3.29$$

Because $\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing}$ *and* $\Delta H_{mixing} = 0$, it follows that:

$$\Delta \overline{G}_{ideal\ mixing} = RT \sum_i X_i \ln X_i \quad 3.30$$

We stated above that the total expression for an extensive property of a solution is the sum of the partial molar properties of the pure phases (times the mole fractions) plus the mixing term. The partial

molar Gibbs Free Energy is the chemical potential, so the full expression for the Gibbs Free Energy of an ideal solution is:

$$\overline{G}_{ideal} = \sum_i X_i \mu_i^o + RT \sum_i X_i \ln X_1 \qquad 3.31$$

Rearranging terms, we can re-express equation 3.31 as:

$$\overline{G}_{ideal} = \sum_i X_i (\mu_i^o + RT \ln X_1) \qquad 3.32$$

The term in parentheses is simply the chemical potential of component *i*, $\mu_i$, as expressed in equation 3.26. Substituting equation 3.26 into 3.32, we have

$$\overline{G}_{ideal} = \sum_i X_i \mu_i \qquad 3.33$$

Note that for an ideal solution, $\mu_i$ is always less than or equal to $\mu_i^o$ because the term $RT\ln X_i$ is always negative (because the log of a fraction is always negative).

Let's consider ideal mixing in the simplest case, namely binary mixing. For a two component (binary) system, $X_1 = (1 - X_2)$, so we can write equation 3.30 for the binary case as:

$$\Delta\overline{G}_{ideal\ mixing} = RT\left[(1-X_2)\ln(1-X_2) + X_2 \ln X_2\right] \qquad 3.34$$

Since $X_2$ is less than *1*, ΔG is negative and becomes increasingly negative with temperature, as illustrated in Figure 3.6. The curve is symmetrical with respect to *X*; i.e., the minimum occurs at $X_2 = 0.5$.

Now let's see how we can recover information on $\mu_i$ from plots such as Figure 3.6, which we will call G-bar—X plots. Substituting $X_1 = (1 - X_2)$ into equation 3.33, it becomes:

$$\overline{G}_{ideal\ solution} = \mu_1(1-X_2) + \mu_2 X_2 = \mu_1 + (\mu_2 - \mu_2)X_2 \qquad 3.35$$

This is the equation of a straight line on such a plot with slope of $(\mu_2 - \mu_1)$ and intercept $\mu_1$. This line is illustrated in Figure 3.7. The curved line is described by equation 3.31. The dashed line is given by equation 3.35. Both equation 3.31 and 3.35 give the same value of $\overline{G}$ for a given value of $X_2$, such as $X'_2$. Thus the straight line and the curved one in Figure 3.7 much touch at $X'_2$. In fact, the straight line is the tangent to the curved one at $X'_2$. The intercept of the tangent at $X_2 = 0$ is $\mu_1$ and the intercept at $X_2 = 1$ is $\mu_2$. The point is, on a plot of molar free energy vs. mole fraction (a G-X diagram), *we can determine the chemical potential of component i in a two component system by extrapolating a tangent of the free energy curve to $X_i = 1$.* We see that in Figure 3.7, as $X_1$ approaches 1 ($X_2$ approaches 0), the intercept of the tangent approaches $\mu_1^o$, i.e., $\mu_1$ approaches $\mu_1^o$. Looking at equation 3.26, this is exactly what we expect. Figure 3.7 illustrates the case of an ideal solution, but the intercept method applies to non-ideal solutions as well, as we shall see.

Finally, the solid line connecting the $\mu^o$'s is the Gibbs Free Energy of a mechanical mixture of components 1 and 2, which we may express as:

$$\Delta\overline{G}_{mixture} = \sum_i X_i \mu_i^o \qquad 3.36$$

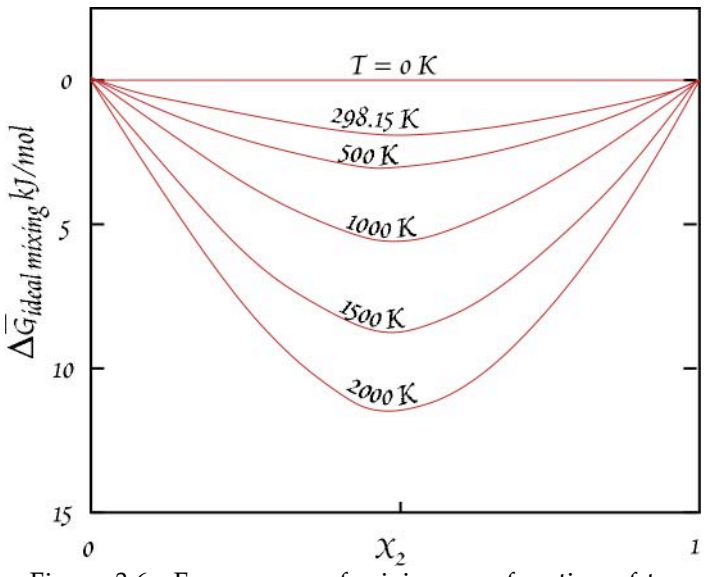



Figure 3.6. Free energy of mixing as a function of temperature in the ideal case.

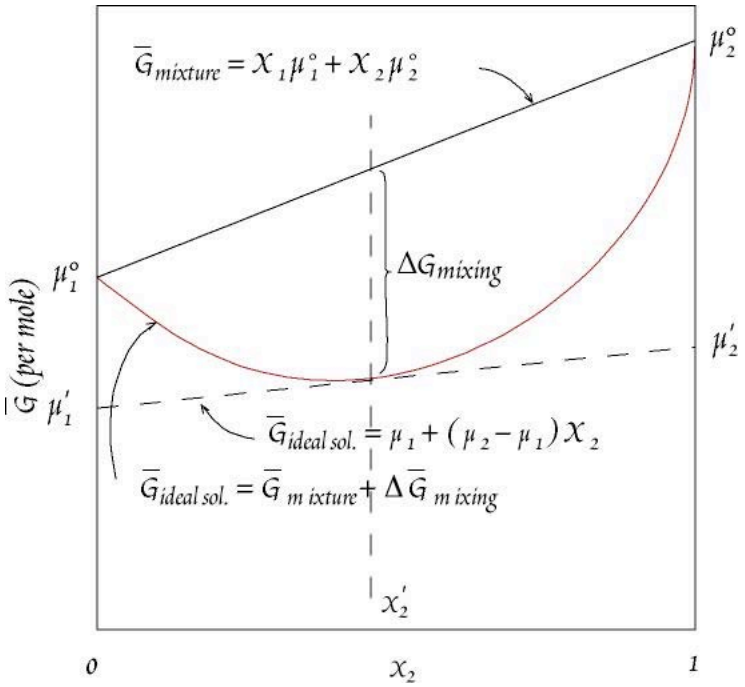



Figure 3.7. Molar free energy in an ideal mixture and graphical illustration of equation 3.31. After Nordstrom & Munoz, 1986.

You should satisfy yourself that the $\Delta G_{mixing}$ is the difference between this line and the free energy curve:

$$\Delta\bar{G}_{ideal\ mix.} = \bar{G}_{ideal\ sol.} - \bar{G}_{mixture}$$

## 3.6 Real solutions

We now turn our attention to real solutions, which are somewhat more complex than ideal ones, as you might imagine. We will need to introduce a few new tools to help us deal with these complexities.

### 3.6.1 Chemical Potential in Real Solutions

Let's consider the behavior of a real solution in view of the two solution models we have already introduced: Raoult's Law and Henry's Law. Figure 3.8 illustrates the variation of chemical potential as a function of composition in a hypothetical real solution. We can identify 3 regions where the behavior of the chemical potential is distinct:

1.) The first is where the mole fraction of component $X_i$ is close to 1 and Raoult's Law holds. In this case, the amount of solute dissolved in *i* is trivially small, so molecular interactions involving solute molecules do not significantly affect the thermodynamic properties of the solution, and the behavior of $\mu_i$ is close to that in an ideal solution:

$$\mu_{i,ideal} = \mu_i^o + RT\ln X_i \qquad (3.26)$$

2.) At the opposite end is the case where $X_i$ is very small. Here interactions between two component i molecules are extremely rare, and the behavior of $\mu_i$ is essentially controlled by interactions between i and those of the solvent. While the behavior of $\mu_i$ is not ideal, it is nonetheless a linear function of $\ln X_i$. This is the region where Henry's Law holds. The compositional dependence of the chemical potential in this region can be expressed as:

$$\mu_i = \mu_i^o + RT\ln h_i X_i \qquad 3.38$$

where *h* is the Henry's Law constant defined in equation 3.10. This equation can be rewritten as:

$$\mu_i = \mu_i^o + RT\ln X_i + RT\ln h_i \qquad 3.39$$

By definition, *h* is independent of composition at constant T and P and can be regarded as adding a fixed amount to the standard state chemical potential (a fixed amount to the intercept in Fig. 3.8). By independent of composition, we mean it is independent of $X_i$, the mole fraction of the component of interest. *h* will, of course depend on the nature of the solution. For example, if Na is our component of interest, $h_{Na}$ will not be the same for an electrolyte solution as for a silicate melt. We can define a new term, $\mu^*$, as:

$$\mu_i^* \equiv \mu_i^o + RT\ln h_i \qquad 3.40$$

Substituting 3.40 into 3.39 we obtain: $\mu_i = \mu_i^* + RT\ln X_i$ 3.41

When plotted against ln $X_i$, the chemical potential of *i* in the range of very dilute solutions is given by a straight line with slope RT and intercept $\mu^*$ (the intercept is at $X_i = 1$ and hence ln $X_i = 0$ and $\mu_i = \mu^*$). Thus $\mu^*$ can be obtained by extrapolating the Henry's Law slope to X = 1. *We can think of $\mu^*$ as the chemical potential in the hypothetical standard state of Henry's Law behavior at X = 1.*

3.) The third region of the plot is that region of real solution behavior between the regions where Henry's Law and Raoult's Law apply. In this region, $\mu$ is not a linear function of ln X. We will introduce a new parameter, *activity*, to deal with this region.

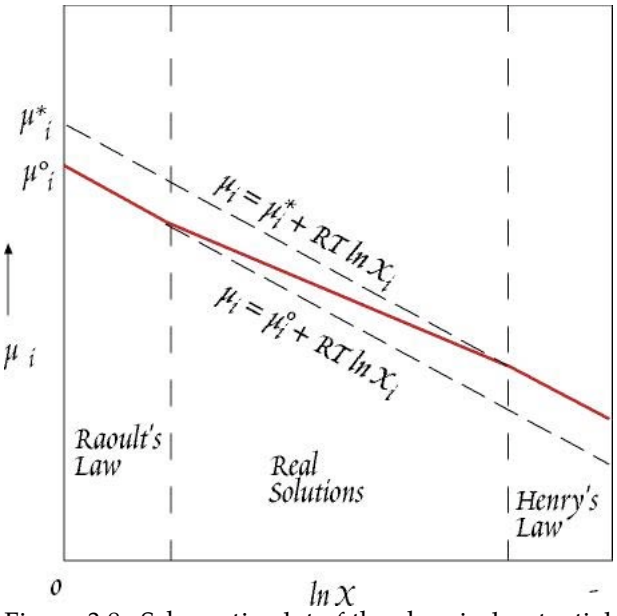



Figure 3.8. Schematic plot of the chemical potential of component *i* in solution as a function of ln $X_i$. Here $\mu^\circ$ is the chemical potential of pure i at the pressure and temperature of the diagram. After Nordstrom and Munoz (1986).

### 3.6.2 Fugacities

The tools we have introduced to deal with ideal solutions and infinitely dilute ones are based on observations of the gaseous state: Raoult's Law and Henry's Law. We will continue to make reference to gases in dealing with real solutions that follow neither law. While this approach has a largely historical basis, it is nevertheless a consistent one. So following this pattern, we will first introduce the concept of fugacity, and derive from it a more general parameter, activity.

In the range of intermediate concentrations, the partial pressure of the vapor of component *i* above a solution is generally not linearly related to the mole fraction of component *i* in solution. Thus chemical potential of *i* cannot be determined from equations such as 3.26, which we derived on the assumption that the partial pressure was proportional to the mole fraction. To deal with this situation, chemists invented a fictitious partial pressure, *fugacity*. Fugacity may be thought of as the 'escaping tendency' of a real gas from a solution. It was defined to have the same relationship to chemical potential as the partial pressure of an ideal gas:

$$\mu_i = \mu_i^o + RT \ln \frac{f_i}{f_i^o} \qquad 3.42$$

where $f^\circ$ is the standard-state fugacity, which is analogous to standard-state partial pressure. We are free to choose the standard state, but the standard state for $f^\circ$ and $\mu^\circ$ must be the same. $f^\circ$ is analogous to the standard state partial pressure, $P^\circ$, of an ideal gas. If we chose our standard state to be the pure substance, then $f^\circ$ is identical to $P^\circ$, but we may wish to choose some other standard state where this will not be the case. Since the behavior of real gases approaches ideal at low pressures, the fugacity will approach the partial pressure under these circumstances. Thus the second part of the definition of fugacity is:

$$\lim_{P \to 0} \frac{f_i}{P_i} = 1 \qquad 3.43$$

For an ideal gas, fugacity is identical to partial pressure. Since, as we stated above, fugacity bears the same relationship to chemical potential (and other state functions) of a non-ideal substance as pressure of a non-ideal gas, we substitute fugacity for pressure in thermodynamic equations.

The relationship between pressure and fugacity can be expressed as:

$$f = \phi P \qquad 3.44$$

where $\phi$ is the *fugacity coefficient*, which will be a function of temperature and pressure differ for each real gas. The fugacity coefficient expresses the difference in the pressure between a real gas and an ideal gas under comparable conditions. Kerrick and Jacobs (1981) fitted the Redlich-Kwong equation (equation 2.15) to observations on the volume, pressure and volume of $H_2O$ and $CO_2$ to obtain values for the coefficients *a* and *b* in equation 2.15. From these, they obtained fugacity coefficients for these gases at a series of temperatures and pressures. These are given in Table 3.1.

### 3.6.3 Activities and Activity Coefficients

*Fugacities* are thermodynamic functions that are directly related to chemical potential and can be calculated from measured P-T-V properties of a gas, though we will not discuss how. However, they have meaning for solids and liquids as well as gases since solids and liquids have finite vapor pressures. Whenever a substance exerts a measurable vapor pressure, a fugacity can be calculated. Fugacities are relevant to the equilibria between species and phase components, because if the vapor phases of the components of some solid or liquid solutions are in equilibrium with each other, and with their respective solid or liquid phases, then the species or phases components in the solid or liquid must be in equilibrium. One important feature of fugacities is that we can use them to define another thermodynamic parameter, the *activity*, *a*:

$$\boxed{a_i \equiv \frac{f_i}{f_i^o}} \qquad 3.45$$

$f°$ is the standard state fugacity. Its value depends on the standard state you choose. You are free to choose a standard state convenient for whatever problem you are addressing.

If we substitute equation 3.45 into equation 3.42, we obtain the important relationship:

$$\boxed{\mu_i = \mu_i^o + RT \ln a_i} \qquad 3.46$$

The 'catch' on selecting a standard state for $f°$, and hence for determining $a_i$ in equation 3.46, is that this state must be the same as the standard state for $\mu°$. Thus we need to bear in mind that standard states are implicit in the definition of activities and that those standard states are tied to the standard-state chemical potential. Until the standard state is specified, activities have no meaning.

Comparing equation 3.46 with 3.26 leads to:

$$a_{i,ideal} = X_i \qquad 3.47$$

*Thus in ideal solutions, the activity is equal to the mole fraction.*

Chemical potentials can be thought of as driving forces that determine the distribution of components between phases of variable composition in a system. *Activities can be thought of as the effective concentration or the availability of components for reaction.* In real solutions, it would be convenient to relate all non-ideal thermodynamic parameters to the composition of the solution, because composition is generally readily and accurately measured. To relate activities to mole fractions, we define a new parameter, the *rational activity coefficient*, $\lambda$. The relationship is:

$$a_i = X_i \lambda_i \qquad 3.48$$

**Table 3.1. $H_2O$ and $CO_2$ Fugacity Coefficients**

| $H_2O$ | T °C | | | |
|---|---|---|---|---|
| P, MPa | 400 | 600 | 800 | 1000 |
| 50 | 0.4 | 0.78 | 0.91 | |
| 200 | 0.2 | 0.52 | 0.79 | 0.94 |
| 400 | 0.21 | 0.54 | 0.84 | 1.03 |
| 600 | 0.28 | 0.67 | 1.01 | 1.22 |
| 800 | 0.4 | 0.89 | 1.27 | 1.49 |

| $CO_2$ | T °C | | | |
|---|---|---|---|---|
| P, MPa | 377 | 577 | 777 | 977 |
| 50 | 1.02 | 1.1 | 1.12 | 1.12 |
| 200 | 1.79 | 1.86 | 1.82 | 1.75 |
| 400 | 4.91 | 4.18 | 3.63 | 3.22 |
| 600 | 13.85 | 9.48 | 7.2 | 5.83 |
| 800 | 38.73 | 21.33 | 14.15 | 10.44 |

From Kerrick and Jacobs (1981).

### EXAMPLE 3.2. USING FUGACITY TO CALCULATE GIBBS FREE ENERGY

The minerals brucite ($Mg(OH)_2$) and periclase (MgO) are related by the reaction:

$$Mg(OH)_2 \rightleftarrows MgO + H_2O$$

Which side of this reaction represent the stable phase assemblage at 600° C and 200 MPa?

*Answer:* We learned how to solve this sort of problem in Chapter 2: the side with the lowest Gibbs Free Energy will be the stable assemblage. Hence, we need only to calculate $\Delta G_r$ at 600° C and 200 MPa. To do so, we use equation 2.129:

$$\Delta G_{T'P'} = \Delta G^o - \int_{T_{ref}}^{T'} \Delta S_r dT + \int_{T_{ref}}^{T'} \Delta V_r dP \qquad (2.129)$$

Our earlier examples dealt with solids, which are incompressible to a good approximation, and we could simply treat $\Delta V_r$ as being independent of pressure. In that case, the solution to the first integral on the left was simply $\Delta V_r(P' - P_{ref})$. The reaction in this case, like most metamorphic reactions, involves $H_2O$, which is certainly not incompressible: the volume of $H_2O$, as steam or a supercritical fluid, is very much a function of pressure. Let's isolate the difficulty by dividing $\Delta V_r$ into two parts: the volume change of reaction due to the solids, in this case the difference between molar volumes of periclase and brucite, and the volume change due to $H_2O$. We will denote the former as $\Delta V^S$ and assume that it is independent of pressure. The second integral in 2.131 then becomes:

$$\int_{P_{ref}}^{P'} \Delta V_r dP = \Delta V^s (P' - P_{ref}) + \int_{P_{ref}}^{P'} V_{H_2O} dP \qquad 3.49$$

How do we solve the pressure integral above? One approach is to assume that $H_2O$ is an ideal gas.

For an ideal gas: $$V = \frac{RT}{P}$$

so that the pressure integral becomes: $$\int_{P_{ref}}^{P'} \frac{RT}{P} dP = RT \ln \frac{P'}{P_{ref}}$$

Steam is a very non-ideal gas, so this approach would not yield a very accurate answer. The concept of fugacity provides us with an alternative solution. For a non-ideal substance, fugacity bears the same relationship to volume as the pressure of an ideal gas. Hence we may substitute fugacity for pressure so that the pressure integral in equation 2.129 becomes:

$$\int_{f_{ref}}^{f'} \frac{RT}{f} df = RT \ln \frac{f'}{f_{ref}}$$

where we take the reference fugacity to be 0.1 MPa. Equation 3.47 thus becomes:

$$\int_{P_{ref}}^{P'} \Delta V_r dP = \Delta V^s (P' - P_{ref}) + \int_{f_{ref}}^{f'} V_{H_2O} df = \Delta V^s (P' - P_{ref}) + RT \ln \frac{f'}{f^{ref}} \qquad 3.50$$

We can then compute fugacity using equation 3.44 and the fugacity coefficients in Table 3.1.

Using the data in Table 2.2 and solving the temperature integral in 2.129 in the usual way (equation 2.131), we calculate the $\Delta G_{T,P}$ is 3.29 kJ. Since it is positive, the left side of the reaction, i.e., brucite, we predict that brucite is stable.

The $\Delta S$ of this reaction is positive, however, implying that at some temperature, periclase plus water will eventually replace brucite. To calculate the actual temperature of the phase boundary requires a trial and error approach: for a given pressure, we must first guess a temperature, then look up a value of $\phi$ in Table 2.1 (interpolating as necessary), and calculate $\Delta G_r$. Depending on our answer, we make a revised guess of T and repeat the process until $\Delta G$ is 0. Using a spreadsheet, however, this goes fairly quickly. Using this method, we calculate that brucite breaks down at 660° C at 200 MPa, in excellent agreement with experimental observations.

The rational activity coefficient differs slightly in definition from the *practical activity coefficient*, γ, used in aqueous solutions. λ is defined in terms of mole fraction, whereas γ is defined in terms of moles of solute per moles of solvent. Consider for example the activity of Na in an aqueous sodium chloride solution. For $\lambda_{Na}$, X is computed as:

$$X_{Na} = \frac{n_{Na}}{n_{Na} + n_{Cl} + n_{H_2O}}$$

whereas for $\gamma_{Na}$, $X_{Na}$ is: $$\frac{n_{Na}}{n_{H_2O}}$$

where *n* indicates moles of substance. In very dilute solution, the difference is trivial. γ is also used for other concentration units that we will introduce in section 3.7.

### 3.6.4 Excess Functions

The ideal solution model provides a useful reference for solution behavior. Comparing real solutions with ideal ones leads to the concept of *excess functions*, for example:

$$G_{excess} \equiv G_{real} - G_{ideal} \qquad 3.51$$

which can be resolved into contributions of excess enthalpy and entropy:

$$G_{excess} = H_{excess} - TS_{excess} \qquad 3.52$$

The excess enthalpy is a measure of the heat released during mixing the pure end-members to form the solution, and the excess entropy is a measure of all the energetic effects resulting from a nonrandom distribution of species in solution. We can express excess enthalpy change in the same way as excess free energy, i.e.:

$$H_{excess} \equiv H_{real} - H_{ideal} \qquad 3.53$$

But since $\Delta H_{ideal\ mixing} = 0$, $\Delta H_{excess} = \Delta H_{real}$; in other words, the enthalpy change upon mixing is the excess enthalpy change. Similar expressions may, of course, be written for volume and entropy (bearing in mind that unlike volume and enthalpy, $\Delta S_{ideal}$ is not zero).

Combining equation 3.46 with equation 3.48 leads to the following:

$$\mu_i = \mu_i^o + RT \ln X_i \lambda_i \qquad 3.54$$

We can rewrite this as: $$\mu_i = \mu_i^o + RT \ln X_i + RT \ln \lambda_i \qquad 3.55$$

Equation 3.55 shows how activity coefficients relate to Henry's and Raoult's Laws. Comparing equation 3.55 with equation 3.39, we see that in the region where Henry's Law holds, that is dilute solutions, the activity coefficient is equal to Henry's law constant. In the region where Raoult's Law holds, the activity coefficient is 1 and equation 3.55 reduces to equation 3.26 since RT $\ln \lambda_i = 0$.

Since we know that $$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j,j\neq i}} = \mu_i = \mu_i^o + RT \ln X_i \lambda_i$$

comparing equations 3.51 and 3.55, we find that:

$$\left(\frac{\partial G_{excess}}{\partial n_i}\right)_{T,P,n_{j,j\neq i}} = RT \ln \lambda_i$$

which is the same as: $$\bar{G}_{excess,i} = RT \ln \lambda_i \qquad 3.56$$

So that the molar excess free energy associated with component *i* is simply RT times the log of the activity coefficient. The total molar excess free energy of the solution is then:

$$\bar{G}_{excess} = RT \sum_i X_i \ln \lambda_i \qquad 3.57$$

We will see the usefulness of the concept of excess free energy shortly when we consider activities in electrolyte solutions. It will also prove important in our treatment of non-ideal solid solutions and exsolution phenomena in the next chapter.

## DEPRESSION OF THE MELTING POINT

In northern climates such as Ithaca, NY salting road and sidewalks to melt snow and ice is a common practice in winter. We have now acquired the thermodynamics tools to show why salt melts ice and that this effect does not depend on any special properties of salt or water. Depression of the melting point by addition of a second component to a pure substance is a general phenomenon. Suppose that we have an aqueous solution containing sodium chloride coexisting with pure ice. If the two phases are at equilibrium, then the chemical potential of water in ice must equal that of water in the solution, i.e.:

$$\mu_{H_2O}^{ice} = \mu_{H_2O}^{aq} \qquad 3.58$$

(we are using subscripts to denote the component, and superscripts to denote the phase; *aq* denotes the liquid aqueous solution). We define our standard state as that of the pure substance. According to equ. 3.48, the chemical potential of water in the solution can be expressed as:

$$\mu_{H_2O}^{aq} = \mu_{H_2O}^{o} + RT \ln a_{H_2O}^{aq} \qquad 3.59$$

$\mu_{H_2O}^{o}$ denotes the chemical potential of pure liquid water. Substituting 3.59 into 3.58 and rearranging, we have:

$$\mu_{H_2O}^{ice} - \mu_{H_2O}^{o,aq} = RT \ln a_{H_2O}^{aq} \qquad 3.60$$

Ice will incorporate very little salt; if we assume it is a pure phase, we may write 3.60 as:

$$\mu_{H_2O}^{o,ice} - \mu_{H_2O}^{o,aq} = RT \ln a_{H_2O}^{aq} \qquad 3.60a$$

or

$$\mu_{H_2O}^{o,aq} - \mu_{H_2O}^{o,ice} = -RT \ln a_{H_2O}^{aq} \qquad 3.61$$

(The order is important: equation 3.60a describes the freezing process, 3.61 the melting process. These processes will have equal and opposite entropies, enthalpies, and free energies). The left hand side of 3.61 is the Gibbs Free Energy of melting for pure water, which we denote as $\Delta G_m^o$ ($\Delta G_m^o$ is 0 at the melting temperature of pure water, which we denote $T_m^o$, but non-zero at any other temperature). We may rewrite 3.61 as:

$$\Delta G_m^o = -RT \ln a_{H_2O}^{aq} \qquad 3.62$$

If we assume that $\Delta H$ and $\Delta S$ are independent of temperature (which is not unreasonable over a limited temperature range) and we assume pressure is constant as well, the left hand side of the equation may also be written as:

$$\Delta G_m^o = \Delta H_m^o - T\Delta S_m^o \qquad 3.63$$

Substituting 3.63 into 3.62:

$$\Delta H_m^o - T\Delta S_m^o = -RT \ln a_{H_2O}^{aq} \qquad 3.64$$

At the melting temperature of pure water, $\Delta G_m^o$ is zero, so that:

$$\Delta H_m^o = T_m^o \Delta S_m^o$$

Substituting this into 3.64 and rearranging:

$$\Delta S_m^o \left(T_m^o - T\right) = -RT \ln a_{H_2O}^{aq} \qquad 3.65$$

Further rearrangement yields:

$$\frac{T_m^o}{T} - 1 = \frac{-R}{\Delta S_m^o} \ln a_{H_2O}^{aq}$$

For a reasonably dilute solution, the activity of water will approximately equal its mole fraction, so that:

$$\frac{T_m^o}{T} - 1 = \frac{-R}{\Delta S_m^o} \ln X_{H_2O}^{aq} \qquad 3.66$$

The entropy of melting is always positive and since X is always less than 1, the left hand side of 3.66 must always be positive. Thus the ratio $T_m^o/T$ must always be greater than 1. So the temperature at which an aqueous solution will freeze will always be less than the melting point of pure water. Salting of roads is not a question of geochemical interest, but there are many examples of depression of the freezing point of geological interest. For example, the freezing point of the ocean is about –2° C. And this phenomenon is important in igneous petrology, as we shall see in the next chapter. A related phenomenon of geological interest is elevation of the boiling point of a liquid: for example hydrothermal solutions boil at temperatures significantly above that of pure water. Can you demonstrate that elevation of the boiling point of an ideal solution depends only on the mole fraction of the solute?

## 3.7 Electrolyte Solutions

Electrolyte solutions are solutions in which the solute dissociates to form ions, which facilitate electric conduction. Seawater is an obvious example of a natural electrolyte solution, but all natural waters are also electrolytes, though generally more dilute ones. These solutions, which Lavoisier* called the "rinsings of the Earth" are of enormous importance in many geologic processes.

### 3.7.1 The Nature of Water and Water-Electrolyte Interaction

There is perhaps no compound more familiar to us than $H_2O$. Common place though it might be, $H_2O$ is the most remarkable compound in nature. Its unusual properties include: the highest heat capacity of all solids and liquids except ammonia, the highest latent heat of vaporization of all substances, the highest surface tension of all liquids, its maximum density is at 4° C, with density decreasing below that temperature (negative coefficient of thermal expansion), the solid form is less dense than the liquid (negative Clapeyron slope), and finally, it is the best solvent known, dissolving more substances and in greater quantity than any other liquid. We will digress here briefly to consider the structure and properties of $H_2O$ and the nature of water-electrolyte interactions from a microscopic perspective.

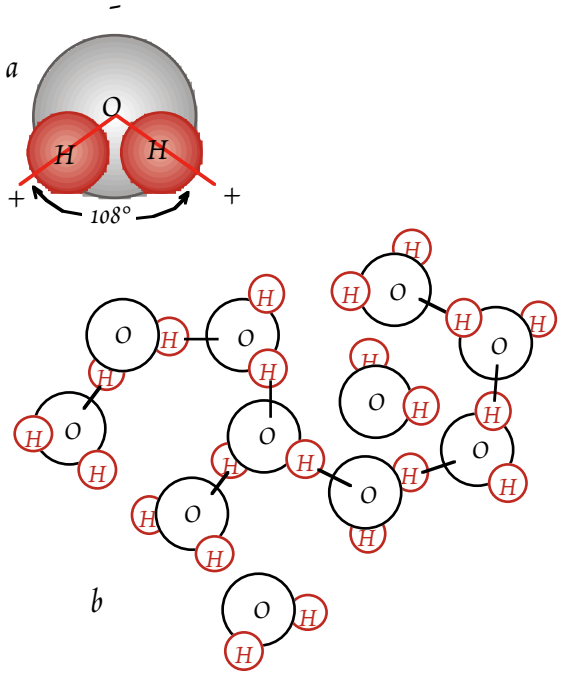



Figure 3.9. (a.) Structure of the water molecule. Bond angle in the liquid phase is 108°, 105° in the gas. The hydrogens retain a partial positive charge and the oxygen retains a partial positive charge. (b.) Partial structure present in liquid water. Lines connecting adjacent molecules illustrate hydrogen bonds.

Many of the unusual properties of water arise from its non-linear polar structure, which is illustrated in Figure 3.9a. The polar nature of water gives rise to van der Waals forces and the hydrogen bond discussed in Chapter 1. The hydrogen bond, which forms between hydrogens and the oxygens of adjacent molecules, imposes a dynamic partial structure on liquid water (Fig. 3.9b). These bonds continually break and new ones reform, and there is always some fraction of unassociated molecules. On average, each water molecule is coordinated by 4 other water molecules. When water boils, all hydrogen bonds are broken. The energy involved in breaking these bonds accounts for the high heat of vaporization.

The dissolving power of water is due to its *dielectric* nature. A dielectric substance is one that reduces the forces acting between electric charges. When placed between two electrically charged plates (a capacitor), water molecules will align themselves in the direction of the electric field. As a result, the molecules oppose the charge on the plates and effectively reduce the transmission of the electric field. The *permittivity*, ε, of a substance is the measure of this effect. The *relative permittivity*, or *dielectric constant*, $\varepsilon_r$, of a substance is defined as the ratio of the capacitance observed when the substance is placed between the plates of a capacitor to the capacitance of the same capacitor when a vacuum is present between the plates:

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_o} \qquad 3.67$$

*Antoine Lavoisier (1743-1794) laid the foundations of modern chemistry in his book, *Traité de Elémentaire de Chemie*, published in 1789. He died at the guillotine during the French Revolution.

where $\varepsilon_0$ is the permittivity of a vacuum ($8.85 \times 10^{-12}$ $C^2/J\ m$). The relative permittivity of water is 78.54 at 25°C and 1 atm. For comparison, the relative permittivity of methane, a typical non-polar molecule, is 1.7.

Water molecules surrounding a dissolved ion will tend to align themselves to oppose the charge of the ion. This insulates the ion from the electric field of other ions. This property of water accounts in large measure for its dissolving power. For example, we could easily calculate that the energy required dissociate NaCl (i.e., the energy required to move $Na^+$ and $Cl^-$ ions from their normal interatomic distance in a lattice, 2.36Å to infinite separation) is about 585 kJ/mol. Because water has a dielectric constant of about 80, this energy is reduced by a factor of 80, so only 7.45 kJ are required for dissociation.

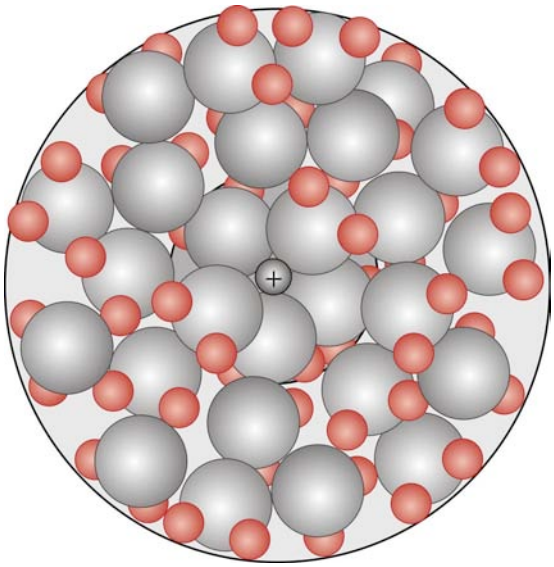


Figure 3.10. Solvation of a cation in aqueous solution. In the first solvation shell, water molecules are bound to the cation and oriented so that the partial negative charge on the oxygen faces the cation. In the second solvation shell molecules are only loosely bound and partially oriented.

The charged nature of ions and the polar nature of water result in the *solvation* of dissolved ions. Immediately adjacent to the ion, water molecules align themselves to oppose the charge on the ion, e.g., the oxygen of the water molecule will be closest to a cation (Figure 3.10). These water molecules are called the *first solvation shell* or layer and they are effectively bound to the ion, moving with it as it moves. Beyond the first solvation shell is a region of more loosely bound molecules that are only partially oriented, called the second solvation shell or layer. The boundary of this latter shell is diffuse: there is no sharp transition between oriented and unaffected water molecules. The energy liberated, called the *solvation energy*, in this process is considerable. For NaCl, for example, it is -765 kJ/mol (it is not possible to deduce the solvation energies of $Na^+$ and $Cl^-$ independently). The total number of water molecules bound to the ion is called the *solvation number*. Solvation effectively increases the electrostatic radius of cations by about 0.9 Å and of anions by about 0.1Å per unit of charge.

An additional effect of solvation is *electrostriction*. Water molecules in the first solvation sphere are packed more tightly than they would otherwise be. This is true, to a lesser extent, of molecules in the secondary shell. In addition, removal of molecules from the liquid water structure causes partial collapse of this structure. The net effect is that the volume occupied by water in an electrolyte solution is less than in pure water, which can lead to negative apparent molar volumes of solutes, as we shall see. The extent of electrostriction depends strongly on temperature and pressure.

A final interesting property of water is that some fraction of water molecules will *autodissociate*. In pure water at standard state conditions, one in every $10^{-7}$ molecules will dissociate to form $H^+$ and $OH^-$ ions. Although in most thermodynamic treatments the protons produced in this process are assumed to be free ions, most will combine with water molecules to form $H_3O^+$ ions. $OH^+$ is called the *hydroxl* ion; the $H_3O^+$ is called *hydronium*.

### 3.7.2 Some Definitions and Conventions

The first two terms we need to define are solvent and solute. *Solvent* is the substance present in greatest abundance in a solution; in the electrolyte solutions the we will discuss here, water is always the solvent. *Solute* refers to the remaining substances present in solution. Thus in seawater, water is the solvent and NaCl, $CaSO_4$, etc., are the solutes. We may also refer to the individual ions as solutes.

### 3.7.2.1 Concentration Units

Geochemists concerned with aqueous solutions commonly use a variety of concentration units other than mole fraction. The first is *molality* (abbreviated as lower-case *m*), which is *moles of solute per kg of solvent* ($H_2O$). Molality can be converted to moles solute per moles solvent unit by dividing by 55.51 mol/kg. A second unit is *molarity* (abbreviated as uppercase *M*), which is *moles of solute per liter* of solution. To convert molality to mole fraction, we would divide by the molecular weight of solvent and use the rational activity coefficient. Natural solutions are often sufficiently dilute that the difference between molality and molarity is trivial (seawater, a relatively concentrated natural solution, contains only 3.5 weight percent dissolved solids). Another common unit is weight fraction (i.e., grams per gram solution), which may take several forms, such as weight percentage, parts per thousand or parts per million (abbreviated %, ppt or ‰, ppm or mg/kg). To convert to mole fraction, one simply divides the weight of solute and $H_2O$ by the respective molecular weights.

### 3.7.2.2 pH

One of the most common parameters in aqueous geochemistry is pH. pH is defined as the negative logarithm of the hydrogen ion activity:

$$\boxed{pH \equiv -\log a_{H^+}} \qquad 3.68$$

### 3.7.2.3 Standard State and Other Conventions

The first problem we must face in determining activities in electrolyte solutions is specifying the standard state. With gases, the standard state is generally the pure substance (generally at 298 K and 1 atm), but this is generally not a reasonable choice for electrolytes. A NaCl solution will become saturated at about 0.1 $X_{NaCl}$, and crystalline NaCl has very different properties from NaCl in aqueous solution. ***By convention, a hypothetical standard state of unit activity at 1 molal concentration is chosen:***

$$a^\circ = m = 1 \qquad 3.69$$

Activity is generally given units of molality in this case (it is dimensionless as we defined it in equation 3.45), so that in this hypothetical standard state, activity equals molality. The standard state is hypothetical because, for most electrolytes, the activity will be less than 1 in a 1 m (molal) solution. Because the *standard state* generally is unattainable in reality, we must also define an attainable *reference state*, from which experimental measurements can be extrapolated. *By convention, the reference state is that of an infinitely dilute solution*, i.e., the Henry's Law state. For multicomponent solutions, we also specify that the concentrations of all other components be held constant. Hence the reference state is:

$$\lim_{m \to 0} \frac{a_i}{m_i} = 1 \ (m_j \ constant) \qquad 3.70$$

This convention is illustrated in Figure 3.11. In such solutions, the activity coefficient can be shown to depend on the charge of the ion, its concentration, and the concentration of other ions in the solution as well as temperature and other parameters of the solute. Comparing 3.70 with equations 3.46 and 3.48, we see that under these conditions, the activity coefficient is 1. By referring to infinite dilution, we are removing the effect of solute-solute interactions. The standard state properties of an electrolyte solution therefore only take account of solvent-solute interactions.

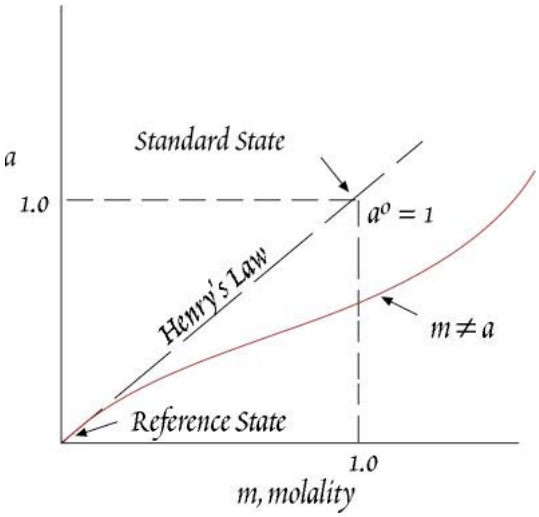



Figure 3.11. Relationship of activity and molality, reference state, and standard state for aqueous solutions. After Nordstrom and Munoz (1986).

Clearly, it is impossible to measure the properties of the solute, such as chemical potential or molar volume, at infinite dilution. In practice, this problem is overcome by measuring properties at some finite dilution and extrapolating the result to infinite dilution. Indeed, even at finite concentrations, it is not possible to measure directly many properties of electrolytes. Volume is a good example. One cannot measure the volume of the solute, but one can measure the volume change of the solution as a function of concentration of the solute. Then by assuming that the partial molar volume of water does not change, a partial molar volume of the solute can be calculated. This is called the *apparent molar volume*, $\bar{V}_A$. The apparent molar volume of NaCl as a function of molarity is shown in Figure 3.12. In essence, this convention assigns all deviations from non-ideality to the solute, and allow us to use the partial molar volume of pure water in the place of the true, but unknown, molar volume of water in the solution. Thus the volume of NaCl solution is given by:

$$V = n_w \bar{V}_w + n_{NaCl} \bar{V}^{aq}_{NaCl} \qquad 3.71$$

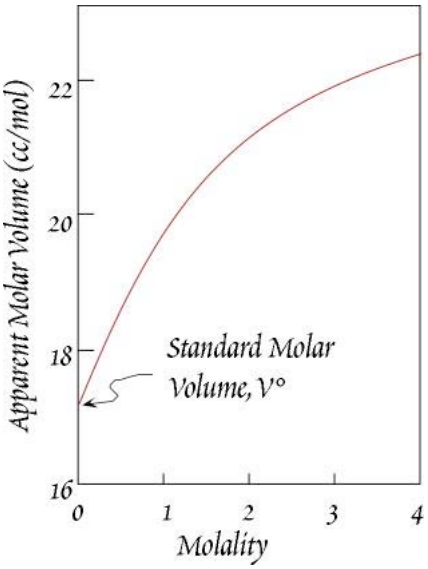



Figure 3.12. Apparent molar volume of NaCl in aqueous solution as a function of molality. The standard molar volume, V°, is the apparent molar volume at infinite dilution.

This convention leads to some interesting effects. For example, the apparent molar volume of magnesium sulfate increases with pressure, and many other salts, including NaCl (Fig. 3.13), exhibit the same behavior. Just as curiously, the apparent molar volume of sodium chloride in saturated aqueous solution becomes negative above ~200° C (Figure 3.13). Many other salts show the same effect. These examples emphasize the "apparent" nature of molar volume when defined in this way. Of course, the molar volume of NaCl does not actually become negative; rather this is result of the interaction between $Na^+$ and $Cl^-$ and $H_2O$ (electrostriction) and the convention of assigning all non-ideality to sodium chloride.

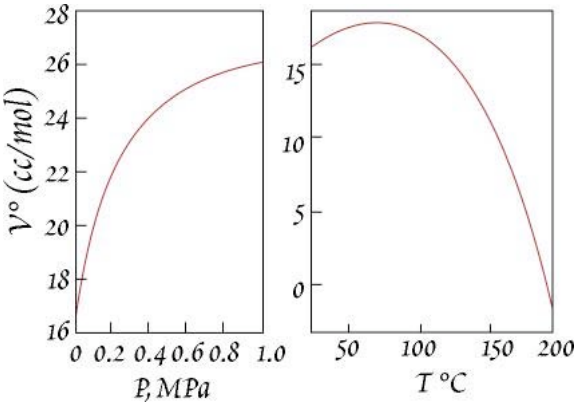



Figure 3.13. Standard molar volume of NaCl in aqueous solution as a function of temperature and pressure.

The concentration of a salt consisting of $\nu_A$ moles of cation A and $\nu_B$ moles of cation B is related to the concentration of its constituent ionic species as:

$$m_A = \nu_A m_{AB}$$

and $$m_B = \nu_B m_{AB} \qquad 3.72$$

By convention, the thermodynamic properties of ionic species A and B are related to those of the salt AB by:

$$\Psi_{AB} \equiv \nu_A \Psi_A + \nu_B \Psi_B \qquad 3.73$$

where $\Psi$ is some thermodynamic property. Thus the chemical potential of $MgCl_2$ is related to that of $Mg^{2+}$ and $Cl^-$ as:

$$\mu_{MgCl_2} = \mu_{Mg^+} + 2 \times \mu_{Cl^-}$$

The same holds for enthalpy of formation, entropy, molar volume, etc.

A final important convention is that *the partial molar properties and energies of formation for the proton are taken to be zero under all conditions.*

### 3.7.3 Activities in Electrolytes

The assumption we made for ideal solution behavior was that interactions between molecules (species might be a better term in the case of electrolyte solutions) of solute and molecules of solvent were not different from those interactions between solvent ions only. In light of the discussion of aqueous solutions earlier, we can see this is clearly not going to be the case for an electrolyte solution. We have seen significant deviations from ideality even where the components have no net charge (e.g., water-ethanol); we can expect greater deviations due to electrostatic interactions between charged species.

The nature of these interactions suggests that a purely macroscopic viewpoint, which takes no account of molecular and ionic interactions, may have severe limitations in predicting equilibria involving electrolyte solutions. Thus chemists and geochemists concerned with the behavior of electrolytes have had to incorporate a microscopic viewpoint into electrolyte theory. On the other hand, they did not want to abandon entirely the useful description of equilibria based on thermodynamics. We have already introduced concepts, the activity and the activity coefficient, which allow us to treat non-ideal behavior within a thermodynamic framework. *The additional task imposed by electrolyte solutions, and indeed all real solutions, therefore, is not to rebuild the framework, but simply to determine activities from readily measurable properties of the solution.* The dependence of all partial molar properties of a solute on concentration can be determined once the activity coefficient and its temperature and pressure dependence are known.

#### 3.7.3.1 The Debye-Hückel and Davies Equations

Both solvent-solute and solute-solute interactions in electrolytes give rise to excess free energies and non-ideal behavior. By developing a model to account for these two kinds of interactions, we can develop an equation that will predict the activity of ions in electrolyte solution.

In an electrolyte solution, each ion will exert an electrostatic force on every other ion. These forces will decrease with the increase square of distance between ions. The forces between ions will be reduced by the presence of water molecules, due to its dielectric nature. As total solute concentration increases, the mean distance between ions will decrease. Thus we can expect that activity will depend on the total ionic concentration in the solution. The extent of electrostatic interaction will also obviously depend on the charge of the ions involved: the force between $Ca^{2+}$ and $Mg^{2+}$ ions will be greater at the same distance than between $Na^{+}$ and $K^{+}$ ions.

In the Debye-Hückel Theory (Fig. 3.14), a given ion is considered to be surrounded by an atmosphere or cloud of oppositely charged ions (this atmosphere is distinct from, and unrelated to, the solvation shell). If it were not for the thermal motion of the ions, the structure would be analogous to that of a crystal lattice, though considerably looser. Thermal motion, however, tends to destroy this structure. The density of charge in this ion atmosphere increases with the *square root* of the ionic concentrations, but increases with the *square* of the charges on those ions. The dielectric effect of intervening water molecules will tend to reduce the interaction between ions. Debye–Hückel Theory also assumes that:

- all electrolytes are completely dissociated into ions,
- the ions are spherically symmetrical charges (hard spheres),
- the solvent is structureless; the sole property is its permittivity,
- the thermal energy of ions exceeds the electrostatic interaction energy.

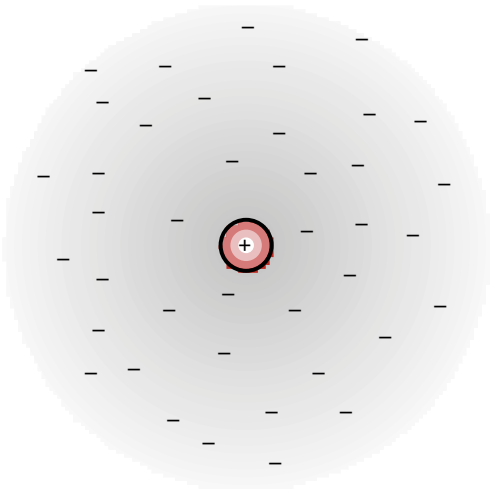


Figure 3.14. An ion surrounded by a cloud of oppositely charged ions, as assumed in Debye-Hückel Theory.

With these assumptions, Debye and Hückel (1923) used the Poisson–Boltzmann equation, which describes the electrostatic interaction energy between ion and a cloud of opposite charges, to derive the following relationship (see Morel and Hering, 1993 for the full derivation):

$$\log_{10}\gamma_i = \frac{-Az_i^2\sqrt{I}}{1+B\mathring{a}_i\sqrt{I}} \qquad 3.74$$

*I* is *ionic strength*, in units of molality or molarity, calculated as:

$$I = \frac{1}{2}\sum_j m_j z_j^2 \qquad 3.75$$

where m is the concentration and z the ionic charge. The parameter å is known as the *hydrated ionic radiu, or effective radius* (significantly larger than the radius of the same ion in a crystal). A and B constants known as solvent parameters and are functions of T and P. Equation 3.74 is known as the *Debye-Hückel Extended Law*; we will refer to it simply as the *Debye-Hückel Equation*. Table 3.2a summarizes the Debye-Hückel solvent parameters over a range of temperature and Table 3.2b gives values of å for a number of ions.

For very dilute solutions, the denominator of equation 3.74 approaches 1 (because I approaches 0), hence equation 3.74 becomes:

$$\log_{10}\gamma_i = -Az_i^2\sqrt{I} \qquad 3.76$$

This equation is known as the *Debye-Hückel Limiting Law* (so called because it applies in the limit of very dilute concentrations).

Davies (1938, 1962) introduced an empirical modification of the Debye-Hückel equation. Davies equation is:

$$\log_{10}\gamma_i = -Az_i^2\left[\frac{\sqrt{I}}{1+\sqrt{I}} - bI\right] \qquad 3.77$$

where A is the same as in the Debye-Hückel equation and *b* is an empirically determined parameter with a value of around 0.3. It is instructive to see how the activity coefficient of $Ca^{2+}$ would vary according to Debye-Hückel and Davies equations if we vary the ionic strength of the solution. This variation is shown in Figure 3.15. The Davies equation predicts that activity coefficients begin to increase above ionic strengths of about 0.5 m. For reasons discussed below and in greater detail in Chapter 4, activity coefficients do actually increase at higher ionic strengths. On the whole, the Davies equation is slightly more accurate for many solutions at ionic strengths in the range of 0.1 to 1 m. Be-

**Table 3.2a Debye-Hückel Solvent Parameters**

| T °C | A | B ($10^8$ cm) |
|---|---|---|
| 0 | 0.4911 | 0.3244 |
| 25 | 0.5092 | 0.3283 |
| 50 | 0.5336 | 0.3325 |
| 75 | 0.5639 | 0.3371 |
| 100 | 0.5998 | 0.3422 |
| 125 | 0.6416 | 0.3476 |
| 150 | 0.6898 | 0.3533 |
| 175 | 0.7454 | 0.3592 |
| 200 | 0.8099 | 0.3655 |
| 225 | 0.8860 | 0.3721 |
| 250 | 0.9785 | 0.3792 |
| 275 | 1.0960 | 0.3871 |
| 300 | 1.2555 | 0.3965 |

from Helgeson and Kirkham (1974).

**Table 3.2b Debye-Hückel Effective Radii**

| Ion | å ($10^{-8}$ cm) |
|---|---|
| $Rb^+$, $Cs^+$, $NH^+$, Ag | 2.5 |
| $K^+$, $Cl^-$, $Br^-$, $I^-$, $NO_3^-$ | 3 |
| $OH^-$, $F^-$, $HS^-$, $BrO_3^-$, $IO_4^-$, $MnO_4^-$ | 3.5 |
| $Na^+$,$HCO_3^-$,$H_2PO_4^-$,$HSO_3^-$,$SO_4^{2-}$,$HPO_3^{2-}$,$PO_3^{3-}$ | 4.0-4.5 |
| $Pb^{2+}$, $CO_3^{2-}$, $SO_3^{2-}$, | 4.5 |
| $Sr^{2+}$, $Ba^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $S^{2-}$ | 5 |
| $Li^+$, $Ca^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Sn^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Ni^{2+}$ | 6 |
| $Mg^{2+}$, $Be^{2+}$ | 8 |
| $H^+$, $Al^{3+}$, trivalent rare earths | 9 |
| $Th^{4+}$, $Zr^{4+}$, $Ce^{4+}$ | 11 |

from Garrels and Christ (1982).

cause of this, as well as its simplicity, the Davies equation is widely used.

### 3.7.3.2 Limitations to the Debye-Hückel Approach

None of the assumptions made by Debye and Hückel hold in the absolute. Furthermore, the Poisson-Boltzmann equation provides only an approximate description of ion interactions, and Debye and Hückel used an approximate solution of this equation. Thus we should not expect the Debye-Hückel equations to provide an exact prediction of activity coefficients under all conditions.

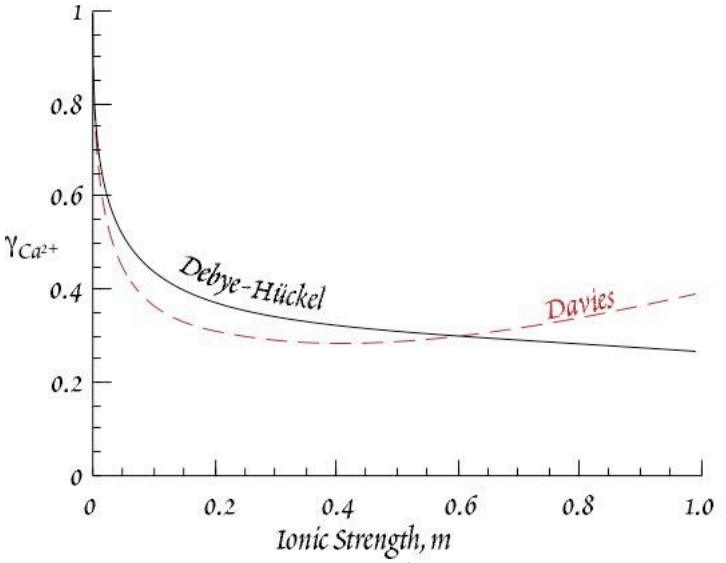



Figure 3.15. Variation of the $Ca^{2+}$ activity coefficient with ionic strength according to the Debye-Hückel (black solid line) and Davies equations (red dashed line).

Perhaps the greatest difficulty is the assumption of complete dissociation. When ions approach each other closely, the electrostatic interaction energy exceeds the thermal energy, which violates the assumption made in the approximate solution of the Poisson-Boltzmann equation. In this case, the ions are said to be associated. Furthermore, the charge on ions is not spherically symmetric and this asymmetry becomes increasingly important at short distances. Close approach is obviously more likely at high ionic strength, so not surprisingly the Debye-Hückel equation breaks down at high ionic strength.

We can distinguish two broad types of ion associations: ion pairs and complexes. These two classes actually form a continuum, but we will define a complex as an association of ions in solution that involves some degree of covalent bonding (i.e., electron sharing). Ion pairs, on the other hand, are held together purely by electrostatic forces. We will discuss formation of ion pairs and complexes in greater detail in subsequent chapters. Here we will attempt to convey only a very qualitative understanding of these effects.

An ion pair† can be considered to have formed when ions approach closer than some critical distance where the electrostatic energy, which tends to bind them, exceeds twice the thermal energy, which tends to move them apart. When this happens, the ions are electrostatically bound and their motions are linked. This critical distance depends on the charge of the ions involved and is therefore much greater for highly charged ions than for singly charged ones. As we will show in Chapter 4, ion pairs involving singly charged ions will never form, even at high ionic strengths. On the other hand, multiply charged ions will tend to form ion pairs even at very low ionic strengths.

Formation of ion pairs will cause further deviations from ideality. We can identify two effects. First, the effective concentration, or activity, of an ionic species than forms ionic associations will be reduced. Consider, for example, a pure solution of $CaSO_4$. If some fraction, $\alpha$, of $Ca^{2+}$ and $SO_4^{2-}$ ions forms ion pairs, then the effective concentration of $Ca^{2+}$ ions is:

$$[Ca^{2+}]_{eff} = [Ca_{2+}]_{tot} (1 - \alpha)$$

(here we follow the usual convention of using brackets to denote concentrations). The second effect is on ionic strength. By assuming complete dissociation, we similarly overestimate the effective concentration in this example by a factor of $(1 - \alpha)$.

† The term *ion pair* is a bit of a misnomer because such associations can involve more than two ions. In concentrated solutions, ion pairs may consist of a cation plus several anions.

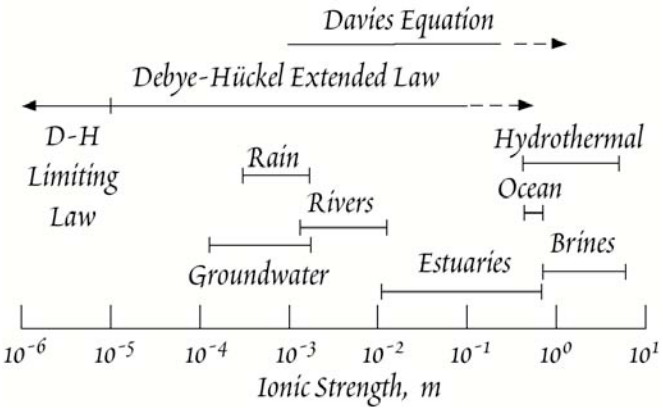



Figure 3.16. Ionic strength of natural electrolyte solutions and the applicability of the Debye-Hückel and Davies equations.

A second phenomenon that causes deviations from ideality not predicted by Debye-Hückel is solvation. As we noted, an ion in aqueous solution are surrounded by a sphere of water molecules that are bound to it. Since those water molecules bound to the ion are effectively unavailable for reaction, the activity of water is reduced by the fraction of water molecules bound in solvation shells. This fraction is trivial in dilution solutions, but is important at high ionic strength. The result of this effect is to increase the activity of ions.

Despite these problems, Debye-Hückel has proved to be remarkably successful in predicting activity coefficients in dilute solution. The extended Debye-Hückel Equation (Equation 3.74) is most useful at concentrations less than 0.1 M, which includes many natural waters and provides adequate approximation for activity coefficients up to ionic strengths of about 1 M, which would include most solutions of geological interest, including seawater. As we noted above, the Davies equation is slightly more accurate in the range of 0.1 to 1 M ionic strength. Above these concentrations, both the Davies and Debye-Hückel equations are increasingly inaccurate. There are thus a variety of geological solutions for which the Debye-Hückel and Davies equations cannot be used, including hydrothermal solutions, highly saline lakes, formation brines, and aerosol particles. Figure 3.16 summarizes the typical ionic strengths of natural solutions and the applicability of these equations. The Debye-Hückel Limiting Law is useful only for very dilution solutions, less than $10^{-5}$ mol/kg, which is more dilute than essentially all solutions of geological interest. We will consider several methods of estimating activities in higher ionic strength solutions in Chapter 4.

## 3.8 Ideal Solid Solutions and Their Activities

When we deal with solid solutions, we are again faced with the inadequacy of the purely macro-

| Ion | A g/kg | B mol/kg × $10^3$ | C $z^2$ | D $mz^2 \times 10^3$ |
|---|---|---|---|---|
| $Cl^-$ | 0.0078 | 0.2201 | 1 | 0.2201 |
| $SO_4^{2-}$ | 0.0112 | 0.1167 | 4 | 0.4667 |
| $HCO_3^-$ | 0.0583 | 0.9557 | 1 | 0.9557 |
| $Mg^{2+}$ | 0.0041 | 0.1687 | 4 | 0.6746 |
| $Ca^{2+}$ | 0.015 | 0.3742 | 4 | 1.4970 |
| $K^+$ | 0.0023 | 0.0588 | 1 | 0.0588 |
| $Na^+$ | 0.0041 | 0.1782 | 1 | 0.1782 |

### Example 3.3: Calculating Activities Using the Debye-Hückel Equation

Given the composition for the average river water in column A in the adjacent table, calculate the activity of the $Ca^{2+}$ ion at 25° C using the Debye-Hückel equation.

*Answer:* Our first step is to convert these concentrations to molality by dividing by the respective molecular weights. We obtain the molal concentrations in column B. We also need to compute $z^2$ (column C), and the product $z^2m$ (column D). Using equation 3.75, we calculate the ionic strength to be 0.00202 m. (note, one must use the ionic strength in molal or molar, and not millimolar, units in the Debye-Hückel Equation.

We substitute this value for I, then find å = 6, A = 0.5092, and B = 0.3283 in Table 3.1, and obtain a value for the activity coefficient of 0.8237, and an activity of 0.308 ×$10^{-3}$ m. If we did the calculation for other temperatures, we would see that for a dilute solution such as this, the activity coefficient is a only weak function of temperature, decreasing to 0.625 at 300° C.

scopic approach of classical thermodynamics. There is little disadvantage to this approach for gases, where the arrangement of molecules is chaotic. But the crystalline state differs from that of gases in that the arrangement of atoms in the crystal lattice is highly ordered, and the properties of the crystal depend strongly on the nature of the ordering. For this reason, we cannot afford to ignore the arrangement of atoms in solids, particularly with respect to solutions.

Solid solutions differ from those of gases and liquids in several respects. First, solution in the solid state inevitably involves substitution. While we can increase the concentration of HCl in water simply by adding HCl gas, we can only increase the concentration of Fe in biotite solid solution if we simultaneously remove Mg. Second, solid solutions involve substitution at crystallographically distinct sites. Thus in biotite a solid solution between phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$) and annite ($KFe_3AlSi_3O_{10}(OH)_2$) occurs as $Fe^{2+}$ replaces $Mg^{2+}$ in the octahedral site; the tetrahedral Si site and the anion (O) sites remain unaffected by this substitution. Third, substitution is often coupled. For example, the solid solution between anorthite ($CaAl_2Si_2O_8$) and albite ($NaAlSi_3O_8$) in plagioclase feldspar involves not only the substitution of $Na^+$ for $Ca^{2+}$, but also the substitution of $Al^{3+}$ for $Si^{4+}$. The anorthite-albite solution problem is clearly simplified if we choose anorthite and albite as our components rather than $Na^+$, $Ca^{2+}$, $Al^{3+}$ and $Si^{4+}$. Such components are known as *phase components*. Choosing pure phase end members as components is not always satisfactory either because substitution on more than one site is possible, leading to an unreasonably large number of components, or because the pure phase does not exist and hence its thermodynamic properties cannot be measured.

However we choose our components, we need a method of calculating activities that takes account of the ordered nature of the crystalline state. Here we will discuss two ideal solution models of crystalline solids. We tackle the problem of non-ideal solid solutions in Chapter 4.

### 3.8.1 Mixing on Site Model

Many crystalline solids can be successfully treated as ideal solutions. Where this is possible, the thermodynamic treatment and assessment of equilibrium are greatly simplified. A simple and often successful model that assumes ideality but takes account of the ordered nature of the crystalline state is the *mixing on site model*, which considers the substitution of species in any site individually. In this model, the activity of an individual species is calculated as:

$$a_{i,ideal} = (X_i)^{\nu} \qquad 3.78$$

where X is the mole fraction of the $i^{th}$ atom and $\nu$ is the number of sites per formula unit on which mixing takes place. For example, $\nu$=2 in the Fe-Mg exchange in olivine, $(Mg,Fe)_2SiO_4$. One trick to simplifying this equation is to pick the formula unit such that $\nu = 1$. For example, we would pick $(Mg,Fe)Si_{1/2}O_2$ as the formula unit for olivine. We must then consistently choose all other thermodynamic parameters to be 1/2 those of $(Mg,Fe)_2SiO_4$.

The entropy of mixing is given by:

$$\Delta S_{ideal\ mixing} = -R\sum_j \left( n_j \sum_i X_{i,j} \ln X_{i,j} \right) \qquad 3.79$$

where the subscript $j$ refers to sites and the subscript $i$ refers to components, and n is the number of sites per formula unit. The entropy of mixing is the same as the configurational entropy, residual entropy, or 'third law entropy', i.e., entropy when T = 0 K. For example, in clinopyroxene, there are two exchangeable sites, a sixfold-coordinated M1 site, (Mg, $Fe^{+2}$, $Fe^{+3}$, $Al^{+3}$), and an eightfold-coordinated M2 site ($Ca^{+2}$, $Na^+$). Here $j$ ranges from 1 to 2 (e.g., 1 = M1, 2 = M2), but n = 1 in both cases (because both sites accept only one atom). $i$ must range over all present ions in each site, so in this example, $i$ ranges from 1 to 4 (1 = Mg, 2 = $Fe^{2+}$, etc.) when $j$=1 and from 1 to 2 when $j$ = 2. Since we have assumed an ideal solution, $\Delta H = 0$ and $\Delta G_{ideal} = -T\Delta S$. In other words, all we need is temperature and equ. 3.79 to calculate the free energy of solution.

In the mixing-on-site model, the activity of a phase component in a solution, for example pyrope in garnet, is the product of the activity of the individual species in each site in the phase:

$$a_\phi = \prod_i X^{\nu_i} \qquad 3.80$$

where $a_f$ is the activity of phase component $\phi$, $i$ are the components of pure $\phi$, and $\nu_i$ is the stoichiometric proportion of $i$ in pure $\phi$. For example, to calculate the activity of aegirine ($NaFe^{3+}Si_2O_6$) in aegirine-augite ($[Na,Ca][Fe^{3+},Fe^{2+},Mg]Si_2O_6$), we would calculate the product: $X_{Na}X_{Fe^{3+}}$. Note that it would not be necessary to include the mole fractions of Si and O, since these are 1.

A slight complication arises when more than one ion occupies a structural site in the pure phase. For example, suppose we wish to calculate the activity of phlogopite ($KMg_3Si_3AlO_{10}(OH)_2$) in a biotite of composition $K_{0.8}Ca_{0.2}(Mg_{0.17}Fe_{0.83})_3Si_{2.8}Al_{1.2}O_{10}(OH)_2$. The tetrahedral site is occupied by Si and Al in the ratio of 3:1 in the pure phase end members. If we were to calculate the activity of phlogopite in pure phlogopite using equation 3.80, the activities in the tetrahedral site would contribute only $X_{Si}^4 X_{Al}^1 = (0.75)^3(0.25)^1 = 0.1055$ in the pure phase. So we would obtain an activity of 0.1055 instead of 1 for phlogopite in pure phlogopite. Since the activity of a phase component must be one when it is pure, we need to normalize the result. Thus we apply a correction by multiplying by the raw activity we obtain from 3.92 by $1/(0.1055) = 9.481$, and thus obtain an activity of phlogopite of 1.

### 3.8.2 Local Charge Balance Model

Yet another model for the calculation of activities in ideal solid solutions is the *local charge balance* model. A common example is the substitution of Ca for Na in the plagioclase solid solution ($NaAlSi_3O_8$—$CaAl_2Si_2O_8$). To maintain charge balance, the substitution of $Ca^{2+}$ for $Na^+$ in the octahedral site requires substitution of $Al^{3+}$ for $Si^{4+}$ in the tetrahedral site to maintain local charge balance. In this model, the activity of the end-member of phase component is equal to the mole fraction of the component (see Example 3.5).

#### Example 3.4. Calculating Activities Using the Mixing on Site Model

Sometimes it is desirable to calculate the activities of pure end member components in solid solutions. Garnet has the general formula $X_3Y_2Si_3O_{12}$. Calculate the activity of pyrope, $Mg_3Al_2Si_3O_{12}$, in a garnet solid solution of composition:

$$(Mg_{.382}Fe^{2+}_{2.316}Mn_{.167}Ca_{.156})(Al_{1.974}Fe^{3+}_{.044})Si_3O_{12}$$

*Answer:* The chemical potential of pyrope in garnet contains mixing contributions from both Mg in the cubic site and Al in the octahedral site:

$$\mu^{gt}_{py} = \mu^{o}_{py} + 3RT \ln X_{Mg} + 2RT \ln X_{Al} = RT \ln(X^3_{Mg} X^2_{Al})$$

The activity of pyrope is thus given by:

$$a^{gt}_{py} = X^{gt}_{py} = X^3_{Mg} X^2_{Al}$$

In the example composition above, the activity of Mg is:

$$a_{Mg} = X^3_{Mg} = \left(\frac{[Mg]}{[Mg]+[Fe^{2+}]+[Mn]+[Ca]}\right) = 0.126^3 = 0.002$$

and that of Al is: $$a_{Al} = X^2_{Al} = \left(\frac{[Al]}{[Al]+[Fe^{3+}]}\right) = 0.976^2 = 0.956$$

The activity of pyrope in the garnet composition above is 0.002 x 0.956 = 0.00191. There is, of course, no mixing contribution from the tetrahedral site because it is occupied only by Si in both the solution and the pure pyrope phase.

### EXAMPLE 3.5: ACTIVITIES USING THE LOCAL CHARGE BALANCE MODEL

**PLAGIOCLASE ANALYSIS**

| Oxide | Wt. percent |
|---|---|
| $SiO_2$ | 44.35 |
| $Al_2O_3$ | 34.85 |
| CaO | 18.63 |
| $Na_2O$ | 0.79 |
| $K_2O$ | 0.05 |

Given the adjacent analysis of a plagioclase crystal, what are the activities of albite and anorthite in the solution?

*Answer*: According to the *local charge balance model*, the activity of albite will be equal to the mole fraction of Na in the octahedral site. To calculate this, we first must convert the weight percent oxides to formula units of cation. The first step is to calculate the moles of cation from the oxide weight percents. First, we can convert weight percent oxide to weight percent cation using the formula:

$$\text{wt. \% cation} = \text{wt \% oxide} \times \frac{\text{atomic wt. cation} \times \text{formula units cation in oxide}}{\text{molecular wt. oxide}}$$

Next, we calculate the moles of cation: $\text{moles cation} = \frac{\text{wt \% cation}}{\text{atomic wt. cation}}$

Combining these two equations, the 'atomic wt. cation' terms cancel and we have:

$$\text{moles cation} = \text{wt \% oxide} \times \frac{\text{formula units cation in oxide}}{\text{molecular wt. oxide}}$$

Next, we want to calculate the number of moles of each cation per formula unit. A general formula for feldspar is: $XY_4O_8$, where X is Na, K, or Ca in the 'A' site and Y is Al or Si in the tetrahedral site. So to calculate formula units in the 'A' site, we divide the number of moles of Na, K, and Ca by the sum of moles of Na, K, and Ca. To calculate formula units in the tetrahedral site, we divide the number of moles of Al and Si by the sum of moles of Al and Si and multiply by 4, since there are 4 ions in this site. Since the number of oxygens is constant, we can refer to these quantities as the moles per 8 oxygens. The table below shows the results of these calculations.

The activity of albite is equal to the mole fraction of Na, 0.07; the activity of anorthite is 0.93.

**CATION FORMULA UNITS**

| | Mol. wt. oxide | moles cation | moles per 8 oxygens |
|---|---|---|---|
| Si | 60.06 | 0.7385 | 2.077 |
| Al | 101.96 | 0.6836 | 1.923 |
| Ca | 56.08 | 0.3322 | 0.926 |
| Na | 61.98 | 0.0255 | 0.071 |
| K | 94.2 | 0.0011 | 0.003 |

## 3.9 EQUILIBRIUM CONSTANTS

Now that we have introduced the concepts of activity and activity coefficients, we are ready for one of the most useful parameters in physical chemistry: the equilibrium constant. Though we can predict the equilibrium state of a system, and therefore the final result of a chemical reaction, from the Gibbs Free Energy alone, the equilibrium constant is a convenient and succinct way express this. As we shall see, it is closely related to, and readily derived from, the Gibbs Free Energy.

### 3.9.1 DERIVATION AND DEFINITION

Consider a chemical reaction such as:

$$aA + bB \rightleftarrows cC + dD$$

carried out under isobaric and isothermal conditions. The Gibbs Free Energy change of this reaction can be expressed as:

$$\Delta G = c\mu_c + d\mu_d - a\mu_a - b\mu_b \qquad 3.81$$

At equilibrium, ΔG must be zero. A general expression then is:

$$\Delta G = \sum_i \nu_i \mu_i = 0 \qquad 3.82$$

where $\nu_i$ is the stoichiometric coefficient of species *i*. Equilibrium in such situations need not mean that all the reactants (i.e., those phases on the left side of the equation) are consumed to leave only products. Indeed, this is generally not so. Substituting 3.46 into 3.82 we obtain:

$$\sum_i \nu_i \mu_i^o + RT \sum_i \nu_i \ln a_i = 0 \qquad 3.83$$

or:

$$\sum \nu_i \mu_l^o + RT \ln \prod_i a_i^{\nu_i} = 0 \qquad 3.84$$

The first term is simply the standard state Gibbs Free Energy change, $\Delta G°$, for the reaction. There can be only one fixed value of $\Delta G°$ for a fixed standard state pressure and temperature, and therefore of the activity products. The activity products are therefore called the *equilibrium constant* K, familiar from elementary chemistry:

$$\boxed{K = \prod_i a_i^{\nu_i}} \qquad 3.85$$

Substituting 3.85 into 3.84 and rearranging, we see that the equilibrium constant is related to the Gibbs Free Energy change of the reaction by the equation:

$$\boxed{\Delta G_r^o = -RT \ln K} \qquad 3.86$$

At this point, it is worth saying some more about 'standard states'. We mentioned that one is free to choose a standard state, but there are pitfalls. In general, there are two kinds of standard states, fixed pressure-temperature standard states and variable P-T standard states. If you chose a fixed temperature standard state, then equation 3.86 is only valid at that standard-state temperature. If you chose a variable-temperature standard state, then 3.86 is valid for all temperatures, but $\Delta G°$ is then a function of temperature. The same goes for pressure.

### 3.9.2 The Law of Mass Action

Let's attempt to understand the implications of equation 3.85. Consider the dissociation of carbonic acid, an important geological reaction:

$$H_2CO_3 = HCO_3^- + H^+$$

For this particular case, equation 3.85 is expressed as:

$$K = \frac{a_{HCO_3^-} a_{H^+}}{a_{H_2CO_3}}$$

The right side of the equation is a quotient, the product of the activities of the products divided by the product of the activities of the reactants, and is called the *reaction quotient*. At equilibrium, the reaction quotient is equal to the equilibrium constant. The equilibrium constant therefore allows us to predict the relative amounts of products and reactants that will be present when a system reaches equilibrium.

Suppose now that we prepare a beaker of carbonic acid solution; it's not hard to prepare: we just allow pure water to equilibrate with the atmosphere. Let's simplify things by assuming that this is an ideal solution. This allows us to replace activities with concentrations (the concentration units will dictate how we define the equilibrium constant; see below). When the solution has reached equilibrium, just enough carbonic acid will have dissociated so that the reaction quotient will be equal to the equilibrium constant. Now let's add some $H^+$ ions, perhaps by adding a little HCl. The value the reaction quotient increases above that of the equilibrium constant and the system is no longer in equilibrium.

Systems will always respond to disturbances by moving toward equilibrium (how fast they respond is another matter, and one that we will address in Chapter 5). The system will respond by adjusting the concentrations of the 3 species until equilibrium is again achieved, in this case, hydrogen and bicarbonate ions will combine to form carbonic acid until the reaction quotient again equals the equilibrium constant. We can also see that had we reduced the number of hydrogen ions in the solution (perhaps by adding a base), the reaction would have been driven the other way: i.e., hydrogen ions would be produced by dissociation. Equation 3.85 is known as the *Law of Mass Action*, which we can state more generally as: *changing the concentration of one species in a system at equilibrium will cause a reaction a direction that minimizes that change.*

### 3.9.2.1 Le Chatelier's Principle

We can generalize this principle to the effects of temperature and pressure as well. Recall that:

$$\left(\frac{\partial \Delta G_r}{\partial P}\right)_T = \Delta V \quad (2.129) \quad \text{and} \quad \left(\frac{\partial \Delta G_r}{\partial T}\right)_T = -\Delta S_r \quad (2.130)$$

and that systems respond to changes imposed on them by minimizing G. Thus a system undergoing reaction will respond to an increase in pressure by minimizing volume. Similarly, it will respond to an increase in temperature by maximizing entropy. The reaction ice → water illustrates this. If the pres-

**Example 3.6. Manipulating Reactions and Equilibrium Constant Expressions**

Often we encounter a reaction for which we have no value of the equilibrium constant. In many cases, however, we can derive an equilibrium constant by considering the reaction of interest to be the algebraic sum of several reactions for which we do have equilibrium constant values. For example, the concentration of carbonate ion is often much lower than that of the bicarbonate ion. In such cases, it is more convenient to write the reaction for the dissolution of calcite as:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^- \qquad 3.87$$

Given the following equilibrium constants, what is the equilibrium constant expression for the above reaction?

$$K_2 = \frac{a_{H^+} a_{CO_3^{2-}}}{a_{HCO_3^-}} \qquad K_{cal} = \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{a_{CaCO_3}} \qquad K_{H_2O} = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}}$$

*Answer:* Reaction 3.87 can be written as the algebraic sum of three reactions:

$$\begin{array}{ll} + & CaCO_3 \rightleftarrows Ca^{2+} + CO_3^{2-} \\ + & H_2O \rightleftarrows H^+ + OH^- \\ - & HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \\ \hline & CaCO_3 - HCO_3^- + H_2O \rightleftarrows Ca^{2+} + OH^- \end{array}$$

The initial inclination might be to think that if we can sum the reactions, the equilibrium constant of the resulting reaction is the sum the equilibrium constants of the components ones. However, this is not the case. Whereas we sum the reactions, we take the product of the equilibrium constants. Thus our new equilibrium constant is:

$$K = \frac{K_{cal} K_{H_2O}}{K_2}$$

For several reasons (chief among them is that equilibrium constants can be very large or very small numbers), it is often more convenient to work with the log of the equilibrium constant. A commonly used notation is pK. pK is the negative logarithm (base 10) of the corresponding equilibrium constant (note this notation is analogous to that used for pH). The pK's sum and our equilibrium constant expression is:

$$pK = pK_{cal} - pK_{H_2O} - pK_2$$

sure is increased on a system containing water and ice, the equilibrium will shift to favor the phase with the least volume, which is water (recall that water is unusual in that the liquid has a smaller molar volume than the solid). If the temperature of that system is increased, the phase with the greatest molar entropy is favored, which is also water.

Another way of looking at the effect of temperature is to recall that:

$$\Delta S \geq \frac{\Delta Q}{T}$$

Combining this with equation 2.130, we can see that if a reaction A + B → C + D generates heat, then increasing the temperature will retard formation of the products, i.e., the reactants will be favored.

A general statement that encompasses both the law of mass action and the effects we have just discussed is then:

**When perturbed, a system reacts to minimize the effect of the perturbation.**

This is known as *Le Chatelier's Principle*.

### 3.9.3 $K_D$ Values, Apparent Equilibrium Constants, and the Solubility Product

It is often difficult to determine activities for phase components or species, and therefore it is more convenient to work with concentrations. We can define a new 'constant', the distribution coefficient, $K_D$, as:

$$K_D = \prod_i X_i^{\nu_i} \qquad 3.88$$

$K_D$ is related to the equilibrium constant K as:

$$K_D = \frac{K_{eq}}{K_\lambda} \qquad 3.89$$

where $K_\lambda$ is simply the ratio of activity coefficients:

$$K_\lambda = \prod_i \lambda_i^{\nu_i} \qquad 3.90$$

Distribution coefficients are functions of temperature and pressure, as are the equilibrium constants, though the dependence of the two may differ. The difference is that $K_D$ values are also functions of composition.

An alternative to the distribution coefficient is the *apparent equilibrium constant*, which we define as:

$$K^{app} = \prod_i m_i^{\nu_i} \qquad 3.91 \qquad\qquad K^{app} = \frac{K_{eq}}{K_\gamma} \qquad 3.92$$

with $K_\gamma$ defined analogously to $K_\lambda$. The difference between the apparent equilibrium constant and the distribution coefficient is that we have defined the former in terms of molality and the latter in terms of mole fraction. Igneous geochemists tend to use the distribution coefficient, aqueous geochemists the apparent equilibrium constant.

Another special form of the equilibrium constant is the *solubility product*. Consider the dissolution of NaCl in water. The equilibrium constant is:

$$K = \frac{a_{Na^+_{aq}} a_{Cl^-_{aq}}}{a_{NaCl_s}}$$

where *aq* denotes the dissolved ion and *s* denotes solid. Because the activity of NaCl in pure sodium chloride solid is 1, this reduces to:

$$K = a_{Na^+_{aq}} a_{Cl^-_{aq}} = K_{sp} \qquad 3.93$$

where $K_{sp}$ is called the *solubility product*. You should note that it is generally the case in dissolution reactions such as this that we take the denominator, i.e., the activity of the solid, to be 1.

### 3.9.4 Henry's Law and Gas Solubilities

Consider a liquid, water for example, in equilibrium with a gas, the atmosphere for example. Earlier in this chapter, we found that the partial pressure of component *i* in the gas could be related to the concentration of a component *i* in the liquid by Henry's Law:

$$P_i = h_i X_i \qquad (3.10)$$

where *h* is Henry's Law constant. We can rearrange this as:

$$h_i = \frac{P_i}{X_i} \qquad 3.94$$

Notice that this equation is analogous in form to the equilibrium constant expression (3.88), except that we have used a partial pressure in place of one of the concentrations. A Henry's Law constant is thus a form of equilibrium constant used for gas solubility: it relates the equilibrium concentration of a substance in a liquid solution to that component's partial pressure in a gas.

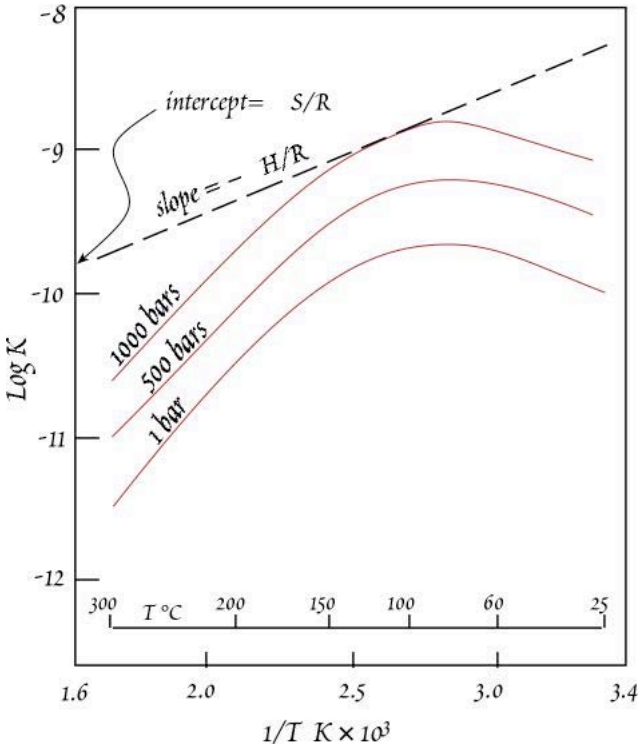



Figure 3.17. Log of the solubility constant of barite plotted against the inverse of temperature. The slope of a tangent to the curve is equal to $-\Delta H/R$. The intercept of the tangent (which occurs at $1/T = 0$ and is off the plot) is equal to $\Delta S/R$. After Blount (1977).

### 3.9.5 Temperature Dependence of Equilibrium Constant

Since $\Delta G° = \Delta H° - T\Delta S°$ and $\Delta G_r^o = -RT \ln K$, it follows that in the standard state, the equilibrium constant is related to enthalpy and entropy change of reaction as:

$$\boxed{\ln K = -\frac{\Delta H_r^o}{RT} + \frac{\Delta S_r^o}{R}} \qquad 3.95$$

Equation 3.95 allows us to calculate an equilibrium constant from fundamental thermodynamic data. Conversely, we can estimate values for $\Delta S°$ and $\Delta H°$ from the equilibrium constant, which is readily calculated if we know the activities of reactants and products. Equation 3.95 has the form:

**Example 3.7: Using the Solubility Product.**

The apparent (molar) solubility product of fluorite ($CaF_2$) at 25° C is $3.9 \times 10^{-11}$. What is the concentration of $Ca^{2+}$ ion in groundwater containing 0.1 mM of $F^-$ in equilibrium with fluorite?

*Answer:* Expressing equation 3.93 for this case we have:

$$K_{sp\text{-}Fl} = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]} = [Ca^{2+}][F^-]^2$$

We take the activity of $CaF_2$ as 1. Rearranging and substituting in values, we have:

$$[Ca^{2+}] = \frac{K_{sp\text{-}Fl}}{[F^-]^2} = \frac{3.9\times10^{-11}}{[0.1\times10^{-3}]^2} = \frac{3.9\times10^{-11}}{1\times10^{-8}} = 3.9\times10^{-3} M = 3.9 mM$$

$$\ln K = \frac{a}{T} + b$$

where $a$ and $b$ are $\Delta H^\circ/R$ and $\Delta S^\circ/R$ respectively. If we can assume that $\Delta H$ and $\Delta S$ are constant over some temperature range (this is likely to be the case provided the temperature interval is small), then a plot of ln K vs. 1/T will have a slope of $\Delta H^\circ/R$ and an intercept of $\Delta S^\circ/R$. Thus measurements of ln K made over a range of temperature and plotted vs. 1/T provide estimates of $\Delta H^\circ$ and $\Delta S^\circ$. Even if $\Delta H$ and $\Delta S$ are not constant, they can be estimated from the instantaneous slope and intercept of a curve of ln K plotted against 1/T. This is illustrated in Figure 3.17, which shows measurements of the solubility constant for barite ($BaSO_4$) plotted in this fashion (though in this case the $\log_{10}$ rather than natural logarithm is used). From changes of $\Delta H$ and $\Delta S$ with changing temperature and knowing the heat capacity of barite, we can also estimate heat capacities of the $Ba^{2+}$ and $SO_4^{2-}$ ions, which would obviously be difficult to measure directly. We can, of course, also calculate $\Delta G$ directly from equation 3.86. Thus a series of measurements of the equilibrium constant for simple systems allows us deduce the fundamental thermodynamic data needed to predict equilibrium in more complex systems.

Taking the derivative with respect to temperature of both sides of equation 3.95 (while holding pressure constant), we have:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H_r^o}{RT^2} \qquad 3.96$$

This equation is known as the *van't Hoff Equation*.

**EXAMPLE 3.8. CALCULATING EQUILIBRIUM CONSTANTS AND EQUILIBRIUM CONCENTRATIONS**

The hydration of olivine to form chrysotile (a serpentine mineral) may represented in a pure Mg system as:

$$H_2O + 2H^+ + 2Mg_2SiO_4 \rightleftarrows Mg_3Si_2O_5(OH)_4 + Mg^{2+}$$

| Species | $\Delta H^\circ$ kJ | $S^\circ$ J/K |
|---|---|---|
| $Mg_3Si_2O_5(OH)_4$ | -4272.87 | 434.84 |
| $Mg^{2+}$ | -366.46 | 109.05 |
| $H^+$ | 44.87 | 106.68 |
| $Mg_2SiO_4$ | -2132.75 | 186.02 |
| $H_2O$ | -232.19 | 211.50 |

If this reaction controlled the concentration of $Mg^{2+}$ of the metamorphic fluid, what would be the activity of $Mg^{2+}$ be in that fluid if it had a pH of 4.0 at 300° C?

*Answer*: Helgeson (1967) gives the thermodynamic data shown in the adjacent table for the reactants at 300° C. From these data, we use Hess's Law to calculate $\Delta H_r$ and $\Delta S_r$ as -231.38 kJ and -253.01 J/K respectively. The equilibrium constant for the reaction may be calculated as:

$$K = \exp\left(-\frac{\Delta H_r^o}{RT} + \frac{\Delta S_r^o}{R}\right) = \exp\left(-\frac{-231.38\times10^3}{8.134\times573} + \frac{253.01}{8.314}\right) = 7.53\times10^7$$

The equilibrium constant for this reaction can be written as:

$K = \dfrac{a_{Mg^{2+}} a_{Cry}}{a_{H^+}^2 a_{Fo}^2 a_{H_2O}}$ which reduces to $K = \dfrac{a_{Mg^{2+}}}{a_{H^+}^2}$ if we take the activities of water, chrysotile, and forsterite as 1. Since pH = - log $a_{H^+}$, we may rearrange and obtain the activity of the magnesium ion as:

$$a_{Mg^{2+}} = K\, a_{H^+}^2 = 7.53\times10^7 \times 10^{-4\times2} = 7.53\times10^{-1}$$

### 3.9.6 Pressure Dependence of Equilibrium Constant

Since $\left(\frac{\partial \Delta G_r}{\partial P}\right)_T = \Delta V$ and $\Delta G_r^o = -RT \ln \mathrm{K}$

then $$\left(\frac{\partial \ln \mathrm{K}}{\partial P}\right)_T = -\frac{\Delta V_r^o}{RT} \qquad 3.97$$

If $\Delta V_r$ does not depend on pressure, this equation can be integrated to obtain:

$$\ln \mathrm{K}_{P_2} = \ln \mathrm{K}_{P_1} - \frac{\Delta V_r^o}{RT}(P_1 - P_2)$$

This assumption will be pretty good for solids because their compressibilities are very low, but slightly less satisfactory for reactions involving liquids (such as dissolution), because they are more compressible. This assumption will be essentially totally invalid for reactions involving gases, because their volumes are highly pressure dependent.

## 3.10 Practical Approach to Electrolyte Equilibrium

With the equilibrium constant now in our geochemical toolbox, we have the tools necessary to roll up our sleeves and get to work on some real geochemical problems. Even setting aside non-ideal behavior, electrolyte solutions, geological ones in particular, often have many components and can be extremely complex. Predicting their equilibrium state can therefore be difficult. There are, however, a few rules for approaching problems of electrolyte solutions that, when properly employed, make the task much more tractable.

### 3.10.1 Choosing Components and Species

We emphasized at the beginning of the chapter the importance of choosing the components in a system. How well we chose components will make a difference in how easily we can solve a given problem. Morel and Hering (1993) suggest these rules for choosing components and species in aqueous systems:

1. *All species should be expressible as stoichiometric functions of the components, the stoichiometry being defined by chemical reactions.*
2. *Each species has a unique stoichiometric expression as a function of the components.*
3. *$H_2O$ should always be chosen as a component.*
4. *$H^+$ should always be chosen as a component.*

$H^+$ activity, or pH, is very often the critical variable, also called the "master variable", in problems in natural waters. In addition, recall that we define the free energy of formation of $H^+$ as 0. For these reasons, it is both convenient and important that $H^+$ be chosen as a component.

### 3.10.2 Mass Balance

This constraint, also sometimes called mole balance, is a very simple one, and as such it is easily overlooked. When a salt is dissolved in water, the anion and cation are added in stoichiometric proportions. If the dissolution of the salt is the only source of these ions in the solution, then for a salt of composition $C_{\nu+}A_{\nu-}$ we may write:

$$\nu^-[\mathrm{C}] = \nu^+[\mathrm{A}] \qquad 3.98$$

Thus, for example, for a solution formed by dissolution of $CaCl_2$ in water the concentration of $Cl^-$ ion will be twice that of the $Ca^{2+}$ ion. Even if $CaCl_2$ is not the only source of these ions in solution, its congruent dissolution allows us to write the mass balance constraint in the form of a differential equation:

**EXAMPLE 3.9. DETERMINING THE PH OF RAIN WATER FROM ITS COMPOSITION**

Determine the pH of the two samples of rain in the adjacent table. Assume that sulfuric and nitric acid are fully dissociated and that the ions in the table, along with $H^+$ and $OH^-$ are the only ones present.

**ANALYSIS OF RAIN WATER**

| | Rain 1 ($\mu$M) | Rain 2 ($\mu$M) |
|---|---|---|
| Na | 9 | 89 |
| Mg | 4 | 16 |
| K | 5 | 9 |
| Ca | 8 | 37 |
| Cl | 17 | 101 |
| $NO_3$ | 10 | 500 |
| $SO_4$ | 18 | 228 |

*Answer:* This problem is simpler than it might first appear. Given the stated conditions, there are no reactions between these species that we need to concern ourselves with. To solve the problem, we observe that this solution must be electrically neutral: any difference in the sum of cations and anions must be due to the one or both of the two species not listed: $OH^-$ and $H^+$.

We start by making an initial guess that the rain is acidic and that the concentration of $H^+$ will be much higher than that of $OH^-$, and that we can therefore neglect the latter (we'll want to verify this assumption when we have obtained a solution). The rest is straightforward. We sum the product of charge times concentration (Equation 3.99) for both cations and anions and find that anions exceed cations in both cases: the difference is equal to the concentration of $H^+$. Taking the log of the concentration (having first converted concentrations to M from $\mu$M by multiplying by $10^{-6}$) we obtain a pH of 4.6 for the first sample and 3.14 for the second.

**CHARGE BALANCE FOR RAINWATER**

| | Rain 1 | Rain 2 |
|---|---|---|
| $\Sigma$ cations | 38 | 204 |
| $\Sigma$ anions | 63 | 1057 |
| $\Delta$ | 25 | 853 |
| pH | 4.60 | 3.07 |

Now we need to check our simplifying assumption that we could neglect $OH^-$. The equilibrium between $OH^-$ and $H^+$ is given by:

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

From this we compute $[OH^-]$ as $10^{-10}$ in the first case and $10^{-11}$ in the second. Including these would not change the anion sum significantly, so our assumption was justified.

$$\frac{\partial Cl^-}{\partial Ca^{2+}} = 2$$

which just says that $CaCl_2$ dissolution adds two $Cl^-$ ions to solution for every $Ca^{2+}$ ion added.

By carefully choosing components and boundaries of our system, we can often write conservation equations for components. For example, suppose we have a liter of water containing dissolved $CO_2$ in equilibrium with calcite (for example, groundwater in limestone). In some circumstances, we may want to choose our system as the water plus the limestone, in which case we may consider Ca conserved and write:

$$\Sigma Ca = Ca^{2+}_{aq} + CaCO_{3s}$$

where $CaCO_{3s}$ is calcite (limestone) and $Ca^{2+}_{aq}$ is aqueous calcium ion. We may want to avoid choosing carbonate as a component and chose carbon instead, since the carbonate ion is not conserved because of association and dissociation reactions such as:

$$CO_3^{2-} + H^+ \rightleftarrows HCO_3^-$$

Choosing carbon as a component has the disadvantage that some carbon will be present as organic compounds, which we may not wish to consider. A wiser choice is to define $CO_2$ as a component. Total $CO_2$ would then include all carbonate species as well as $CO_2$ (very often, total $CO_2$ is expressed instead as total carbonate). The conservation equation for total $CO_2$ for our system would be:

$$\Sigma CO_2 = CaCO_{3s} + CO_2 + H_2CO_3 + HCO_3^- + CO_3^{2-}$$

Here we see the importance of the distinction we made between components and species earlier in the chapter.

### 3.10.3 Electrical Neutrality

There is an additional condition that electrolyte solutions must meet: *electrical neutrality*. Thus the sum of the positive charges in solutions must equal the sum of the negative ones, or:

$$\boxed{\sum_i m_i z_i = 0} \qquad 3.99$$

While this presents some experimental obstacles, for example we cannot add only $Na^+$ ion to an aqueous solution while holding other compositional parameters constant, it also allows placement of an addition mathematical constraint on the solution. It is often convenient to rearrange equ. 3.99 so as to place anions and cations on different sides of the equation:

$$\sum_i m_i^+ z_i^+ = \sum_n m_n^- z_n^- \qquad 3.100$$

As an example, consider an natural water in equilibrium with atmospheric $CO_2$ and containing no other species. The charge balance equation in this case is:

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

As example 3.9 illustrates, the electrical neutrality constraint can prove extremely useful.

### 3.10.4 Equilibrium Constant Expressions

For each chemical reaction in our system, we can write one version of equation 3.85. This allows us to relate the equilibrium activities of the species undergoing reaction in our system to one another.

Solution of aqueous equilibria problems often hinge on the degree to which we can simplify the problem by minimizing the number of equilibrium constant expressions we must solve. For example, $H_2SO_4$ will be completely dissociated in all but the most acidic natural waters, so we need not deal with equilibrium between $H^+$, $SO_4^{2-}$, $HSO_4^-$, and $H_2SO_4$, and need not consider the two latter in our list of species. Similarly, though many natural waters contain $Na^+$ and $Cl^-$, NaCl will precipitate only from concentrated brines, so we generally need not consider equilibrium between NaCl, $Na^+$, and $Cl^-$.

Carbonate is a somewhat different matter. Over the range of compositions of natural waters, $H_2CO_3$,

**Example 3.10: Soil Organic Acid**

Consider soil water with a pH of 7 containing a weak organic acid, which we will designate HA, at a concentration of $1 \times 10^{-4}$ M. If the apparent dissociation constant of the acid is $10^{-4.5}$, what fraction of the acid is dissociated?

*Answer:* We have two unknowns: the concentration of the dissociated and undissociated acid and we have two equations: the equilibrium constant expression for dissociation, and mass balance equation. We'll have to solve the two simultaneously to obtain the answer. Our two equations are:

$$K_{dis} = \frac{[H^+][A^-]}{[HA]} = 10^{-4.5} \qquad \Sigma HA = [HA] + [A^-]$$

Solving the dissociation constant expression for $[A^-]$ we have:

$$[A^-] = \frac{[HA]K_{dis}}{[H^+]}$$

Then solving the conservation equation for [HA] and substituting, we have

$$[A^-] = \frac{(\Sigma HA - [A^-])K_{dis}}{[H^+]}$$

Setting $H^+$ to $10^{-7}$ and $\Sigma HA$ to $10^{-4}$, we calculate $[A^-]$ as $3.16 \times 10^{-5}$ M, so 31.6% of the acid is dissociated.

$HCO_3^-$, and $CO_3^{2-}$ may all be present. In most cases, however, one of these forms will dominate and the concentrations of the remaining ones will be an order of magnitude or more lower than that of the dominant one. In some cases, two of the above species may have comparable concentrations and will be have to consider equilibrium between them, but it is rarely necessary to consider equilibrium between all three. Thus at most we will have to consider equilibrium between $H_2CO_3$ and $HCO_3^-$, or $HCO_3^-$ and $CO_3^{2-}$, and we can safely ignore the existence of the remaining species. A successful solution of problems involving carbonate equilibria often requires correctly deciding which reactions to ignore. We will discuss carbonate equilibrium in greater detail in Chapter 6.

## 3.11 Oxidation and Reduction

An important geochemical variable that we have not yet considered is the *oxidation state* of a system. Many elements exist in nature in more than one valence state. Iron and carbon are the most important of these because of their abundance. Other elements, including transition metals such as Ti, Mn, Cr, Ce, Eu, and U, and non-metals such as C, N, S, and As, are found in more than one valence state in nature. The valence state of an element can significantly affect its geochemical behavior. For example, U is quite soluble in water in its oxidized state, $U^{6+}$, but is much less soluble in its reduced state, $U^{4+}$. Many uranium deposits have formed when an oxidized, U-bearing solution was reduced. Iron is reasonably soluble in reduced form, $Fe^{2+}$, but much less soluble in oxidized form, $Fe^{3+}$. The same is true of manganese. Thus iron is leached from rocks by reduced hydrothermal fluids and precipitated when these fluids mix with oxidized seawater. $Eu^{2+}$ in magmas substitutes readily for Ca in plagioclase, whereas $Eu^{3+}$ does not. The mobility of pollutants, particularly toxic metals, will depend strongly on the whether the environment is reducing or oxidizing. Thus the oxidation state of a system is an important geochemical variable.

The *valence number* of an element is defined as the electrical charge an atom would acquire if it formed ions in solution. For strongly electronegative and electropositive elements that form dominantly ionic bonds, valence number corresponds to the actual state of the element in ionic form. However, for elements that predominantly or exclusively form covalent bonds, valence state is a somewhat hypothetical concept. Carbon, for example, is never present in solution as a monatomic ion. Because of this, assignment of valence number can be a bit ambiguous. A few simple conventions guide assignment of valence number:

- The valence number of all elements in pure form is 0.
- The sum of valence numbers assigned to atoms in molecules or complex species must equal the actual charge on the species.
- The valence number of hydrogen is +1, except in metal hydrides, when it is -1.
- The valence number of oxygen is -2 except in peroxides, when it is -1.

The valence state in which an element will be present in a system is governed by the availability of electrons. Oxidation-reduction *(redox)* reactions involve the transfer of electrons and the resultant change in valence. *Oxidation is the loss of electrons; reduction is the gain of electrons*‡. An example is the oxidation of magnetite (which consists of 1 $Fe^{2+}$ and 2 $Fe^{3+}$) to hematite:

$$2Fe_3O_4 + \tfrac{1}{2}O_2 \rightleftarrows 3Fe_2O_3 \qquad 3.101$$

The $Fe^{2+}$ in magnetite looses an electron in this reaction and thereby oxidized; conversely oxygen gains an electron and is thereby reduced.

We can divide the elements into *electron donors* and *electron acceptors*; this division is closely related to electronegativity, as you might expect. Electron acceptors are electronegative; electron donors are electropositive. Metals in 0 valence state are electron donors, non-metals in 0 valence state are usually electron acceptors. Some elements, such as carbon and sulfur, can be either electron donors or recep-

‡ A useful mnemonic to remember this is **LEO** the lion says **GRR**! (**L**oss **E**quals **O**xidation, **G**ain **R**efers to **R**eduction.) Silly, perhaps, but effective. Try it!

tors. Oxygen is the most common electron acceptor, hence the term *oxidation*. It is nevertheless important to remember that oxidation and reduction may take place in the absence of oxygen.

A reduced system is one in which the availability of electrons is high, due to an excess of electron donors over electron acceptors. In such a system, metals will be in a low valence state, e.g., $Fe^{2+}$. Conversely, when the availability of electrons is low, due to an abundance of electron acceptors, a system is said to be oxidized. Since it is the most common electron acceptor, the abundance of oxygen usually controls the oxidation state of a system, but this need not be the case.

To predict the equilibrium oxidation state of a system we need a means of characterizing the availability of electrons, and the valence state of elements as a function of that availability. Low-temperature geochemists and high-temperature geochemists do this in different ways. The former use electrochemical potential while the latter use oxygen fugacity. We will consider both.

### 3.11.1 Redox in Aqueous Solutions

The simplest form of the chemical equation for the reduction of ferric iron would be:

$$Fe^{3+}_{aq} + e^- \rightleftarrows Fe^{2+}_{aq} \qquad 3.102$$

where the subscript *aq* denotes the aqueous species. This form suggests that the energy involved might be most conveniently measured in an electrochemical cell.

The Daniell cell pictured in Figure 3.18 can be used to measure the energy involved in the exchange of electrons between elements, for example, zinc and copper:

$$Zn_s + Cu^{2+}_{aq} \rightleftarrows Zn^{2+}_{aq} + Cu_s \qquad 3.103$$

where the subscript *s* denotes the solid. Such a cell provides a measure of the *relative* preference of Zn and Cu for electrons. In practice, such measurements are made by applying a voltage to the system that is just sufficient to halt the flow of electrons from the zinc plate to the copper one. What is actually measured then is a potential energy, denoted E, and referred to as the *electrode potential*, or simply the *potential* of the reaction.

If we could measure the potential of two separate half-cell reactions:

$$Zn_s \rightleftarrows Zn^{2+}_{aq} + 2e^-$$

$$Cu_s \rightleftarrows Cu^{2+}_{aq} + 2e^-$$

we could determine the energy gain/loss in the transfer of an electron from an individual element. Unfortunately, such measurements are not possible (nor would these reactions occur in the natural environment: electrons are not given up except to another element or species*). This requires the establishment of an arbitrary reference value. Once such a reference value is established, the potential in-

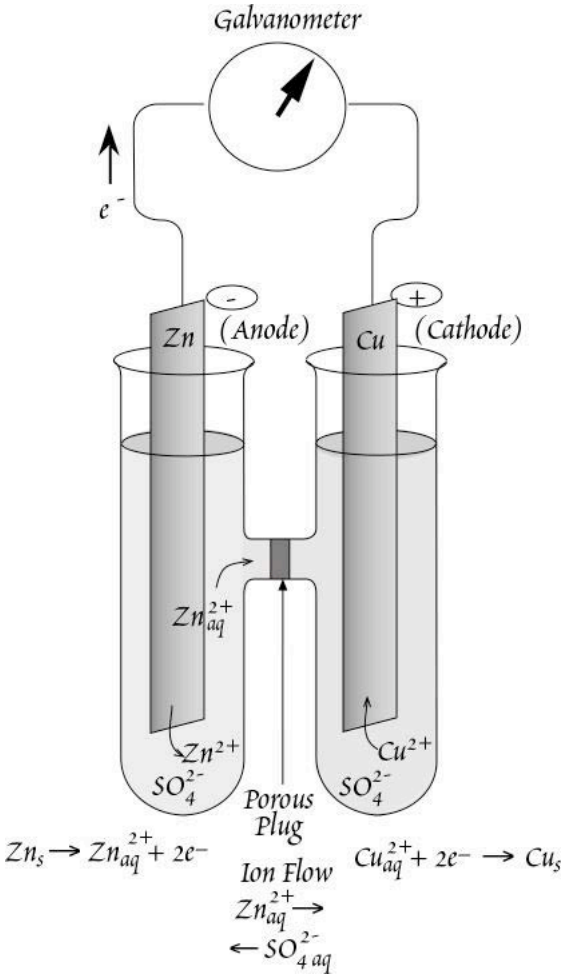



Figure 3.18. Electrode reactions in the Daniell Cell.

* Ionization reactions, where free electrons are formed, do occur in nature at very high temperatures. They occur, for example, in stars or other very energetic environments in the universe.

volved in reactions such as 3.102 can be established.

### 3.11.1.1 Hydrogen scale potential, $E_H$

The established convention is to measure potentials in a standard hydrogen electrode cell (at standard temperature and pressure). The cell consists on one side of a platinum plate coated with fine Pt powder that is surrounded by $H_2$ gas maintained at a partial pressure of 1 atm and immersed in a solution of unit $H^+$ activity. The other side consists of the electrode and solution under investigation. A potential of 0 is assigned to the half-cell reaction:

$$\frac{1}{2}H_{2(g)} \rightleftarrows H^+_{aq} + e^- \qquad 3.104$$

where the subscript $g$ denotes the gas phase. The potential measured for the entire reaction is then assigned to the half-cell reaction of interest. Thus for example, the potential of the reaction:

$$Zn^{2+}_{aq} + H_{2(g)} \rightleftarrows Zn_s + 2H^+$$

is –0.763 V. This value is assigned to the reaction:

$$Zn^{2+}_{aq} + 2e^- \rightleftarrows Zn_s \qquad 3.105$$

and called the *hydrogen scale potential*, or $E_H$, of this reaction. Thus the $E_H$ for the reduction of $Zn^{+2}$ to $Zn^0$ is -0.763 V. The hydrogen scale potentials of a few half-cell reactions are listed in Table 3.3. The sign convention for $E_H$ is that the sign of the potential is positive when the reaction proceeds from left to right (i.e., from reactants to products). Thus if a reaction has positive $E_H$, the metal ion will be reduced by hydrogen gas to the metal. If a reaction has negative $E_H$, the metal will be oxidized to the ion and $H^+$ reduced. The standard state potentials (298 K, 0.1 MPa) of more complex reactions can be predicted by algebraic combinations of the reactions and potentials in Table 3.3.

The half-cell reactions in Table 3.3 are arranged in order increasing E°. Thus a species on the product (right) side of a given reaction will reduce (give up electrons to) the species on the reactant side in all reactions listed below it. Thus in the Daniell Cell reaction in Figure 3.18, Zn metal will reduce $Cu^{2+}$ in solution. Zn may thus be said to be a stronger reducing agent than Cu.

**TABLE 3.3. $E_H^\circ$ AND $p\varepsilon^\circ$ FOR SOME HALF-CELL REACTIONS**

| Half Cell Reaction | $E_H°$ (V) | $p\varepsilon°$ |
|---|---|---|
| $Li^+ + e^- \rightleftarrows Li$ | -3.05 | –51.58 |
| $Ca^{2+} + 2e^- \rightleftarrows Ca$ | -2.93 | –49.55 |
| $Th^{4+} + 4e^- \rightleftarrows Th$ | -1.83 | –30.95 |
| $U^{+4} + 4e^- \rightleftarrows U$ | -1.38 | –23.34 |
| $Mn^{2+} + 2e^- \rightleftarrows Mn$ | -1.18 | –19.95 |
| $Zn^{2+} + 2e^- \rightleftarrows Zn$ | -0.76 | –12.85 |
| $Cr^{3+} + 3e^- \rightleftarrows Cr$ | -0.74 | –12.51 |
| $Fe^{2+} + 2e^- \rightleftarrows Fe$ | -0.44 | –7.44 |
| $Eu^{3+} + e^- \rightleftarrows Eu^{2+}$ | -0.36 | -6.08 |
| $Pb^{2+} + 2e^- \rightleftarrows Pb$ | -0.13 | –2.2 |
| $CO_{2(g)} + 4H^+ + 4e^- \rightleftarrows CH_2O^* + 2H_2O$ | -0.71 | –1.2 |
| $2H^+ + 2e^- \rightleftarrows H_{2(g)}$ | 0 | 0 |
| $N_{2(g)} + 6H^+ + 6e^- \rightleftarrows 2NH_3$ | 0.093 | 1.58 |
| $Cu^{2+} + 2e^- \rightleftarrows Cu$ | 0.34 | 5.75 |
| $UO_2^{2+} + 2e^- \rightleftarrows UO_2$ | 0.41 | 6.85 |
| $S + 2e^- \rightleftarrows S^{2-}$ | 0.44 | 7.44 |
| $Cu^+ + e^- \rightleftarrows Cu$ | 0.52 | 8.79 |
| $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ | 0.77 | 13.02 |
| $NO_3^- + 2H^+ + e^- \rightleftarrows NO_{2(g)} + H_2O$ | 0.80 | 13.53 |
| $Ag^+ + e^- \rightleftarrows Ag$ | 0.80 | 13.53 |
| $Hg^{2+} + 2e^- \rightleftarrows Hg$ | 0.85 | 14.37 |
| $MnO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$ | 1.23 | 20.8 |
| $O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$ | 1.23 | 20.8 |
| $MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$ | 1.51 | 25.53 |
| $Au^+ + e^- \rightleftarrows Au$ | 1.69 | 28.58 |
| $Ce^{4+} + e^- \rightleftarrows Ce^{3+}$ | 1.72 | 29.05 |
| $Pt^+ + e^- \rightleftarrows Pt$ | 2.64 | 44.64 |

*$CH_2O$ refers to carbohydrate, the basic product of photosynthesis.

Electrochemical energy is another form of free energy and can be related to the Gibbs Free Energy of reaction as:

$$\boxed{\Delta G = -z\mathcal{F}E} \qquad 3.106$$

and

$$\Delta G^\circ = -z\mathcal{F}E^\circ \qquad 3.107$$

where $z$ is the number of electrons per mole exchanged (e.g., 2 in the reduction of zinc) and $\mathcal{F}$ is the Faraday constant ($\mathcal{F}$ = 96,485 coulombs; 1 joule = 1 volt-coulomb). The free energy of formation of a pure element is 0 (by convention). Thus, the ΔG in a reaction that is opposite one such as 3.105, i.e.:

$$Zn_{(s)} \rightleftarrows Zn^{2+} + 2e^-$$

is the free energy of formation of the ion from the pure element. From equ. 3.106 we can calculate the ΔG for the reduction of zinc as 147.24 kJ/mol. The free energy of formation of $Zn^{2+}$ would be –147.24 kJ/mol. Given the free energy of formation of an ion, we can also use 3.105 to calculate the hydrogen scale potential. Since

$$\Delta G = \Delta G^o + RT \ln \prod_i a_i^{\nu_i} \qquad 3.108$$

we can substitute 3.106 and 3.107 into 3.108 and also write

$$\boxed{E = E^\circ - \frac{RT}{z\mathcal{F}} \ln \prod_i a_i^{\nu_i}} \qquad 3.109$$

Equation 3.108 is known as the *Nernst Equation*‡. At 298K and 0.1 MPa it reduces to:

$$E = E^o - \frac{0.0592}{z} \log \prod_i a_i^{\nu_i} \qquad 3.110$$

We can deduce the meaning of this relationship from the relationship between ΔG and E in equ. 3.106. At equilibrium ΔG is zero. Thus in equation 3.108, *activities will adjust themselves such that E is 0.*

### 3.11.1.2 Alternative Representation of Redox State: pε

Consider again the reaction: $Fe^{3+}_{aq} + e^- \rightleftarrows Fe^{2+}_{aq}$ (3.102)

If we were to express the equilibrium constant for this reaction, we would write:

$$K = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}} a_{e^-}}$$

Thus we might find it convenient to define an activity for the electron. For this reason, chemists have defined an analogous parameter to pH, called *pε*. pε is the negative log of the activity of electrons in solution:

$$\boxed{p\varepsilon \equiv -\log a_{e^-}} \qquad 3.111$$

The log of the equilibrium constant for 3.101 may then be written as:

$$\log K = \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} + p\varepsilon$$

upon rearranging we have:

$$p\varepsilon = \log K - \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad 3.112$$

‡ Named for Walther Nernst (1864-1941). Nernst was born in Briesau, Prussia (now in Poland) and completed a PhD at the University of Würzburg in 1887. Nernst made many contributions to thermodynamics and kinetics, including an early version of the third law. He was awarded the Nobel Prize in 1920.

**EXAMPLE 3.11: CALCULATING THE $E_H$ OF NET REACTIONS**

We can calculate $E_H$ values for reactions not listed in Table 3.3 by algebraic combinations of the reactions and potentials that are listed. There is, however, a "catch". Let's see how this works.

Calculate the $E_H$ for the reaction:0

$$Fe^{3+} + 3e^- \rightleftarrows Fe$$

*Answer:* This reaction is the algebraic sum of two reactions listed in Table 3.2:

$$Fe^{3+} + e^- \rightleftarrows Fe^{+2}$$

$$Fe^{2+} + 2e^- \rightleftarrows Fe$$

Since the reactions sum, we might assume that we can simply sum the $E_H$ values to obtain the $E_H$ of the net reaction. Doing so, we obtain an $E_H$ of 0.33 V. However, the true $E_H$ of this reaction is –0.037 V. What have we done wrong?

We have neglected to take into consideration the number of electrons exchanged. In the algebraic combination of $E_H$ values, we need to multiply the $E_H$ for each component reaction by the number of electrons exchanged. We then divide the sum of these values by number of electrons exchanged in the net reaction to obtain the $E_H$ of the net reaction, i.e.,

$$E_{H(net)} = \frac{1}{z_{net}} \sum_i z_i E_{Hi} \qquad 3.113$$

where the sum is over the component reactions *i*. Looking at equation 3.105, we can see why this is the case. By Hess's Law, the $\Delta G$ of the net reaction must be the simple sum of the component reaction $\Delta G$'s, but $E_H$ values are obtained by multiplying $\Delta G$ by z. Equation 3.107 is derived by combining equ. 3.105 and Hess's Law. Using equ. 3.107, we obtain the correct $E_H$ of -0.037 V.

When the activities of reactants and products are in their standard states, i.e., a = 1, then

$$p\varepsilon^o = \frac{1}{z}\log K \qquad 3.114$$

(where z again is the number of electrons exchanged: 1 in reaction 3.102). $p\varepsilon°$ values are empirically determined and may be found in various tables. Table 3.3 lists values for some of the more important reactions. For any state other than the standard state, $p\varepsilon$ is related to the standard state $p\varepsilon$ by:

$$p\varepsilon = p\varepsilon^o - \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad 3.115$$

$p\varepsilon$ and $E_H$ are related by the following equation:

$$p\varepsilon = \frac{\mathcal{F} E_H}{2.303RT} = \frac{5039 E_H}{T} \qquad 3.116$$

(the factor 2.303 arises from the switch from natural log units to base 10 log units).

In defining electron activity and representing it in log units, there is a clear analogy between $p\varepsilon$ and pH. However, the analogy is purely mathematical, and not physical. Natural waters do not contain significant concentrations of free electrons. Also, though a system at equilibrium can have only one value for $p\varepsilon$, just as it will have only one value of pH, redox equilibrium is often not achieved in natural waters. The $p\varepsilon$ of a natural system is therefore often difficult to determine. *Thus $p\varepsilon$ is a hypothetical unit*, defined for convenience of incorporating a representation of redox state that fits readily into established thermodynamic constructs such as the equilibrium constant. In this sense, equation 3.116 provides a more accurate definition of $p\varepsilon$ than does equ. 3.112.

The greater the $p\varepsilon$, the greater the tendency of species to lose their transferable, or valence, electrons. In a qualitative way we can think of the negative of $p\varepsilon$ as a measure of the availability of electrons. $p\varepsilon$ can be related in a general way to the relative abundance of electron acceptors. When an electron acceptor, such as oxygen, is abundant relative to the abundance of electron donors, the $p\varepsilon$ is high and

electron donors will be in electron-poor valence states, e.g., $Mn^{4+}$ instead of $Mn^{2+}$. pε, and $E_H$, are particularly useful concepts when combined with pH to produce diagrams representing the stability fields of various species. We will briefly consider how these are constructed.

### 3.11.1.3 pε – pH Diagrams

pε – pH and $E_H$–pH diagrams are commonly used tools of aqueous geochemistry, and it is important to become familiar with them. An example, the pε–pH diagram for iron, is shown in Figure 3.19. pε–pH diagrams look much like phase diagrams, and indeed there are many similarities. There are, however, some important differences. First, labeled regions do not represent conditions of stability for phases, rather they show which *species* will be *predominate* under the pε–pH conditions within the regions. Indeed, in Fig. 3.19 we consider only a single phase: an aqueous solution. The bounded regions are called *predominance areas*. Second, species are stable beyond their region: boundaries represent the conditions under which the activities of species predominating in two adjoining fields are equal. However, since the plot is logarithmic, activities of species decrease rapidly beyond their predominance areas.

More generally, a pε-pH diagram is a type of *activity diagram*, or predominance diagram, in which the region of predominance of a species is represented as a function of activities of two or more species or ratios of species. We will meet variants of such diagrams in later chapters.

Let's now see how Figure 3.19 can be constructed from basic chemical and thermodynamic data. We will consider only a very simple Fe-bearing aqueous solution. Thus our solution contains only species of iron, the dissociation products of water and species formed by reactions between them. Thermodynamics allows us to calculate the predominance region for each species. To draw boundaries on this plot, we will want to obtain equations in the form of $p\varepsilon = a + b \times pH$. With an equation in this form, $b$ is a slope and $a$ is an intercept on a pε-pH diagram. Hence we will want to write all redox reactions so that they contain $e^-$ and all acid-base reactions so that they contain $H^+$.

In Fig. 3.18, we are only interested in the region where water is stable. So to begin construction of our diagram, we want to draw boundaries outlining the region of stability of water. The upper limit is the reduction of oxygen to water:

$$\tfrac{1}{2}O_{2(g)} + 2e^- + 2H^+_{aq} \rightleftarrows H_2O$$

The equilibrium constant for this reaction is: $$K = \frac{a_{H_2O}}{P_{O_2}^{1/2} a_{e^-}^2 a_{H^+}^2} \qquad 3.117$$

Expressed in log form: $$\log K = \log a_{H_2O} - \frac{1}{2}\log P_{O_2} + 2p\varepsilon + 2pH$$

The value of log K is 41.56 (at 25° C and 0.1 MPa). In the standard state, the activity of water and partial pressure of oxygen are 1 so that 3.117 becomes:

$$p\varepsilon = 20.78 - pH \qquad 3.118$$

Equation 3.118 plots on a pε—pH diagram as a straight line with a slope of -1 intersecting the vertical axis at 20.78. This is labeled as line ① on Figure 3.19.

Similarly, the lower limit of the stability of water is the reduction of hydrogen:

$$H^+_{aq} + e^- \rightleftarrows \frac{1}{2}H_{2(g)}$$

Because $\Delta G_r^o = 0$ and log K = 0 (by convention), we have pε = –pH for this reaction, i.e., a slope of 1 and intercept of 0. This is labeled as line ② on Figure 3.19. Water is stable between these 2 lines (region shown in gray on Figure 3.19).

Now let's consider the stabilities of a few simple aqueous iron species. One of the more important reactions is the hydrolysis of $Fe^{3+}$:

$$Fe^{3+}_{aq} + H_2O \rightleftarrows Fe(OH)^{2+}_{aq} + H^+$$

The equilibrium constant for this reaction is 0.00631. The equilibrium constant expression is then:

$$\log K = \log \frac{a_{Fe(OH)^{2+}}}{a_{Fe^{3+}}} - pH = -2.2$$

Region boundaries on pε–pH diagrams represent the conditions under which the activities of two species are equal. When the activities of $FeOH^{+2}$ and $Fe^{+3}$ are equal the equation reduces to:

$$-\log K = pH = 2.2$$

Thus this equation defines the boundary between regions of predominance of $Fe^{3+}$ and $Fe(OH)^{2+}$. The reaction is independent of pε (no oxidation or reduction is involved), and it plots as a straight vertical line pH = 2.2 (line ③ on Figure 3.19). Boundaries between the successive hydrolysis products, e.g., $Fe(OH)^0_3$ and $Fe(OH)^-_4$ can be similarly drawn as vertical lines at the pH equal to their equilibrium constants, and occur at pH values of 3.5, 7.3, and 8.8. The boundary between $Fe^{2+}$ and $Fe(OH)^-$ can be similarly calculated and occurs at a pH of 9.5.

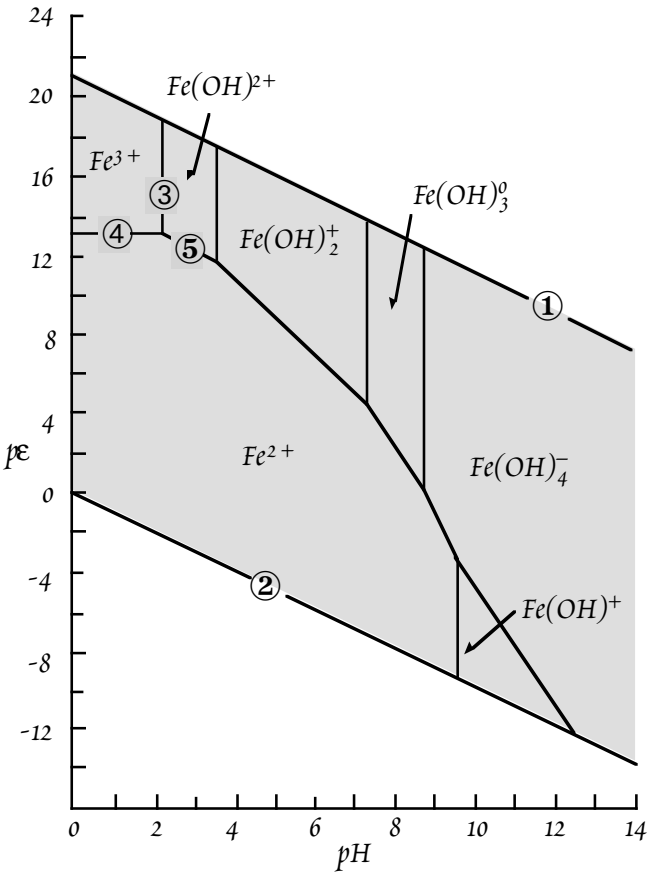



Figure 3.19. pε—pH diagram showing predominance regions for ferric and ferrous iron and their hydrolysis products in aqueous solution at 25°C and 1 bar.

Now consider equilibrium between $Fe^{+2}$ and $Fe^{+3}$. The pε° for this reaction is 13.0 (Table 3.3), hence from equation 3.112 we have:

$$p\varepsilon = 13.0 - \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

When the activities are equal, this equation reduces to:

$$p\varepsilon = 13.0 \qquad 3.119$$

and therefore plots as a horizontal line at pε = 13 that intersects the $FeOH^{+2}$—$Fe^{+3}$ line at an invariant point at pH = 2.2 (line ④ on Figure 3.19).

The equilibrium between $Fe^{+2}$, and $Fe(OH)^{+2}$ is defined by the reaction:

$$Fe(OH)^{2+}_{aq} + e^- + H^+ \rightleftarrows Fe^{2+}_{aq} + H_2O$$

Two things are occurring in this reaction: reduction of ferric to ferrous iron, and reaction of $H^+$ ions with the $OH^-$ radical to form water. Thus we can treat it as the algebraic sum of the two reactions we just considered:

$$Fe^{3+}_{aq} + e^- \rightleftarrows Fe^{2+}_{aq} \qquad p\varepsilon = 13.0$$

$$Fe(OH)^{2+}_{aq} + H^+ \rightleftarrows Fe^{3+}_{aq} + H_2O \qquad pH = 2.2$$

$$Fe(OH)^{2+}_{aq} + e^- + H^+ \rightleftarrows Fe^{2+}_{aq} + H_2O \qquad p\varepsilon + pH = 15.2$$

or:

$$p\varepsilon = 15.2 - pH$$

Thus this boundary has a slope of -1 and an intercept of 15.2 (line ⑤ on Figure 3.19). Slopes and intercepts of other reactions may be derived in a similar manner.

Now let's consider some solid phases of iron as well, specifically hematite ($Fe_2O_3$) and magnetite ($Fe_3O_4$). First, let's consider the oxidation of magnetite to hematite. We could write this reaction as we did in equation 3.101, however, that reaction does not explicitly involve electrons, so that we would not be able to derive an expression containing $p\varepsilon$ or $pH$ from it. Instead, we'll use water as the source of oxygen and write the reaction as:

$$2Fe_3O_4+H_2O \rightleftarrows 3Fe_2O_3+2H^++2e^- \qquad 3.120$$

Assuming unit activity of all phases, the equilibrium constant expression for this reaction is:

$$\log K = -2pH - 2p\varepsilon \qquad 3.121$$

From the free energy of formation of the phases ($\Delta G_f$ = -742.2 kJ/mol for hematite, -1015.4 kJ/mol for magnetite, and -237.2 kJ/mol for water) we can calculate $\Delta G_r$ using Hess's Law and the equilibrium constant using Equ. 3.86. Doing so, we find log K = -5.77. Rearranging equation 3.121 we have:

$$p\varepsilon = 2.88 - pH$$

The boundary between hematite and magnetite will plot as a line with a slope of -1 and an intercept of 2.88. Above this line, i.e., at higher pε, hematite will be stable, below that magnetite will be stable (Figure 3.20). Thus this line is equivalent to a phase boundary.

Next let's consider the dissolution of magnetite to form $Fe^{2+}$ ions. The relevant reaction is:

$$Fe_3O_4 + 8H^+ + 2e^- \rightleftarrows 3Fe^{2+} + 4H_2O$$

The equilibrium constant for this reaction is $7 \times 10^{29}$. Written in log form:

$$\log K = 3\log a_{Fe^{2+}} + 8pH - 2p\varepsilon = 29.85$$

or: $$p\varepsilon = 14.92 - 4pH - \frac{3}{2}\log a_{Fe^{2+}}$$

We have assumed that the activity of water is 1 and that magnetite is pure and therefore that its activity is 1. If we again assume unit activity of $Fe^{2+}$, the predominance area of magnetite would plot as the line:

$$p\varepsilon = 14.92 - 4pH$$

i.e., a slope of –4 and intercept of 0.58. However, such a high activity of $Fe^{2+}$ would be highly unusual in a natural solution. A more relevant activity for $Fe^{2+}$ would be perhaps $10^{-6}$. Adopting this value for the activity of $Fe^{2+}$, we can draw a line corresponding to the equation:

$$p\varepsilon = 23.92 - 4pH$$

This line represents the conditions under which magnetite is in equilibrium with an activity of aqueous $Fe^{2+}$ of $10^{-6}$. For any other activity, the line will be shifted, as illustrated in Figure 3.20. For higher concentrations, the magnetite region will expand, for lower con-

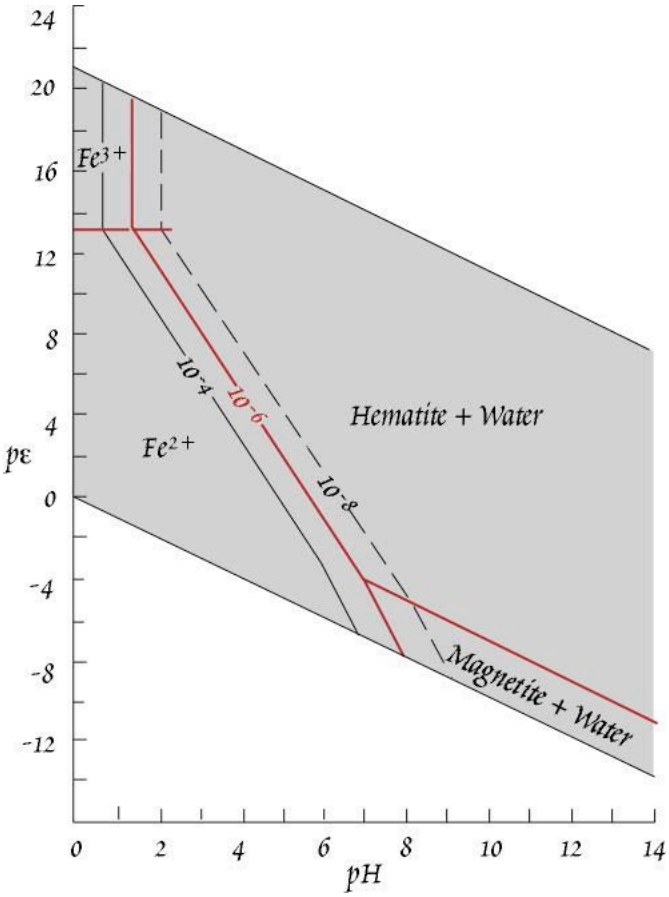



Figure 3.20. Stability regions for magnetite and hematite in equilibrium with an iron-bearing aqueous solution. Thick lines are for a $Fe_{aq}$ activity of $10^{-6}$, finer lines for activities of $10^{-4}$ and $10^{-8}$. The latter is dashed.

centrations it will contract.

Now consider the equilibrium between hematite and $Fe^{2+}$. We can describe this with the reaction:

$$Fe_2O_3 + 6H^+ + 2e^- \rightleftarrows 2Fe^{2+} + 3H_2O$$

The equilibrium constant (which may again be calculated from $\Delta G_r$) for this reaction is 23.79.

Expressed in log form:

$$\log K = 2\log a_{Fe^{2+}} + 6pH + 2p\varepsilon = 23.79$$

Using an activity of 1 for $Fe^{2+}$, we can solve for pε as:

$$p\varepsilon = 11.9 - 3pH - \log a_{Fe^{2+}}$$

For an activity of $Fe^{2+}$ of $10^{-6}$, this is a line with a slope of 3 and an intercept of 17.9. This line represents the conditions under which hematite is in equilibrium with $a_{Fe^{2+}} = 10^{-6}$. Again, for any other activity, the line will be shifted as shown in Figure 3.20.

Finally, equilibrium between hematite and $Fe^{3+}$ may be expressed as:

$$Fe_2O_3 + 6H^+ \rightleftarrows 2Fe^{3+} + 3H_2O$$

The equilibrium constant expression is:

$$\log K = 2\log a_{Fe^{3+}} + 6pH = -3.93$$

For a $Fe^{3+}$ activity of $10^{-6}$, this reduces to:

$$pH = 1.34$$

Since the reaction does not involve transfer of electrons, this boundary depends only on pH.

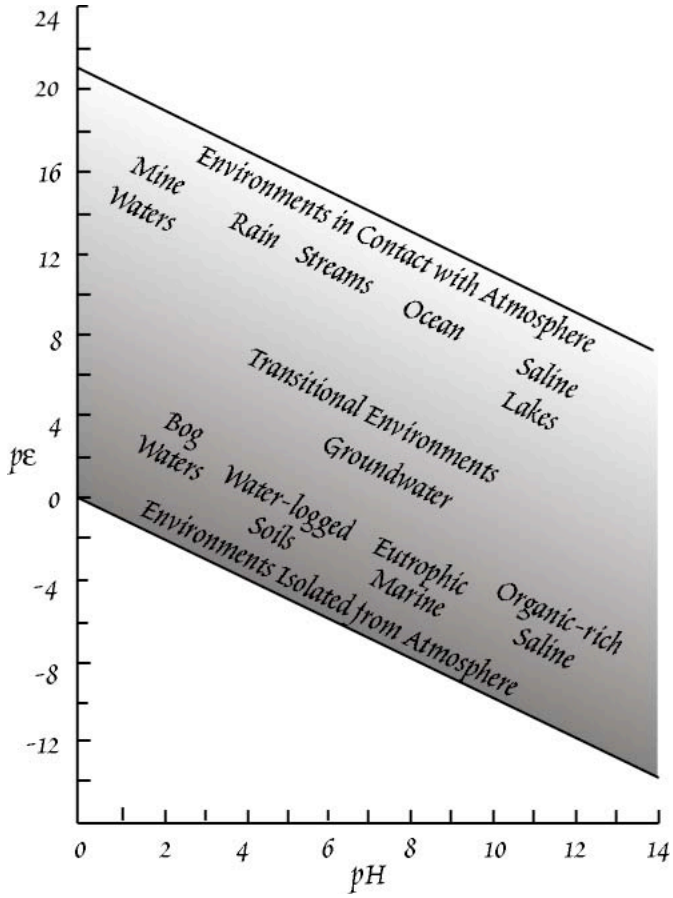



Figure 3.21. pε and pH of various waters on and near the surface of the earth. After Garrels and Christ (1965).

The boundary between predominance of $Fe^{3+}$ and $Fe^{2+}$ is independent of the Fe concentration in solution, and is the same as equ. 3.119 and Fig. 3.18, namely pε = 13.

Examining this diagram, we see that for realistic dissolved Fe concentrations magnetite can be in equilibrium only with a fairly reduced, neutral to alkaline solution. At pH of about 7 or less, it dissolves and would not be stable in equilibrium with acidic waters unless the Fe concentration were very high. Hematite is stable over a larger range of conditions, and becomes stable over a wider range of pH as pε increases. Significant concentrations of the $Fe^{3+}$ ion (> $10^{-6}$ m) will be found only very acidic, oxidizing environments.

Figure 3.21 illustrates the pH and pε values that characterize a variety of environments on and near the surface of the Earth. Comparing this figure with pH–pε diagrams allows us to predict the species we might expect to find in various environments. For example, $Fe^{3+}$ would be a significant dissolved species only in the acidic, oxidized waters that sometimes occur in mine drainages (the acidity of these waters results from high concentrations of sulfuric acid that is produced by oxidation of sulfides). We would expect to find magnetite precipitating only from reduced seawater or in organic-rich, highly saline waters.

**BALANCING REDOX REACTIONS FOR pε–pH DIAGRAMS**

While many redox reactions are straightforward, balancing more complex redox reactions for *pε–pH* diagrams can be a bit more difficult, but a few simple rules make is easier. Let's take as an example the oxidation of ammonium to nitrate. We begin by writing the species of interest on each side of the reaction:

$$NH_4^+ = NO_3^-$$

The next step is to balance the oxygen. We don't want to use $O_2$ gas to do this. We used $O_2$ at a partial pressure of 1 to define the top boundary for the water stability region. Within the region of stability of water, the $O_2$ concentration will be lower and we don't necessarily know its value. This is usually best done using water:

$$3H_2O + NH_4^+ = NO_3^-$$

Next balance the hydrogen using $H^+$:

$$3H_2O + NH_4^+ = NO_3^- + 10H^+$$

Finally, we use electrons to balance charge:

$$3H_2O + NH_4^+ = NO_3^- + 10H^+ + 8e^-$$

As a check, we can consider the valance change of our principal species and be sure that our reaction makes sense. In ammonium, nitrogen is in the 3– state, in nitrate, it is in the 5+ state, a net change of 8. This is just the number of electrons exchanged in the reaction we have written.

## 3.11.2 REDOX IN MAGMATIC SYSTEMS

High temperature geochemists use *oxygen fugacity* to characterize the oxidation state of systems. Consequently, we want to write redox reactions that contain $O_2$. Thus, equilibrium between magnetite and hematite would be written as:

$$4Fe_3O_4 + O_{2(g)} \rightleftarrows 6Fe_2O_3 \qquad 3.122$$

(or alternatively, as we wrote in in equation 3.101) rather than the way we expressed it in equ. 3.120. We note, however, there is negligible molecular oxygen in magmatic systems, and other species are often responsible for transfer of electrons and $O^{2-}$. For example, the equilibrium between magnetite and hematite may be mediated by water:

$$2Fe_3O_4 + H_2O_{(g)} \rightleftarrows 3Fe_2O_3 + H_2 \qquad 3.123$$

The above two reactions are thermodynamically equivalent in terms of magnetite oxidation. The first reaction is simpler, of course, and hence preferred, but it may sometimes be necessary to consider the proportions of the actual gas species present.

If we can regard magnetite and hematite as pure phases, then their activities are equal to one and the equilibrium constant for reaction 3.121 is the inverse of the oxygen fugacity:

$$K_{MH} = \frac{1}{f_{O_2}} \qquad 3.124$$

We can rewrite equ. 3.86 as:

$$K = e^{-\Delta G_f^o / RT} \qquad 3.125$$

and taking the standard state as 1000 K and 1 bar, we can write:

$$-\log K = \log f_{O_2} = \left( \frac{6\Delta G^o_{f(Fe_2O_3,1000)} - 4\Delta G^o_{f(Fe_3O_4,1000)}}{2.303RT} \right)$$

Thus oxygen fugacity can be calculated directly from the difference in the free energy of formation of magnetite and hematite at the appropriate T and P. Substituting appropriate values into this equation yields a value for log $f_{O_2}$ of –10.86.

It is important to understand that the oxygen fugacity is fixed at this level (though the exact level at which it is fixed is still disputed because of uncertainties in the thermodynamic data) simply by the equilibrium coexistence of magnetite and hematite. The oxygen fugacity does not depend on the proportion of these minerals. For this reason, it is appropriately called a buffer. To understand how this works, imagine some amount of magnetite, hematite and oxygen present in a magma. If the oxygen fugacity is increased by the addition of oxygen to the system, equilibrium in the reaction in equation 3.121 is driven to the right until the log of the oxygen fugacity returns to a value of -10.86. Only when all magnetite is converted to hematite can the oxygen fugacity rise. A drop in oxygen fugacity would be buffered in exactly the opposite way until all hematite were gone. A number of other buffers can be constructed based on reactions such as:

$$3Fe_2SiO_4 + O_2 \rightleftarrows 2Fe_3O_4 + 3SiO_2$$

(fayalite) (magnetite) (quartz)

and

$$Fe + \frac{1}{2}O_2 \rightleftarrows FeO$$

(iron) (wüstite)

These can be used to construct the oxygen buffer curves in Figure 3.21.

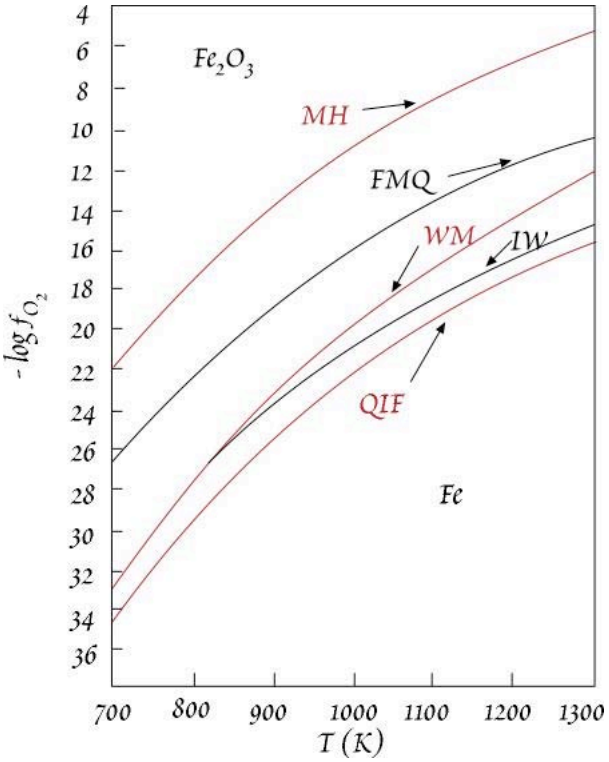



Figure 3.22. Oxygen buffer curves in the system Fe-Si-O at 1 bar. QIF, IW, WM, FMQ, and MH refer to the quartz-iron-fayalite, iron-wüstite, wüstite-magnetite, fayalite-magnetite-quartz and magnetite-hematite buffers respectively.

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## PROBLEMS

1. Consider the following minerals:

anhydrite: $CaSO_4$

bassanite: $CaSO_4.{}^1/_2H_2O$ (the stuff of which plaster of paris is made)

gyspum: $CaSO_4.2H_2O$

a.) If water vapor is the only phase of pure water in the system, how many phases are there in this system and how many components are there?

b.) How many phases are present at invariant points in such a system? How many univariant reactions are possible? Write all univariant reactions, labeling each according the phase that does not participate in the reaction.

2. Consider a system consisting of olivine of variable composition ($(Mg,Fe)_2SiO_4$) and orthopyroxene of variable composition ($(Mg,Fe)SiO_3$). What is the *minimum* number of components needed to describe this system?

3. In section 3.2.1.3, we showed that a system containing $H_2O$, $H_2CO_3$, $HCO_3^-$, $CO_3^{2-}$, $H^+$, and $OH^-$ could be described in terms of components $CO_3^{2-}$, $H^+$, and $OH^-$. Find a different set of components that describe the system equally well. Show that each of the species in the system is an algebraic sum of your chosen components.

4. Use the data in Table 2.2 to construct a temperature-pressure phase diagram that showing the stability fields of calcite and aragonite.

5. Consider the following hypothetical gaseous solution: gases 1 and 2 form an ideal binary solution; at 1000°K, the free energies of formation from the elements are -50kJ/mol for species 1 and -60kJ/mol for species 2.

a.) Calculate $\Delta G_{mixing}$ for the solution at 0.1 increments of $X_2$. Plot your results.

b.) Calculate $\bar{G}$ for *ideal* solution at 0.1 increments of $X_2$. Plot your results.

c.) Using the method of intercepts, find $\mu^1$ and $\mu^2$ in the solution at $X_2 = 0.2$

6. Using the thermodynamic data in Table 2.2, determine which side of the reaction:

$$2Al(OH)_3 \rightleftarrows Al_2O_3 + 3H_2O$$

is stable at 600° C and 400 MPa.

7. The following analysis of water is from the Rhine River as it leaves the Swiss Alps:

| | | | |
|---|---|---|---|
| $HCO_3^-$ | 113.5 ppm | $SO_4^{2-}$ | 36.0 ppm |
| $Cl^-$ | 1.1 ppm | $NO_3^-$ | 1.9 ppm |
| $Ca^{2+}$ | 40.7 ppm | $Mg^{2+}$ | 7.2 ppm |
| $Na^+$ | 1.4 ppm | $K^+$ | 1.2 ppm |

a. Calculate the ionic strength of this water. (Recall that concentrations in ppm are equal to concentrations in mmol $kg^{-1}$ multiplied by formula weight.)

b. Using the Debye-Hückel equation and the data in Table 3.2, calculate the practical activity coefficients for each of these species at 25°C.

8. Seawater has the following composition:

| | | | |
|---|---|---|---|
| $Na^+$ | 0.481 M | $Cl^-$ | 0.560 M |
| $Mg^{2+}$ | 0.0544 M | $SO_4^{2-}$ | 0.0283 M |
| $Ca^{2+}$ | 0.0105 M | $HCO_3^-$ | 0.00238 M |
| $K^+$ | 0.0105 M | | |

a. Calculate the ionic strength.

b. Using the Davies equation and the data in Table 3.2, calculate the practical activity coefficients for each of these species at 25°C.

9. Water from Thonon, France has the following composition:

| Anions | mg/L | Cations | mg/L |
|---|---|---|---|
| $HCO_3^-$ | 332 | $Ca^{2+}$ | 103.2 |
| $SO_4^{2-}$ | 14 | $Mg^{2+}$ | 16.1 |
| $NO_3^-$ | 14 | $K^+$ | 1.4 |
| $Cl^-$ | 8.2 | $Na^+$ | 5.1 |

a. What is the ionic strength of this water?

b. What are the activity coefficients for $HCO_3^-$ and $CO_3^{2-}$ in this water?

c. Assuming an equilibrium constant for the dissociation of bicarbonate:

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$$

of $4.68 \times 10^{-11}$ and a pH of 7.3, what is the equilibrium concentration of $CO_3^{2-}$ in this water?

10. Given the following analysis of biotite and assuming a *mixing-on-site model* for all sites, calculate the activities of the following components:

a.) $KMg_3Si_3AlO_{10}(OH)_2$ (phlogopite)

b.) $KFe_3^{+2}Si_3AlO_{10}(OH)_2$ (annite)

| Site | Ion | Ions per site |
|---|---|---|
| Tetrahedral | Si | 2.773 |
| | Al | 1.228 |
| Octahedral | Al | 0.414 |
| | Ti | 0.136 |
| | $Fe^{+3}$ | 0.085 |
| | $Fe^{+2}$ | 1.390 |
| | Mn | 0.009 |
| | Mg | 0.850 |
| Interlayer | Ca | 0.013 |
| | Na | 0.063 |
| | K | 0.894 |
| Anion | OH | 1.687 |
| | F | 0.037 |

*Hint*: Check your result by making sure the activity of phlogopite in pure phlogopite is 1.

11. Write the equilibrium constant expression for the reaction:

$$CaCO_{3(s)} + 2H^{+}_{(aq)} + SO^{2-}_{4} + H_2O_{(liq)} \Leftrightarrow CaSO_4 \cdot 2H_2O + CO_{2(g)}$$

assuming the solids are pure crystalline phases and that the gas is ideal.

12. The equilibrium constant for the dissolution of galena:

$$PbS_{solid} + 2H^{+} \rightleftarrows Pb^{2+}_{aq} + H_2S^{aq}$$

is $9.12 \times 10^{-7}$ at 80° C. Using the $\gamma_{Pb^{2+}} = 0.11$ and $\gamma_{H_2S} = 1.77$, calculate the equilibrium concentration of $Pb^{2+}$ in aqueous solution at this temperature and at pH's of 6, 5 and 4. Assume the dissolution of galena is the only source of Pb and $H_2S$ in the solution and that there is no significant dissociation of $H_2S$. *Hint:* mass balance requires that $[H_2S] = [Pb^{2+}]$.

13. The first and second dissociation constants for phosphoric acid ($H_3PO_4$) are:

$$K_1 = \frac{\left[H^+\right]\left[H_2PO_4^-\right]}{\left[H_3PO_4\right]} = 7.52 \times 10^{-3}$$

$$K_2 = \frac{\left[H^+\right]\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 6.23 \times 10^{-8}$$

Assuming ideal behavior ($\gamma = 1$), a pH of 3.5, and a third dissociation constant is 0. If you added 1 mole of phosphoric acid to 1 liter water, what will the concentration of $H_2PO_4^-$ be?

14. The first dissociation constant for $H_2S$ is $K_1 = 9.1 \times 10^{-3}$. Neglecting the second dissociation and assuming ideality (i.e. activity equals concentration), what is the pH of 1 liter of pure water if you dissolve 0.01 moles of $H_2S$ in it? What fraction of $H_2S$ has dissociated? *(HINT: assume that the concentration of $OH^-$ is negligible (in other words, no autodissociation of water and use the quadratic equation for your final solution).*

15. Assuming ideal solution behavior for the following:

a.) Show that the boiling point of a substance is increased when another substance is dissolved in it assuming the concentration of the solute in the vapor is small.

b.) By how much will the boiling point of water be elevated when 10% salt is dissolved in it?

15. Find $\Delta\bar{G}$ for the reaction:

$$Pb^{2+} + Mn \rightleftarrows Pb + Mn^{2+}$$

Which side of the reaction is favored? (HINT: use the data in Table 3.3)

16. What is the $\Delta\bar{G}$ for the reaction:

$$Cu^{2+} + e^- \rightleftarrows Cu^+$$

What is the $p\varepsilon°$ for this reaction?

17. Consider a stream with a pH of 6.7 and a total dissolved Fe concentration of 1 mg/L. Assume ideal behavior for this problem.

a. If the stream water is in equilibrium with the atmospheric $O_2$ (partial pressure of 0.2 MPa), what is the $p\varepsilon$ of the water?

b. Assuming they are the only species of Fe in the water, what are the concentrations of $Fe^{3+}$ and $Fe^{2+}$. Use the $p\varepsilon$ you determined in part a.

18. Write reactions for the oxidation of nitrogen gas to aqueous nitrite and nitrate ions that contain the electron and hydrogen ion (i.e., reactions suitable for a *pε-pH* diagram). Write the log equilibrium constant expression for these reactions. Using the data below, calculate the log equilibrium constant for these reactions under standard state conditions). Calculate $p\varepsilon^\circ$ and $E_H^o$ for these reactions. *Hint*: remember, in the standard state, *all* reactants and products have activities of 1.

| species | $\Delta G_f^o$ kJ/mol |
|---|---|
| $H_2O$ | -237.19 |
| $N_2$ (gas) | 0 |
| $NO_3^-$ | -111.3 |
| $NO_2^-$ | -32.2 |

Standard state is 25°C and 0.1 MPa. R = 8.314 J/mole-K.

18. Construct a pε–pH diagram for the following species of sulfur: $HSO_4^-$, $SO_4^{2-}$, $H_2S$, $HS^-$, and $S^{2-}$ at 25°C and 0.1 MPa. The following free energies of formation should provide sufficient information to complete this task.

| species | $\Delta G_f^o$ | species | $\Delta G_f^o$ |
|---|---|---|---|
| $S^{2-}$ (aq) | +85.81 | $H_2O$ | -237.19 |
| $HS^-$ (aq) | +12.09 | $H^+$ | 0 |
| $H_2S$ (aq) | -27.82 | $H_2$ (g) | 0 |
| $SO_4^{2-}$ (aq) | -744.54 | $O_2$ (g) | 0 |
| $HSO_4^-$ (aq) | -755.92 | | |

Values are in kJ/mole, standard state is 25°C and 0.1 MPa. R = 8.314 J/mole-K.

19. Construct a pε–pH diagram for dissolve species of uranium: $UO_2^{2+}$and $U(OH)_5^-$, and the two solid phases $UO_2$ and $U_3O_8$ at 25°C and 0.1 MPa. Assume the activity of dissolved uranium is fixed at $10^{-6}$. The following free energies of formation should provide sufficient information to complete this task.

| species | $\Delta G_f^o$ |
|---|---|
| $U(OH)_5^-$ (aq) | –1630.80 |
| $UO_2^{2+}$ (aq) | -952.53 |
| $UO_2$ (s) | -1031.86 |
| $U_3O_8$ (s) | -3369.58 |
| $H_2O$ | -237.19 |

Values are in kJ/mole, standard state is 25°C and 0.1 MPa. R = 8.314 J/mole-K.