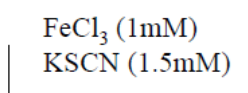
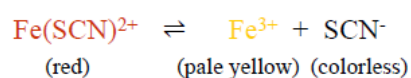


Activity and the systematic treatment of Equilibrium

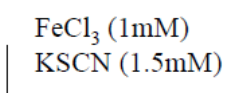
Chapter 7, Sec 7.1, 7.2, 7.3, 7.4 and 7.5

7-1. The Effect of Ionic Strength on Solubility of Salts

< Color plate 3 >



$\mu \cong 0 \text{ M}$
(red)

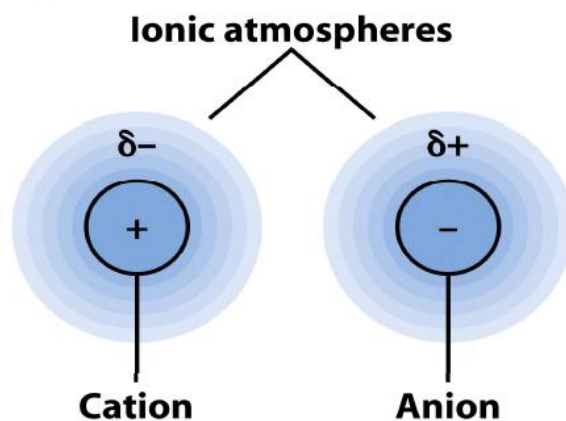


$\mu \cong 0.4 \text{ M}$ (by adding KNO_3)
(the red color fades)

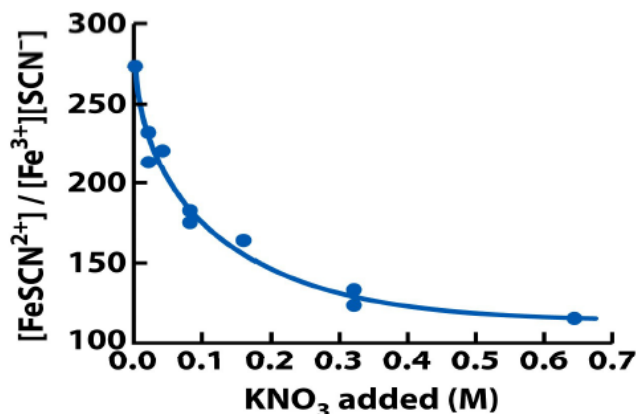
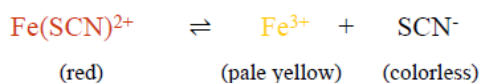
- Adding any “inert” salt to any sparingly soluble salt (or complex) increases the solubility of the latter.
→ Ionic Atmosphere Model

Ionic Atmosphere Model

- An ionic atmosphere surrounds ions in solution.
- The greater the ionic strength of a solution, the higher the charge in the ionic atmosphere.
- Each ion-plus-atmosphere contains less net charge and there is less attraction between any particular cation and anion.

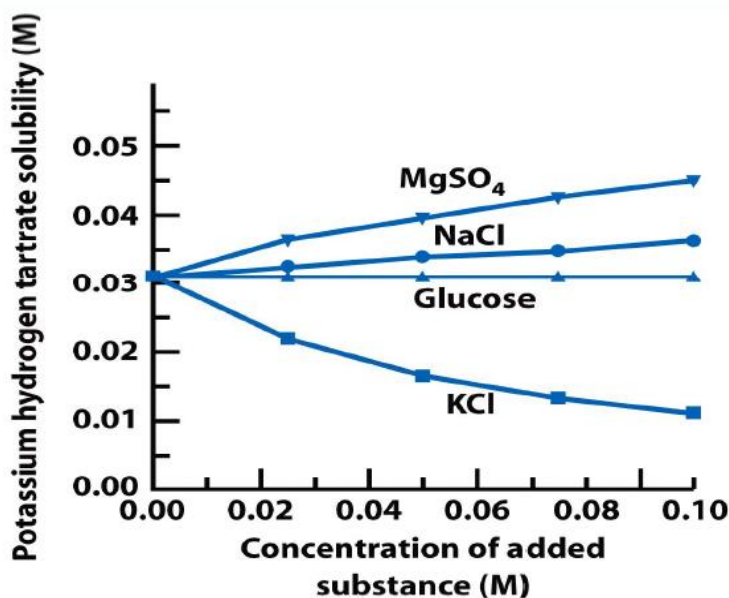


7-1. The Effect of Ionic Strength on Solubility of Salts



Adding any “inert” salt to any sparingly soluble salt (or complex) increases the solubility of the latter.

Solubility of potassium hydrogen tartrate (p.144)



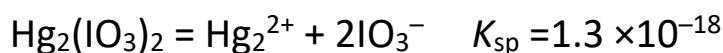
Solubility of potassium hydrogen tartrate increases when the salts MgSO₄ or NaCl are added. There is no effect when the neutral compound glucose is added.

Addition of KCl decreases the solubility. (Why?)

Bitartrate," J. Chem. Ed. 1998, 75, 1628.]

Example: Molar solubility of $\text{Hg}_2(\text{IO}_3)_2$ in distilled water and in 0.050M KNO_3 + saturated solution of mercurous iodate

Mercurous iodate in distilled water



$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{IO}_3^-]^2 = x(2x)^2 = 4x^3 = 1.3 \times 10^{-18}$$

$$x = [\text{Hg}_2^{2+}] = 6.9 \times 10^{-7} \text{M}$$

0.050M KNO_3 + saturated solution of mercurous iodate

$$[\text{Hg}_2^{2+}] = 1.0 \times 10^{-6} \text{M}$$

\Rightarrow Ion dissociation is increased by increasing the ionic strength

What Do We Mean by “Ionic Strength”?

Ionic strength, μ , is a measure of the total concentration of ions in solution. The more highly charged an ion, the more it is counted.

Or Ionic strength, μ is a measure of the average electrostatic interactions among ions in an electrolyte.

$$\mu = \frac{1}{2} \sum_i c_i z_i^2 = \frac{1}{2} (c_1 z_1^2 + c_2 z_2^2 \pm \dots)$$

where c_i is the concentration of the i th species and z_i is its charge. The sum extends over *all* ions in solution.

Example 1) Find the ionic strength of (a) 0.010 M KNO_3 ; (b) 0.010 M K_2SO_4 ; (c) 0.010 M $\text{Al}(\text{NO}_3)_3$.

Answer:

$$(a) \quad \mu = \frac{1}{2} [0.010 (1)^2 + 0.010 (-1)^2] = 0.010 \text{ M}$$

$$(b) \quad \mu = \frac{1}{2} [0.020 (1)^2 + 0.010 (-2)^2] = 0.030 \text{ M}$$

$$(c) \quad \mu = \frac{1}{2} [0.010 (+3)^2 + 0.030 (-1)^2] = 0.060 \text{ M}$$

Example 2) Find the ionic strength of 0.1 mM Na₂SO₄ + 0.1 mM KCl

$$\mu = (1/2)\{(0.1 \times 2)(+1)^2 + (0.1)(-2)^2 + (0.1)(+1)^2 + (0.1)(-1)^2\} \\ = 0.4 \text{ mM}$$

Q) What is the ionic strength of 0.5 mM CaCl₂? (Answer: 1.5 mM)

Effect of Ionic Charge on Ionic Strength

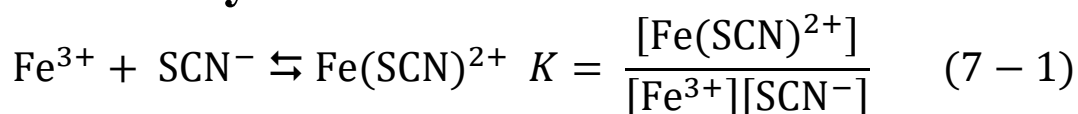
| Electrolyte | Molarity | Ionic strength |
|-------------|----------|---|
| 1:1 | M | M {NaCl} |
| 2:1 | M | 3M {Ba(NO ₃) ₂ ; Na ₂ SO ₄ } |
| 3:1 | M | 6M {Al(NO ₃) ₃ ; Na ₃ PO ₄ } |
| 2:2 | M | 4M {MgSO ₄ } |

The salt effect (also called the electrolyte effect)

Influence of ions on the activities of reagents.

The electrolyte effect results from the electrostatic attractive and repulsive forces that exist between the ions of an electrolyte and the ions involved in an equilibrium. These forces cause each ion from the dissociated reactant to be surrounded by a sheath of solution that contains a slight excess of electrolyte ions of opposite charge.

7.2 Activity Coefficients



Equation 7-1 does not predict any effect of ionic strength on a chemical reaction. To account for the effect of ionic strength, concentrations are replaced by **activities**:

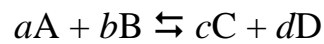
$$\text{Activity of } C: \quad A_C = [C]\gamma_C$$

where A_C : Activity of C

$[C]$: Concentration of C

γ_C : Activity coefficient of C

The activity of species C is its concentration multiplied by its **activity coefficient**. The activity coefficient measures the deviation of behavior from ideality. If the activity coefficient were 1, then the behavior would be ideal and the form of the equilibrium constant in Equation 7-1 would be correct.



The correct form of the equilibrium constant is

$$K = \frac{A_C^c A_D^d}{A_A^a A_B^b} = \frac{[C]^c \gamma_C^c [D]^d \gamma_D^d}{[A]^a \gamma_A^a [B]^b \gamma_B^b} \quad (7-5)$$

K is called thermodynamic equilibrium constant or real equilibrium constant.

Equation 7-5 allows for the effect of ionic strength on a chemical equilibrium because the activity coefficients depend on ionic strength.

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (6-2)$$

K_C is called the concentration equilibrium constant.

Very commonly, tabulated equilibrium constants are not K but K_C , measured under a particular set of conditions.

For Reaction 7-2: $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$, the equilibrium constant is $K_{sp} = A_{Ca^{2+}} A_{SO_4^{2-}} = [Ca^{2+}] \gamma_{Ca^{2+}} [SO_4^{2-}] \gamma_{SO_4^{2-}}$

If the concentrations of Ca^{2+} and SO_4^{2-} are to increase when a second salt is added to increase ionic strength, the activity coefficients must decrease with increasing ionic strength.

At low ionic strength, activity coefficients approach unity, and the thermodynamic equilibrium constant (7-5) approaches the “concentration” equilibrium constant (6-2).

If $\mu \rightarrow 0$, then $K_C \rightarrow K$

One way to measure a thermodynamic equilibrium constant is to measure the concentration ratio (6-2) at successively lower ionic strengths and extrapolate to zero ionic strength.

EXAMPLE: Write the solubility product expression for $\text{La}_2(\text{SO}_4)_3$ with activity coefficients.

Solution: Exponents of activity coefficients are the same as exponents of concentrations:

$$K_{sp} = A_{\text{La}^{3+}}^2 A_{\text{SO}_4^{2-}}^3 = [\text{La}^{3+}]^2 \gamma_{\text{La}^{3+}}^2 [\text{SO}_4^{2-}]^3 \gamma_{\text{SO}_4^{2-}}^3$$

Q) Write the equilibrium expression for $\text{Ca}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CaCl}_2(\text{aq})$ with activity coefficients.

$$K = \frac{A_{\text{CaCl}_2}}{A_{\text{Ca}^{2+}} A_{\text{Cl}^-}^2} = \frac{[\text{CaCl}_2] \gamma_{\text{CaCl}_2}}{[\text{Ca}^{2+}] \gamma_{\text{CaCl}_2} [\text{Cl}^-]^2 \gamma_{\text{Cl}^-}^2}$$

Activity Coefficients of Ions

The ionic atmosphere model leads to the **extended Debye-Hückel equation**, relating activity coefficients to ionic strength:

$$\text{Extended Debye-Hückel equation: } \log \gamma = \frac{-0.51 z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu}/305)} \quad \mu \leq 0.1 \text{ M at } 25^\circ\text{C} \quad (7-6)$$

α : hydrated radius in unit of picometer (10^{-12} m)

Table 7-1 lists sizes (α) and activity coefficients of many ions.

Activity coefficients for aqueous solutions at 25°C

| Ion | Ion size (α , pm) | Ionic strength (μ , M) | | | | |
|---|------------------------------|-----------------------------|-------|-------|-------|-------|
| | | 0.001 | 0.005 | 0.01 | 0.05 | 0.1 |
| Charge = ± 1 | | | | | | |
| H ⁺ | 900 | 0.967 | 0.933 | 0.914 | 0.86 | 0.83 |
| (C ₆ H ₅) ₂ CHCO ₂ ⁻ , (C ₃ H ₇) ₄ N ⁺ | 800 | 0.966 | 0.931 | 0.912 | 0.85 | 0.82 |
| (O ₂ N) ₃ C ₆ H ₂ O ⁻ , (C ₃ H ₇) ₃ NH ⁺ , CH ₃ OC ₆ H ₄ CO ₂ ⁻ | 700 | 0.965 | 0.930 | 0.909 | 0.845 | 0.81 |
| Li ⁺ , C ₆ H ₅ CO ₂ ⁻ , HOC ₆ H ₄ CO ₂ ⁻ , ClC ₆ H ₄ CO ₂ ⁻ , C ₆ H ₅ CH ₂ CO ₂ ⁻ , CH ₂ =CHCH ₂ CO ₂ ⁻ , (CH ₃) ₂ CHCH ₂ CO ₂ ⁻ , (CH ₃ CH ₂) ₄ N ⁺ , (C ₃ H ₇) ₂ NH ⁺ | 600 | 0.965 | 0.929 | 0.907 | 0.835 | 0.80 |
| Cl ₂ CHCO ₂ ⁻ , Cl ₃ CCO ₂ ⁻ , (CH ₃ CH ₂) ₃ NH ⁺ , (C ₃ H ₇)NH ₃ ⁺ | 500 | 0.964 | 0.928 | 0.904 | 0.83 | 0.79 |
| Na ⁺ , CdCl ⁺ , ClO ₂ ⁻ , IO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , H ₂ AsO ₄ ⁻ , Co(NH ₃) ₄ (NO ₂) ₂ ⁺ , CH ₃ CO ₂ ⁻ , ClCH ₂ CO ₂ ⁻ , (CH ₃) ₄ N ⁺ , (CH ₃ CH ₂) ₂ NH ₂ ⁺ , H ₂ NCH ₂ CO ₂ ⁻ | 450 | 0.964 | 0.928 | 0.902 | 0.82 | 0.775 |
| ⁺ H ₃ NCH ₂ CO ₂ H, (CH ₃) ₃ NH ⁺ , CH ₃ CH ₂ NH ₃ ⁺ | 400 | 0.964 | 0.927 | 0.901 | 0.815 | 0.77 |
| OH ⁻ , F ⁻ , SCN ⁻ , OCN ⁻ , HS ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , IO ₄ ⁻ , MnO ₄ ⁻ , HCO ₂ ⁻ , H ₂ citrate ⁻ , CH ₃ NH ₃ ⁺ , (CH ₃) ₂ NH ₂ ⁺ | 350 | 0.964 | 0.926 | 0.900 | 0.81 | 0.76 |
| K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻ | 300 | 0.964 | 0.925 | 0.899 | 0.805 | 0.755 |
| Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , TI ⁺ , Ag ⁺ | 250 | 0.964 | 0.924 | 0.898 | 0.80 | 0.75 |

a. Lanthanides are elements 57–71 in the periodic table.

SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, 59, 1675.

| Ion | Ion size (α , pm) | Ionic strength (μ , M) | | | | |
|---|------------------------------|-----------------------------|-------|-------|-------|-------|
| | | 0.001 | 0.005 | 0.01 | 0.05 | 0.1 |
| Charge = ± 2 | | | | | | |
| Mg ²⁺ , Be ²⁺ | 800 | 0.872 | 0.755 | 0.69 | 0.52 | 0.45 |
| CH ₃ (CH ₂ CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CH ₂ CO ₂ ⁻) ₂ | 700 | 0.872 | 0.755 | 0.685 | 0.50 | 0.425 |
| Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , C ₆ H ₄ (CO ₂ ⁻) ₂ , H ₂ C(CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CO ₂ ⁻) ₂ | 600 | 0.870 | 0.749 | 0.675 | 0.485 | 0.405 |
| Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , S ₂ O ₄ ²⁻ , WO ₄ ²⁻ , H ₂ C(CO ₂ ⁻) ₂ , (CH ₂ CO ₂ ⁻) ₂ , (CHOHCO ₂ ⁻) ₂ | 500 | 0.868 | 0.744 | 0.67 | 0.465 | 0.38 |
| Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , MoO ₄ ²⁻ , Co(NH ₃) ₅ Cl ²⁺ , Fe(CN) ₅ NO ²⁻ , C ₂ O ₄ ²⁻ , Hcitrate ²⁻ | 450 | 0.867 | 0.742 | 0.665 | 0.455 | 0.37 |
| Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₆ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻ | 400 | 0.867 | 0.740 | 0.660 | 0.445 | 0.355 |
| Charge = ± 3 | | | | | | |
| Al ³⁺ , Fe ³⁺ , Cr ³⁺ , Sc ³⁺ , Y ³⁺ , In ³⁺ , lanthanides ^a | 900 | 0.738 | 0.54 | 0.445 | 0.245 | 0.18 |
| citrate ³⁻ | 500 | 0.728 | 0.51 | 0.405 | 0.18 | 0.115 |
| PO ₄ ³⁻ , Fe(CN) ₆ ³⁻ , Cr(NH ₃) ₆ ³⁺ , Co(NH ₃) ₆ ³⁺ , Co(NH ₃) ₅ H ₂ O ³⁺ | 400 | 0.725 | 0.505 | 0.395 | 0.16 | 0.095 |
| Charge = ± 4 | | | | | | |
| Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺ | 1 100 | 0.588 | 0.35 | 0.255 | 0.10 | 0.065 |
| Fe(CN) ₆ ⁴⁻ | 500 | 0.57 | 0.31 | 0.20 | 0.048 | 0.021 |

a. Lanthanides are elements 57–71 in the periodic table.

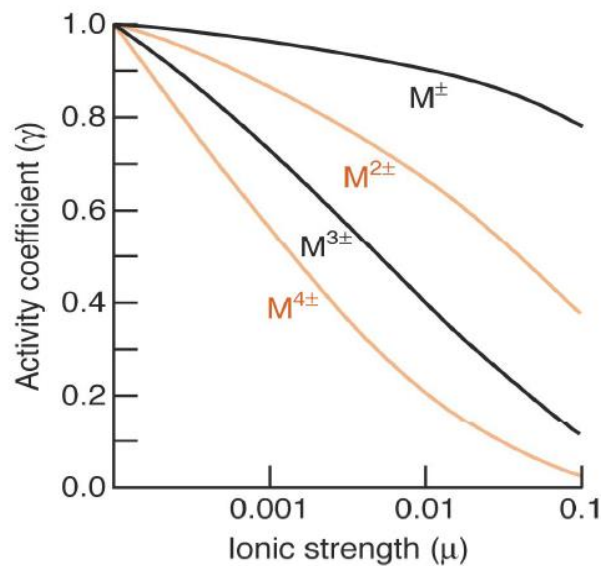
SOURCE: J. Kielland, J. Am. Chem. Soc. 1937, 59, 1675.

Effect of Ionic Strength, Ion Charge, and Ion Size on the Activity Coefficient

Over the range of ionic strengths from 0 to 0.1 M, the effect of each variable on activity coefficients is as follows:

1. As ionic strength increases, the activity coefficient decreases (Figure 7-4). The activity coefficient (γ) approaches unity as the ionic strength (μ) approaches 0.
2. As the magnitude of the charge of the ion increases, the departure of its activity coefficient from unity increases. Activity corrections are more important for ions with a charge of ± 3 than for ions with a charge of ± 1 (Figure 7-4).
3. The smaller the ion size (α), the more important activity effects become.

Fig. 7-4. Activity coefficients for differently charged ions with a constant hydrated radius of 500 pm



The greater the charge of the ion, the more rapidly γ decreases as ionic strength increases.

EXAMPLE Using Table 7-1

Find the activity coefficient of Ca^{2+} in a solution of 3.3 mM CaCl_2 .

Solution The ionic strength is

$$\begin{aligned}\mu &= \frac{1}{2} ([\text{Ca}^{2+}] \cdot 2^2 + [\text{Cl}^-] \cdot (-1)^2) \\ &= \frac{1}{2} ((0.0033) \cdot 4 + (0.0066) \cdot 1) = 0.010 \text{ M}\end{aligned}$$

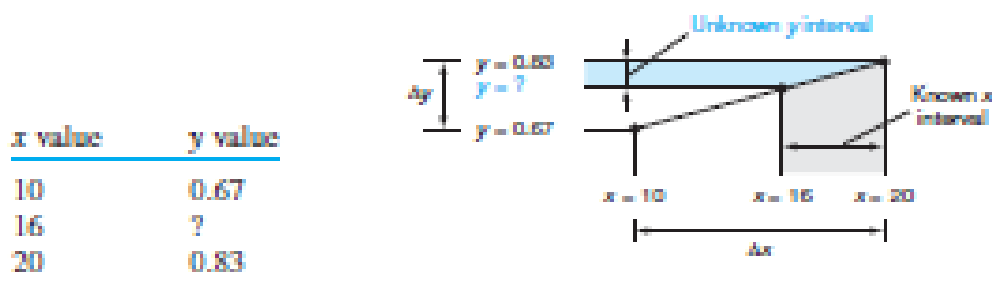
In Table 7-1, Ca^{2+} is listed under the charge ± 2 and has a size of 600 pm. Thus $\gamma = 0.675$ when $\mu = 0.010 \text{ M}$.

Example: Find γ for Cl^- in 0.33 mM CaCl_2 .

$$\mu = 3 \times (0.33 \text{ mM}) = 0.99 \text{ mM} \approx 1.0 \text{ mM} = 0.001 \text{ M}$$

From table 7-1 γ for $\text{Cl}^- = 0.964$

How to interpolate



Interpolation:

$$\frac{\text{Unknown } y \text{ interval}}{\Delta y} = \frac{\text{known } x \text{ interval}}{\Delta x}$$

$$\frac{0.83 - y}{0.83 - 0.67} = \frac{20 - 16}{20 - 10} \Rightarrow y = 0.76_6$$

For $x = 16$, our estimate of y is 0.76_6 .

EXAMPLE interpolating Activity Coefficients

Calculate the activity coefficient of H^+ when $\mu = 0.025 \text{ M}$.

Solution H^+ is the first entry in Table 7-1.

| μ | γ for H^+ |
|-------|---------------------------|
| 0.01 | 0.914 |
| 0.025 | ? |
| 0.05 | 0.86 |

The linear interpolation is set up as follows:

$$\frac{\text{Unknown } \gamma \text{ interval}}{\Delta \gamma} = \frac{\text{known } \mu \text{ interval}}{\Delta \mu}$$

$$\frac{0.86 - \gamma}{0.86 - 0.914} = \frac{0.05 - 0.025}{0.05 - 0.01}$$

$$\gamma = 0.89_4$$

Another Solution A better and slightly more tedious calculation uses Equation 7-6, with the ion size $\alpha = 900 \text{ pm}$ listed for H^+ in Table 7-1:

$$\log \gamma_{\text{H}^+} = \frac{(-0.51)(1^2)\sqrt{0.025}}{1 + (900\sqrt{0.025}/305)} = -0.054_{98}$$

$$\gamma_{\text{H}^+} = 10^{-0.054_{98}} = 0.88_1$$

Activity Coefficients of Nonionic Compounds

Neutral molecules, such as benzene and acetic acid, have no ionic atmosphere because they have no charge. To a good approximation, their activity coefficients are unity when the ionic strength is less than 0.1 M.

In this book, we set $\gamma = 1$ for neutral molecules. That is, *the activity of a neutral molecule will be assumed to be equal to its concentration.*

For gases such as H_2 , the activity is written

$$A_{H_2} = P_{H_2} \gamma_{H_2}$$

where P_{H_2} is pressure in bars. The activity of a gas is called its *fugacity*, and the activity coefficient is called the *fugacity coefficient*. Deviation of gas behavior from the ideal gas law results in deviation of the fugacity coefficient from unity. For gases at or below 1 bar, $\gamma = 1$. Therefore, for gases, *we will set* $A = P(\text{bar})$.

High Ionic Strengths

Above an ionic strength of 1 M, activity coefficients of most ions increase.

Solubility using activity coefficients

EXAMPLE Using Activity Coefficients

Find the concentration of Ca^{2+} in equilibrium with 0.050 M NaF saturated with CaF_2 . The solubility of CaF_2 is small, so the concentration of F^- is 0.050 M from NaF.

Solution We find $[Ca^{2+}]$ from the solubility product expression, including activity coefficients. The ionic strength of 0.050 M NaF is 0.050 M. At $\mu = 0.050$ M in Table 7-1, we find $\gamma_{Ca^{2+}} = 0.485$ and $\gamma_{F^-} = 0.81$.

$$\begin{aligned} K_{sp} &= [Ca^{2+}] \gamma_{Ca^{2+}} [F^-]^2 \gamma_{F^-}^2 \\ 3.2 \times 10^{-11} &= [Ca^{2+}] (0.485) (0.050)^2 (0.81)^2 \\ [Ca^{2+}] &= 4.0 \times 10^{-8} \text{ M} \end{aligned}$$

$[\text{Ca}^{2+}] = ?$ 0.0125M MgSO_4 soln saturate
d with CaF_2 .

$$0.0125\text{M } \text{MgSO}_4 \Rightarrow \mu = (1/2)[(0.0125)(+2)^2 + (0.0125)(-2)^2]$$

$$\gamma_{\text{Ca}^{2+}} = 0.485, \gamma_{\text{F}^-} = 0.81$$

$$\text{CaF}_2(\text{s}) = \text{Ca}^{2+} + 2\text{F}^- \quad K_s$$

$$K_s = 3.9 \times 10^{-11}$$

| | | | |
|---------|-------|---|---|
| Initial | solid | 0 | 0 |
|---------|-------|---|---|

| | | | |
|-------|-------|-----|------|
| Final | solid | x | $2x$ |
|-------|-------|-----|------|

$$K_{\text{sp}} = [\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}} [\text{F}^-]^2 \gamma_{\text{F}^-}^2 = (x)(0.485)(2x)^2 (0.81)^2 = 3.9 \times 10^{-11}$$

$$x = [\text{Ca}^{2+}] = 3.1 \times 10^{-4} \text{ M}$$

7-3 pH Revisited

The definition $\text{pH} \approx -\log[\text{H}^+]$ in Chapter 6 is not exact. A better definition is

$$\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log[\text{H}^+]\gamma_{\text{H}^+} \quad (7-8)$$

When we measure pH with a pH meter, we are measuring the negative logarithm of the hydrogen ion activity, not its concentration.

EXAMPLE pH of Pure Water at 25°C

Let's calculate the pH of pure water by using activity coefficients.

Solution The relevant equilibrium is



$$K_w = \mathcal{A}_{\text{H}^+}\mathcal{A}_{\text{OH}^-} = [\text{H}^+]\gamma_{\text{H}^+}[\text{OH}^-]\gamma_{\text{OH}^-} \quad (7-10)$$

H^+ and OH^- are produced in a 1:1 mole ratio, so their concentrations must be equal. Calling each concentration x , we write

$$K_w = 1.0 \times 10^{-14} = (x)\gamma_{\text{H}^+}(x)\gamma_{\text{OH}^-}$$

But the ionic strength of pure water is so small that it is reasonable to guess that $\gamma_{\text{H}^+} = \gamma_{\text{OH}^-} = 1$. Using these values in the preceding equation gives

$$1.0 \times 10^{-14} = (x)(1)(x)(1) = x^2 \Rightarrow x = 1.0 \times 10^{-7} \text{ M}$$

The concentrations of H^+ and OH^- are both $1.0 \times 10^{-7} \text{ M}$. The ionic strength is $1.0 \times 10^{-7} \text{ M}$, so each activity coefficient is very close to 1.00. The pH is

$$\text{pH} = -\log[\text{H}^+]\gamma_{\text{H}^+} = -\log(1.0 \times 10^{-7})(1.00) = 7.00$$

EXAMPLE pH of Water Containing a Salt

Now let's calculate the pH of water containing 0.10 M KCl at 25°C.

Solution Reaction 7-9 tells us that $[\text{H}^+] = [\text{OH}^-]$. However, the ionic strength of 0.10 M KCl is 0.10 M. The activity coefficients of H^+ and OH^- in Table 7-1 are 0.83 and 0.76, respectively, when $\mu = 0.10 \text{ M}$. Putting these values into Equation 7-10 gives

$$\begin{aligned} K_w &= [\text{H}^+]\gamma_{\text{H}^+}[\text{OH}^-]\gamma_{\text{OH}^-} \\ 1.0 \times 10^{-14} &= (x)(0.83)(x)(0.76) \\ x &= 1.26 \times 10^{-7} \text{ M} \end{aligned}$$

The concentrations of H^+ and OH^- are equal and are both greater than $1.0 \times 10^{-7} \text{ M}$. The activities of H^+ and OH^- are not equal in this solution:

$$\begin{aligned} \mathcal{A}_{\text{H}^+} &= [\text{H}^+]\gamma_{\text{H}^+} = (1.26 \times 10^{-7})(0.83) = 1.05 \times 10^{-7} \\ \mathcal{A}_{\text{OH}^-} &= [\text{OH}^-]\gamma_{\text{OH}^-} = (1.26 \times 10^{-7})(0.76) = 0.96 \times 10^{-7} \end{aligned}$$

Finally, we calculate $\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log(1.05 \times 10^{-7}) = 6.98$.

Q) Find $[\text{H}^+]$ and the pH of 0.05 M LiNO_3 . (Answer: $1.2_0 \times 10^{-7} \text{ M}$,

6.99)

SYSTEMATIC TREATMENT OF EQUILIBRIUM

General strategy for determining the concentrations of species involved in chemical equilibria

- Write as many independent algebraic equations as there are unknowns. These equations come from the chemical equilibria, the charge balance, and the mass balance.
- Often, approximations make the problem less daunting!

Charge balance

Sum of positive charges in solution = sum of negative charges in solution

Example: solution that contains H^+ , OH^- , K^+ , $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-}

$$[H^+] + [K^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

Coefficient in front of ion = magnitude of charge on that ion

This statement is true because a mole of, say, PO_4^{3-} contributes three moles of negative charge. If $[PO_4^{3-}] = 0.01 \text{ M}$, the negative charge is $3[PO_4^{3-}] = 3(0.01) = 0.03 \text{ M}$.

The general form of the charge balance for any solution is

$$\text{Charge balance: } n_1[C_1] + n_2[C_2] + \dots = m_1[A_1] + m_2[A_2] + \dots \quad (7-12)$$

where $[C]$ is the concentration of a cation, n is the charge of the cation, $[A]$ is the concentration of an anion, and m is the magnitude of the charge of the anion.

EXAMPLE: Write the charge balance for a solution containing H_2O , H^+ , OH^- , ClO_4^- , $Fe(CN)_6^{3-}$, CN^- , Fe^{3+} , Mg^{2+} , CH_3OH , HCN , NH_3 , and NH_4^+ .

Solution Neutral species (H_2O , CH_3OH , HCN , and NH_3) contribute no charge, so the charge balance is

$$[H^+] + 3[Fe^{3+}] + 2[Mg^{2+}] + [NH_4^+] = [OH^-] + [ClO_4^-] + 3[Fe(CN)_6^{3-}] + [CN^-]$$

Q) What would be the charge balance if you add $MgCl_2$ to the solution and it dissociates into $Mg^{2+} + 2Cl^-$? (Answer: $[H^+] + 3[Fe^{3+}] + 2[Mg^{2+}] + [NH_4^+] = [OH^-] + [ClO_4^-] + 3[Fe(CN)_6^{3-}] + [CN^-] + [Cl^-]$)

Mass Balance

The **mass balance**, also called the *material balance*, is a statement of the conservation of matter. The mass balance states that *the quantity of all species in a solution containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution.*

Example 1: 0.050 M CH₃COOH



Mass balance for

acetic acid in water:

$$\begin{array}{ccccccc} 0.050 \text{ M} & = & [\text{CH}_3\text{CO}_2\text{H}] & + & [\text{CH}_3\text{COO}^-] \\ \text{What we put} & & \text{Dissociated} & & \text{Undissociated} \\ \text{into the solution} & & \text{product} & & \text{product} \end{array}$$

Example 2: 0.0250 M H₃PO₄

$$0.0250 \text{ M} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$$

EXAMPLE Mass Balance When the Total Concentration Is Known

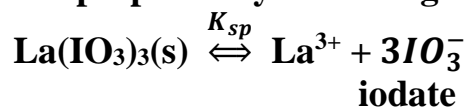
Write the mass balances for K⁺ and for phosphate in a solution prepared by mixing 0.0250 mol KH₂PO₄ plus 0.0300 mol KOH and diluting to 1.00 L.

$$[\text{K}^+] = 0.0250 + 0.030 = 0.0550 \text{ M}$$

$$[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = 0.0250 \text{ M}$$

Q) Write two mass balances for a 1.00-L solution containing 0.100 mol of sodium acetate. (Answer: [Na⁺] = 0.100 M; [CH₃CO₂H] + [CH₃CO₂⁻] = 0.100 M)

Now consider a solution prepared by dissolving La(IO₃)₃ in water.



the mass balance is

$$[\text{IO}_3^-] = 3[\text{La}^{3+}]$$

If the solution also contains the ion pair LaIO_3^{2+} and the hydrolysis product LaOH^{2+} , the mass balance would be

$$[\text{Total iodate}] = 3[\text{total lanthanum}]$$

$$[\text{IO}_3^-] + [\text{LaIO}_3^{2+}] = 3\{[\text{La}^{3+}] + [\text{LaIO}_3^{2+}] + [\text{LaOH}^{2+}]\}$$

EXAMPLE Mass Balance When the Total Concentration Is Unknown

Write the mass balance for a saturated solution of the slightly soluble salt Ag₃PO₄, which produces PO₄³⁻ and 3Ag⁺ when it dissolves.

Solution If the phosphate in solution remained as PO₄³⁻, we could write

$$[\text{Ag}^+] = 3[\text{PO}_4^{3-}]$$

because three silver ions are produced for each phosphate ion. However, phosphate (PO_4^{3-}) reacts with water to give, HPO_4^{2-} , H_2PO_4^- and H_3PO_4 , so the mass balance is

$$[\text{Ag}^+] = 3\{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]\}$$

the number of atoms of Ag^+ must equal three times the total number of atoms of phosphorus, regardless of how many species contain phosphorus.

Q) Write the mass balance for a saturated solution of $\text{Ba}(\text{HSO}_4)_2$ if the species in solution are Ba^{2+} , $\text{BaSO}_4(\text{aq})$, HSO_4^- , SO_4^{2-} , and BaOH^+ . (Answer: $2 \times \text{total barium} = \text{total sulfate}$, or $2\{[\text{Ba}^{2+}] + [\text{BaSO}_4(\text{aq})] + [\text{BaOH}^+]\} = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{BaSO}_4(\text{aq})]$)

Systematic Treatment of Equilibrium

Now that we have considered the charge and mass balances, we are ready for the systematic treatment of equilibrium.¹¹ Here is the general prescription:

Step 1 Write the *pertinent reactions*.

Step 2 Write the *charge balance* equation.

Step 3 Write *mass balance* equations. There may be more than one.

Step 4 Write the *equilibrium constant expression* for each chemical reaction. This step is the only one in which activity coefficients appear.

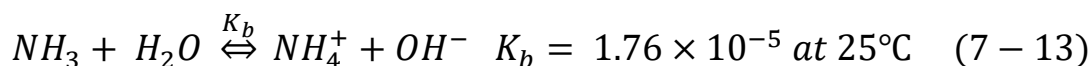
Step 5 *Count the equations and unknowns*. There should be as many equations as unknowns (chemical species). If not, you must either find more equilibria or fix some concentrations at known values.

Step 6 *Solve* for all unknowns.

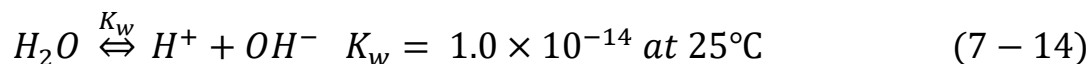
7.5 Applying the Systematic Treatment of Equilibrium

A Solution of Ammonia

Let's find the concentrations of species in an aqueous solution containing 0.010 0 mol NH_3 in 1.000 L. The primary equilibrium is



A second equilibrium in every aqueous solution is



Our goal is to find $[NH_3]$, $[NH_4^+]$, $[H^+]$, and $[OH^-]$.

Step 1 Pertinent reactions. They are 7-13 and 7-14.

Step 2 Charge balance. The sum of positive charge equals the sum of negative charge:

$$[NH_4^+] + [H^+] = [OH^-] \quad (7-15)$$

Step 3 Mass balance. All of the ammonia delivered to the solution is either in the form NH_3 or NH_4^+ . These two must add up to 0.0100 M.

$$[NH_3] + [NH_4^+] = 0.0100 \text{ M} \equiv F \quad (7-16)$$

Step 4 Equilibrium expressions.

$$K_b = \frac{[NH_4^+]\gamma_{NH_4^+} [OH^-]\gamma_{OH^-}}{[NH_3]\gamma_{[NH_3]}} = 1.76 \times 10^{-5} \quad (7-17)$$

$$K_w = [H^+]\gamma_{H^+} [OH^-]\gamma_{OH^-} = 1.0 \times 10^{-14} \quad (7-18)$$

This is the only step in which activity coefficients enter the problem.

Step 5 Count equations and unknowns. We have four equations, 7-15 to 7-18, and four unknowns ($[NH_3]$, $[NH_4^+]$, $[H^+]$, and $[OH^-]$). We have enough information to solve the problem.

Step 6 Solve.

$$[NH_4^+] + [H^+] = \frac{K_w}{[H^+]} \quad (7-15)$$

$$[NH_4^+] = \frac{K_w}{[H^+]} - [H^+] \quad (7-19)$$

From equation (7-16)

$$[NH_3] = F - [NH_4^+] = F - \left(\frac{K_w}{[H^+]} - [H^+] \right) \quad (7-20)$$

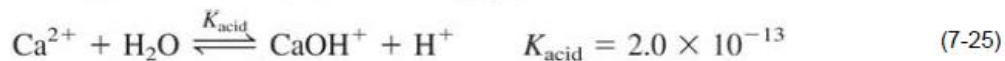
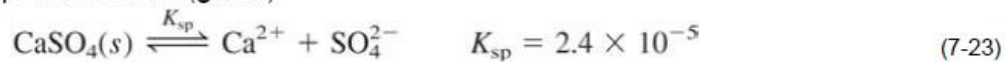
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{\left(\frac{K_w}{[H^+]} - [H^+] \right) \left(\frac{K_w}{[H^+]} \right)}{\left(F - \frac{K_w}{[H^+]} + [H^+] \right)} \quad (7-21)$$

Equation 7-21 is horrible, but $[H^+]$ is the only unknown. One way you could solve for $[H^+]$ is to *guess* a value of $[H^+]$, put it into the right side of the equation, and see if the right side is equal to K_b on the left side.

After solving for $[H^+]$, we could calculate $[OH^-] = K_w/[H^+]$. We could find $[NH_4^+]$ from Equation 7-19 and we could compute $[NH_3]$ from the K_b equilibrium expression. Then we would have all four concentrations.

EXAMPLE: Solubility of $CaSO_4$: find the concentration of the major species in a saturated solution of $CaSO_4$

Step 1: reactions (given)



Step 2: charge balance

$$2[Ca^{2+}] + [CaOH^+] + [H^+] = 2[SO_4^{2-}] + [HSO_4^-] + [OH^-] \quad (7-28)$$

Step 3: mass balance

$$[\text{Total calcium}] = [\text{total sulfate}]$$

$$[Ca^{2+}] + [CaSO_4(aq)] + [CaOH^+] = [SO_4^{2-}] + [HSO_4^-] + [CaSO_4(aq)] \quad (7-29)$$

Step 4: equilibrium constant expressions

$$K_{sp} = [\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}} [\text{SO}_4^{2-}] \gamma_{\text{SO}_4^{2-}} = 2.4 \times 10^{-5} \quad (7-30)$$

$$K_{\text{ion pair}} = [\text{CaSO}_4(aq)] = 5.0 \times 10^{-3} \quad (7-31)$$

$$K_{\text{acid}} = \frac{[\text{CaOH}^+] \gamma_{\text{CaOH}^+} [\text{H}^+] \gamma_{\text{H}^+}}{[\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}}} = 2.0 \times 10^{-13} \quad (7-32)$$

$$K_{\text{base}} = \frac{[\text{HSO}_4^-] \gamma_{\text{HSO}_4^-} [\text{OH}^-] \gamma_{\text{OH}^-}}{[\text{SO}_4^{2-}] \gamma_{\text{SO}_4^{2-}}} = 9.8 \times 10^{-13} \quad (7-33)$$

$$K_w = [\text{H}^+] \gamma_{\text{H}^+} [\text{OH}^-] \gamma_{\text{OH}^-} = 1.0 \times 10^{-14} \quad (7-34)$$

Step 5: count equations and unknowns

7 equations and 7 unknown concentrations

Step 6: solve – make approximations!

- Disregard the activity coefficients for now
- Check magnitude of equilibrium constants; reactions 7-25 and 7-26 are likely negligible compared to 7-23 and 7-24

Reaction 7-27 has also a small K, but this involves other species! From this reaction, we also know that $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$

New charge balance: $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$

New mass balance: $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$

We are left with 3 unknowns ($[\text{Ca}^{2+}]$, $[\text{SO}_4^{2-}]$ and $[\text{CaSO}_4(aq)]$), and 3 equations: 7-30, 7-31, and $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$

But $[\text{CaSO}_4(aq)]$ is known: $5.0 \times 10^{-3} \text{ M}$

So we are left with:

$$[\text{Ca}^{2+}]_1 \gamma_{\text{Ca}^{2+}} [\text{SO}_4^{2-}]_1 \gamma_{\text{SO}_4^{2-}} = 2.4 \times 10^{-5}$$

$$[\text{Ca}^{2+}]_1(1) [\text{SO}_4^{2-}]_1(1) = 2.4 \times 10^{-5}$$

$$[\text{Ca}^{2+}]_1(1) [\text{Ca}^{2+}]_1(1) = 2.4 \times 10^{-5} \Rightarrow [\text{Ca}^{2+}]_1 = 4.9 \times 10^{-3} \text{ M}$$

(The subscript 1 here means first approximation)

Calculate ionic strength of the solution: $\mu = \frac{1}{2} \sum c_i z_i^2$

$$\mu = \frac{1}{2} (4.9 \times 10^{-3} \times 2^2 + 4.9 \times 10^{-3} \times 2^2) = 0.020 \text{ M}$$

From this value for the ionic strength, we can either calculate the activity coefficients, or interpolate them from Table 7-1. This gives:

$$\gamma(\text{Ca}^{2+}) = 0.628 \text{ and } \gamma(\text{SO}_4^{2-}) = 0.606$$

Putting these coefficients back into equation 7-30:

$$0.628 [\text{Ca}^{2+}]_2 0.606 [\text{SO}_4^{2-}]_2 = 2.4 \times 10^{-5}$$

$$[\text{Ca}^{2+}] = 7.9 \times 10^{-3} \text{ M} \rightarrow \mu = 0.032 \text{ M}$$

Repeating this process (*iteration*) a number of times eventually leads to a consistent value of $[\text{Ca}^{2+}] = 9.2 \times 10^{-3} \text{ M}$ and $\mu = 0.037 \text{ M}$

Finally, convince yourself that the original approximations were valid:

Estimate $[\text{CaOH}^+]$ and $[\text{HSO}_4^-]$ (ignore activity coefficients) from 7-32 and 7-33:

$$[\text{CaOH}^+] = 2 \times 10^{-8} \text{ M} \text{ and } [\text{HSO}_4^-] = 9 \times 10^{-8} \text{ M}$$

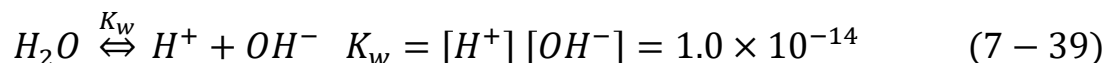
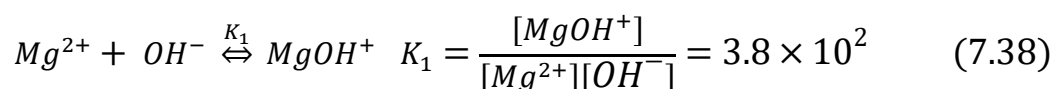
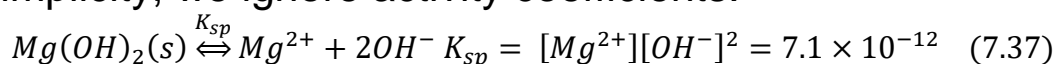
i.e. they are both $\sim 10^5$ times less than $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}] = \text{OK!}$

We Will Usually Omit Activity Coefficients

Although it is proper to write equilibrium constants in terms of activities, the complexity of manipulating activity coefficients is a nuisance. Most of the time, we will omit activity coefficients unless there is a particular point to be made. Occasional problems will remind you how to use activities.

Solubility of Magnesium Hydroxide

Let's find the concentrations of species in a saturated solution of $\text{Mg}(\text{OH})_2$, given the following chemistry. For simplicity, we ignore activity coefficients.



Step 1 Pertinent reactions are listed above.

Step 2 Charge balance:

$$2[\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{H}^+] = [\text{OH}^-] \quad (7-40)$$

Step 3 Mass balance.

From Reaction 7-37, we could say that the concentrations of all species containing OH^- equal two times the concentrations of all magnesium species. However, Reaction 7-39 also creates 1 OH^- for each H^+ . The mass balance accounts for both sources of OH^- :

$$\underbrace{[\text{OH}^-] + [\text{MgOH}^+]}_{\text{Species containing OH}^-} = 2 \underbrace{\{[\text{Mg}^{2+}] + [\text{MgOH}^+]\}}_{\text{Species containing Mg}^{2+}} + [\text{H}^+] \quad (7-41)$$

Step 4 Equilibrium constant expressions are in Equations 7-37 through 7-39.

Step 5 Count equations and unknowns. We have four equations (7-37 to 7-40) and four unknowns: $[\text{Mg}^{2+}]$, $[\text{MgOH}^+]$, $[\text{H}^+]$, and $[\text{OH}^-]$.

Step 6 Solve.

Before hitting the algebra, we can make one simplification. The solution must be basic because we made it from $\text{Mg}(\text{OH})_2$. In basic solution, $[\text{OH}^-] \gg [\text{H}^+]$, so we can neglect $[\text{H}^+]$ on the left side of Equation 7-40 in comparison with $[\text{OH}^-]$ on the right side. The charge balance simplifies to **(7-42)**

$$2[\text{Mg}^{2+}] + [\text{MgOH}^+] = [\text{OH}^-] \quad (7-42)$$

From the K_1 expression 7-38, we write $[\text{MgOH}^+] = K_1[\text{Mg}^{2+}][\text{OH}^-]$. Substituting this expression for $[\text{MgOH}^+]$ into Equation 7-42 gives

$$2[\text{Mg}^{2+}] + K_1[\text{Mg}^{2+}][\text{OH}^-] = [\text{OH}^-]$$

which we solve for $[\text{Mg}^{2+}]$:

$$[\text{Mg}^{2+}] = \frac{[\text{OH}^-]}{2 + K_1[\text{OH}^-]}$$

Substituting this expression for $[\text{Mg}^{2+}]$ into the solubility product reduces the equation to a single variable:

$$K_{sp} = [Mg^{2+}][OH^-]^2 = \left(\frac{[OH^-]}{2 + K_1[OH^-]} \right) [OH^-]^2 = \frac{[OH^-]^3}{2 + K_1[OH^-]} \quad (7-43)$$

Solubility of LiF in distilled water (approximation):

$$K_{sp} \approx [\text{Li}^+][\text{F}^-] = x^2 = 1.7 \times 10^{-3}$$

$$x = [\text{Li}^+] = [\text{F}^-] = 0.041 \text{ M}$$

1) assume $\mu = 0.041$. $\Rightarrow f_{\text{Li}^+} = 0.851$, $f_{\text{F}^-} = 0.830$

$$K_{sp} = [\text{Li}^+] f_{\text{Li}^+} [\text{F}^-] f_{\text{F}^-} = (x)(0.851)(x)(0.830) = 1.7 \times 10^{-3}$$

$$x = [\text{Li}^+] = 0.049 \text{ M}$$

2) assume $\mu = 0.049$. $\Rightarrow f_{\text{Li}^+} = 0.837$, $f_{\text{F}^-} = 0.812$

$$K_{sp} = [\text{Li}^+] f_{\text{Li}^+} [\text{F}^-] f_{\text{F}^-} = (x)(0.837)(x)(0.812) = 1.7 \times 10^{-3}$$

$$x = [\text{Li}^+] = 0.050 \text{ M}$$

3) assume $\mu = 0.050$. $\Rightarrow f_{\text{Li}^+} = 0.835$, $f_{\text{F}^-} = 0.81$

$$K_{sp} = [\text{Li}^+] f_{\text{Li}^+} [\text{F}^-] f_{\text{F}^-} = (x)(0.835)(x)(0.81) = 1.7 \times 10^{-3}$$

$$\begin{array}{l} x = [\text{Li}^+] = 0.050 \text{ M} \\ \text{ty} \uparrow \end{array} \quad \therefore \mu \uparrow \Rightarrow \text{solubility} \uparrow$$