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

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 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

3.9.1   Derivation and definition

Consider a chemical reaction such as:

$$aA + bB \rightleftharpoons cC + dD$$
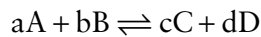
carried out under isobaric and isothermal conditions. The Gibbs free energy change of this reaction can be expressed as:

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

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

$$\Delta G = \sum_i v_i \mu_i = 0 \quad (3.82)$$

where v_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 eqn. 3.46 into 3.82 we obtain:

$$\sum_i v_i \mu_i^o + RT \sum_i v_i \ln a_i = 0 \quad (3.83)$$

or:

$$\sum_i v_i \mu_i^o + RT \ln \prod_i a_i^{v_i} = 0 \quad (3.84)$$

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:

$$K = \prod_i a_i^{v_i} \qquad (3.85)$$

Substituting eqn. 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:

$$\Delta G_r^o = -RT \ln K \qquad (3.86)$$

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 eqn. 3.86 is only valid at that standard-state temperature. If you chose a variable-temperature standard state, then eqn. 3.86 is valid for all temperatures, but $\Delta G°$ is then a function of temperature. The same goes for pressure. Whereas most thermodynamic quantities we have dealt with thus far are additive, equilibrium constants are multiplicative (see Example 3.6).

Example 3.6   Manipulating reactions and equilibrium constant expressions
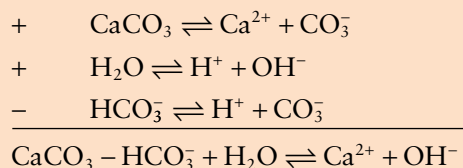
Often we encounter a reaction for which we have no value of the equilibrium constant. In many cases, however, we can derive an equilibrium constant by considering the reaction of interest to be the algebraic sum of several reactions for which we do have equilibrium constant values. For example, the concentration 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:

$$CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^- \qquad (3.87)$$
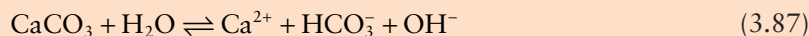
Given the following equilibrium constants, what is the equilibrium constant expression for the above reaction?

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

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

$$
\begin{aligned}
+ \quad & CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^- \\
+ \quad & H_2O \rightleftharpoons H^+ + OH^- \\
- \quad & HCO_3^- \rightleftharpoons H^+ + CO_3^- \\
\hline
& CaCO_3 - HCO_3^- + H_2O \rightleftharpoons Ca^{2+} + OH^-
\end{aligned}
$$

The initial inclination might be to think that if we can sum the reactions, the equilibrium constant of the resulting reaction is the sum of the equilibrium constants of the components. 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 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:

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

3.9.2   The Law of Mass Action

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

$$H_2CO_3 = HCO_3^- + H^+$$
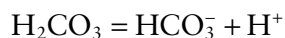
For this particular case, eqn. 3.85 is expressed as:

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

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 is 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 later). 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 of 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 three 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:

$$\left(\frac{\partial \Delta G_r}{\partial P}\right)_T = \Delta V \qquad (2.128)$$

and

$$\left(\frac{\partial \Delta G_r}{\partial T}\right)_T = -\Delta S_r \qquad (2.129)$$

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 pressure 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 eqn. 2.129, we can see that if a reaction A + B → C + D generates heat, then increasing the temperature will retard formation of the products, that is, 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:

$$K_D = \prod_i X_i^{v_i} \qquad (3.88)$$

K_D is related to the equilibrium constant K as:

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

where K_λ is simply the ratio of activity coefficients:

$$K_\lambda = \prod_i \lambda_i^{v_i} \qquad (3.90)$$

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:

$$K^{app} = \prod_i m_i^{v_i} \qquad (3.91)$$

$$K^{app} = \frac{K_{eq}}{K_\gamma} \qquad (3.92)$$

with K_γ defined analogously to K_λ. 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 (see Example 3.7).

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

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Example 3.7   Using the solubility product

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

Answer: Expressing eqn. 3.93 for this case we have:

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

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

$$[Ca^{2+}] = \frac{K_{sp-Fl}}{[F^-]^2} = \frac{3.9 \times 10^{-11}}{[0.1 \times 10^{-3}]^2} = \frac{3.9 \times 10^{-11}}{1 \times 10^{-8}} = 3.9 \times 10^{-3} \text{ M} = 3.9 \text{ mM}$$

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.

3.9.5 Temperature dependence of equilibrium constant

Since $\Delta G° = \Delta H° - T\Delta S°$ and $\Delta G_r° = -RT\ln K$, 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 (see Example 3.8). 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:

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

Example 3.8   Calculating equilibrium constants and equilibrium concentrations

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

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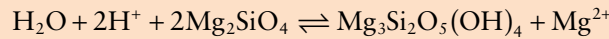
Species	$\Delta H°$ (kJ)	$S°$ (J/K)
$Mg_3Si_2O_5(OH)_4$	−4272.87	434.84
Mg^{2+}	−366.46	109.05
H^+	44.87	106.68
Mg_2SiO_4	−2132.75	186.02
H_2O	−232.19	211.50

If this reaction controlled the concentration of Mg^{2+} of the metamorphic fluid, what would be the activity of Mg^{2+} in that fluid if it had a pH of 4.0 at 300°C?
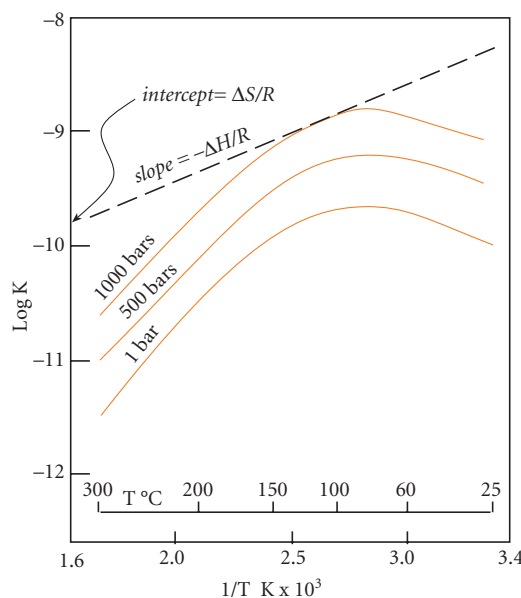
Answer: Helgeson (1967) gives the thermodynamic data shown in the adjacent table for the reactants at 300°C. From these data, we use Hess's Law to calculate ΔH_r and ΔS_r as −231.38 kJ and −253.01 J/K respectively. The equilibrium constant for the reaction may be calculated as:

$$K = \exp\left(-\frac{\Delta H_r^o}{RT} + \frac{\Delta S_r^o}{R}\right) = \exp\left(-\frac{-231.38 \times 10^3}{8.134 \times 573} + \frac{253.01}{8.314}\right) = 7.53 \times 10^7$$

The equilibrium constant for this reaction can be written as: $K = \dfrac{a_{Mg^{2+}} a_{Cry}}{a_{H^+}^2 a_{Fo}^2 a_{H2O}}$ 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:

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

where a and b are $\Delta H°/R$ and $\Delta S°/R$ respectively. If we can assume that ΔH and ΔS 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 $\Delta H°/R$ and an intercept of $\Delta S°/R$. Thus measurements of ln K made over a range of temperatures and plotted vs. $1/T$ provide estimates of $\Delta H°$ and $\Delta S°$. Even if ΔH and ΔS 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 ΔH and ΔS 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 ΔG directly from eqn. 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 eqn. 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*.

3.9.6 Pressure dependence of equilibrium constant

Since

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

and

$$\Delta G_r^o = -RT \ln K$$

then

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

If ΔV_r does not depend on pressure, this equation can be integrated to obtain:

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

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,

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). With permission from Mineralogical Society of America.

geologic 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 choose components will make a difference to how easily we can solve a given problem. Morel and Hering (1993) suggested 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 $C_{v+}A_{v-}$ we may write:

$$v^-[C] = v^+[A] \qquad (3.98)$$

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:

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

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:

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

where $CaCO_{3s}$ is calcite (limestone) and Ca_{aq}^{2+} 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:

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$
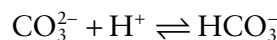
Choosing carbon as a component has the disadvantage that some carbon will be present as organic compounds, which we may not wish to consider. A wiser choice is to define CO_2 as a component. Total CO_2 would then include all carbonate species as well as CO_2 (very often, total CO_2 is expressed instead 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. Example 3.9 illustrates the use of mass balance.

3.10.3 Electrical neutrality

There is an additional condition that electrolyte solutions must meet: *electrical neutrality*.

Example 3.9   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 1×10^{-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 the mass balance equation. We will have to solve the two simultaneously to obtain the answer. Our two equations are:

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

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 ΣHA to 10^{-4}, we calculate $[A^-]$ as $3.16 \cdot 10^{-5}$ M, so 31.6% of the acid is dissociated.

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 additional mathematical constraint on the solution. It is often convenient to rearrange eqn. 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 water in equilibrium with atmospheric CO_2 and containing no other species. The charge balance equation in this case is:

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_2^+]$$

As Example 3.10 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 eqn. 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 reactions between H^+, SO_4^{2-}, HSO_4^-, and H_2SO_4, and need not consider the latter two 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 reaction between NaCl, Na^+, and Cl^-.

Example 3.10   Determining the pH of rainwater 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 rainwater		
	Rain 1 (μM)	Rain 2 (μM)
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 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 will want to verify this assumption when we have obtained a solution). The rest is straightforward. We sum the product of charge times concentration (eqn. 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 μM by multiplying by 10^{-6}) we obtain a pH of 4.6 for the first sample and 3.14 for the second.

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.

Charge balance for rainwater		
	Rain 1	Rain 2
Σ cations	38	204
Σ anions	63	1057
Δ	25	853
pH	4.60	3.07

Carbonate is a somewhat different matter. Over the range of compositions of natural waters, H_2CO_3, 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 concen-trations and we will 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 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:

$$2Fe_3O_4 + \frac{1}{2}O_2 \rightleftharpoons 3Fe_2O_3 \quad (3.101)$$
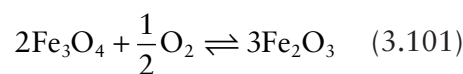
The Fe^{2+} in magnetite loses an electron in this reaction and thereby oxidized; conversely, oxygen gains an electron and is thereby reduced.

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 receptors. 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.

---

[*] 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!

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.
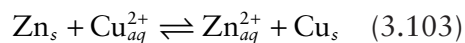
3.11.1   Redox in aqueous solutions

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

$$Fe^{3+}_{aq} + e^- \rightleftharpoons Fe^{2+}_{aq} \qquad (3.102)$$
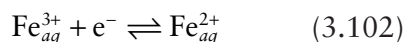
where the subscript aq denotes the aqueous species. This form suggests that the energy involved might be most conveniently measured in an electrochemical cell.

The Daniell cell pictured in Figure 3.18 can be used to measure the energy involved in the

Figure 3.18   Electrode reactions in the Daniell Cell.

exchange of electrons between elements, for example, zinc and copper:

$$Zn_s + Cu^{2+}_{aq} \rightleftharpoons Zn^{2+}_{aq} + Cu_s \quad (3.103)$$

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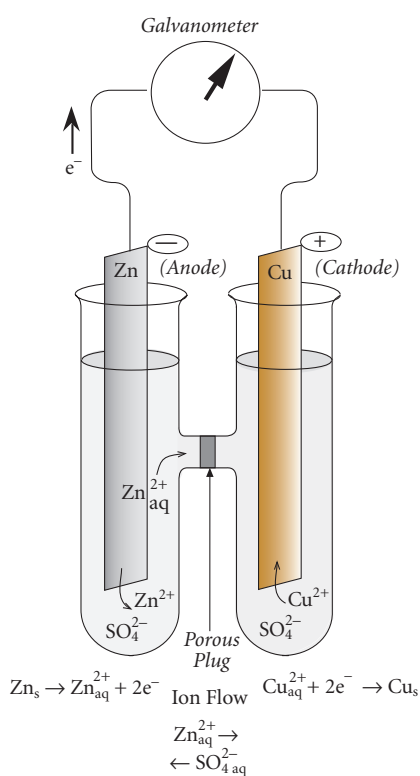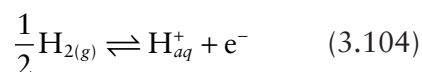
If we could measure the potential of two separate half-cell reactions:

$$Zn_s \rightleftharpoons Zn^{2+}_{aq} + 2e^-$$
$$Cu_s \rightleftharpoons Cu^{2+}_{aq} + 2e^-$$

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 involved in reactions such as 3.102 can be established.
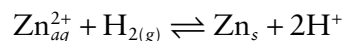
3.11.1.1   Hydrogen scale potential, E_H

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:

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

---

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

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:

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

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

$$Zn^{2+}_{aq} + 2e^- \rightleftharpoons Zn_s \qquad (3.105)$$
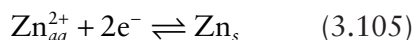
and called the *hydrogen scale potential*, or E_H, of this reaction. Thus the E_H for the reduction of Zn^{+2} to Zn^0 is −0.763 V. The hydrogen scale potentials of a few half-cell reactions are listed in Table 3.3. The sign convention for E_H is that the sign of the potential is positive when the reaction 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 (see Example 3.11).

The half-cell reactions in Table 3.3 are arranged in order of 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° and $p\varepsilon^\circ$ for some half-cell reactions.

Half-cell reaction	E_H°(V)	$p\varepsilon^\circ$
$Li^+ + e^- \rightleftharpoons Li$	−3.05	−51.58
$Ca^{2+} + 2\,e^- \rightleftharpoons Ca$	−2.93	−49.55
$Th^{4+} + 4e^- \rightleftharpoons Th$	−1.83	−30.95
$U^{4+} + 4e^- \rightleftharpoons U$	−1.38	−23.34
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1.18	−19.95
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76	−12.85
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	−0.74	−12.51
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44	−7.44
$Eu^{3+} + e^- \rightleftharpoons Eu^{2+}$	−0.36	−6.08
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13	−2.13
$CO_{2(g)} + 4H^+ + 4e^- \rightleftharpoons CH_2O^* + 2H_2O$	−0.71	−1.2
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.26	−4.34
$2H^+ + 2e^- \rightleftharpoons H_{2(g)}$	0	0
$N_{2(g)} + 6H^+ + 6e^- \rightleftharpoons 2NH_3$	0.093	1.58
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0.34	5.75
$UO_2^{2+} + 2e^- \rightleftharpoons UO_2$	0.41	6.85
$S + 2e^- \rightleftharpoons S^{2-}$	0.44	7.44
$Cu^+ + e^- \rightleftharpoons Cu$	0.52	8.79
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77	13.02
$NO^{3+} + 2H^+ + e^- \rightleftharpoons NO_{2(g)} + H_2O$	0.80	13.53
$Ag^+ + e^- \rightleftharpoons Ag$	0.80	13.53
$Hg^{2+} + 2e^- \rightleftharpoons Hg$	0.85	14.37
$MnO_{2(s)} + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	1.22	20.63
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.23	20.80
$MnO^{4-} + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.51	25.53
$Au^+ + e^- \rightleftharpoons Au$	1.69	28.58
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.72	29.05
$Pt^+ + e^- \rightleftharpoons Pt$	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:

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

and

$$\Delta G° = -z\mathcal{F}E° \qquad (3.107)$$

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, such as:

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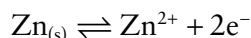
is the free energy of formation of the ion from the pure element. From eqn. 3.106 we can calculate the ΔG for the reduction of zinc as 147.24 kJ/mol. The free energy of formation of Zn^{2+} would be -147.24 kJ/mol. Given the free energy of formation of an ion, we can also use eqn. 3.105 to calculate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

$$\Delta G = \Delta G° + RT \ln \prod_i a_i^{v_i} \qquad (3.108)$$

we can substitute eqns. 3.106 and 3.107 into 3.108 and also write

$$E = E° - \frac{RT}{z\mathcal{F}} \ln \prod_i a_i^{v_i} \qquad (3.109)$$

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

$$E = E° - \frac{0.0592}{z} \log \prod_i a_i^{v_i} \qquad (3.110)$$

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

3.11.1.2   Alternative representation of redox state: $p\varepsilon$

Consider again the reaction:

$$Fe_{aq}^{3+} + e^- \rightleftharpoons Fe_{aq}^{2+} \qquad (3.102)$$
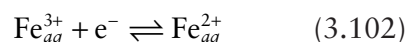
If we were to express the equilibrium constant for this reaction, we would write:

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

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 $p\varepsilon$, which is the negative log of the activity of electrons in solution:

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

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

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

Upon rearranging we have:

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

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

$$p\varepsilon° = \frac{1}{z}\log K \qquad (3.113)$$

(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:

$$p\varepsilon = p\varepsilon° - \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad (3.114)$$

---

[*] 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:

$$Fe^{3+} + 3e^- \rightleftharpoons Fe$$
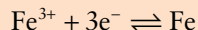
Answer: This reaction is the algebraic sum of two reactions listed in Table 3.3:

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

$$Fe^{2+} + 2e^- \rightleftharpoons Fe$$
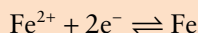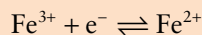
Since the reactions sum, we might assume that we can simply sum the E_H values to obtain the E_H of the net reaction. Doing so, we obtain an E_H of 0.33 V. However, the true E_H of this reaction is -0.037 V. What have we done wrong?
   We have neglected to take into consideration the number of electrons 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.,

$$E_{H(net)} = \frac{1}{z_{net}} \sum_i z_i E_{Hi} \tag{3.115}$$

where the sum is over the component reactions i. Looking at eqn. 3.106, we can see why this is the case. By Hess's Law, the ΔG of the net reaction must be the simple sum of the component reaction ΔGs, but E_H values are obtained by multiplying ΔG by z. Equation 3.115 is derived by combining eqn. 3.106 and Hess's Law. Using eqn. 3.115, we obtain the correct E_H of -0.037 V.

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

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

(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, although 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, eqn, 3.116 provides a more accurate definition of $p\varepsilon$ than does eqn. 3.111.
   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+}). $p\varepsilon$, and E_H, are particularly useful concepts when
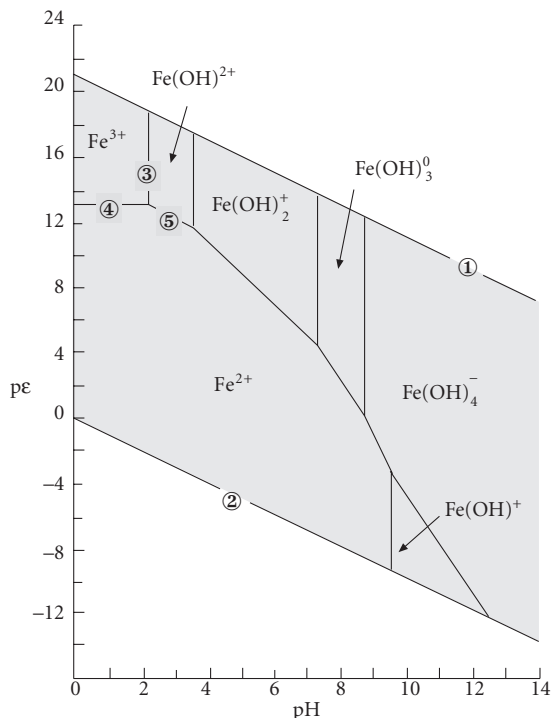
Figure 3.19 $p\varepsilon$–pH diagram showing predominance regions for ferric and ferrous iron and their hydrolysis products in aqueous solution at 25°C and 1 bar. After Nordstrom and Munoz (1986). With permission from John Wiley & Sons.

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 $p\varepsilon$–pH diagrams

$p\varepsilon$–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 $p\varepsilon$–pH diagram for iron, is shown in Figure 3.19. $p\varepsilon$–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 *predominate* under the $p\varepsilon$–pH conditions within the regions. Indeed, in Figure 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 condi-

tions 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 $p\varepsilon$–pH diagram is a type of *activity* 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 $p\varepsilon = a + b \cdot$ pH. With an equation in this form, b is a slope and a is an intercept on a $p\varepsilon$–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 Figure 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:

$$\frac{1}{2}O_{2(g)} + 2e^- + 2H^+_{aq} \rightleftharpoons H_2O$$
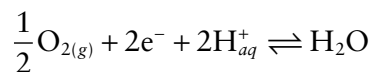
The equilibrium constant for this reaction is:

$$K = \frac{a_{H_2O}}{P_{O_2}^{1/2} a_{e^-}^2 a_{H^+}^2} \tag{3.117}$$

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:

$$p\varepsilon = 20.78 - pH \tag{3.118}$$

Equation 3.118 plots on a $p\varepsilon$–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:

$$H^+_{aq} + e^- \rightleftharpoons \frac{1}{2} H_{2(g)}$$
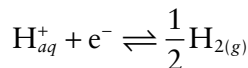
Because $\Delta G^\circ_r = 0$ and log K = 0 (by convention), we have $p\varepsilon = -pH$ for this reaction: a slope of 1 and intercept of 0. This is labeled as line ② on Figure 3.19. Water is stable between these two lines (region shown in gray on Figure 3.19).

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+}:

$$Fe^{3+}_{aq} + H_2O \rightleftharpoons Fe(OH)^{2+}_{aq} + H^+$$
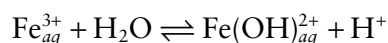
The equilibrium constant for this reaction is 0.00631. The equilibrium constant expression is then:

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

Region boundaries on $p\varepsilon$–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 $p\varepsilon$ (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, such as $Fe(OH)^0_3$ 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.

Now consider equilibrium between Fe^{2+} and Fe^{3+} (eqn. 3.102). The $p\varepsilon^\circ$ for this reac-

tion is 13.0 (Table 3.3), hence from eqn. 3.112 we have:

$$p\varepsilon = 13.0 - \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad (3.119)$$

When the activities are equal, this equation reduces to:

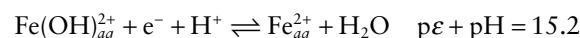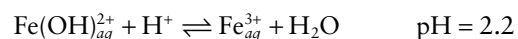$$p\varepsilon = 13.0$$

and therefore plots as a horizontal line at $p\varepsilon = 13$ 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:

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

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:

$Fe^{3+}_{aq} + e^- \rightleftharpoons Fe^{2+}_{aq}$	$p\varepsilon = 13.0$
$Fe(OH)^{2+}_{aq} + H^+ \rightleftharpoons Fe^{3+}_{aq} + H_2O$	pH = 2.2

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

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 eqn. 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:

$$2Fe_3O_4 + H_2O \rightleftharpoons 3Fe_2O_3 + 2H^+ + 2e^-$$
$$(3.120)$$
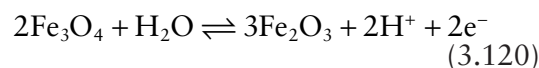
Assuming unit activity of all phases, the equilibrium constant expression for this reaction is:

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

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 ΔG_r using Hess's Law and the equilibrium constant using eqn. 3.86. Doing so, we find log $K = -5.77$. Rearranging eqn. 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 $p\varepsilon$) 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:

$$Fe_3O_4 + 8H^+ + 2e^- \rightleftharpoons 3Fe^{2+} + 4H_2O$$
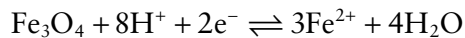
The equilibrium constant for this reaction is 7×10^{29}. Written in log form:

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

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:

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

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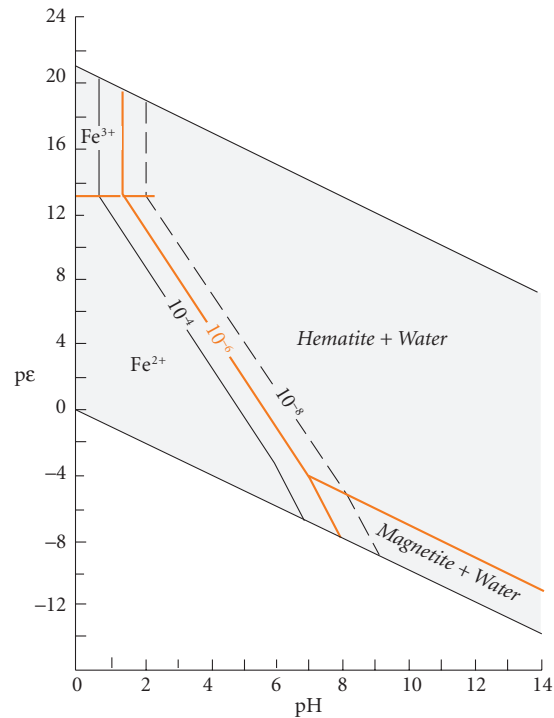
Figure 3.20   Stability regions for magnetite and hematite in equilibrium with an iron-bearing aqueous solution. Red lines are for a Fe_{aq} activity of 10^{-6}, black lines for activities of 10^{-4} and 10^{-8}. The latter is dashed.

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, while for lower concentrations it will contract.

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

$$Fe_2O_3 + 6H^+ + 2e^- \rightleftharpoons 2Fe^{2+} + 3H_2O$$
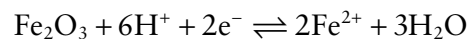
The equilibrium constant (which may again be calculated from ΔG_r) for this reaction is 23.79.

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 $p\varepsilon$ 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:

$$Fe_2O_3 + 6H^+ \rightleftharpoons 2Fe^{3+} + 3H_2O$$
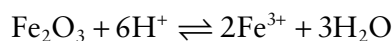
The equilibrium constant expression is:

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

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.

The boundary between predominance of Fe^{3+} and Fe^{2+} is independent of the Fe concentration in solution, and is the same as eqn. 3.119 and Figure 3.18, namely $p\varepsilon = 13$.

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 $p\varepsilon$ increases. Significant concentrations of the Fe^{3+} ion ($>10^{-6}$ m) will be found only in very acidic, oxidizing environments.

Figure 3.21 illustrates the pH and $p\varepsilon$ values that characterize a variety of environments on and near the surface of the Earth. Comparing this figure with pH–$p\varepsilon$ 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
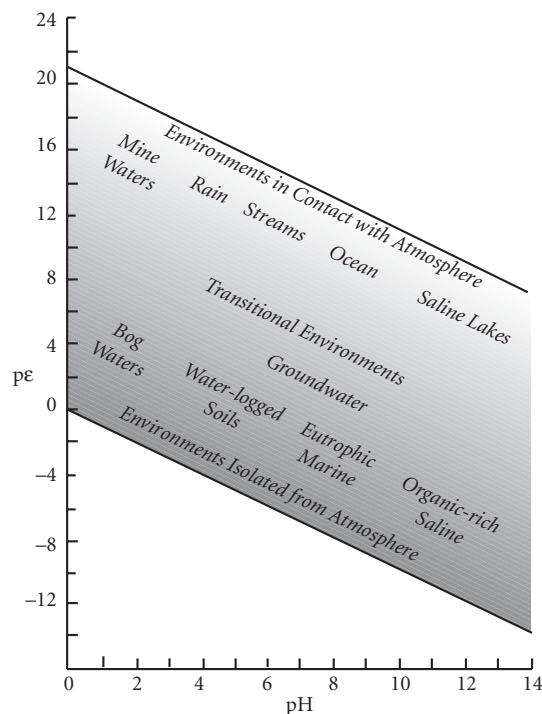

Figure 3.21 pε and pH of various waters on and near the surface of the Earth. From Garrels and Christ (1965).

expect to find magnetite precipitating only from reduced seawater or in organic-rich, highly saline waters.

### 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:

$$4Fe_3O_4 + O_{2(g)} \rightleftharpoons 6Fe_2O_3 \quad (3.122)$$
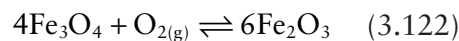
(or alternatively, as we wrote in eqn. 3.101) rather than the way we expressed it in eqn. 3.120. We note, however, there is negligible molecular oxygen in magmatic systems, and other species are often responsible for transfer of electrons and O^{2-}. For example, the equilibrium between magnetite and hematite may be mediated by water:

Balancing redox reactions for pε–pH diagrams

While many redox reactions are straightforward, balancing more complex redox reactions for $p\varepsilon$–pH diagrams can be a bit more difficult, but a few simple rules make it 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:

$$NH_4^+ = NO_3^-$$
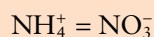
The next step is to balance the oxygen. We don't want to use O_2 gas to do this. We used O_2 at a partial pressure of 1 to define the top boundary for the water stability region. Within the region of stability of water, the O_2 concentration will be lower and we don't necessarily know its value. This is usually best done using water:

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

Next balance the hydrogen using H^+:

$$3H_2O + NH_4^+ = NO_3^- + 10H^+$$
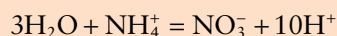
Finally, we use electrons to balance charge:

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

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, while 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.

$$2Fe_3O_4 + H_2O_{(g)} \rightleftharpoons 3Fe_2O_3 + H_2 \quad (3.123)$$
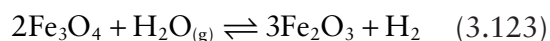
The above two reactions are thermodynamically equivalent in terms of magnetite oxidation. The first reaction is simpler, of course, and hence preferred, but it may sometimes be necessary to consider the proportions of the actual gas species present.

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:

$$K_{MH} = \frac{1}{f_{O_2}} \quad (3.124)$$

We can rewrite eqn. 3.86 as:

$$K = e^{-\Delta G_f^o / RT} \quad (3.125)$$

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

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

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.
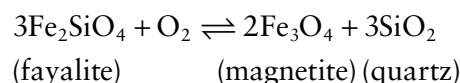
It is important to understand that the oxygen fugacity is fixed at this level (though the exact level at which it is fixed is still disputed because of uncertainties in the thermodynamic data) simply by the equilibrium coexistence of magnetite and hematite. The
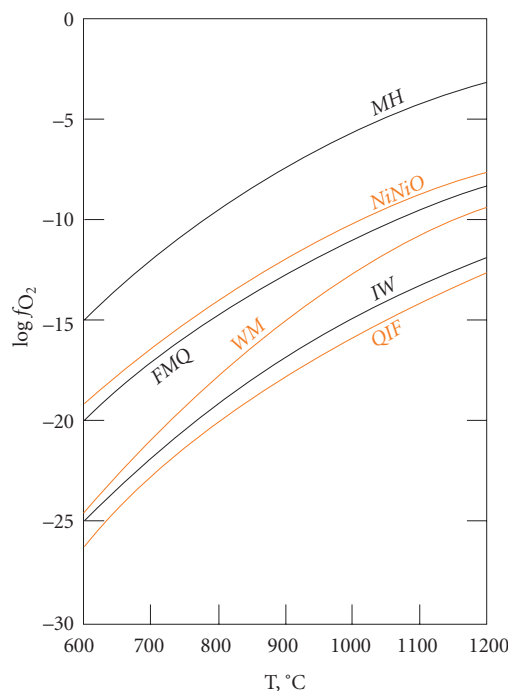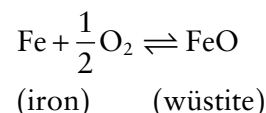
Figure 3.22 Oxygen buffer curves in the system Fe-Si-O at 1 bar. QIF, IW, WM, FMQ, and MH refer to the quartz–iron–fayalite, iron–wüstite, wüstite–magnetite, fayalite–magnetite–quartz and magnetite–hematite buffers respectively. After Nordstrom and Munoz (1986). With permission from John Wiley & Sons.

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 eqn. 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:

$$3Fe_2SiO_4 + O_2 \rightleftharpoons 2Fe_3O_4 + 3SiO_2$$
$$\text{(fayalite)} \qquad \text{(magnetite)} \text{(quartz)}$$

and

$$Fe + \frac{1}{2}O_2 \rightleftharpoons FeO$$
$$\text{(iron)} \qquad \text{(wüstite)}$$

These can be used to construct the oxygen buffer curves in Figure 3.22.

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