

## CHAPTER 7 SOLUTIONS

### 7.1 Solutions

From your basic chemistry, **solution** may be defined as a homogeneous mixture. They are usually classified according to the physical state such as: gaseous, liquid and solid solutions. Dalton's law of partial pressure describes the behavior of gaseous solutions and air is the most common example. Alloys are also solid solutions; coinage silver is copper dissolved in silver, and that brass is a solid solution of zinc in copper but not all alloys are solid solutions. Liquid solutions are the most common among the solutions and are usually the most common employed by chemists.

When several non-reacting substances are mixed, three possible types of mixtures may be obtained:

- A coarse mixture, such as that of salt and sugar
- Colloidal dispersion, such as results when fine clay is shaken in water, or
- A true solution, obtained when a substance like sugar dissolves in water.

In the coarse mixture, the individual particles are readily discernable and may be separated from each other by mechanical means.

Although, in a colloidal dispersion the particles are much finer and the heterogeneity is not so readily apparent, the dispersion, is nevertheless, not homogeneous.

On the other hand, in the true solution the conditions the conditions cannot be separated from each other by mechanical means, and every part of the solution is found to be like every other part; i.e. a true solution constitutes a homogeneous phase.

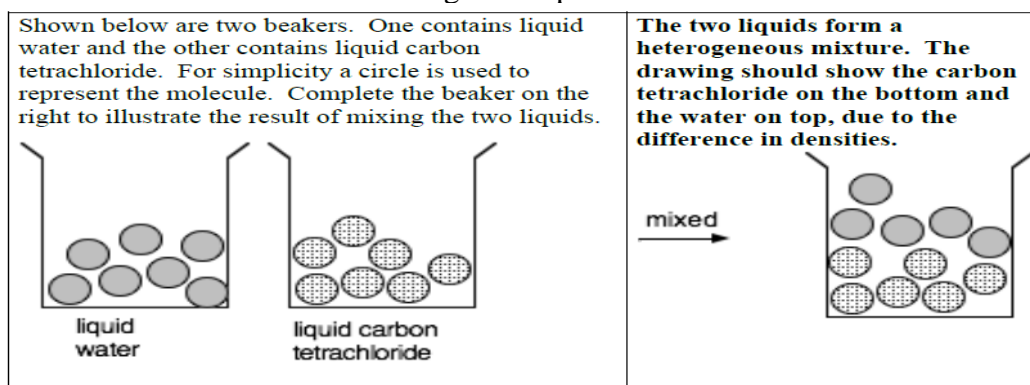


Figure 7.1 Heterogeneous Mixture

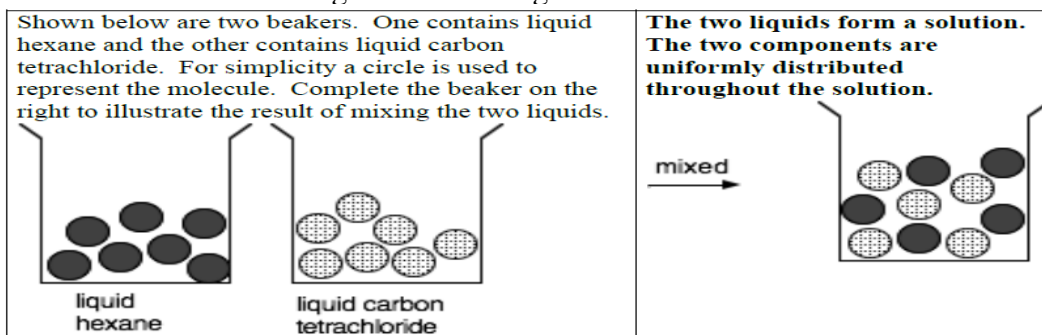


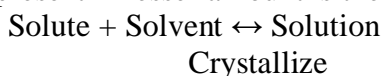
Figure 7.2 Homogeneous Mixture (Solution)

### 7.1.1 Parts of Solution

**Solute** is the substance that dissolves, present in small amount and the **solvent** is the substance in which solution takes place usually present in large amount

### 7.1.2 Nature of Solutions

Solutions have two components, namely, the solute and the solvent. The component of a solution usually present in greater amount is the **solvent**. It is the dissolving medium. And the component that is dissolved and it is usually present in lesser amount is the **solute**.



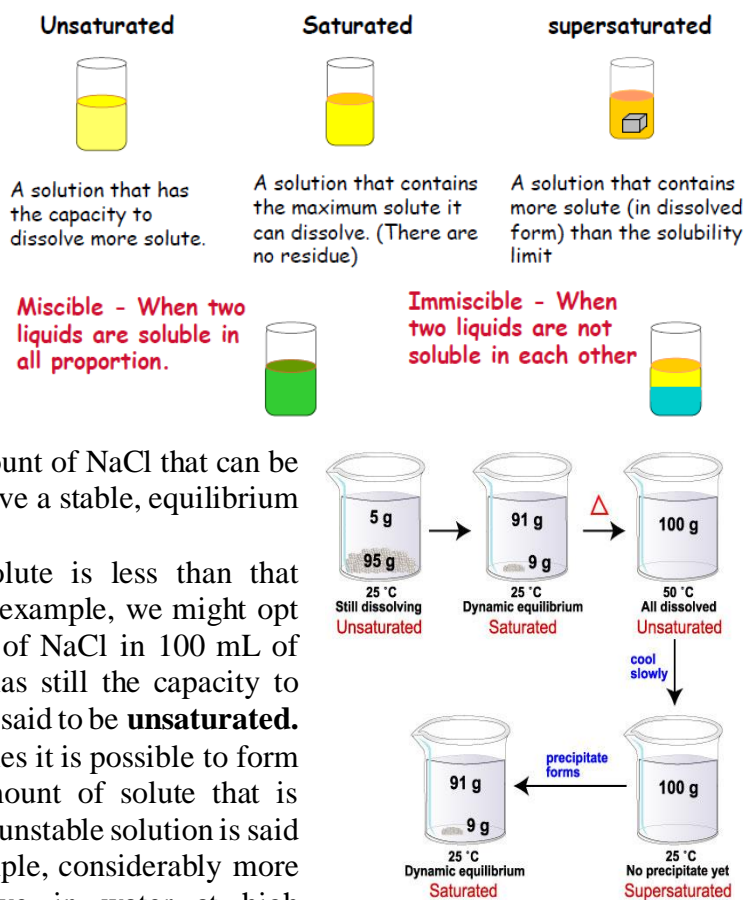
### 7.1.3 Saturated Solutions and Solubility

As a solid solute starts to dissolve in a solvent, the concentration of solute particles in solution, increases, their chances of colliding with the surface of the solid also increase. Such collision will make the solute reattached to the solid which is the opposite of solution process. Such process is called **crystallization**, such as in the reaction given above.

As the process continues, the rates of the opposing processes will be equal achieving a state of equilibrium. A solution that is in equilibrium with the undissolved solute is said to be **saturated**. Any addition of solute to the solution, will not be dissolved. The amount of solute required to form that saturated solution in a given quantity of solvent is known as the **solubility** of that solvent. For example, the solubility of NaCl in water at 0°C is 35.7g per 100 mL of water. This gives the maximum amount of NaCl that can be dissolved in a given quantity of water to give a stable, equilibrium solution at that temperature.

In cases, where the dissolved solute is less than that required to form a saturated solution. For example, we might opt to form a solution containing only 15.0g of NaCl in 100 mL of water at 0°C. In this case, the solution has still the capacity to dissolve more of the solute. This solution is said to be **unsaturated**.

Under suitable conditions, sometimes it is possible to form solutions that contain more than the amount of solute that is required to form a saturated solution. Such unstable solution is said to be **supersaturated** solution. For example, considerably more sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2$ , can dissolve in water at high temperatures than at low temperatures. When saturated solution of sodium acetate is made at high



temperature and then cooled slowly, all of the solute may remain dissolved even though the solubility decreases as the temperature is reduced. Because the solute in a supersaturated solution is present in a concentration higher than the equilibrium concentration, supersaturated solutions are unstable. In order for crystallization to occur, the molecules or ions of solute must arrange themselves properly to form crystals. Addition of small crystal of solute ( seed crystal in the process called **seeding**) provides a template for crystallization of the excess solute, leading to a saturated solution in contact with excess solid. This process is applicable in the sugar industry where syrup is allowed to undergo evaporation process producing a supersaturated solution. Addition of sugar crystal (**seeding**) will crystallize the sugar and will be separated from the excess liquid called **molasses**. Also in the caramelization of sugar. During caramelization process, addition of small amount of sugar crystal will re-crystallize the excess sugar known as **graining**.

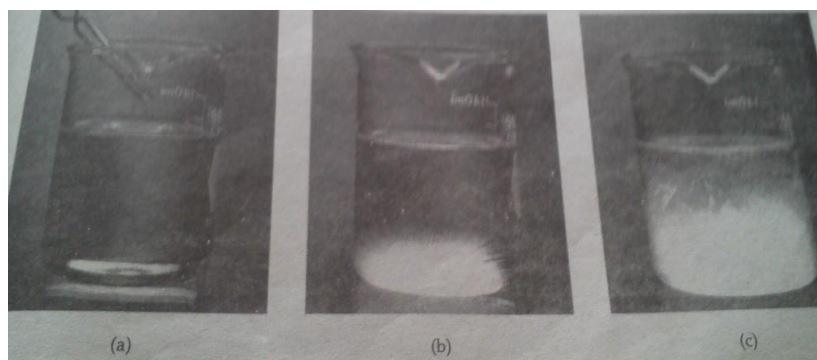
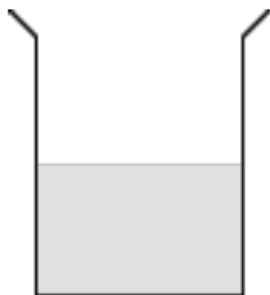


Figure 8.3 Sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) readily forms supersaturated solutions in water. (a) when a seed crystal of  $\text{NaC}_2\text{H}_3\text{O}_2$  is added, excess sodium acetate crystallizes from the solution, as in (b) and (c).



Given that the beaker to the left contains an aqueous solution of  $\text{NaCl}$ , describe a simple test to determine whether the solution is unsaturated, saturated or supersaturated. What would you expect to happen during the test if the solution were unsaturated? saturated? supersaturated?

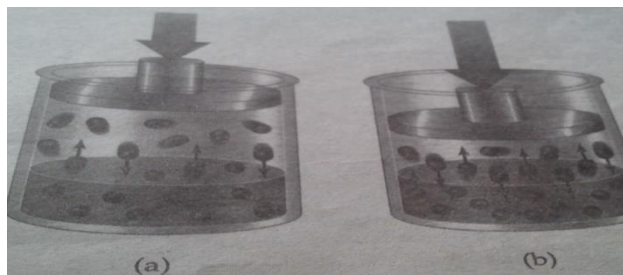
**Adding a crystal of sodium chloride is all that is necessary to determine whether the solution is unsaturated, saturated or supersaturated. If the solution is unsaturated, the crystal of  $\text{NaCl}$  will dissolve. If the solution is saturated, the crystal will fall to the bottom of the beaker and will not dissolve. If the solution is supersaturated, the addition of the crystal will cause the extra  $\text{NaCl}$  to precipitate out of the solution causing it to increase in quantity.**

## 7.2 Factors Affecting Solubility

The extent in which a substance is dissolved in another substance is dependent upon the nature of both the solute and the solvent. And it also depends on the temperature and, for gases, on pressure. In this topic, we will only discuss briefly the effect temperature and pressure on the solubility.

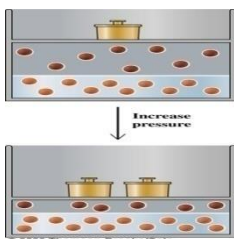
## 7.2.1 Pressure Effects

The solubility of a gas in any solvent increases as the pressure of the gas over the solvent increases. On the contrary, the solubilities of solids and liquids are not appreciably affected by pressure.



### 7.2.1.1 Effect of pressure on the solubility of a gas.

When the pressure is increased, as in (b), the rate at which gas molecules enter the solution increases. The concentration of solute molecules at equilibrium increases in proportion to the pressure.



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The solubility of the gas increases in direct proportion to its partial pressure above the solution.

Bottlers use the effect of pressure on solubility in producing carbonated beverages such as champagne, beer and soft drinks. These are bottled under a carbon dioxide pressure slightly greater than 1 atm in the process called **carbonation**.

When the bottles are opened to the air, the partial pressure of  $\text{CO}_2$  above the solution is decreased and its solubility decreases causing it to bubble out of the solution.

Because the solubility of gases increases with increasing pressure, divers who breathe compressed air must be concerned about the solubility of gases in their blood. Although the gases are not very soluble at sea level, their solubilities can become appreciable deep underwater where their partial pressures are greater. The deep-sea divers must ascend slowly to prevent dissolved gases from being released rapidly from blood and other fluids in the body. These bubbles affect nerve impulses and give rise to the affliction known as

#### Pressure - (Gas)

**Solubility of gas is greatly affected by pressure**

Gas solute is very sensitive to pressure. Gas particles are separated by large void space, an increase in pressure will increase these particles to come closer together thereby increasing the solubility of the gas.

Divers must be careful when diving to great depth because the potential of dissolved  $\text{N}_2$  gas in blood. Clinical term is the **Bends**.



#### Pressure - (Solid and Liquid)

The solubility of solids and liquids are hardly affected by pressure.

Solids and liquids are already very close to each other. An increase in pressure will not affect solubility



decompression sickness or “the bends” which is very painful and can be fatal. Nitrogen is the main problem because it has highest partial pressure in air because it can be removed only through the respiratory system. Oxygen, on the other hand is consumed by metabolism.

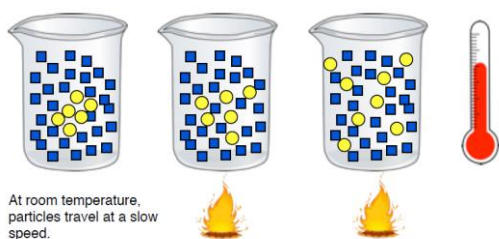
Deep-sea divers sometimes substitute helium for nitrogen in the air they breathe, because helium has a much lower solubility in biological fluids than nitrogen does. For example, divers working at a depth of 100ft experience a pressure of about

four atm. At this pressure a mixture of 95 mole percent helium and 5 mole percent oxygen will give an oxygen a partial pressure of about 0.20 atm, which is the partial pressure of oxygen in normal air at 1 atm. If the oxygen partial pressures become too great, the urge to breathe is reduced,



carbon dioxide is not removed from the body, and carbon dioxide poisoning occurs. At excessive concentrations, carbon dioxide acts as neurotoxin, interfering with nerve conduction and transmission.

## 7.2.2 Temperature Effects

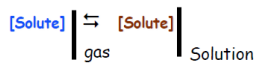


At room temperature, particles travel at a slow speed.

At higher temperature, particles are moving faster.

### Temperature - (Gas)

Consider the extent in which  $O_2$  or  $CO_2$  dissolves in water. What are the conditions which will increase the solubility of gas in water.



As the temperature increase, both solute and solvent will be moving faster, the gas solute however will now have enough energy to leave the liquid interface.

The solubility of most solid solutes in water increases with the increasing temperature of the solution. Thus more sucrose (table sugar,  $C_{12}H_{22}O_{11}$ ) can be dissolved in hot water than in cold water, the basis for making rock candy and some other confections. Generally, solubility of solids increases as the temperature increases.

In contrast to solid solutes, the solubility of gaseous substances in water decreases with increasing temperature. If a glass of cold tap water is warmed, bubbles of air are seen on the inside of the glass. Similarly, carbonated beverages taste flat as they are allowed to warm; as the temperature of the solution increases, the solubility of carbon dioxide decreases and escapes from the solution. The carbon dioxide gas imparts a “bite” on the beverage, as the gas escapes, so the flat taste. The decreased solubility of oxygen in water as temperature increases is one of the

effects of thermal pollution of lakes and streams. The effect is particularly serious in deep lakes because warm water is less dense than cold water and tends to remain on top of cold water at the surface. This situation impedes the dissolving of oxygen into the deeper layers, thus stifling the respiration of all aquatic life needing oxygen. Fish may suffocate and die under these conditions.

## Disaster: (1700 dead) from Gas Solubility



Lake Nyos in Cameroon, the site of a natural disaster. In 1986 a huge bubble of  $CO_2$  escaped from the lake and asphyxiated more than 1700 people.

In the African nation of Cameroon in 1986 a huge bubble of  $CO_2$  gas escaped from Lake Nyos and moved down a river valley at 20 m/s (about 45 mph). Because  $CO_2$  is denser than air, it hugged the ground and displaced the air in its path. More than 1700 people suffocated. The  $CO_2$  came from springs of carbonated groundwater at the bottom of the lake. Because the lake is so deep, the  $CO_2$  mixed little with the upper layers of water, and the bottom layer became supersaturated with  $CO_2$ . When this delicate situation was changed, perhaps because of an earthquake or landslide, the  $CO_2$  came out of the lake water just like it does when a can of soda is opened.

**Dissolving Process:** Why is water soluble in alcohol yet water is insoluble in oil ?

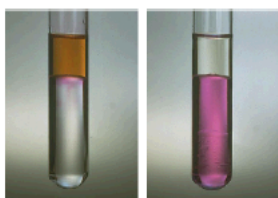
Solubility Factor:

Solute and Solvent characteristic:

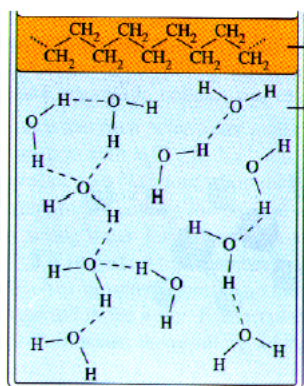
- In aqueous solution, water will form strong intermolecular forces with only other polar molecules (the dissolution process)
- Oil is a nonpolar substance and therefore will only form strong IMF with other nonpolar substances such as organic compounds.
- The result is the immiscibility of water and oil.

(Later the Energetics of this process will be discuss)

Organic Chemist saying  
"Like Dissolves Like"



An oil layer floating on water. For a substance to dissolve, the water-water hydrogen bonds must be broken to make a "hole" for each solute particle. However, the water-water interactions will break only if they are replaced by similar strong interactions with the solute.



## 7.3 Methods of Expressing Concentration of Solutions

1. Percent by Mass
2. Percent by Volume
3. Parts Per Million, ppm
4. Mole Fraction, X
5. Molality, m
6. Molarity, M
7. Normality, N

### 7.3.1. Percent by Mass, %w/w

$$\% \text{ w/w} = \frac{\text{mass of Solute}}{\text{mass of Solution}} \times 100\% \quad \text{but Mass of Solution} = \text{mass of solute} + \text{mass of solvent, then}$$

$$\% \frac{w}{w} = \frac{\text{mass of solute, g}}{\text{mass of solute, g} + \text{mass of solvent, g}} \times 100\%$$

#### Sample Problem 7.1

A solution is made by dissolving 20g of NaCl in 80g of water. What is the concentration of the solution expressed as % by mass?

Given:

Solvent – water; Solute – NaCl

Mass of solute = 10g

Mass of solvent = 90g

$$\% \frac{w}{w} = \frac{20g}{20g + 80g} \times 100\% = 20\%$$

### 7.3.2. Percent by Volume, %v/v

$\% \text{ v/v} = \frac{\text{Volume of solute}}{\text{Volume of Solution}} \times 100\%$  but volume of solution = volume of solute + volume solvent

$$\% \frac{v}{v} = \frac{\text{Volume of Solute}}{\text{Volume of solute} + \text{Volume of Solvent}} \times 100\%$$

Sample Problem 7.2:

A 12 mL of toluene and 88 mL of benzene are mixed to form a solution. What is the concentration of toluene-benzene solution in percent by volume.

Given:

Solvent – benzene, Solute – toluene

Volume of solute = 12mL

Volume of solvent = 80mL

$$\% \frac{v}{v} = \frac{12\text{mL}}{12\text{mL} + 80\text{mL}} \times 100\% = 13.04\%$$

Note: if the given does not specify  $\% \frac{v}{v}$ , it is understood to be  $\% \frac{w}{w}$ .

### 7.3.3. Parts Per Million, ppm

$\text{ppm} = \frac{\text{part of solute}}{\text{part of solution}} \times 100\%$ , but part of solution = part of solute + part of solvent, so

$$\text{ppm} = \frac{\text{part of solute}}{\text{part of solute} + \text{part of solvent}} \times 1,000,000$$

$$\text{ppt} = \frac{\text{part of solute}}{\text{part of solute} + \text{part of solvent}} \times 10,000$$

$$\text{ppb} = \frac{\text{part of solute}}{\text{part of solute} + \text{part of solvent}} \times 1,000,000,000$$

Sample Problem 7.3:

In our example No. 2, let us compute for the ppm.

Given:

Part of solute = 15 part

Part of solvent = 80 part

$$\text{ppm} = \frac{15 \text{ part}}{15 \text{ part} + 80 \text{ part}} \times 1,000,000 = 157,895 \text{ ppm}$$

$$\text{ppt} = \frac{15 \text{ part}}{15 \text{ part} + 80 \text{ part}} \times 10,000 = 1,578.95 \text{ ppt}$$

$$\text{ppb} = \frac{15 \text{ part}}{15 \text{ part} + 80 \text{ part}} \times 1,000,000,000 = 157,895,000 \text{ ppb}$$

ppt – parts per ten thousand; ppb = parts per billion

### 7.3.4. Mole Fraction, X

Mole fraction is the ratio of the number of moles of that component to the total number of moles of all the components present in the solution.

$$X = \frac{\text{Number of moles of one component, } n}{\text{Total number of moles of all the components, } nt}$$

Suppose, we have a three-component solution containing component A, component B, and component C.

$X_A$  – the mole fraction of component A and  $n_A$  – number of moles of component A

$X_B$  – the mole fraction of component B and  $n_B$  – number of moles of component B

$X_C$  – the mole fraction of component C and  $n_C$  – number of moles of component C

Solving for the mole fractions of each component:

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

$$X_B = \frac{n_B}{n_A + n_B + n_C}$$

$$X_C = \frac{n_C}{n_A + n_B + n_C}$$

Solving for the number of moles of any component, n:  $n = \frac{\text{mass of component, g}}{\text{Molar Mass of Component, g/mol}}$

Since mole fractions are expressed in terms of fractions, the total mole fractions of all the components should be equal to 1.00.

Sample Problem 7.4:

A gaseous solution containing 2 mol of  $H_2$  and 5 mol  $O_2$ . What are the mole fractions of  $O_2$  and  $H_2$ ?

Solution:

$$n_{H_2} = 2.0 \text{ mol}$$

$$n_{O_2} = 5.0 \text{ mol}$$

$$X_{H_2} = \frac{2.0 \text{ mol}}{2.0 \text{ mol} + 5.0 \text{ mol}} = 0.29 \quad X_{O_2} = \frac{5.0 \text{ mol}}{2.0 \text{ mol} + 5.0 \text{ mol}} = 0.71$$

$$\text{Checking: } N_{H_2} + N_{O_2} = 0.29 + 0.71 = 1.00$$

Sample Problem 7.5: What is the mole fraction of ethyl alcohol, ( $CH_3CH_2OH$ ), is 39.0% by ethyl alcohol by mass?

Solution:

Atomic mass: C = 12.0; H = 1.0; O = 16.0

Molar mass:

$$CH_3CH_2OH = 46.0 \text{ g/mol}$$

$$H_2O = 18.0 \text{ g/mol}$$

$$\text{Mass of } CH_3CH_2OH = 39.0\% = 39.0 \text{ g}$$

$$\text{Mass of } H_2O = 100.0 \text{ g} - 39.0 \text{ g} = 61.0 \text{ g}$$

$$? \text{ mol } CH_3CH_2OH = 39.0 \text{ g } CH_3CH_2OH \left( \frac{1.0 \text{ mol } CH_3CH_2OH}{46.0 \text{ g } CH_3CH_2OH} \right) = 0.848 \text{ mol}$$

$$? \text{ mol } H_2O = 61.0 \text{ g } H_2O \left( \frac{1.0 \text{ mol } H_2O}{18.0 \text{ g } H_2O} \right) = 3.39 \text{ mol}$$

Mole Fractions:



$$X_{CH_3CH_2OH} = \frac{0.848 \text{ mol}}{0.848 \text{ mol} + 3.39 \text{ mol}} = 0.200 \quad X_{H_2O} = \frac{3.39 \text{ mol}}{0.848 \text{ mol} + 3.39 \text{ mol}} = 0.800$$

$$\text{Or } X_{H_2O} = 1.0 - X_{CH_3CH_2OH} = 1.000 - 0.200 = 0.800$$

### 7.3.5. Molality, m

Molality is often used to express the concentration of solutions that uses solvents other than water. And is defined as the number of moles of solute dissolved in a kilogram of solvent. It is expressed in mol/kg or simply molal, m.

$$m = \frac{\text{moles of solute}, n}{\text{kg of solvent}} \quad \text{but number of moles solute}, n = \frac{\text{mass of solute}, g}{\text{Molar mass of solute}, g/mol} \text{ so,}$$

$$m = \frac{\text{mass of solute}, g}{\text{Molar Mass of solute}(kg \text{ solvent})} = \frac{\cancel{g}}{\frac{\cancel{g}}{mol} (kg)} = \frac{mol}{kg} = \text{molal}$$

Sample Problem 7.6:

A solution is made by dissolving 4.35g of glucose,  $C_6H_{12}O_6$ , in 25.0 mL of water. Calculate the molality of glucose in the solution.

Given:

Atomic mass: C = 12.0; H = 1.0; O = 16.0

Mass of solute ( $C_6H_{12}O_6$ ) = 4.35g

Density of water = 1.00 g/mL

Converting volume to mass of water:

$$? \text{ kg } H_2O = 25.0 \cancel{mL} \left( \frac{1.00 \cancel{g}}{1.00 \cancel{mL}} \right) \left( \frac{1.00 \text{ kg}}{1,000 \cancel{g}} \right) = 0.025 \text{ kg}$$

Molar mass:

$$C_6H_{12}O_6 = [(6 \times 12.0) + (12 \times 1.0) + (16.0 \times 6)] = 180.0 \text{ g/mol}$$

$$m = \frac{4.35 \text{ g}}{180.0 \frac{g}{mol} (0.025 \text{ kg})} = 0.967 \frac{mol}{kg} = 0.967 \text{ molal} = 0.967 \text{ m}$$

Sample problem 7.7:

What is the molality of a 12.5% glucose ( $C_6H_{12}O_6$ ), in water.

Solution:

Atomic mass: C = 12.0; H = 1.0; O = 16.0

Given:

Solute: glucose, ( $C_6H_{12}O_6$ )

Solvent:  $H_2O$

Mass of glucose, ( $C_6H_{12}O_6$ ) = 12.5% ( understood to be % by mass) = 12.5 g

Mass of solvent,  $H_2O$  = 100.0 g – 12.5 g = 87.5 g

Molar mass: glucose, ( $C_6H_{12}O_6$ )

Molar mass of glucose = 180 g/mol

$$m = \frac{12.5 \text{ g}}{180 \frac{g}{mol} (0.0875 \text{ kg})} = 0.79 \text{ molal or } 0.79 \text{ m}$$

### 7.3.6. Molarity, M

$$M = \frac{\text{Moles of solute}}{\text{Volume of Solution, L}} = \frac{\text{mol}}{\text{L}} \text{ or Molar but: } n = \frac{\text{mass of solute, g}}{\text{Molar mass of solute, g/mol}}$$

$$M = \frac{\text{mass of solute, g}}{\text{Molar mass of solute, } \frac{\text{g}}{\text{mol}} (\text{liter of Solution})} = \frac{\text{mol}}{\text{L}} = \text{Molar} = M$$

Sample Problem 7.8:

What is the molarity of a solution prepared by dissolving 15.0g of NaOH in enough water to make a total of 225mL solution?

Solution:

Atomic mass: Na = 23.0; O = 16.0; H = 1.0

Molar mass, NaOH = (1)(23.0) + (1)(16.0) + (1)(1.0) = 40.0 g/mol Given:

Solute: NaOH

Solvent: H<sub>2</sub>O

Mass of solute = 15.0g NaOH

Volume of solvent = 225mL

Converting volume from mL to L ( liter of solution):

$$? \text{ L} = 225 \text{ mL} \times \frac{1.0 \text{ L}}{1000 \text{ mL}} = 0.225 \text{ L}$$

$$M = \frac{15.0 \text{ g}}{40.0 \frac{\text{g}}{\text{mol}} (0.225 \text{ L})} = 1.67 \frac{\text{mol}}{\text{L}} = 1.67 \text{ Molar} = 1.67 \text{ M}$$

$$M = \frac{15.0 \text{ g}}{40 \frac{\text{g}}{\text{mol}} (0.225 \text{ L})} = 1.67 \text{ Molar or } 1.67 \text{ M}$$

Sample Problem 7.9:

What mass of solute should be used to prepare 2.000L of 1.500 M KOH?

Solution:

Atomic mass: H = 1.0; O = 16.0; K = 39.1

Molar mass: KOH = 39.1 + 16.0 + 1.0 = 56.1 g/mol

Solute: KOH

Solvent: H<sub>2</sub>O

V solution = 2.000 L

M of solution = 1.500 M = 1.500 mol/L

Mass of solute = ?

$$1.500 \frac{\text{mol}}{\text{L}} = \frac{\text{KOH, mass of solute, g}}{56.1 \frac{\text{g}}{\text{mol}} (2.000 \text{ L})}$$

$$\text{g KOH} = 1.500 \frac{\text{mol}}{\text{L}} \times 56.1 \frac{\text{g}}{\text{mol}} \times 2.000 \text{ L} = 168.3 \text{ g}$$

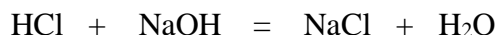
Using the 4 analytical balance, weigh exactly 168.300 g of KOH, dissolve in 100.0 mL of distilled water in a 250-mL beaker. Once all the crystals have been dissolved, transfer into a clean

2.000-L volumetric flask. Fill with distilled water up to the mark. Cap and mix thoroughly. You have prepared a 2.000L of 1.500 M KOH solution.

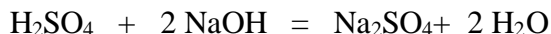
### 7.3.7 Equivalents and Normality

Chemists often find it convenient to use “equivalents” rather than “moles” in quantifying the amount of a substance. Equivalents are also used in biology, environmental science, pharmacy and other health professions. Solution concentrations of equivalents are expressed in “normality” instead of “molarity”. In this introduction to equivalents and normality, the discussion will be limited hydrogen ion in acids and hydroxide bases in acid-base reactions. Equivalents are also employed for the determination of the amounts of oxidizing agents and reducing agents in redox reactions involving the titration of sodium oxalate with potassium permanganate, etc.

The purpose for using equivalents instead of moles is that equivalents are defined so that one equivalent of any acid will react with one equivalent of any base. Recall that this is not true for moles. One mole of any acid will not always react with one mole of any base. Consider the following two chemical equations:



In this first reaction one mole of HCl reacts with one mole of NaOH.



In this second reaction one mole of H<sub>2</sub>SO<sub>4</sub> reacts with two moles of NaOH.

## EQUIVALENTS OF ACIDS AND BASES

### 7.3.7.1 Acids

An equivalent of a protonic acid is defined as the amount of the acid that will donate one mole of hydrogen ions in reactions with bases. The number of equivalents of an acid equal to one mole of the acid can be determined from its chemical formula.

- HCl has only one acidic hydrogen. Thus one mole of HCl is equal to one equivalent (abbreviated “eq”) of HCl, since one mole of HCl donates one mole of H<sup>+</sup> ions. 1 mol HCl = 1 eq HCl.
- H<sub>2</sub>SO<sub>4</sub> has two acidic hydrogens. Thus one mole of H<sub>2</sub>SO<sub>4</sub> donates two moles of H<sup>+</sup> ions and contains two equivalents of H<sub>2</sub>SO<sub>4</sub>. 1 mol H<sub>2</sub>SO<sub>4</sub> = 2 eq H<sub>2</sub>SO<sub>4</sub>.
- Consider acetic acid, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> or CH<sub>3</sub>COOH. The chemical formulas for acids shows the acidic hydrogens first. There is only one acidic hydrogen in acetic acid and three non-acidic hydrogens. For organic acids, the H that is attached to the COO is the available H<sup>+</sup>, hence, only one H.  
1 mol HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> = 1 eq HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>.

A generalized equation is: 1 mol acid = n eq acid, where n is the number of acidic hydrogens in the chemical formula for the acid.

### 7.3.7.2 Bases

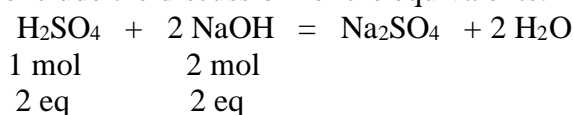
An equivalent of an hydroxide base is defined as the amount of the base that will react with one mole of hydrogen ions. Since one mole of hydroxide ions reacts with one mole of hydrogen ions ( $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ ), the number of equivalents of an hydroxide base in one mole of the hydroxide base equals the number of hydroxide ions in the chemical formula of the base. 1 mol base = n eq base, where **n** is the number of hydroxides in the chemical formula.

Therefore for:

<u>Base</u>	<u>Mol</u>	<u>Eq</u>
NaOH	1	1 (1 OH)
Ca (OH) <sub>2</sub>	1	2 (2 OH)
Al (OH) <sub>3</sub>	1	3 (3 OH)

Note that the #eq of an acid or base is > #mol of an acid or base.

Examples below conclude the discussion for the equivalents.



We see that the #eq acid = #eq base, which is true for all acid-base reactions. In the future discussion, the number of H and the number of OH in the formula are equivalent the number of replaceable Hydrogen ion ( $\text{H}^+$ ) and number of replaceable hydroxide ion ( $\text{OH}^-$ ), respectively.

### 7.3.7.3 Equivalent Weight

One mole of a substance is defined as the weight (mass) in grams equal to its molecular weight (MW). Similarly, one equivalent of a substance is the weight in grams equal to its “equivalent weight” (EW).

- a) For HCl, 1 mol HCl = 1 eq HCl. MW of HCl = 36.46; EW of HCl = 36.46.
- b) For  $\text{H}_2\text{SO}_4$ , 1mol  $\text{H}_2\text{SO}_4$  = 2 eq  $\text{H}_2\text{SO}_4$ . MW of  $\text{H}_2\text{SO}_4$  = 98.08; EW of  $\text{H}_2\text{SO}_4$  = 49.04.

$$\text{EW (Equivalent Weight)} = \frac{\text{Molecular weight or Molar Mass}}{\text{number of replaceable H+or OH-or its equivalent for a salt}}$$

For acids,  $\text{EW} = \text{MW}/\mathbf{n}$ , where **n** is the number of acidic hydrogens in the chemical formula.

For hydroxide bases,  $\text{EW} = \text{MW}/\mathbf{n}$ , where **n** is the number of hydroxide ions in the chemical formula.

The EW is always less than or equal to the MW.  $\text{EW} \leq \text{MW}$ .

#### Molecular Weights and Equivalent Weights of some Acids and Bases

<u>Compound</u>	<u>MW</u>	<u>EW</u>
$\text{HNO}_3$	63.01	63.01
$\text{H}_3\text{PO}_4$	98.00	32.67
NaOH	40.00	40.00
$\text{Ca}(\text{OH})_2$	74.09	37.05
$\text{Al}(\text{OH})_3$	78.00	26.00

In some cases, milli-equivalent is used such as:

$$\text{GEW (Gram Eq. Weight)} = \frac{\text{Molecular weight or Molar Mass}}{(\text{number of replaceable H+or OH-or its equivalent for a salt})1000}$$

For acids,  $GEW = \frac{MW}{1000 n}$ , where **n** is the number of acidic hydrogens in the chemical formula.

For hydroxide bases,  $GEW = \frac{MW}{1000 n}$ , where **n** is the number of hydroxide ions in the chemical formula.

Sample Problem 7.10:

Calculate the #eq of  $\text{Ca(OH)}_2$  in 6.32 g of  $\text{Ca(OH)}_2$ . What is its meq (milliequivalent):

Solution:

Atomic mass: Ca = 40.0; O = 16.0; H = 1.0

Molar Mass:

$\text{Ca(OH)}_2 = 74.0 \text{ g/mol}$

Number of replaceable  $\text{OH}^- = 2 \text{ eq/mol}$

$$\text{Number of g/equivalent} = \frac{74.0 \text{ g/mol}}{2 \text{ eq/mol}} = 37 \frac{\text{g}}{\text{eq}}$$

$$\text{Number of g/milliequivalent (meq)} = \frac{74.0 \text{ g/mol}}{2000 \text{ meq/mol}} = 0.037 \frac{\text{g}}{\text{meq}}$$

$$\text{Number of equivalent} = \frac{6.32 \text{ g Ca(OH)}_2}{37 \text{ g/eq}} = 0.171 \text{ eq Ca(OH)}_2$$

$$\text{Number of meq} = \frac{6.32 \text{ g Ca(OH)}_2}{0.037 \text{ g/eq}} = 171 \text{ meq (Ca(OH)}_2)$$

#### 7.3.7.4 Normality

The “normality” (N) of a substance in solution is equal to the number of equivalents of the substance in one liter of solution.

$$\text{In general, } N = \frac{\text{number equivalent of a substance}}{\text{Volume of the solution expressed in L}} = \frac{\text{Eq}}{\text{L}}$$

$$\text{First; no. of equivalent} = \frac{\frac{\text{Mass of Substance}}{\text{MW or MM}}}{\text{no. of replaceable H+ or OH}^-}$$

$$\text{Substituting to the equation: } N = \frac{\frac{\text{Mass of Substance}}{\text{MW or MM}}}{\text{no. of replaceable H+ or OH}^-} = \frac{\frac{\frac{\text{g}}{\text{mol}}}{\text{eq/mol}}}{\text{L of solution}} = \frac{\frac{\text{g}}{\text{mol}}}{\text{eq/mol}} \left\{ \begin{array}{l} \boxed{1} \end{array} \right\} \left\{ \begin{array}{l} \boxed{2} \end{array} \right\} \left\{ \begin{array}{l} \boxed{3} \end{array} \right\}$$

In performing the mathematical operations, step 1 (represented by Box, should be performed first, followed by step 2 (Box 2) and finally step 3 (Box 3).

Sample Problem 7.11

Calculate the normality of a  $\text{Ca(OH)}_2$  solution containing 5.52 g of  $\text{Ca(OH)}_2$  in 5.75 L of solution.

Solution:

Atomic mass: Ca = 40.0; O = 16.0; H = 1.0

Molar Mass:

$\text{Ca(OH)}_2 = 74.0 \text{ g/mol}$

Mass a  $\text{Ca(OH)}_2 = 5.52 \text{ g}$

Volume of solution = 5.75 L

No. of replaceable OH<sup>-</sup> = 2.0 eq/mol

$$N = \frac{\frac{5.52 \text{ g}}{74.0 \text{ g/mol}}}{\frac{2.0 \text{ eq/mol}}{5.75 \text{ L}}} = \frac{5.52 \text{ g}}{37.0 \text{ g/eq}} = \frac{0.149 \text{ eq}}{5.75 \text{ L}} = 0.0259 \text{ N}$$

Sample Problem 7.12:

What mass of solute should be used to prepare 1.000 L of 0.1250 N H<sub>2</sub>SO<sub>4</sub>?

Solution:

Atomic mass: H = 1.0; S = 32.0; O = 16.0

Molar mass:

H<sub>2</sub>SO<sub>4</sub> = 98.0 g/mol

Volume of solution = 1.000 L

Normality = 0.125 N = 0.1250 eq/L

No. of replaceable H<sup>+</sup> = 2.0

$$0.1250 \text{ eq/L} = \frac{\frac{\text{Mass, g}}{98.0 \text{ g/mol}}}{\frac{2.0 \text{ eq/mol}}{1.000 \text{ L}}}$$

$$\text{Mass, g} = 0.1250 \text{ eq/L} \times \frac{98.0 \text{ g/mol}}{2.0 \text{ eq/mol}} \times 1.000 \text{ L} = 6.125 \text{ g}$$

### 7.3.7.5 Conversion of Normality to Molarity and Molarity to Normality

A problem that comes up frequently is to calculate the normality of a molar solution and vice versa.

For acids, N = **nM**, where **n** is the number of acidic hydrogen in the chemical formula of the acid.

For hydroxide bases, N = **nM**, where **n** is the number of hydroxide ions in the chemical formula of the base.

$$N = \frac{\frac{\text{Mass, g}}{\text{g/mol}}}{\frac{\text{eq/mol}}{\text{L}}}$$

$$M = \frac{\text{mass of solute, g}}{\text{Molar mass of solute, } \frac{\text{g}}{\text{mol}} \text{ (liter of Solution)}}$$

Given a solution of same mass of solute:

$$\text{Mass, g} = N \frac{\text{g/mol}}{\text{No. of replaceable H+ or OH-}} \times L$$

$$\text{Mass} = M \times \text{g/mol} \times L$$

Equating them:

$$N \frac{\text{g/mol}}{\text{No. of replaceable H+ or OH-}} \times L =$$

Solving for N:

$$N = \frac{M \times \frac{\text{g/mol} \times L}{\text{mol} \text{ (L)}}}{\text{No. of replaceable H+ or OH-}} = M \times \text{No. of replaceable H+ or OH-}$$



### Sample Problem 7.13:

Convert 3.0M H<sub>2</sub>SO<sub>4</sub> to N H<sub>2</sub>SO<sub>4</sub>

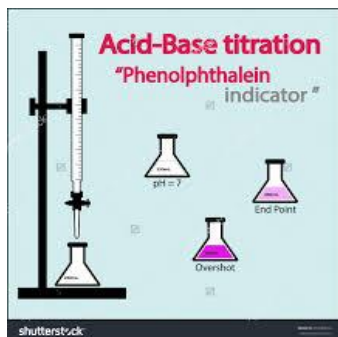
### Solution

No. of replaceable H<sup>+</sup> = 2.0 eq/mol

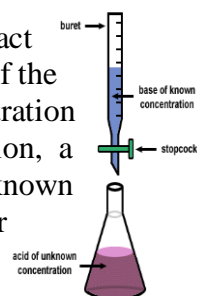
M = 3.0 mol/L

$$N = 3.0 \text{ mol/L} \times 2.0 \text{ eq/mol} = 6.0 \text{ eq/L} = 6.0 \text{ N}$$

## 7.4 Titrations



**Standardization** is the process of determining the exact concentration of an unknown solution with the use of the technique called **titration**. Acid-base titration is the titration process between an acid and a base. In the titration, a **primary standard** of highest purity and known concentration is used. An example primary standard for the acid-base titration is the **potassium acid phthalate** (KHP), C<sub>6</sub>H<sub>4</sub>COOHCOOK.



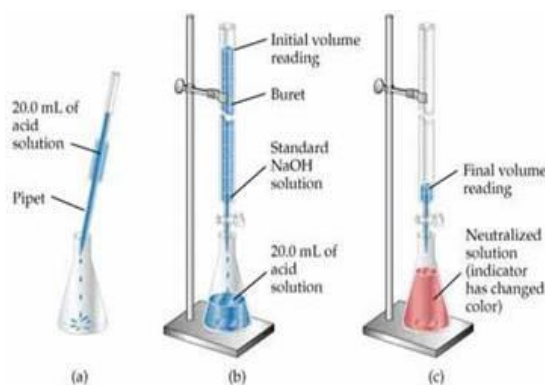
In titration, an **indicator** is used to change the color of the solution at the end point. Addition of the base to the acid is done drop by drop until **equivalence point** is reached (the point at which an equivalent amount of acid reacts with the equivalent amount of the base). A little more in excess above the equivalence point is the **end point** where the indicator changes its color. A very faint end point in order to have an exact point color of the indicating **over-titration** acid-base titration, indicator is used for a to faint (pale) pink (base).

In calculations involving titrations, the equation,  $N_A \times L_{\text{soln}} = A$ .

Titrations are reactions in which we measure the volume of a standardized solution (e.g. NaOH) that reacts stoichiometrically with an acid. In an acid-base reaction, using the concept of equivalents, we know that at the endpoint of a titration:

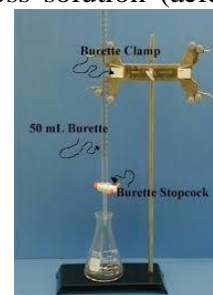
$$\#eq \text{ base} = \#eq \text{ acid.}$$

Table 7.1 Common Concentrated Reagents



should serve as the basis volume of the base used. after the equivalence solution becomes darker (overrun). In the case of **phenolphthalein** colorless solution (acid)

#eq



Reagent	Formula	Percent By Mass	Molarity
Acetic acid	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	100	17.5
Hydrochloric acid	HCl	37	12
Nitric acid	HNO <sub>3</sub>	70	15.8
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	85	14.7
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	96	18.0
Ammonia	NH <sub>3</sub>	28	14.8

### 7.4.1 Standardization of an Acid Solution by Titration with a Standardized Base

Acid solutions for titrating bases are usually standardized by titration with standardized base. At the titration endpoint, #eq base = #eq acid. Therefore, using the dilution method:

$$C_1 V_1 = C_2 V_2$$

Where  $C_1$  - is the concentrated solution,  $V_1$  - is the volume of the concentrated solution,  $C_2$  - is the concentration of the diluted or final solution and  $V_2$  is the volume of the diluted solution or the final volume. Using the normality and volume of the solutions involved:

$$N_1 V_1 = N_2 V_2 \text{ between an acid and a base: } N_{\text{Acid}} V_{\text{Acid}} = N_{\text{Base}} V_{\text{base}}$$

Sample Problem 7.14:

It takes 35.75 mL of 0.1835N NaOH to titrate 25.45 mL of an HCl solution. Calculate the normality of the HCl solution.

Solution:

$$V_{\text{NaOH}} = 35.75 \text{ mL}$$

$$N_{\text{NaOH}} = 0.1835 \text{ N}$$

$$V_{\text{HCl}} = 25.45 \text{ mL}$$

Using the equation:  $N_{\text{Acid}} V_{\text{Acid}} = N_{\text{Base}} V_{\text{base}}$

Solving for  $N_{\text{Acid}}$ :

$$N_{\text{Acid}} = \frac{N_{\text{base}} V_{\text{Base}}}{V_{\text{Acid}}} = \frac{(0.1835 \text{ N})(35.75 \text{ mL})}{25.45 \text{ mL}} = 0.2578 \text{ N}$$

Sample Problem 7.15:

What volume of 12.00 N HCl should be used to prepare 250.0 mL of 2.000N HCl?

Solution:

This is a dilution problem where a diluted solution is prepared from more concentrated solution.

$$N_1 \text{ (concentrated solution)} = 12.0 \text{ N}$$

$$V_1 = \text{the volume of 12.0N required} = ?$$

$$N_2 = \text{final or diluted concentration} = 2.0 \text{ N}$$

$$V_2 = \text{final volume or diluted volume} = 250.0 \text{ mL}$$

$$\text{Using: } N_1 V_1 = N_2 V_2; V_1 = \frac{N_2 V_2}{N_1} = \frac{(2.000 \text{ N})(250.0 \text{ mL})}{12.00 \text{ N}} = 41.67 \text{ mL}$$

Using a pipet, measure 41.67 mL of 12.00 N HCl and transfer it to a 250-mL volumetric flask containing 100 mL of distilled water. Complete to the mark with distilled water. Mix thoroughly.

## 7.5 Properties of Electrolytes

Substances particularly salts and inorganic acids and bases, which when dissolved in water or other appropriate solvents yield solutions which conduct electricity to a greater extent or lesser extent. Such solutions, as has been previously discussed are called **electrolytes**.

Solutions of electrolytes also exhibit the colligative properties of vapor pressure lowering, boiling point elevation, freezing point lowering and osmotic pressure, but they do not obey the simple relations deduced for non-electrolytes.

The colligative effects observed are always greater than those to be expected from the concentration. Stated differently, solutions of electrolytes behave as if the solute had in solution a molecular weight lower than the simplest formula weight of the substance.

As has been said, the freezing point lowering, boiling point elevation, vapor pressure lowering, and osmotic pressure of solutions of electrolytes are all higher than the corresponding effects for solutions of non-electrolytes of the same total concentrations.

To represent the colligative properties of electrolytes by means of the relations for non-electrolytes, **Van't Hoff** suggested the use of a factor  $\hat{i}$ , which is defined as the ratio of the colligative effect produced by a concentration of electrolyte divided by the effect observed for the same concentration of non-electrolyte.

$\hat{i} = \frac{\Delta T_f}{(\Delta T_f)_o} = \frac{\Delta P}{\Delta P_o} = \frac{\Pi}{\Pi_o}$  where:  $\Delta T_f$  – the freezing point lowering;  $(\Delta T_f)_o$  – the freezing point depression of the same concentration.

$\Delta T_f = \hat{i}K_fm$  ;  $\Delta T_b = \hat{i}K_bm$  ;  $\Delta P = \hat{i}P_oN_2$  ;  $\Pi = \hat{i}\frac{N_2}{V}RT = \hat{i}(CRT)$ ;  $(\Delta T_f)_o = K_fm$  and  
 $\hat{i} = \frac{\Delta T_f}{(\Delta T_f)_o} = \frac{\Delta T_b}{(\Delta T_b)_o} = \frac{\Delta P}{(\Delta P)_o} = \frac{\Pi}{\Pi_o}$  where the quantities without subscripts refer to the electrolytes and those with subscripts refer to non-electrolytes.

And for dilute solutions:

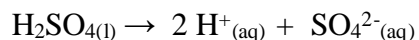
$$\Delta P = \hat{i}(\Delta P)_o ; \Delta T_b = \hat{i}(\Delta T_b)_o = \hat{i}K_bm ; \Pi = \hat{i}(\Pi)_o = \frac{\hat{i}N_2RT}{V}$$

A 1 *m* solution of NaCl, an ionic compound, freezes at -3.37°C, instead of -1.86°C, the expected freezing point of a 1 *m* molecular compound dissolved in water. This much greater depression of the freezing point by the salt - almost twice as much - is not hard to understand if we remember that colligative properties depend upon the concentrations of *particles*, not their chemical identities.

In a 1 *m* NaCl solution, the solute is dissociated.



So, 1 *m* NaCl actually has a 2 *m* concentration in dissolved solute particles. Theoretically, then 1 *m* NaCl should freeze at 2 X (-1.86°C) = -3.72°C. If we made up a solution of 1 *m* H<sub>2</sub>SO<sub>4</sub>, we would have to consider the following dissociation.

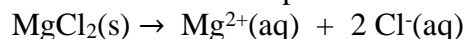


Thus, 1 mol H<sub>2</sub>SO<sub>4</sub> can give a total of 3 mol of ions - 2 mol of H<sup>+</sup> ions and 1 mol of SO<sub>4</sub><sup>2-</sup> ions. A 1 *m* solution of this acid has a calculated freezing point of -5.58°C (3 X -1.86°C). It actually freezes at -4.22°C.

#### Sample Problem 7.16:

Estimate the freezing point of a 0.106 *m* aqueous MgCl<sub>2</sub>, assuming that it ionizes completely.

Solution:  $\text{MgCl}_2$  dissolves in water and breaks up as follows:



1.0 mol  $\text{MgCl}_2$  = 3.0 mol of ions (1  $\text{Mg}^{+2}$  ion and 2  $\text{Cl}^{-}$  ions)

Molality = 0.106 m

$$K_f = 1.86^{\circ}\text{C} \frac{\text{kg-solvent}}{\text{mol-solute}}$$

$$\text{Effective molality} = \text{no. of ions} \times \text{molality} = 3.0 \times 0.106 \frac{\text{mol-solute}}{\text{kg-solvent}} = 0.318 \frac{\text{mol-solute}}{\text{kg-solvent}}$$

$$\Delta t = K_{fm}; \Delta t = 1.86^{\circ}\text{C} \frac{\text{kg-solvent}}{\text{mol-solute}} \times 0.318 \frac{\text{mol-solute}}{\text{kg-solvent}} = 0.592^{\circ}\text{C}$$

Thus the freezing point is depressed below  $0.000^{\circ}\text{C}$  by  $0.519^{\circ}\text{C}$ , so we calculate that this solution freezes at  $0.000^{\circ}\text{C} - 0.519^{\circ}\text{C} = -0.519^{\circ}\text{C}$ . It actually freezes at  $-0.517^{\circ}\text{C}$ .

## 7.6 Colligative Properties of Electrolytes in Aqueous Solution

When one mole of an acid, base, or salt is dissolved, more than one mole of ions is present in the solution. For example, one mole of  $\text{NaCl}$  yields two moles of ions in solution – one mole of  $\text{Na}^{+}$  and one mole of  $\text{Cl}^{-}$ . Since more dissolved particles (ions) are present the colligative properties such as vapor pressure, boiling point, freezing point, and osmotic pressure, which depend upon the number of dissolved particles, are affected more for an electrolyte than for a non-electrolyte. One mole of  $\text{NaCl}$  which gives two moles of ions would be expected to have double the effect of one mole of something like sugar (a non-electrolyte) which yields just one mole of dissolved particles (molecules).

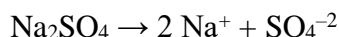
In describing boiling and freezing point changes, a general equation may be modified to allow for the dissociation of electrolytes by inserting an “ion multiplier”,  $\hat{I}$ , that is equal to the number of moles of ions resulting from the dissociation of one mole of solute:

$$\Delta T = \hat{I} K_b m; \Delta T = \hat{I} K_f m \quad \text{For NaCl, } \hat{I} = 2, \text{ for CaCl}_2, \hat{I} = 3, \text{ and for Na}_3\text{PO}_4, \hat{I} = 4.$$

Sample Problem 7.17 :

Calculate the freezing point of 0.20 m  $\text{Na}_2\text{SO}_4$ .

Solution:



$$\hat{I} = 3 (2 \text{Na}^{+} + 1 \text{SO}_4^{-2})$$

$$K_f = 1.86^{\circ}\text{C} \frac{\text{kg-solvent}}{\text{mol-solute}}$$

Using:  $\Delta T = \hat{I} K_f m$

$$\Delta T = \hat{I} K_f m = 3.0 \times 1.86^{\circ}\text{C} \frac{\text{kg-solvent}}{\text{mol-solute}} \times 0.20 \frac{\text{mol-solute}}{\text{kg-solvent}} = 1.12^{\circ}\text{C}$$

$$T_f = 0.0 - 1.1 = -1.1^{\circ}\text{C}.$$

Even if dissociation of the solute is considered, most solutions do not conform precisely with calculated values. This is because the solute and/or the solvent particles interact with each other or with themselves, which reduces the “effective” concentration to a value below that calculated from the amounts of solute and solvent present in the solution. These interactions are electrical in character.

For weak electrolytes, an apparent degree of dissociation,  $\alpha$  (alpha), can be calculated simply from values of the “ion multipliers”. Taking **n**, as the **maximum number of ions formed**

**per molecule of solute**,  $\alpha$  is:

$$\alpha = \frac{\hat{I}-1}{n-1} \times 100$$

Sample Problem 7.18:

A solution of 10.0 g of HF in 500 g water freezes at  $-1.98^{\circ}\text{C}$ . Find the degree of ionization of HF.

Solution:

Atomic mass: H = 1.0; F = 19.0

Molar Mass:

HF = 1.0 + 19.0 = 20.0 g/mol

Mass of solvent, kg =  $500 \cancel{\text{g}} \times \frac{1.0 \text{ kg}}{1000 \cancel{\text{g}}} = 0.500 \text{ kg}$

$$m = \frac{10.0 \cancel{\text{g}} \text{ HF}}{20.0 \frac{\cancel{\text{g}}}{\text{mol}} (0.500 \text{ kg})} = 1.00 \text{ m or } 1.00 \frac{\text{mol-solute}}{\text{kg-solvent}}$$

The HF is only partially ionized according to the equation:  $\text{HF} \leftrightarrow \text{H}^+ + \text{F}^-$

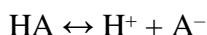
Here,  $n = 2$  and  $i$  is less than 2.0.

$$\Delta T = \hat{K}_f m \quad \text{and} \quad \hat{I} = \frac{\Delta T_f}{K_f m} = \frac{1.98}{(1.86)(1.00)} = 1.06 \quad \text{and} \quad \alpha = \frac{\hat{I}-1}{n-1} \times 100 = \frac{1.06-1}{2-1} \times 100 = 6\%$$

Sample 7.19 :

Determine the freezing point of a 0.500 m aqueous solution of a weak acid, HA, if it is 10% ionized.

Solution:



$n = 2$  (1  $\text{H}^+$  1  $\text{A}^-$ )

Using the equation:  $\alpha = \frac{\hat{I}-1}{n-1} \times 100\%$ , we can solve for the  $i$ .

$\alpha = 10\%$

$m = 0.500 \text{ mol/kg}$

$$\begin{aligned} 10\% &= \frac{\hat{I}-1}{2-1} \times 100\% \\ 10\% &= \frac{\hat{I}-1}{1} \times 100\% \\ 10\% (1) &= (\hat{I}-1)100\% \\ 10\% &= 100\% \hat{I} - 100\% \\ 10\% + 100\% &= 100\% \hat{I} \\ \hat{I} &= \frac{110\%}{100\%} = 1.10 \end{aligned}$$

$$\begin{aligned} \Delta T &= \hat{K}_f m = (1.10)(1.86^{\circ}\text{C} \frac{\text{kg-solvent}}{\text{mol-solute}})(0.50 \frac{\text{mol-solute}}{\text{kg-solvent}}) \\ \Delta T &= 1.023^{\circ}\text{C} \end{aligned}$$

The solution freezes  $1.0^{\circ}\text{C}$  below the normal freezing point of water:

$T_f = 0.0 - 1.023 = -1.023^{\circ}\text{C}$ .

## 7.7 Properties of Non-Electrolytes

### 7.7.1 Colligative Properties

The Colligative properties of non-electrolyte solutions deserve serious considerations because they supply valuable methods for estimating the molecular weight of the dissolved substance and for evaluating a number of highly important thermodynamic quantities.

In this topic, we will consider four properties of solutions containing non-volatile solutes;

1. Vapor pressure lowering of the solvent
2. Freezing point lowering
3. Boiling point elevation; and
4. Osmotic pressure of the solution.

The above properties are called **Colligative properties**. A **Colligative property** is defined as any property which depends only on the number of particles in solution and not in any way on the nature of these.

### 7.7.1.1 Lowering of Vapor Pressure of Solvent

A dissolve solute lowers the vapor pressure of a liquid solvent in which it is dissolved. The vapor pressure lowering suffered by the solvent can be readily understood in terms of Raoult's Law.

Let  $X_1$  be the mole fraction of the solvent,  $X_2$  be the mole fraction of the solute,  $P^o$  the vapor pressure of the pure solvent, and  $P$ , the vapor pressure of the solvent above a given solution. Then according to Raoult's Law,

$$P = P^o X_1 \text{ which pertains to the ideal solutions.}$$

**Ideal solution** is one in which the intermolecular forces between the molecules are essentially the same.

Since  $X_1$ , in any solution is always less than the unity,  $P$ , must always be less than  $P^o$ . Consequently, solution of a solute in a solvent leads to a lowering of the vapor pressure of the latter below that of the pure solvent.

Furthermore, when the solute is nonvolatile it does not contribute to the total vapor pressure, and hence, the above equation gives as well the total vapor pressure above the solution, which in this case is due to solvent only and is always less than  $P^o$ .

The extent of the vapor pressure lowering,  $\Delta P$ , is:

$$\Delta P = P^o - P = P^o - P^o X_1 = P^o (1 - X_1) = P^o X_2$$

According to the above equation, the vapor pressure lowering of the solvent depends both on the vapor pressure of the solvent and the mol fraction of solution. In other words, it depends on the nature of the solvent and on the concentration of the solute, but not on the nature of the latter.

If we consider the relative vapor pressure lowering, i.e.  $X_2 = \frac{\Delta P}{P^o} = \frac{P^o - P}{P^o}$ .

The relative vapor pressure lowering of the solvent depends only on the mol fraction of solute and is completely independent of either the nature of the solute or solvent.

The vapor pressure could also be equal to the sum of the two partial pressures:

$$P_{\text{total}} = P_1^o X_1 + P_2^o X_2$$

where  $X_1$  is the mole fraction of component 1 in the solution and  $P_1^o$  is the vapor pressure of pure component 1.  $P_2^o$  is the vapor pressure of pure component 2 and  $X_2$  is the mole fraction of component B.



Sample problem 7.20:

Heptane, (C<sub>7</sub>H<sub>16</sub>) and octane (C<sub>8</sub>H<sub>18</sub>) form ideal solutions. What is the vapor pressure at 40°C of a solution that contains 3.00 mol heptane and 5.00 mol of octane? At 40°C, the vapor pressure of heptane is 0.121 atm and the vapor pressure of octane is 0.041 atm.

Solution:

$$\begin{aligned} n_{\text{heptane}} &= 3.00 \text{ mol (component 1)} \\ n_{\text{octane}} &= 5.00 \text{ mol (component 2)} \\ n_{\text{total}} &= 3.00 \text{ mol} + 5.00 \text{ mol} = 8.00 \text{ mol} \\ X_{\text{heptane}} &= \frac{3.00 \text{ mol}}{8.00 \text{ mol}} = 0.375; & X_{\text{octane}} &= \frac{5.00 \text{ mol}}{8.00 \text{ mol}} = 0.625; \\ P_1^o &= 0.121 \text{ atm}; & P_2^o &= 0.041 \text{ atm} \end{aligned}$$

$$P_{\text{total}} = P_1^o X_1 + P_2^o X_2$$

$$P_{\text{total}} = (0.121 \text{ atm})(0.375) + (0.041 \text{ atm})(0.625) = 0.0454 \text{ atm} + 0.0256 \text{ atm} = 0.071 \text{ atm}$$

For dilute solutions from a non-volatile solute, the vapor pressure is caused by solvent alone. It follows Raoult's law:

$$P_{\text{total}} = P_1^o X_1, \text{ but, } X_1 + X_2 = 1 \text{ and that } X_1 = 1 - X_2, \text{ therefore, } P_{\text{total}} = (1 - X_2) P_1^o \text{ or}$$

$$P_{\text{total}} = P_1^o - X_2 P_1^o$$

The vapor pressure of pure component 1 is lowered by an amount equal to  $X_2 P_1^o$ .

Sample Problem 7.21:

Assuming ideality, calculate the vapor pressure of a 1.00 m solution of a non-volatile, nondissociating solute in water at 50°C. The vapor pressure of water at 50°C is 0.122 atm.

Solution:

Molar mass:

$$\text{H}_2\text{O} = 18.0 \text{ g/mol}$$

$$m = 1.00 \text{ molal} = 1 \text{ mol solute/kg solvent}$$

Mole fractions:

$$n_{\text{water}} = 1.0 \text{ kg} \times \frac{1000 \text{ g}}{1.0 \text{ kg}} = 1000 \text{ g} \times \frac{1.0 \text{ mol}}{18.0 \text{ g}} = 55.6 \text{ mol}$$

$$n_{\text{solute}} = 1.00 \text{ mol}$$

$$n_{\text{total}} = 1.00 \text{ mol} + 55.6 \text{ mol} = 56.6 \text{ mol}$$

$$X_{\text{water}} = \frac{55.6 \text{ mol}}{56.6 \text{ mol}} = 0.982$$

$$P_{\text{total}} = X_2 P_1^o = (0.982)(0.122 \text{ atm}) = 0.120 \text{ atm}$$

### 7.7.1.2 Boiling Point Elevation of Solutions

Solutions containing nonvolatile solutes boil at temperatures higher than the boiling point of pure solvent. The difference between the boiling points of the solution and pure solvent at any given constant pressure is referred to as the **boiling point elevation of the solution**. **Boiling point** is the temperature in which the vapor pressure of the liquid is equal to the atmospheric pressure. Boiling points taken under 1 atm pressure are **normal boiling points**.

The boiling point of the solution depends on:

- The nature of the solvent, and

b. The concentration of solute

$$\Delta T_b = \frac{RT_o^2}{\Delta H_v} \times X_2$$

Where,  $T_o$  is the boiling point of solvent,  $H_v$  is the heat of vaporization and  $X_2$  is the mole fraction of solute and  $R$  is the universal gas constant 1.987 cal/g-K or 0.08206L-atm/K-mol.

$$\text{In terms of molality, } m, \Delta T_b = \frac{RT_o^2}{\Delta H_v n_1} \times m.$$

For any given solvent, all the quantities in the bracket are constants, and hence have the whole term in constant, therefore,  $K_b = \left[ \frac{RT_o^2}{\Delta H_v n_1} \right]$  and  $\Delta T_b = K_b m$ .

The boiling point of any dilute solution is directly proportional to the molality of the solution.

The proportionality constant  $K_b$ , is referred to as either **molal boiling point elevation constant**, or **Ebulloscopic constant** which signifies the rise in boiling point for a 1 molal solution of a solute in a solvent. Actually, it is the boiling point elevation per mole calculated by proportion from the boiling point elevation of very dilute solutions.

Sample Problem 7.21:

What is the boiling point of a solution prepared by dissolving 2.40 g of biphenyl ( $C_{12}H_{10}$ ) in 75.0 g of benzene. The molar mass of biphenyl is 154.0.

Solution:

Molar Mass:

Biphenyl = 154.0 g/mol

Mass of biphenyl = 2.40 g (solute)

Mass of benzene = 75g (solvent)  $\times \frac{1.0 \text{ kg}}{1000\text{g}} = 0.075 \text{ kg}$

Solving for molality:

$$m = \frac{2.40 \text{ g}}{154.0 \frac{\text{g}}{\text{mol}} (0.075 \text{ kg})} = 0.208 \text{ mol/kg}$$

$$\Delta T_b = K_b m = 0.208 \text{ m} \times 2.53^\circ \text{C/m} = 0.526^\circ \text{C}$$

The boiling point elevation:  $80.1^\circ \text{C} + 0.5^\circ \text{C} = 80.6^\circ \text{C}$

### 7.7.1.3 Freezing Point Lowering of Solutions

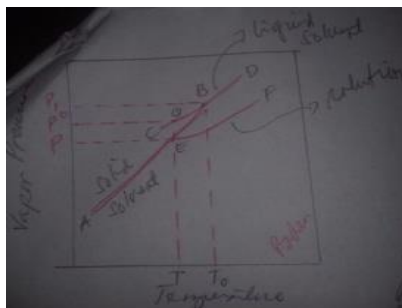
When a dilute solution is cooled, a temperature is eventually reached at which solid solvent begins to separate from solution. The temperature at which the separation begins is referred to as the **freezing point of solution**. In other words it is the temperature at which a particular solution is in equilibrium with solid solvent.

Solutions freeze at lower temperature than the pure solvent. The freezing point lowering of a solution is again a direct consequence of the vapor pressure lowering of the solvent by dissolved solute.

$$\Delta T_f = T_o - T, \quad \Delta T_f = mK_f$$

Where:  $\Delta T_f$  = freezing point depression

$K_f$  = Molal freezing point constant



$\Delta H_f$  = Heat of Fusion

In the diagram, AB is the sublimation curve of the solid solvent, while CD is the vapor pressure curve of pure liquid solvent. At the freezing point of the pure solvent the solid and liquid phases are in equilibrium, and consequently they must both have at this temperature identical vapor pressures. The only point on the diagram at which the two forms of the pure solvent have the same vapor pressure is B, the intersection of AB and CD, and therefore,  $T_0$  the temperature corresponding to B, must be the freezing point of the pure solvent. When a solute is dissolved in the solvent, however, the vapor pressure of the latter is lowered, and equilibrium can no longer exist at  $T_0$ . To ascertain the new point of equilibrium between the solution of the solute and the solid solvent, the temperature must be found at which the vapor pressure of the solution becomes equal to that of the solid, i.e. the temperature at which the vapor pressure curve of the solution intersects the sublimation curve and this will be the freezing point of the solution. Since the vapor pressure curve of the solution, EF, always lies below that of the pure solvent, the intersection of EF and AB can occur only at a point such as E for which the temperature is lower than  $T_0$ . Hence, any solution of the solute in the solvent must have a freezing point,  $T$ , lower than that of the solvent,  $T_0$ .

The freezing point depression of a solution is defined as  $\Delta T_f$ , and represents the number of degrees of freedom by which the freezing point of a solution is lower than that of the pure solvent.

Let,  $P_0$ , be the vapor pressure of solid and pure liquid solvent at temperature  $T_0$  and  $P$  be the vapor pressure of both solid solvent and solution at temperature  $T$ . Again let  $P_0$  be the vapor pressure of pure supercooled solvent liquid at  $T$ , point G. Then since G and B lie on the same vapor pressure curve, they must both be related by the Clausius-Clapeyron equation:

$$\ln \frac{P_0}{P} = \frac{\Delta H_v (T_0 - T)}{RT_0 T}$$

where  $\Delta H_v$  – heat of vaporization of pure solvent since points E and B lie on the same sublimation curve.

$$\ln \frac{P_0}{P} = \frac{\Delta H_v (T_0 - T)}{RT_0 T}$$

where  $\Delta H_v$  – heat of sublimation of the solid solvent.

Or

$$\Delta T_f = \left( \frac{RT_0^2}{\Delta H_f N_1} \right) m = K_f m \text{ or } K_f = \frac{RT_0^2}{\Delta H_f N_1}$$

The above equation is the fundamental relation of cryoscopy and is directly analogous to boiling point elevation and is referred to as the **molal freezing point lowering** or the **cryoscopic constant of a solvent**.

Sample Problem 7.22:

What is the boiling point of a solution prepared by dissolving 2.40 g of biphenyl ( $C_{12}H_{10}$ ) in 75.0 g of benzene. The molar mass of biphenyl is 154.0. The molal freezing-point depression constant for benzene is  $-5.12^\circ\text{C/m}$  ( $K_b$ ). The normal freezing point of benzene is  $5.5^\circ\text{C}$ .

Solution:

Molar Mass:

Biphenyl = 154.0 g/mol

Mass of biphenyl = 2.40 g (solute)

Mass of benzene = 75g (solvent)  $\times \frac{1.0 \text{ kg}}{1000\text{-g}} = 0.075 \text{ kg}$

$K_b = -5.12 \text{ }^\circ\text{C/m}$

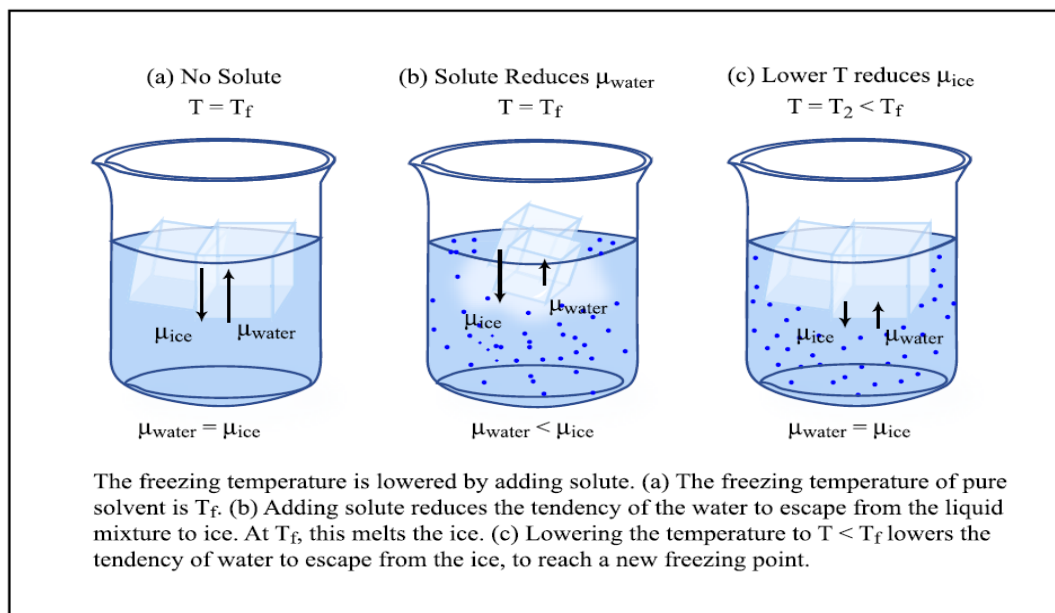
Solving for molality:

$$m = \frac{2.40 \text{ g}}{154.0 \frac{\text{g}}{\text{mol}} (0.075 \text{ kg})} = 0.208 \text{ mol/kg}$$

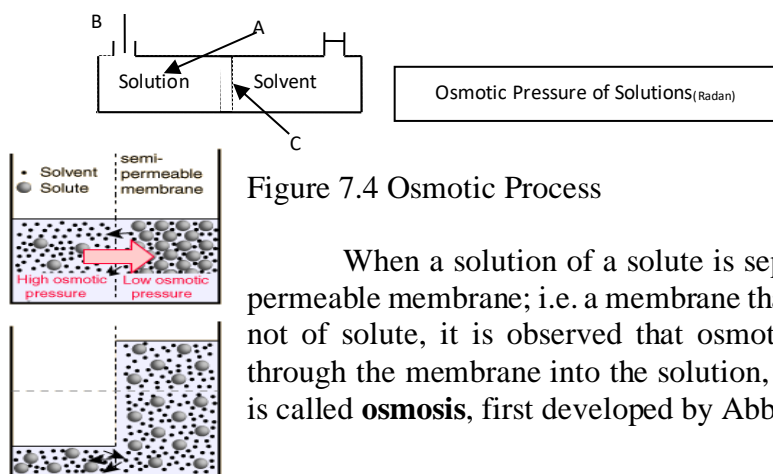
$$\Delta T_f = mK_f = (0.208 \text{ m})(-5.12^\circ\text{C/m}) = -1.06 \text{ }^\circ\text{C}$$

$$T = T_o + \Delta T_f = 5.5 \text{ }^\circ\text{C} + (-1.06 \text{ }^\circ\text{C}) = 4.44 \text{ }^\circ\text{C}$$

*During winter, in countries where there is snow formation, one cannot imagine what will happen if highways have thick snows. To prevent formation of thick snows on roads and highways, salts are laid on roads and highways to prevent accidents.*

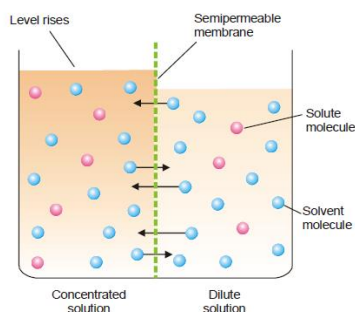


#### 7.7.1.4 Osmosis and Osmotic Pressure

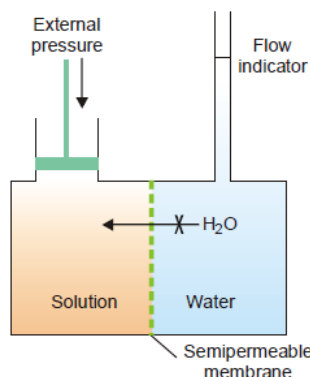


For low molecular weight solutes in water the best semi-permeable membrane known is a film of copper ferrocyanide,  $\text{Cu}_2\text{Fe}(\text{CN})_6$  prepared by the contact of cupric salt with one of potassium ferrocyanide.

For high molecular weight solutes in organic solvents the membranes used most frequently are thin film of either cellulose or cellulose nitrate.



In the figure above, chamber open at one end fitted at the other end movable piston B. The chamber is divided by of a semi-permeable membrane C into two sections, of which the one is filled with pure solvent, the other end



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some solution of a solute in the solvent. Due to osmosis, solvent will tend to pass through the membrane into the solution and displaces the piston upward. The motion of the piston and osmosis of the solvent can be prevented, however, by the application of pressure to the piston to keep it in its original position. The mechanical pressure which must be applied on a solution to prevent osmosis of the solvent into the solution through a semi-permeable membrane is called the **osmotic pressure of the solution**.

$\Pi V = nRT$  where:  $\Pi$  is the osmotic pressure,  $n$  is the number of moles solute and  $V$  is the volume in Liters (L),  $T$  is the absolute temperature and  $r$  is the universal gas constant  $R = \frac{0.08206 \text{ L-atm}}{\text{K-mol}}$ .

Rearranging the equation:

$$\Pi = \frac{n}{V} RT \text{ where, } \frac{n}{V} = \frac{\text{mol}}{\text{L}} = \text{Molarity} = M, \text{ therefore, } \Pi = MRT$$

Sample Problem 7.23:

Biochemists have discovered more than 400 mutant varieties of hemoglobin, the blood protein that carries  $\text{O}_2$ . A physician dissolves 21.5 mg of one variety in water to make 1.50 mL of solution at  $5.0^\circ\text{C}$ . She measures an osmotic pressure of 3.61 torr. What is the molar mass of the protein?

Solution:

$$\Pi = 3.61 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.00475 \text{ atm}$$

$$V = 1.50 \text{ mL} \times \frac{1.0 \text{ L}}{1000 \text{ mL}} = 0.0015 \text{ L}$$

$$T = 5.0^\circ\text{C} + 273.15 = 278.15 \text{ K}$$

$$\Pi = MRT \text{ and } M = \frac{\Pi}{RT} = \frac{0.00475 \text{ atm}}{0.08206 \frac{\text{L-atm}}{\text{K-mol}} (278.15 \text{ K})} = 2.08 \times 10^{-4} \text{ mol/L}$$

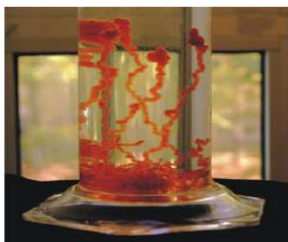
$$n = \frac{2.08 \times 10^{-4} \text{ mol}}{\text{L}} \times 0.0015 \text{ L} = 3.12 \times 10^{-7} \text{ mol}$$

$$\text{mass} = 21.5 \text{ mg} \times \frac{1.0 \text{ g}}{1000 \text{ mg}} = 0.0215 \text{ g}$$

$$\text{Molar mass} = \frac{0.0215 \text{ g}}{3.12 \times 10^{-7} \text{ mol}} = 6.89 \times 10^4 \text{ g/mol}$$

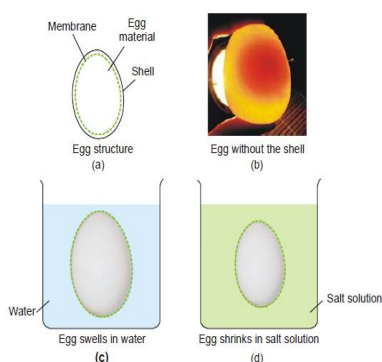
## 7.8 Some Applications of Osmosis

### 1. Silica Garden



Crystals of many salts *e.g.*, ferrous sulfate, nickel chloride, cobalt nitrate and ferric chloride are placed in a solution of glass material (sodium silicate). The layers of metallic silicates formed on the surface of crystals by double decomposition are semipermeable. The water from outside enters through these membranes which burst and form what we call a *Silica Garden*.

### 2. The Egg Experiment



The outer hard shell of two eggs of the same size is removed by dissolving in dilute hydrochloric acid. One of these is placed in distilled water and the other in saturated salt solution. After a few hours it will be noticed that the egg placed in water swells and the one in salt solution shrinks. In the first case, water diffuses through the skin (a semipermeable membrane) into the egg material which swells. In the second case, the concentration of the salt solution being higher than the egg material, the water content of the egg moves out and goes into the solution, the egg shrinks.

## Chapter Exercises

7.1 Calculate the mole fraction, molarity and molality of  $\text{NH}_3$ , if it is in a solution composed of 30.6g  $\text{NH}_3$  in 18.3g of water. The density of the solution is 0.982 g/mL and the density of water is 1.00g/mL.

7.2 A concentrated phosphoric acid is 90% by mass. The molarity of the  $\text{H}_3\text{PO}_4$  in 90%  $\text{H}_3\text{PO}_4$  is 12.2M at room temperature.

7.3 A solution of  $\text{HCl}(\text{aq})$  contains 36%  $\text{HCl}$  by mass.  
a. Calculate the mole fraction of  $\text{HCl}$  in the solution  
b. Calculate the molality of  $\text{HCl}$  in the solution.

7.4 Given the density of a solution of 5.0g toluene ( $\text{C}_7\text{H}_8$ ), and 225g benzene ( $\text{C}_6\text{H}_6$ ) is 0.876 g/mL. Calculate the molarity of the solution.

7.5 a. How many grams of concentrated nitric acid solution should be used to prepare 250.0 mL of 2.00M  $\text{HNO}_3$ ? The concentrated nitric acid is 70%  $\text{HNO}_3$ .



b. If the density of the concentrated nitric acid solution is 1.42g/mL, what volume should be used?

7.6 A 15.0mL sample of an acid requires 37.3mL of 0.303N NaOH for neutralization. Calculate the normality of the acid. What is the molarity of the acid?

7.7 A 2.5g sample of groundwater was found to contain 5.4 $\mu$ g of  $\text{Zn}^{+2}$ . What is the concentration of  $\text{Zn}^{+2}$  in ppm?

7.8 In a geographical area at sea level measuring 56 km by 24 km by 1 km, the ozone concentration is 0.145 ppm. How many moles of ozone must be removed from the atmosphere to reach a concentration of 0.080 ppm, assuming a constant pressure of 1 atm and a constant temperature of 30 degrees Celsius.

7.9 The maximum concentration of  $\text{O}_2$  in seawater is  $2.2 \times 10^{-4}$  M at 25.0 °C. What is this concentration in ppm?

7.10 What is the ppm concentration of calcium ion in 0.010 M  $\text{CaCO}_3$ ?

7.11 Determine concentration of a solution that contains 825 mg of  $\text{Na}_2\text{HPO}_4$  dissolved in 450.0 mL of water in (a) molarity, (b) molality, (c) mole fraction, (d) mass %, and (e) ppm. Assume the density of the solution is the same as water (1.00 g/mL). Assume no volume change upon the addition of the solute.

7.12. An aqueous solution is prepared by diluting 3.30 mL acetone ( $d = 0.789$  g/mL) with water to a final volume of 75.0 mL. The density of the solution is 0.993 g/mL. What is the molarity, molality and mole fraction of acetone in this solution?

7.13. What are the mole fractions of solute and solvent in 1.00 m aqueous solution?

7.14 Hydrogen peroxide is a powerful oxidizing agent, it is used in concentrated solution in rocket fuel, but in dilute solution in hair bleach. An aqueous solution of  $\text{H}_2\text{O}_2$  is 30.0% by mass and has a density of 1.11 g/mL. Calculate a). molality, b). mole fraction of  $\text{H}_2\text{O}_2$ , and c). molarity.

7.15 Concentrated hydrochloric acid is 11.8 M HCl and has a density of 1.190 g/mL. Calculate the mass %, molality, and mole fraction of HCl?

7.16 Find the osmotic pressure of blood at normal body temperature (37°C) if the blood behaves as if it were a 0.296 M solution of nonionizing solute.

7.17 An aqueous solution contains 30.0 g of a protein in 1.00 L. The osmotic pressure of the solution is 0.0167 atm at 27°C. What is the approximate molar mass of the protein?

7.18 At 37°C, 0.30 M sucrose has about the same osmotic pressure as blood. What is the osmotic pressure of blood?

7.20 A solution that contains 9.30 g hemoglobin per 200. mL of solution has an osmotic pressure of 0.0171 atm at 27°C. What is the molecular weight of hemoglobin?

7.21 A protein has a molecular weight of 3000. The osmotic pressure of a saturated solution of this protein in water is 0.274 atm at 25°C. a). How many grams of this protein are dissolved in one liter of the saturated solution. b). What is the molarity of the solution?

7.22 A solution containing 2.00 g of  $\text{CaCl}_2$  in 98.00 g water freezes at -0.880 °C. What is the van't Hoff factor,  $i$ , for the freezing point of this solution?

7.23 A solution is prepared from 3.00 g of NaOH and 75.00 g of water. If the van't Hoff factor for the freezing point of this solution is 1.83, at what temperature will the solution freeze?

7.24 A solution that contains 13.2 g of solute in 250. g of  $\text{CCl}_4$  freezes at -33.0 °C. What is the molecular weight of the solute?

7.25 The antifreeze used in car radiators is ethylene glycol,  $\text{C}_2\text{H}_4(\text{OH})_2$ . How many grams of ethylene glycol should be added to 1.00 kg of water to produce a solution that freezes at -15.0 °C?

7.26 Methyl alcohol,  $\text{CH}_3\text{OH}$ , and ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , form ideal solutions. At 50°C, the vapor pressure of pure methyl alcohol is 0.529 atm, and the vapor pressure of pure ethyl alcohol is 0.292 atm. What is the vapor pressure at 50°C of a solution containing 24.00 g of methyl alcohol and 5.76 g of ethyl alcohol?

7.27 A solution that contains 4.32 g of naphthalene,  $\text{C}_{10}\text{H}_8$ , in 150. g of ethylene dibromide freezes at 7.13°C. The normal freezing point of ethylene dibromide is 9.79°C. What is the freezing point constant,  $K_f$  for ethylene dibromide?

7.28 What is the freezing point of a 0.125 m aqueous solution of a weak acid, HX, if the acid is 4.00% ionized. Ignore interionic attractions.

7.29 A solution prepared from 96.0 g of a non-volatile non-dissociating solute in 5.00 mole of toluene has a vapor pressure of 0.161 atm at 60°C. What is the molecular weight of the solute? The vapor pressure of pure toluene at 60°C is 0.184 atm.

7.30 Concentrated HBr is 48.0% by mass and has a density of 1.50 g/mL. a). How many grams of concentrated HBr should be used to prepare 750 mL of 1.50 M HBr solution? b). How many milliliters of concentrated HBr should be used to prepare this solution?

7.31 What mass of  $\text{H}_3\text{PO}_4$  should be used to prepare 255 mL of 1.25 N  $\text{H}_3\text{PO}_4$ ?

7.32 What volume of concentrated nitric acid should be used to prepare a). 3.50L of 1.50 M  $\text{HNO}_3$  solution? b). 250. mL of 6.00 M  $\text{HNO}_3$ ?

7.33 A 150. mL sample of concentrated  $\text{NH}_3$  is diluted to a final volume of 500. mL. What is the resulting molarity of the solution?