

## Solution Concentrations

### Key terms and concepts

- Defining solution; Types of solution
- Ways to express solution concentration: percent by weight, percent by volume, Molarity, Molality, Normality, parts per million
- Solution preparation from solid solute
- Solution preparation from liquid solute
- Interconverting concentration units

## Solution Concentrations

- Solutions are a **homogeneous mixture** composed of two or more substances. They consist of a solvent (a liquid, such as water) and one or more solutes (substances that are dissolved in the solvent)
- The **dissolving of a solute** in a solvent is a **physical change**. However, chemical reactions often occur between substances that are in solution. These chemical changes can depend on the amount of substances—that is, their concentrations—in the solution.

### A solution may be dilute or concentrated:

- A dilute solution is one that contains a relatively small amount of the solute in a given volume of solvent.
- A concentrated solution contains a relatively large amount of the solute in the same volume of solvent.
- Generally, a dilute solution
  - ❖ Contains a smaller amount of solute than does a concentrated solution
  - ❖ Moreover, a dilute solution contains more solvent than an equal volume of concentrated solution does

- For many solutions, there is a limit to the amount of solute that can be dissolved in the solvent.
- A solution in which no more solute will dissolve is called a **saturated solution**.
- A solution that contains an excess of dissolved solute is called **supersaturated**.
- Actually, a supersaturated solution is unstable and some solute will crystallize if the solution is disturbed. For example, adding a small crystal of the solute can start the crystallization
- An **aqueous** solution is a solution in which the solvent is water.

- The terms “dilute,” “concentrated,” and “saturated” can be useful when talking about how much solute is in a solution, but they do not tell us exactly how much solute is present
- Chemists often need to express concentrations in more precise terms. There are different **ways to express solution concentration** in chemistry—Weight Percent, Volume Percent, Molarity, Molality, Normality, Parts Per Million, etc.

#### Weight Percent (percentage by mass)

- Weight percent is often used to express the concentration of a solid substance dissolved in a liquid. The weight percent is equal to the weight of the solute divided by the total weight of the solution and multiplied by 100 to get a percentage

$$\text{weight percent} = \frac{\text{weight of solute}}{\text{total weight of solution}} \times 100$$

- The total mass of the system is the mass of the solute plus the mass of the solvent.

#### Sample problem:

- What is the percentage by mass of a solution made by dissolving 0.49 g of potassium sulfate in 12.70 g of water?

#### Volume Percent (percentage by volume)

- Volume percent is often used to express the concentration of a liquid solute in a liquid solvent. The volume percent is equal to the volume of the solvent divided by the total volume of the solution and multiplied by 100 to get a percentage

$$\text{volume percent} = \frac{\text{volume of solute}}{\text{total volume of solution}} \times 100$$

#### Sample problem:

- A solution is prepared by diluting 10 mL acetic acid with distilled or deionized water to make 100 mL of solution. Calculate the volume percent concentration

#### Molarity

- Molarity is the most common way to express concentration in chemistry. Molarity is the number of moles of solute per liter of solution and is given as a number followed by a capital M.

$$\text{Molarity(M)} = \frac{\text{moles of solute(mol)}}{\text{volume of solution in liters(L)}}$$

#### Sample problem:

- What is the molarity of a solution prepared by dissolving 37.94 g of potassium hydroxide in some water and then diluting the solution to a volume of 500.00 mL?

**Example Molarity of Salts in the Sea**

(a) Typical seawater contains 2.7 g of salt (sodium chloride, NaCl) per 100 mL ( $= 100 \times 10^{-3}$  L). What is the molarity of NaCl in the ocean? (b)  $\text{MgCl}_2$  has a concentration of 0.054 M in the ocean. How many grams of  $\text{MgCl}_2$  are present in 25 mL of seawater?

**Solution** (a) The molecular mass of NaCl is 22.99 g/mol (Na) + 35.45 g/mol (Cl) = 58.44 g/mol. The moles of salt in 2.7 g are  $(2.7 \text{ g}) / (58.44 \text{ g/mol}) = 0.046$  mol, so the molarity is

$$\text{Molarity of NaCl} = \frac{\text{mol NaCl}}{\text{L of seawater}} = \frac{0.046 \text{ mol}}{100 \times 10^{-3} \text{ L}} = 0.46 \text{ M}$$

(b) The molecular mass of  $\text{MgCl}_2$  is 24.30 g/mol (Mg) +  $2 \times 35.45$  g/mol (Cl) = 95.20 g/mol. The number of grams in 25 mL is

$$\text{Grams of } \text{MgCl}_2 = \left(0.054 \frac{\text{mol}}{\text{L}}\right) \left(95.20 \frac{\text{g}}{\text{mol}}\right) (25 \times 10^{-3} \text{ L}) = 0.13 \text{ g}$$

**Molality**

➤ Molality is the amount in moles of solute per kilogram of solvent and is given by a number followed by an italic lowercase *m*. Molal concentration is important primarily in working with colligative properties of solutions.

$$\text{Molality} = m = \frac{\text{mols of solute}}{\text{kg of solvent}}$$

**Sample problem:**

➤ Determine the molal concentration of a solution containing 81.3 g of ethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , dissolved in 166 g of water.

**Normality**

➤ It is defined as **the number of equivalents per liter** rather than the number of moles per liter. It is dependent on the specific chemistry (or reaction) of the analysis. It is calculated as:

$$\text{normality} = N = \frac{\text{number of equivalents of solute}}{1 \text{ liter of solution}} = \frac{\text{equivalents}}{\text{liter}}$$

where

$$\text{number of equivalents of solute} = \frac{\text{grams of solute}}{\text{equivalent weight of solute}}$$

then

$$N = \frac{\text{grams of solute}}{\text{eq wt solute} \times \text{L solution}} = \frac{\text{grams}}{\text{eq wt} \times \text{L}}$$

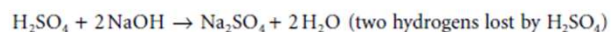
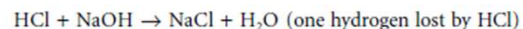
➤ Alternative expressions for normality are shown below:

$$\begin{aligned} \text{normality} &= \frac{\text{equivalents of solute}}{\text{liter of solution}} \\ &= \frac{\text{moles of solute} \times \text{equivalents per mole}}{\text{liters of solution}} \end{aligned}$$

➤ The equivalent is either the same as the mole or some fraction of the mole, depending on the reaction involved, and the **equivalent weight**, or **the weight of one equivalent**, is either the same as the formula weight or some fraction of the formula weight.

➤ Normality is either the same as molarity or some multiple of molarity:  $N = nM$  where *n* is an integer constant  $\geq 1$  and *n* for a particular species is defined by the reaction type and the balanced chemical reaction.

➤ The **equivalent weight of an acid in an acid–base neutralization reaction** is defined as the formula weight divided by the number of hydrogen lost per formula of the acid in the reaction. Acids may lose one or more hydrogen (per formula) when reacting with a base.



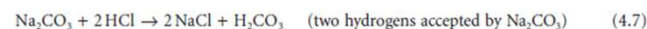
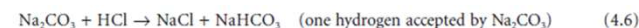
➤ The equivalent weight of HCl is the same as its formula weight, and the equivalent weight of H<sub>2</sub>SO<sub>4</sub> is half the formula weight.

✓ In the case of HCl, there is one hydrogen lost per formula; one equivalent is therefore the same as the mole, and the equivalent weight is the same as the formula weight.

✓ In the case of H<sub>2</sub>SO<sub>4</sub> in the above reaction, there are two hydrogen lost per formula—two equivalents per mole when used as in the above reaction; the equivalent weight is half the formula weight.

➤ The **equivalent weight of a base in an acid–base neutralization reaction** is defined as the formula weight divided by the number of hydrogen accepted per formula of the base in the reaction.

➤ Bases may accept one or more hydrogen (per formula) when reacting with an acid. For example: sodium carbonate is capable of accepting either one or two hydrogen per formula:

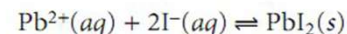


➤ Thus, the equivalent weight of sodium carbonate may be equal to either the formula weight divided by 1 (105.99 g per equivalent, Equation (4.6)) or the formula weight divided by 2 (52.995 g per equivalent, Equation (4.7)), depending on which reaction is involved.

#### Sample problem:

➤ What is the normality of a solution of sodium carbonate if 0.6003 g of it is dissolved in 500.00 mL of solution and it is to be used as in Equation (4.7)?

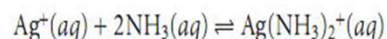
➤ For a **precipitation reaction**, the **reaction unit** is the charge of the cation or anion involved in the reaction; thus for the reaction,



Where  $n = 2$  for Pb<sup>2+</sup> and  $n = 1$  for I<sup>−</sup>.

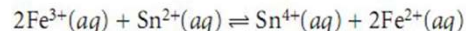
➤ In the case of Pb<sup>2+</sup>, the equivalent weight is half the formula weight. but for I<sup>−</sup> the equivalent weight is the same as the formula weight.

- **For a complexation reaction, the reaction unit** is the number of electron pairs that can be accepted by the metal or donated by the ligand.



the value of n for Ag ion is 2 and for NH<sub>3</sub> is 1

- **For a redox reaction, the reaction unit** is the number of electrons released by the reducing agent or accepted by the oxidizing agent; thus, for the reaction



n=1 for Fe<sup>3+</sup> and n=2 for Sn<sup>2+</sup>.

### Parts per million:

- It is usually applied to very dilute solutions. Many environmental samples contain trace amounts of solute impurities and the concentration of these impurities are reported in *parts per million* (ppm). It is defined as,

$$\text{Parts per million, ppm} = (\text{mass of solute/mass of solution}) \times 10^6$$

- Assuming the density of water is 1.00 g/mL, 1 liter of solution = 1 kg and hence, 1 mg/L = 1 ppm. This is generally true for freshwater and other dilute aqueous solutions
- Alternatively, the number of milligrams of solute per kg of solution is equal to 1 ppm, since 1 mg = 10<sup>-3</sup> g and 1 kg = 10<sup>3</sup> g

Other variations on this theme include:

- ppt – parts per thousand (used for common ions in sea water)
- ppb – parts per billion (used for heavy metals and organics)
- ppt – parts per trillion (used for trace metals and trace organics)

The following table summarizes common mass ratios for solutions and solids.

Unit	Solutions		Solids	
ppm	mg/L	µg/mL	mg/kg	µg/g
ppb	µg/L	ng/mL	µg/kg	ng/g
ppt	ng/L	pg/mL	ng/kg	pg/g

**Sample problem:** A 0.186 mg of zinc per milliliter of blood plasma is considered normal for an adult male. Calculate the ppm of zinc in blood plasma given this data. The density of blood plasma at 37 °C is 1.00 g/mL.

### Preparing Solutions

#### Solid solute and Molarity

- To prepare a solution with a desired molarity from a pure solid or liquid, we weigh out the correct mass of reagent and dissolve it in the desired volume in a volumetric flask
- The grams of solute that are required can be calculated from the desired molarity and volume of solution

$$\text{grams to weigh} = L_D \times M_D \times \text{FW}_{\text{sol}}$$

Where,  $L_D$  refers to the liters desired,  
 $M_D$  to the desired molarity, and  
 $\text{FW}_{\text{sol}}$  to the formula weight of solute

- The grams of solute thus calculated is weighed and placed in the container.
- Water is added to dissolve the solute and to dilute the solution to volume. Following this, the solution is shaken to make it homogeneous.

### Sample problem

- How would you prepare 500.0 mL of a 0.20 M solution of NaOH from pure, solid NaOH?

### Solid solute and Normality

- To determine the weight of a solid that is needed to prepare a solution of a given normality, we first calculate the grams of solute that are required using the following equation:

$$\text{grams to weigh} = L_D \times N_D \times EW_{\text{SOL}}$$

Where,  $L_D$  is the liters of solution desired

$N_D$  is the normality desired, and

$EW_{\text{SOL}}$  is the equivalent weight of the solute

- In order to calculate the equivalent weight of an acid, the balanced equation representing the reaction in which the solution is to be used is needed so that the number of hydrogen lost per formula in the reaction can be determined.

### Solution preparation by dilution

- If a solution is prepared by diluting another solution whose concentration is precisely known, the following dilution equation may be used to calculate the volume of the solution to be diluted (the volume before dilution):

$$C_B \times V_B = C_A \times V_A$$

Here C refers to concentration

V refers to volume

B refers to before dilution, and A refers to after dilution

- Thus, the analyst can know how much of this more concentrated solution to measure out in order to prepare the less concentrated solution.

### Example Preparing a Solution with a Desired Molarity

Copper(II) sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , has 5 moles of  $\text{H}_2\text{O}$  for each mole of  $\text{CuSO}_4$  in the solid crystal. The formula mass of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  ( $= \text{CuSO}_4\text{H}_{10}$ ) is 249.69 g/mol. (Copper(II) sulfate without water in the crystal has the formula  $\text{CuSO}_4$  and is said to be **anhydrous**.) How many grams of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  should be dissolved in a volume of 500.0 mL to make 8.00 mM  $\text{Cu}^{2+}$ ?

**Solution** An 8.00 mM solution contains  $8.00 \times 10^{-3}$  mol/L. We need

$$8.00 \times 10^{-3} \frac{\text{mol}}{\text{L}} \times 0.500 \text{ L} = 4.00 \times 10^{-3} \text{ mol } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$$

The mass of reagent is  $(4.00 \times 10^{-3} \text{ mol}) \times \left( 249.69 \frac{\text{g}}{\text{mol}} \right) = 0.999 \text{ g}$ .

### Example Preparing 0.100 M HCl

The molarity of "concentrated" HCl purchased for laboratory use is approximately 12.1 M. How many milliliters of this reagent should be diluted to 1.000 L to make 0.100 M HCl?

**Solution** The dilution formula handles this problem directly:

$$M_{\text{conc}} \cdot V_{\text{conc}} = M_{\text{dil}} \cdot V_{\text{dil}}$$

$$(12.1 \text{ M}) \cdot (x \text{ mL}) = (0.100 \text{ M}) \cdot (1000 \text{ mL}) \Rightarrow x = 8.26 \text{ mL}$$

To make 0.100 M HCl, we would dilute 8.26 mL of concentrated HCl up to 1.000 L. The concentration will not be exactly 0.100 M, because the reagent is not exactly 12.1 M. A table inside the cover of this book gives volumes of common reagents required to make 1.0 M solutions.

**Example A More Complicated Dilution Calculation**

A solution of ammonia in water is called "ammonium hydroxide" because of the equilibrium



The density of concentrated ammonium hydroxide, which contains 28.0 wt%  $\text{NH}_3$ , is 0.899 g/mL. What volume of this reagent should be diluted to 500.0 mL to make 0.250 M  $\text{NH}_3$ ?

**Solution** To use Equation 1-3, we need to know the molarity of the concentrated reagent. The solution contains 0.899 g of solution per milliliter and there is 0.280 g of  $\text{NH}_3$  per gram of solution (28.0 wt%), so we can write

$$\text{Molarity of NH}_3 = \frac{0.899 \frac{\text{g-solution}}{\text{L}} \times 0.280 \frac{\text{g-NH}_3}{\text{g-solution}}}{17.03 \frac{\text{g-NH}_3}{\text{mol NH}_3}} = 14.8 \text{ M}$$

Now we find the volume of 14.8 M  $\text{NH}_3$  required to prepare 500.0 mL of 0.250 M  $\text{NH}_3$ :

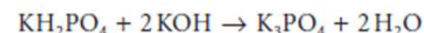
$$M_{\text{conc}} \cdot V_{\text{conc}} = M_{\text{dil}} \cdot V_{\text{dil}}$$

$$14.8 \text{ M} \times V_{\text{conc}} = 0.250 \text{ M} \times 500.0 \text{ mL} \Rightarrow V_{\text{conc}} = 8.45 \text{ mL}$$

The procedure is to place 8.45 mL of concentrated reagent in a 500-mL volumetric flask, add about 400 mL of water, and swirl to mix. Then dilute to exactly 500 mL with water and invert the flask many times to mix well.

**Sample problems****Sample problem 2:**

- How many grams of  $\text{KH}_2\text{PO}_4$  are needed to prepare 500.0 mL of a 0.200 N solution if it is to be used as in the following reaction?

**Sample problem 1:**

- How many milliliters of 12 M hydrochloric acid are needed to prepare 500.0 mL of a 0.60 M solution?

**Interconverting concentration units****Example Converting Weight Percent into Molarity and Molality**

Find the molarity and molality of 37.0 wt% HCl. The density of a substance is the mass per unit volume. The table inside the back cover of this book tells us that the density of the reagent is 1.19 g/mL.

**Solution** For *molarity*, we need to find the moles of HCl per liter of solution. The mass of a liter of solution is  $(1.19 \text{ g/mL})(1000 \text{ mL}) = 1.19 \times 10^3 \text{ g}$ . The mass of HCl in a liter is

$$\text{Mass of HCl per liter} = \left( 1.19 \times 10^3 \frac{\text{g-solution}}{\text{L}} \right) \left( 0.370 \frac{\text{g HCl}}{\text{g-solution}} \right) = 4.40 \times 10^2 \frac{\text{g HCl}}{\text{L}}$$

This is what  
37.0 wt% means

The molecular mass of HCl is 36.46 g/mol, so the molarity is

$$\text{Molarity} = \frac{\text{mol HCl}}{\text{L solution}} = \frac{4.40 \times 10^2 \text{ g-HCl/L}}{36.46 \text{ g-HCl/mol}} = 12.1 \frac{\text{mol}}{\text{L}} = 12.1 \text{ M}$$

For *molality*, we need to find the moles of HCl per kilogram of solvent (which is  $\text{H}_2\text{O}$ ). The solution is 37.0 wt% HCl, so we know that 100.0 g of solution contains 37.0 g of HCl and  $100.0 - 37.0 = 63.0 \text{ g}$  of  $\text{H}_2\text{O}$  ( $= 0.0630 \text{ kg}$ ). But 37.0 g of HCl contains  $37.0 \text{ g} / (36.46 \text{ g/mol}) = 1.01 \text{ mol}$ . The molality is therefore

$$\text{Molality} = \frac{\text{mol HCl}}{\text{kg of solvent}} = \frac{1.01 \text{ mol HCl}}{0.0630 \text{ kg H}_2\text{O}} = 16.1 \text{ m}$$

**Example Converting Parts per Billion into Molarity**

Normal alkanes are hydrocarbons with the formula  $\text{C}_n\text{H}_{2n+2}$ . Plants selectively synthesize alkanes with an odd number of carbon atoms. The concentration of  $\text{C}_{29}\text{H}_{60}$  in summer rainwater collected in Hannover, Germany, is 34 ppb. Find the molarity of  $\text{C}_{29}\text{H}_{60}$  and express the answer with a prefix from Table 1-3.

**Solution** A concentration of 34 ppb means there are 34 ng of  $\text{C}_{29}\text{H}_{60}$  per gram of rainwater, a value that we equate to 34 ng/mL. Multiplying nanograms and milliliters by 1 000 gives 34  $\mu\text{g}$  of  $\text{C}_{29}\text{H}_{60}$  per liter of rainwater. Because the molecular mass of  $\text{C}_{29}\text{H}_{60}$  is 408.8 g/mol, the molarity is

$$\text{Molarity of C}_{29}\text{H}_{60} \text{ in rainwater} = \frac{34 \times 10^{-6} \text{ g/L}}{408.8 \text{ g/mol}} = 8.3 \times 10^{-8} \text{ M}$$

An appropriate prefix from Table 1-3 would be nano (n), which is a multiple of  $10^{-9}$ :

$$8.3 \times 10^{-8} \text{ M} \left( \frac{1 \text{ nM}}{10^{-9} \text{ M}} \right) = 83 \text{ nM}$$



### What Do We Mean by "Ionic Strength"?

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

$$\text{Ionic strength: } \mu = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + \cdots) = \frac{1}{2} \sum_i c_i z_i^2 \quad (8-3)$$

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 Calculation of Ionic Strength

Find the ionic strength of (a) 0.10 M NaNO<sub>3</sub>; (b) 0.010 M Na<sub>2</sub>SO<sub>4</sub>; and (c) 0.020 M KBr plus 0.010 M Na<sub>2</sub>SO<sub>4</sub>.

#### Solution

$$\begin{aligned} \text{(a) } \mu &= \frac{1}{2} \{ [\text{Na}^+] \cdot (+1)^2 + [\text{NO}_3^-] \cdot (-1)^2 \} \\ &= \frac{1}{2} \{ 0.10 \cdot 1 + 0.10 \cdot 1 \} = 0.10 \text{ M} \end{aligned}$$

$$\begin{aligned} \text{(b) } \mu &= \frac{1}{2} \{ [\text{Na}^+] \cdot (+1)^2 + [\text{SO}_4^{2-}] \cdot (-2)^2 \} \\ &= \frac{1}{2} \{ (0.020 \cdot 1) + (0.010 \cdot 4) \} = 0.030 \text{ M} \end{aligned}$$

Note that  $[\text{Na}^+] = 0.020 \text{ M}$  because there are two moles of Na<sup>+</sup> per mole of Na<sub>2</sub>SO<sub>4</sub>.

$$\begin{aligned} \text{(c) } \mu &= \frac{1}{2} \{ [\text{K}^+] \cdot (+1)^2 + [\text{Br}^-] \cdot (-1)^2 + [\text{Na}^+] \cdot (+1)^2 + [\text{SO}_4^{2-}] \cdot (-2)^2 \} \\ &= \frac{1}{2} \{ (0.020 \cdot 1) + (0.020 \cdot 1) + (0.020 \cdot 1) + (0.010 \cdot 4) \} = 0.050 \text{ M} \end{aligned}$$

NaNO<sub>3</sub> is called a 1:1 electrolyte because the cation and the anion both have a charge of 1. For 1:1 electrolytes, the ionic strength equals the molarity. For other stoichiometries (such as the 2:1 electrolyte Na<sub>2</sub>SO<sub>4</sub>), the ionic strength is greater than the molarity.

Computing the ionic strength of any but the most dilute solutions is complicated because salts with ions of charge  $\geq 2$  are not fully dissociated. In Box 8-1 we find that, at a formal concentration of 0.025 M MgSO<sub>4</sub>, 35% of Mg<sup>2+</sup> is bound in the ion pair, MgSO<sub>4</sub>(aq). The higher the concentration and the higher the ionic charge, the more the ion pairing. There is no simple way to find the ionic strength of 0.025 M MgSO<sub>4</sub>.

## 8-2 Activity Coefficients

The equilibrium constant expression in Equation 8-1 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**:

Activity of C:

$$\mathcal{A}_C = [\text{C}] \gamma_C \quad (8-4)$$

$\uparrow$                        $\uparrow$                        $\nwarrow$   
 Activity      Concentration      Activity coefficient  
 of C              of C                      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 8-1 would be correct.

The correct form of the equilibrium constant is

$$\text{General form of equilibrium constant: } K = \frac{\mathcal{A}_C \mathcal{A}_D}{\mathcal{A}_A \mathcal{A}_B} = \frac{[\text{C}]^c \gamma_C [\text{D}]^d \gamma_D}{[\text{A}]^a \gamma_A [\text{B}]^b \gamma_B} \quad (8-5)$$

Equation 8-5 allows for the effect of ionic strength on a chemical equilibrium because the activity coefficients depend on ionic strength.

For Reaction 8-2, the equilibrium constant is

$$K_{sp} = \mathcal{A}_{\text{Ca}^{2+}} \mathcal{A}_{\text{SO}_4^{2-}} = [\text{Ca}^{2+}] \gamma_{\text{Ca}^{2+}} [\text{SO}_4^{2-}] \gamma_{\text{SO}_4^{2-}}$$

If the concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> 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 (8-5) approaches the "concentration" equilibrium constant (6-2). 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. Commonly, tabulated equilibrium constants are not thermodynamic constants but just the concentration ratio (6-2) measured under a particular set of conditions.

#### Example Exponents of Activity Coefficients

Write the solubility product expression for La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> with activity coefficients.

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

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



### Activity Coefficients of Ions

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

Extended Debye-Hückel equation:

$$\log \gamma = \frac{-0.51z^2\sqrt{\mu}}{1 + (\alpha\sqrt{\mu}/305)} \quad (\text{at } 25^\circ\text{C}) \quad (8-6)$$

In Equation 8-6,  $\gamma$  is the activity coefficient of an ion of charge  $\pm z$  and size  $\alpha$  (picometers, pm) in an aqueous solution of ionic strength  $\mu$ . The equation works fairly well for  $\mu \leq 0.1$  M. To find activity coefficients for ionic strengths above 0.1 M (up to molalities of 2–6 mol/kg for many salts), more complicated *Pitzer equations* are usually used.<sup>7</sup>

Table 8-1 lists sizes ( $\alpha$ ) and activity coefficients of many ions. All ions of the same size and charge appear in the same group and have the same activity coefficients. For example,  $\text{Ba}^{2+}$  and succinate ion  $[\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2^-]$ , listed as  $(\text{CH}_2\text{CO}_2^-)_2$  each have a size of 500 pm and are listed among the charge =  $\pm 2$  ions. At an ionic strength of 0.001 M, both of these ions have an activity coefficient of 0.868.

### Example Using Table 8-1

Find the activity coefficient of  $\text{Ca}^{2+}$  in a solution of 3.3 mM  $\text{CaCl}_2$ .

**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 8-1,  $\text{Ca}^{2+}$  is listed under the charge  $\pm 2$  and has a size of 600 pm. Thus  $\gamma = 0.675$  when  $\mu = 0.010$  M.

**Another Solution** A better and slightly more tedious calculation uses Equation 8-6, with the ion size  $\alpha = 900$  pm listed for  $\text{H}^+$  in Table 8-1:

$$\begin{aligned} \log \gamma_{\text{H}^+} &= \frac{(-0.51)(1^2)\sqrt{0.025}}{1 + (900\sqrt{0.025}/305)} = -0.054_{98} \\ \gamma_{\text{H}^+} &= 10^{-0.054_{98}} = 0.88_1 \end{aligned}$$

### 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  $\text{H}_2$ , the activity is written

$$\mathcal{A}_{\text{H}_2} = P_{\text{H}_2} \gamma_{\text{H}_2}$$

where  $P_{\text{H}_2}$  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,  $\gamma \approx 1$ . Therefore, for all gases, we will set  $\mathcal{A} = P(\text{bar})$ .

### High Ionic Strengths

Above an ionic strength of approximately 1 M, activity coefficients of most ions increase, as shown for  $\text{H}^+$  in  $\text{NaClO}_4$  solutions in Figure 8-5. We should not be too surprised that activity coefficients in concentrated salt solutions are not the same as those in dilute aqueous solution. The “solvent” is no longer  $\text{H}_2\text{O}$  but, rather, a mixture of  $\text{H}_2\text{O}$  and  $\text{NaClO}_4$ . Hereafter, we limit our attention to dilute aqueous solutions.

### Practice Exercises

- How many grams of perchloric acid are contained in 37.6 g of 70.5 % (w/w) aqueous perchloric acid? How many grams of water are in the same solution?
- Citric acid (molar mass 192.12 g) is a weak acid with three acidic hydrogens. Suppose a solution is prepared by dissolving 2.136 g of citric acid in water to give 1.43 L of solution.
  - What is the equivalent weight of citric acid?
  - What is the normality of the resulting solution?
- An aqueous solution containing 20.0 % (w/w) KI has a density of 1.168 g/mL. Find the molality of the KI solution.

# Thank you

