Careful measurements on the metal–ligand complex Fe(SCN)$^{2+}$ suggest that its stability decreases in the presence of inert ions. We can demonstrate this by adding an inert salt to an equilibrium mixture of Fe$^{3+}$ and SCN$^\text{-}$. Figure 6.15a shows the result of mixing together equal volumes of 1.0 mM FeCl$_3$ and 1.5 mM KSCN, both of which are colorless. The solution's reddish–orange color is due to the formation of Fe(SCN)$^{2+}$ (the 1mM FeCl$_3$ also contains a few drops of concentrated HNO$_3$ to prevent the precipitation of Fe(OH)$_3$.)

$$\text{Fe}^{3+}(aq)+\text{SCN}^\text{-}(aq)\rightleftharpoons\text{Fe(SCN)}^{2+}(aq)\label{6.61}$$

Adding 10 g of KNO$_3$ to the solution and stirring to dissolve the solid, produces the result shown in Figure 6.15b. The solution's lighter color suggests that adding KNO$_3$ shifts reaction \(\ref{6.61}\) to the left, decreasing the concentration of Fe(SCN)$^{2+}$ and increasing the concentrations of Fe$^{3+}$ and SCN$^\text{-}$. The result is a decrease in the complex's formation constant, $K_1$.

$$K_1=\frac{[\text{Fe(SCN)}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^\text{-}]}\label{6.62}$$

**Figure 6.15:** The effect of a inert salt on a reaction’s equilibrium position is shown by the solutions in these two beakers. The beaker on the left contains equal volumes of 1.0 mM FeCl$_3$ and 1.5 mM KSCN. The solution’s color is due to the formation of the metal–ligand complex Fe(SCN)$^{2+}$. Adding 10 g of KNO$_3$ to the beaker on the left produces the result shown on the right. The lighter color suggests that there is less Fe(SCN)$^{2+}$ as a result of the equilibrium in reaction 6.61 shifting to the left.

Why should adding an inert electrolyte affect a reaction’s equilibrium position? We can explain the effect of KNO$_3$ on the formation of Fe(SCN)$^{2+}$ by considering the reaction on a microscopic scale. The solution in Figure 6.15b contains a variety of cations and anions—Fe$^{3+}$, SCN$^\text{-}$, K$^+$, NO$_3^-$, H$_3$O$^+$, and OH$^-$. Although the solution is homogeneous, on average, there are slightly more anions in regions near Fe$^{3+}$ ions, and slightly more cations in regions near SCN$^\text{-}$ ions. As shown in Figure 6.16, each Fe$^{3+}$ ion and SCN$^\text{-}$ ion is surrounded by an ionic atmosphere of opposite charge ($\delta^-$ and $\delta^+$) that partially screen the ions from each other. Because each ion’s apparent charge at the edge of its ionic atmosphere is less than its actual charge, the force of attraction between the two ions is smaller. As a result, the formation of the Fe(SCN)$^{2+}$ is slightly less favorable and the formation constant in Equation \(\ref{6.62}\) is slightly smaller. Higher concentrations of
KNO$_3$ increase $\delta^-$ and $\delta^+$, resulting in even smaller values for the formation constant.

**Figure 6.16:** Ions of Fe$^{3+}$ and SCN$^-$ are surrounded by ionic atmospheres with net charges of $\delta^-$ and $\delta^+$. Because of these ionic atmospheres, each ion’s apparent charge at the edge of its ionic atmosphere is less than the ion’s actual charge.

### Ionic Strength

To factor the concentration of ions into the formation constant for Fe(SCN)$_{2}^{2+}$, we need a way to express that concentration in a meaningful way. Because both an ion’s concentration and its charge are important, we define the solution’s **ionic strength**, $\mu$ as

$$\mu = \frac{1}{2} \sum ic_i z_i^2$$

where $c_i$ and $z_i$ are the concentration and charge of the $i$th ion.

**Example 6.13**

Calculate the ionic strength for a solution of 0.10 M NaCl. Repeat the calculation for a solution of 0.10 M Na$_2$SO$_4$.

**Solution**

The ionic strength for 0.10 M NaCl is

$$\begin{align*}
&= \frac{1}{2} \left\{ [\text{Na}^+] \times (+1)^2 + [\text{Cl}^-] \times (-1)^2 \right\} \\
&= \frac{1}{2} \left\{ (0.10) \times (+1)^2 + (0.10) \times (-1)^2 \right\} \\
&= 0.10 \text{ M}
\end{align*}$$

For 0.10 M Na$_2$SO$_4$ the ionic strength is
\[\begin{align*}
&= \frac{1}{2} \left\{ [Na^+] \times (+1)^2 + [SO_4^{2-}] \times (-2)^2 \right\} \\
&= \frac{1}{2} \left\{ (0.10) \times (+1)^2 + (0.20) \times (-2)^2 \right\} \\
&= 0.30 \text{ M}
\end{align*}\]

In calculating the ionic strengths of these solutions we are ignoring the presence of \( H_3O^+ \) and \( OH^- \), and, in the case of \( Na_2SO_4 \), the presence of \( HSO_4^- \) from the base dissociation reaction of \( SO_4^{2-} \).

In the case of 0.10 M \( NaCl \), the concentrations of \( H_3O^+ \) and \( OH^- \) are \( 1.0 \times 10^{-7} \), which is significantly smaller than the concentrations of \( Na^+ \) and \( Cl^- \).

Because \( SO_4^{2-} \) is a very weak base (\( K_b = 1.0 \times 10^{-12} \)), the solution is only slightly basic (\( pH = 7.5 \)), and the concentrations of \( HSO_4^- \), \( OH^- \), and \( Cl^- \) are negligible.

Although we can ignore the presence of \( H_3O^+ \), \( OH^- \), and \( HSO_4^- \) when calculating the ionic strength of these two solutions, be aware that an equilibrium reaction may well generate ions that affect the solution’s ionic strength.

Note that the unit for ionic strength is molarity, but that a salt’s ionic strength need not match its molar concentration. For a 1:1 salt, such as \( NaCl \), ionic strength and molar concentration are identical. The ionic strength of a 2:1 electrolyte, such as \( Na_2SO_4 \), is three times larger than the electrolyte’s molar concentration.

### Activity and Activity Coefficients

Figure 6.15 shows that adding \( KNO_3 \) to a mixture of \( Fe^{3+} \) and \( SCN^- \) decreases the formation constant for \( Fe(SCN)^{2+} \). This creates a contradiction. Earlier in this chapter we showed that there is a relationship between a reaction’s standard-state free energy, \( \Delta G^0 \), and its equilibrium constant, \( K \).

\[ \Delta G^\circ = -RT \ln K \]

Because a reaction has only one standard-state, its equilibrium constant must be independent of solution conditions. Although ionic strength affects the apparent formation constant for \( Fe(SCN)^{2+} \), reaction 6.61 must have an underlying thermodynamic formation constant that is independent of ionic strength.

The apparent formation constant for \( \langle Fe(SCN)^{2+} \rangle \), as shown in Equation 6.62, is a function of concentrations. In place of concentrations, we define the true thermodynamic equilibrium constant using activities. The activity of species \( A \), \( a_A \), is the product of its concentration, \( [A] \), and a solution-dependent activity coefficient, \( \gamma_A \).

\[ a_A = [A] \gamma_A \]

The true thermodynamic formation constant for \( Fe(SCN)^{2+} \), therefore, is

\[ K_1 = \frac{[Fe(SCN)^{2+}][Fe^{3+}][SCN^-]}{[Fe^{3+}][SCN^-]} \]
Unless otherwise specified, the equilibrium constants in the appendices are thermodynamic equilibrium constants.

The activity coefficient for a species corrects for any deviation between its physical concentration and its ideal value. For a gas, a pure solid, a pure liquid, or a non-ionic solute, the activity coefficient is approximately one under most reasonable experimental conditions. For a gas the proper terms are fugacity and fugacity coefficient, instead of activity and activity coefficient.) For reactions involving only these species, the difference between activity and concentration is negligible. The activity coefficient for an ion, however, depends on the solution’s ionic strength, the ion’s charge, and the ion’s size. It is possible to calculate activity coefficients using the extended Debye-Hückel equation

\[
\log\gamma_A = \frac{-0.51 \times z_A^2 \times \sqrt{\mu}}{1 + 3.3 \times \alpha_A \times \sqrt{\mu}} \tag{6.63}
\]

where \(z_A\) is the ion’s charge, \(\alpha_A\) is the effective diameter of the hydrated ion in nanometers (Table 6.2), \(\mu\) is the solution’s ionic strength, and 0.51 and 3.3 are constants appropriate for an aqueous solution at 25\(^\circ\)C. An ion’s effective hydrated radius is the radius of the ion plus those water molecules closely bound to the ion. The effective radius is greater for smaller, more highly charged ions than it is for larger, less highly charged ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Effective Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_3)O(^+)</td>
<td>0.9</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>0.6</td>
</tr>
<tr>
<td>Na(^+), IO(_3)(^-), HSO(_3)(^-), HCO(_3)(^-), H(_2)PO(_4)(^-)</td>
<td>0.45</td>
</tr>
<tr>
<td>OH(^-), F(^-), SCN(^-), HS(^-), ClO(_3)(^-), ClO(_4)(^-), MnO(_4)(^-)</td>
<td>0.35</td>
</tr>
<tr>
<td>K(^+), Cl(^-), Br(^-), I(^-), CN(^-), NO(_2)(^-), NO(_3)(^-)</td>
<td>0.3</td>
</tr>
<tr>
<td>Cs(^+), Tl(^+), Ag(^+), NH(_4)(^+)</td>
<td>0.25</td>
</tr>
<tr>
<td>Mg(_2)(^+), Be(_2)(^+)</td>
<td>0.8</td>
</tr>
<tr>
<td>Ca(_2)(^+), Cu(_2)(^+), Zn(_2)(^+), Sn(_2)(^+), Mn(_2)(^+), Fe(_2)(^+), Ni(_2)(^+), Co(_2)(^+)</td>
<td>0.6</td>
</tr>
<tr>
<td>Sr(_2)(^+), Ba(_2)(^+), Cd(_2)(^+), Hg(_2)(^+), S(_2)(^-)</td>
<td>0.5</td>
</tr>
<tr>
<td>Pb(_2)(^+), CO(_3)(^2-), SO(_3)(^2-)</td>
<td>0.45</td>
</tr>
<tr>
<td>Hg(_2)(^2+), SO(_4)(^2-), S(_2)O(_3)(^2-), CrO(_4)(^2-), HPO(_4)(^2-)</td>
<td>0.40</td>
</tr>
<tr>
<td>Al(_3)(^+), Fe(_3)(^+), Cr(_3)(^+)</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Several features of Equation \ref{6.63} deserve mention. First, as the ionic strength approaches zero an ion's activity coefficient approaches a value of one. In a solution where \( \mu = 0 \), an ion’s activity and its concentration are identical. We can take advantage of this fact to determine a reaction’s thermodynamic equilibrium constant by measuring the apparent equilibrium constant for several increasingly smaller ionic strengths and extrapolating back to an ionic strength of zero. Second, an activity coefficient is smaller, and the effect of activity is more important, for an ion with a higher charge and a smaller effective radius. Finally, the extended Debye-Hückel equation provides a reasonable value for an ion’s activity coefficient when the ionic strength is less than 0.1. Modifications to Equation \ref{6.63} extend the calculation of activity coefficients to higher ionic strengths.\(^6\)

### Including Activity Coefficients When Solving Equilibrium Problems

Earlier in this chapter we calculated the solubility of \( \text{Pb(IO}_3\text{)}_2 \) in deionized water, obtaining a result of \( 4.0 \times 10^{-5} \text{ mol/L} \). Because the only significant source of ions is from the solubility reaction, the ionic strength is very low and we can assume that \( \gamma \approx 1 \) for both \( \text{Pb}^{2+} \) and \( \text{IO}_3^- \). In calculating the solubility of \( \text{Pb(IO}_3\text{)}_2 \) in deionized water, we do not need to account for ionic strength. But what if the we need to know the solubility of \( \text{Pb(IO}_3\text{)}_2 \) in a solution containing other, inert ions? In this case we need to include activity coefficients in our calculation.

**Example 6.14**

Calculate the solubility of \( \text{Pb(IO}_3\text{)}_2 \) in a matrix of 0.020 M \( \text{Mg(NO}_3\text{)}_2 \).

**Solution**

We begin by calculating the solution’s ionic strength. Since \( \text{Pb(IO}_3\text{)}_2 \) is only sparingly soluble, we will assume that we can ignore its contribution to the ionic strength; thus

\[
\left( \frac{1}{2} \right) \left( 0.020 \text{ M} \times 2^2 + 0.040 \text{ M} \times (-1) \right) = 0.060 \text{ M}
\]

As is true for any assumption, we will need to verify that it does not introduce too much error into our calculation.

Next, we use Equation \ref{6.63} to calculate the activity coefficients for \( \text{Pb}^{2+} \) and \( \text{IO}_3^- \).

\[
\log \gamma_{\text{Pb}^{2+}} = -0.51 \times 2 \times 0.060 - 0.1 \times 2 \times 0.45 \times 0.060 = -0.366
\]
\[\gamma_{\text{Pb}^{2+}}=0.431\]
\[\log\gamma_{\text{IO}_3^-}=\dfrac{-0.51\times(-1)^2\times\sqrt{0.060}}{1+3.3\times0.45\times\sqrt{0.060}}=-0.0916\]
\[\gamma_{\text{IO}_3^-}=0.810\]

Defining the equilibrium concentrations of Pb\(^{2+}\) and IO\(_3^-\) in terms of the variable \(x\)

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>Pb(IO(_3))(_2) (s)</th>
<th>⇌</th>
<th>Pb(^{2+}) (aq)</th>
<th>+</th>
<th>2IO(_3^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>solid</td>
<td></td>
<td>0</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>solid</td>
<td></td>
<td>+(x)</td>
<td></td>
<td>+2x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>solid</td>
<td></td>
<td>(x)</td>
<td></td>
<td>2x</td>
</tr>
</tbody>
</table>

and substituting into the thermodynamic solubility product for Pb(IO\(_3\))\(_2\) leaves us with

\[K_{\text{sp}}=a_{\text{Pb}^{2+}}a_{\text{IO}_3^-}^2=\gamma_{\text{Pb}^{2+}}[\text{Pb}^{2+}]\gamma_{\text{IO}_3^-}^2[\text{IO}_3^-]^2=2.5\times10^{-13}\]

\[K_{\text{sp}}=(0.431)(x)(0.810)^2(2x)^2=2.5\times10^{-13}\]

\[K_{\text{sp}}=1.131x^3=2.5\times10^{-13}\]

Solving for \(x\) gives \(6.0 \times 10^{-5}\), or a molar solubility of \(6.0 \times 10^{-5}\) mol/L. Ignoring activity, as we did in our earlier calculation, gives the molar solubility as \(4.0 \times 10^{-5}\) mol/L. Failing to account for activity in this case underestimates the molar solubility of Pb(IO\(_3\))\(_2\) by 33%.

The solution’s equilibrium composition is

\[\gamma_{\text{Pb}^{2+}}=6.0\times10^{-5}\;\text{M}\]
\[\gamma_{\text{IO}_3^-}=1.2\times10^{-4}\;\text{M}\]
\[\gamma_{\text{Mg}^{2+}}=0.020\;\text{M}\]
\[\gamma_{\text{NO}_3^-}=0.040\;\text{M}\]

Because the concentrations of Pb\(^{2+}\) and IO\(_3^-\) are much smaller than the concentrations of Mg\(^{2+}\) and NO\(_3^-\), our decision to ignore the contribution of Pb\(^{2+}\) and IO\(_3^-\) to the ionic strength is reasonable.

How do we handle the calculation if we can not ignore the concentrations of Pb\(^{2+}\) and IO\(_3^-\)? One approach is to use
the method of successive approximations. First, we recalculate the ionic strength using the concentrations of all ions, including Pb\(^{2+}\) and IO\(_3^-\). Next, we recalculate the activity coefficients for Pb\(^{2+}\) and IO\(_3^-\), and then recalculate the molar solubility. We continue this cycle until two successive calculations yield the same molar solubility within an acceptable margin of error.

As this example shows, failing to correct for the effect of ionic strength can lead to a significant error in an equilibrium calculation. Nevertheless, it is not unusual to ignore activities and to assume that the equilibrium constant is expressed in terms of concentrations. There is a practical reason for this—in an analysis we rarely know the exact composition, much less the ionic strength of aqueous samples or of solid samples brought into solution. Equilibrium calculations are a useful guide when developing an analytical method; however, only by completing an analysis and evaluating the results can we judge whether our theory matches reality. In the end, our work in the laboratory is the most critical step in developing a reliable analytical method.

This is a good place to revisit the meaning of pH. In Chapter 2, we defined pH as

\[
\text{pH} = -\log[H_3O^+]
\]

Now we see that the correct definition is

\[
\text{pH} = -\log[a_{H_3O^+}] = -\log[\gamma_{H_3O^+}[H_3O^+]]
\]

Failing to account for the effect of ionic strength can lead to a significant error in the reported concentration of H\(_3\)O\(^+\). For example, if the pH of a solution is 7.00 and the activity coefficient for H\(_3\)O\(^+\) is 0.90, then the concentration of H\(_3\)O\(^+\) is 1.11 \times 10^{-7} \text{ M}, not 1.00 \times 10^{-7} \text{ M}, an error of +11\%. Fortunately, in developing and carrying out analytical methods, we are more interested in controlling pH than in calculating [H\(_3\)O\(^+\)]. As a result, the difference between the two definitions of pH is rarely a significant concern.

Exercise 6.13

Calculate the molar solubility of Hg\(_2\)Cl\(_2\) in 0.10 M NaCl, taking into account the effect of ionic strength. Compare your answer to that from Practice Exercise 6.8 in which you ignored the effect of ionic strength.

Click here to review your answer to this exercise.

Contributors

- David Harvey (DePauw University)