

# **Chapter 12: Solution Properties**

### **Section 12.1: Solutions**

A solution is a homogeneous mixture of a solute and a solvent. Solutions can exist in any one of the three physical states.

- **1. A gaseous solution** is a homogenous mixture of two or more gases. Example: Air is mainly a mixture of nitrogen and oxygen.
- **2.** A liquid solution is a homogenous mixture of a solute dissolved in a liquid (solvent). The solute can be a solid, a liquid or a gas dissolved in a liquid. Whenever the solvent is water, the solution is called an aqueous solution. Aqueous solutions are emphasized in general chemistry.
- **3.** A solid solution is a homogenous mixture of two or more solids. Example: Metal alloys are solid solutions.

In all cases, the solution concentration specifies the relative amounts of solute and solvent.

# **Section 12.2: Molarity and Mole Fraction**

**Molarity** is the unit of concentration that is most commonly used in problems dealing with solution stoichiometry.

Recall: molarity = 
$$\frac{\text{moles}}{\text{Liter}}$$

Recall: the symbols for molarity are: M or []. The definitions of moles and molarity have been covered in <a href="Chapter 3">Chapter 3</a> & <a href="Chapter 4">Chapter 4</a>. Please review these topics if necessary for a better understanding of the chapters to follow. Molarity is often expressed as big brackets [].

Thus, [] = 
$$M = \frac{\text{moles of solute}}{\text{Liters of solution}}$$

**Mole fraction** is expressed by the symbol X.

Thus, mole fraction of a component = 
$$\frac{\text{moles of a component}}{\text{total moles of all components}}$$

Mole fraction is covered in Chapter 5 in the context of gas mixtures. If you need to review this concept, please go to <a href="Chapter 5">Chapter 5</a>.

## **Section 12.3: Mass Percent and Volume Percent**

The **mass percent** of a solute in a solution is expressed as:

Mass percent (%) of a solute = 
$$\frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$$

Mass percent is often written as **% (w/w)**. Here w/w indicates that the percent is the ratio of weights or masses. The volume of a solute in a solution is expressed as:

Volume percent (%) of a solute = 
$$\frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$$

Volume percent is often written as % (v/v).

Example: A solution is made by dissolving 0.200 moles of NaCl in 4.30 moles of water. Calculate % (w/w) of NaCl.

Recall: 
$$moles (mol) = \frac{mass (g)}{molar mass (g/mol)}$$

Thus, mass (g) = moles (mol) x molar mass (g/mol)

Using this relationship: mass NaCl = 0.200 mol x 58.5 g/mol = 11.7g

Similarly, mass  $H_2O = 4.30 \text{ mol } \times 18.0 \text{ g/mol} = 77.4 \text{ g}$ 

Total mass of solution = 11.7 g + 77.4 g = 89.1 g

% (w/w) NaCl = 
$$\frac{17.7g}{89.1g} \times 100$$
  
=13.1 %

In this section, practice the Interactive Problem.

# Section 12.4: Parts per Million

When the amount of solute in solution is very small, the concentration is expressed in **parts per million (ppm)**.

ppm solute = 
$$\frac{\text{mass of solute}}{\text{total mass of solution}} \times 10^6$$

Example: Wastewater from a manufacturing plant contains 0.11 g Ca<sup>+2</sup> ion and 0.033 g Mg<sup>+2</sup> ion per 50.0 L solution. The solution density is 1.001 g/mL. Calculate the Ca<sup>+2</sup> and Mg<sup>+2</sup> concentrations in ppm.

The solution density is 1.001 g/mL. The masses of Ca<sup>+2</sup> and Mg<sup>+2</sup> ions are given in grams.

Recall: density = 
$$\frac{\text{mass}}{\text{volume}}$$
  
mass = density x volume  
mass = 1.001  $\frac{\text{g}}{\text{mL}}$  x 50.0 L x  $\frac{1000 \text{ mL}}{1\text{L}}$   
mass = 50050 g

Thus, the total mass of the solution is 50050 g.

$$ppm Ca^{+2} ion = \frac{mass of Ca^{+2}}{total mass of solution} \times 10^6$$

$$ppm Ca^{+2} ion = \frac{0.11g}{50050 g} \times 10^6$$

$$ppm Ca^{+2} ion = 2.2 ppm$$

Continue with the Interactive Problem to practice these concepts.

# **Section 12.5: Molality**

**Molality** (m) is defined as the number of moles of solute per kilogram of solvent.

Recall: 
$$1000 \text{ g} = 1 \text{ kg}$$
  
Thus, Molality (m) =  $\frac{\text{moles of solute}}{\text{kg of solvent}}$ 

Example: A solution has 2.40 g of glucose ( $C_6H_{12}O_6$ ) in 80.0 g of water. Calculate the molality of  $C_6H_{12}O_6$ .

$$\begin{split} \text{moles of C}_6 H_{12} O_6 &= \frac{\text{mass of C}_6 H_{12} O_6}{\text{molar mass of C}_6 H_{12} O_6} \\ &= \frac{2.40 \text{ g}}{180.0 \text{ g/mol}} \\ &= 0.0133 \text{ mol} \\ \text{moles of C}_6 H_{12} O_6 = 0.0133 \text{ mol} \end{split}$$

Now, we calculate the mass of water in kilograms.

mass H<sub>2</sub>O = 80.0 g H<sub>2</sub>O x 
$$\frac{1 \text{ kg}}{1000 \text{ g}}$$
  
= 0.0800 kg H<sub>2</sub>O  
molality (m) =  $\frac{0.0133 \text{ mol } C_6H_{12}O_6}{0.0800 \text{ kg H}_2O}$   
= 0.166 m

Practice the Interactive Problem.

# **Section 12.6: Solubility**

Solubility is the property that characterizes the maximum extent to which a solute can dissolve in a particular solvent. Dissolution implies that solvent and solute become intimately mixed at the molecular level.

The solubility of a solute in a solvent is controlled primarily by three factors:

- (1) Solute-Solvent Interactions
- (2) Temperature
- (3) Pressure

Let us examine each of these three factors, in turn.

#### Section 12.6a: Solute-Solvent Interactions

The dissolution process can be expressed by the equation:

Pure Solvent + Pure Solute → Mixed (Solvent + Solute)

We will learn in <u>Chapter 18</u> that to accurately assess whether dissolution does or does not occur, one must consider changes in both the energy and the disorder resulting from mixing. Mixing increases the disorder in the system, hence, it favors the formation of a solution. Therefore, whether dissolution does or does not occur depends mainly on the relative strength of intermolecular interactions within the pure solvent, within the pure solute, and between solvent and solute.

Qualitatively, we will say that two compounds are likely to be soluble in each other if they exhibit intermolecular forces that are similar in nature and strength.

This important statement can be remembered by the rule of thumb:

#### "Like Dissolves Like."

Recall the definition of polar and non-polar molecules from <u>Chapter 10</u>. Thus, polar compounds are likely to be soluble in other polar compounds, and non-polar compounds are likely to be soluble in other non-polar compounds.

**Consider a hydrocarbon:** Hydrocarbons (i.e. molecular compounds containing carbon and hydrogen) form the backbone of organic compounds.

The only intermolecular forces in hydrocarbons are dispersion forces. Hence, hydrocarbons are non-polar. Water is a polar substance. The water molecules actually interact with each other through hydrogen bonding.

Hence, hydrocarbons and water exhibit very different intermolecular forces and are not be soluble in each other. The lack of solubility of hydrocarbons in water can be understood from the difference in strength of the intermolecular forces.

To make a homogeneous mixture of water and hydrocarbons requires:

- Breaking the strong hydrogen bonds between water molecules and the weak dispersive interactions between hydrocarbon molecules
- 2. Establishing even weaker dispersive interactions between water and hydrocarbon.

We conclude that to make a homogeneous mixture of water and hydrocarbon would require a large and positive change in energy. Hence, dissolution of hydrocarbon in water does not take place.

## Consider methanol (CH<sub>3</sub>OH), ethanol (C<sub>2</sub>H<sub>5</sub>OH) and 1-octanol (C<sub>8</sub>H<sub>17</sub>OH).

Methanol and ethanol are very soluble in water, but octanol is not.

## Why?

Organic compounds bearing a hydroxyl group (-OH) are called alcohols. While OH groups exhibit similar intermolecular forces as  $H_2O$  molecules, the hydrocarbon pieces ( $CH_3$ ,  $C_2H_5$ ,  $C_8H_{17}$ ) do not.

Hence, when alcohols are added to water, their –OH group can form hydrogen bonds with water. Now, intermolecular forces in hydrocarbons are dispersive forces. The strength of these forces increases with the size of the hydrocarbon.

In methanol and ethanol, the hydrogen bonding interactions are stronger than the dispersive interactions. Hence, these alcohols dissolve in water. In octanol, dispersive forces are stronger than hydrogen bonding. Hence, octanol has higher solubility in hydrocarbons than in water.

#### Now, let us consider an ionic solid, NaCl.

NaCl is stable in the solid state because of the strong coulombic forces of attraction between oppositely charged ions (i.e.  $Na^+$  and  $Cl^-$ ). However, when solid NaCl is mixed with water, the forces of attraction between  $H_2O$  molecules and these ions ( $Na^+$  and  $Cl^-$ ) are greater than the forces between

the ions or the water molecules themselves. Hence, NaCl, like many other salts, readily dissolves in water.

lonic solids like  $CaCO_3$  are only slightly soluble in water because the forces of attraction between oppositely charged ions ( $Ca^{+2}$  and  $CO_3^{-2}$ ) are greater than the force of attraction between  $H_2O$  molecules and these ions.

## Section 12.6b: Effect of Temperature

The solubility of a solute in a solvent generally depends on the temperature. In this section we will examine the effect of temperature on the solubility of solids and gases in liquids.

#### Solid solutes

We all know that sugar (sucrose) dissolves when added to water. Sucrose has the chemical formula  $C_{12}H_{22}O_{11}$ . The chemical equation for dissolution is written as:

$$C_{12}H_{22}O_{11 (s)} \leftrightarrows C_{12}H_{22}O_{11 (s)}$$

The two arrows indicate that the reaction is at equilibrium. When an excess amount of sucrose is added to a given quantity of water, a saturated sucrose solution is formed. We also know that the amount of sucrose dissolved in water increases when the water is heated.

Hence, we conclude that the solubility of sucrose in water increases with temperature.

A similar conclusion is reached for <u>most, but not all</u> solid compounds. For instance, for a number of cerium compounds, the solubility actually decreases with increasing temperature.

In <u>Chapter 14</u>, we will learn that it is possible to predict the direction in which an equilibrium shifts, from the sign of the enthalpy change for that process (Le Châtelier's principle).

Specifically, using this principle we conclude that:

- 1. Solubility increases with increasing temperature if the dissolution process is endothermic ( $\Delta H_{sol} > 0$ )
- 2. Solubility decreases with increasing temperature if the dissolution process is exothermic ( $\Delta H_{sol} < 0$ )

In most cases,  $\Delta H_{sol} > 0$  (endothermic dissolution), because the intermolecular attractive forces are stronger in the solid than in solution.

#### Gas solutes

The solubility of gases in liquids always decreases with increasing temperature. Gases in general have very weak intermolecular forces because molecules in the gas state are on the average far from each other. When a gas is dissolved in a liquid, the gas molecules become surrounded by solvent molecules.

Hence, the solute molecules exhibit much stronger intermolecular interactions in the solution state than in the gas state. Dissolving a gas in a liquid is therefore an endothermic process.

Thus, 
$$\Delta H_{sol} < 0$$

#### Section 12.6c: Effect of Pressure

Solids and liquids are generally considered incompressible. Hence, pressure has a negligible effect on their solubility. In contrast, gases are highly compressible. Hence, pressure has a major effect on their solubility in liquids or solids.

## Section 12.6d: Henry's Law

Henry's law expresses the relationship between gas pressure and solubility. According to Henry's law, at moderate pressures the gas solubility is directly proportional to the partial pressure of the gas. Mathematically, this is expressed as:

In this equation,  $S_{gas}$  = Solubility of the gas expressed in mol/L

K<sub>H</sub> = Henry's constant expressed in mol.L<sup>-1</sup>.atm<sup>-1</sup>

P<sub>gas</sub> = Partial pressure of the gas expressed in atm

One takes advantage of the dependence of solubility on partial pressure when making carbonated beverages. A second important example of the

effect of pressure on gas solubility explains the decompression sickness experienced by scuba divers when they ascend too rapidly from deep water to the surface. While the solubility of nitrogen gas in the scuba diver's blood is very low at ambient pressure, it can become significant as the diver reaches significant depths and experiences notable compression. Too rapid an ascension leads to a rapid decompression and may force the excess nitrogen to bubble out of the diver's blood. These bubbles can impair the blood circulation, result in pain and possibly cause fatality.

In order to minimize risks, deep sea divers breathe a helium-oxygen mixture rather than a nitrogen-oxygen mixture. Because helium is much less soluble in blood than nitrogen, much less gas needs to be released from the diver's blood during decompression as he ascends rapidly to the surface.

In Section 12.6(d), practice the Interactive Problems.

## **Section 12.7: Colligative Properties of Solutions**

Some properties of solutions depend primarily on the solute concentration and on the properties of the solvent, but not those of the solute. These properties are:

- Vapor Pressure Lowering
- Osmotic Pressure
- Boiling Point Elevation
- Freezing Point Depression

These properties are called **colligative properties**.

### Sections 12.7a - 12.7.b: Vapor Pressure Lowering

Here, we only consider non-electrolyte solutions containing a non-volatile solute. Recall, a non-electrolyte solution does not conduct electricity. In solutions containing a non-volatile solute, the solute vapor pressure is negligible compared to the solvent vapor pressure. For such solutions, it is observed that the vapor pressure of the solution is lower than the vapor pressure of the pure solvent.

This is called **Vapor Pressure Lowering**.

The Vapor Pressure Lowering is expressed by the symbol  $\Delta P$ .

$$\Delta P = P^{o}_{solvent} - P_{solvent}$$

Here.

 $P^{o}_{solvent}$  = Vapor pressure of the solvent above the pure solvent  $P_{solvent}$  = Vapor pressure of the solvent above the solution

The vapor pressure of the solvent above the solution equals the vapor pressure of the pure solvent times the mole fraction of the solvent in the solution. This relationship is called **Raoult's law**. Mathematically, Raoult's law is expressed as:

$$P_{solvent} = X_{solvent} P^{o}_{solvent}$$

An ideal solution is defined as a solution that follows Raoult's law at any concentration (or mole fraction). However, solutions behave ideally only under limited circumstances. In general, Raoult's law works well for the solvent only when the solvent is almost pure, that is, when the solution is dilute.

Use Raoult's law in the expression for the Vapor Pressure Lowering.

$$\Delta P = P^{o}_{solvent} - X_{solvent} P^{o}_{solvent}$$
  
Thus,  $\Delta P = P^{o}_{solvent} [1 - X_{solvent}]$ 

A solution consists of solvent + solute. Hence, the sum of their mole fractions must be equal to 1.

i.e. 
$$X_{solute} + X_{solvent} = 1$$
  
Hence,  $X_{solute} = 1 - X_{solvent}$   
 $\Delta P = P^{o}_{solvent} X_{solute}$ 

This equation indicates that the Vapor Pressure Lowering increases with an increasing concentration of solute.

Example: 4.60 g of glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, is dissolved in 12.2 g of water at 25°C. Calculate the vapor pressure lowering of water given that the vapor pressure of water at 25°C is 23.8 mmHg.

Recall:

$$\Delta P = P^{o}_{solvent} \quad X_{solute}$$
 
$$\Delta P = Vapor \ \, Pressure \ \, Lowering$$
 The solvent is H<sub>2</sub>O and the solute is C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. 
$$P^{o}_{solvent} = 23.8 \ \, mmHg \ \, at \ \, 25^{o}C.$$
 
$$X_{solute} = \frac{{}^{n}C_{6}H_{12}O_{6}}{{}^{n}C_{6}H_{12}O_{6} + {}^{n}H_{2}O}$$
 
$${}^{n}C_{6}H_{12}O_{6} = \frac{4.60 \ \, g}{180.0 \ \, g/mol} = 0.0256 \ \, mol$$
 
$${}^{n}H_{2}O = \frac{12.2 \ \, g}{18.0 \ \, g/mol} = 0.678 \ \, mol$$
 Thus, 
$$X_{solute} = \frac{0.0256}{0.0256 + 0.678} = 0.0364$$
 Thus, 
$$\Delta P = 23.8 \ \, mmHg \times 0.0364$$
 
$$\Delta P = 0.0866 \ \, mmHg$$

Hence, pure water by itself has a vapor pressure of 23.8 mmHg at 25°C. However, when 4.60 g of glucose is added to 12.2 g of water, the vapor pressure above the solution is reduced by 0.0866 mmHg. Lowering of the vapor pressure results from the favorable solute-solvent intermolecular forces, which tend to keep the water molecules in solution.

In Section 12.7b, practice the Interactive Problem.

### Sections 12.7c - 12.7d: Osmotic Pressure

**Osmosis** is the flow of a solvent through a semi-permeable membrane to equalize the solute concentration on both sides of the membrane. A semi-permeable membrane allows solvent but not solute molecules to pass through.

When two solutions with the same solvent are separated by a semipermeable membrane, solvent molecules pass through the membrane from the low concentration solution to the high concentration solution. The **osmotic pressure**  $(\pi)$  is the pressure, which, when applied to the solution, stops the osmosis phenomenon. The osmotic pressure  $(\pi)$  is a colligative property of the solution. Hence, the osmotic pressure is proportional to the concentration of solute in solution.

Recall that the molar concentration can be expressed in terms of the molarity, M.

Thus, 
$$\pi \alpha$$
 M

The proportionality constant is equal to the product of the gas constant and the temperature.

Hence, 
$$\pi = MRT$$

where R = gas constant and T = absolute temperature. For an osmotic pressure in atmosphere, the value of R must be 0.0821 L.atm.mol<sup>-1</sup>.K<sup>-1</sup>.

Osmosis is often used to determine the molar masses of macromolecules (very large molecules making up plastics or biomaterials). Osmosis plays also a very important role in many biological processes.

Note: In osmosis, the solvent flows from the dilute solution side to the concentrated solution side through a semi-permeable membrane. By applying a pressure equal to the osmotic pressure to a concentrated solution, the process of osmosis can be stopped. By applying a pressure greater than the osmotic pressure ( $\pi$ ), the process is reversed. In this latter case, the solvent flows from the concentrated solution through the semipermeable membrane into the dilute solution. This process is called **Reverse Osmosis**. Reverse osmosis is often used to desalinate ocean water. Desalination means removing salts from seawater to make it drinkable.

Example: A polymer scientist dissolves 12.062 g of a polymer in water to make a 50.0 mL solution. Given that at 25 deg.C, the osmotic pressure of this solution is 0.372 atm, calculate the molar mass of the polymer.

Recall 
$$\pi$$
 = MRT

$$M = \frac{\text{moles solute}}{\text{Liter solution}} = \frac{\text{mass solute}}{\text{molar mass solute } \times \text{Liter solution}}$$

$$= \frac{12.062 \text{ g}}{\text{molar mass } \times 0.050 \text{ L}}$$

$$R = 0.0821 \text{ L.atm.mol}^{-1}.\text{K}^{-1}$$
 
$$T = 25 \text{ deg.C} = 298 \text{ K}$$
 
$$\pi = 0.372 \text{ atm}$$
 Thus, 
$$0.372 \text{ atm} = \frac{12.062 \text{ g} \times 0.0821 \text{L.atm.mol}^{-1}.\text{K}^{-1} \times 298 \text{K}}{\text{molar mass} \times 0.050 \text{ L}}$$
 or Molar Mass = 
$$\frac{12.062 \text{ g} \times 0.0821 \text{L.atm.mol}^{-1}.\text{K}^{-1} \times 298 \text{K}}{0.372 \text{ atm} \times 0.050 \text{ L}}$$
 Molar mass = 
$$1.6 \times 10^4 \text{ g/mol}$$

In Section 12.7d, practice the Interactive Problem.

## Section 12.7e: Boiling Point Elevation

The boiling point of a liquid is the temperature at which the vapor pressure of the liquid is equal to the atmospheric pressure. Adding a nonvolatile solute to a solvent produces a lowering of the vapor pressure of the solvent.

Hence, this in turn affects the boiling point of the solution. In fact, the boiling point of the solution is higher than that of the pure solvent.

If  $T_b$  is the boiling point of the solvent in the solution and  $T_b{}^o$  is the boiling point of the pure solvent,

Then, 
$$\Delta T_b = T_b - T_b^0$$

 $\Delta T_b$  is called the Boiling Point Elevation.

 $\Delta T_{\text{b}}$  is proportional to the vapor pressure lowering of the solution.

 $\Delta T_b$  is another colligative property of the solution.

 $\Delta T_{\text{b}}$  is proportional to the concentration of solute in the solution.

Thus, 
$$\Delta T_{\rm b} \, \propto m$$

Here, m is the molal concentration (i.e. the molality) of the solute in solution.

Hence, 
$$\Delta T_b = K_b m$$

 $K_b$  is the proportionality constant called the **molal boiling point elevation** constant or the **molal ebullioscopic constant**. The value of  $K_b$  depends only on the solvent.

## **Section 12.7f: Freezing Point Depression**

The freezing point depression is defined as the difference between the freezing point of a solvent and that of a solution. Mathematically, this is expressed as:

$$\Delta T_f = T_f^o - T_f$$

 $\Delta T_f$  = Freezing point depression

T<sub>f</sub>° = Freezing point of the pure solvent

 $T_f$  = Freezing point of the solvent in the solution

 $\Delta T_f$  is proportional to m, the molal concentration of solute in the solution.

Thus, 
$$\Delta T_f \propto m$$

Hence, 
$$\Delta T_f = K_f m$$

K<sub>f</sub> is the proportionality constant called the **molal freezing point depression** constant or the molal cryoscopic constant.

There are many common examples of freezing point depression. In winter, the snow can be kept off highways by sprinkling them with salts. The salt is a solute which depresses the freezing point of water. Hence, when snow falls on a road and comes in contact with the salt, its melting temperature is lowered below the ambient temperature. As a consequence, the snow melts.

Another application of the concept of freezing point depression is the preparation of antifreeze for a car's radiator. During winter, pouring antifreeze into your radiator prevent the radiator's water from transforming into ice. Antifreeze is a mixture of water and ethylene glycol, a liquid which dissolves in water and decreases water's freezing point. In freezing point depression applications, the solute can be nonvolatile or volatile, electrolyte or nonelectrolyte. However, the solute must not crystallize in the presence of the solvent.

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