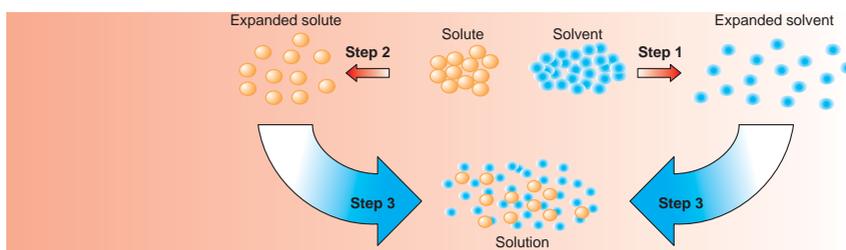# Solutions

Unit Outcomes

At the end of this unit, you should be able to:

- ☛ *know the types of solutions;*

- ☛ *understand the process of solution formation, the rate of solution, the heat of solution and solubility;*

- ☛ *describe the dependence of solubility on the temperature and pressure of the solution;*

- ☛ *know how to solve problems involving the concentration of solutions and to express the result in various units;*

- ☛ *describe, the behaviour of ionic solute in unsaturated, saturated and supersaturated solutions using the concept of equilibrium;*

- ☛ *prepare solutions of a required concentration by dissolving a solute or diluting a concentrated solution;*

- ☛ *understand the relationship between the colligative properties of solutions and know how to solve problems involving colligative properties of solutions;*

- ☛ *describe scientific inquiry skills along this unit: observing, classifying, comparing and contrasting, measuring, asking questions, drawing conclusion, applying concept and problem solving.*

MAIN CONTENTS

Most of the materials around us are mixtures. In this unit, we shall be concerned with properties and types of mixtures, and with the relationships of their properties to those of the individual components.

A homogeneous mixture, also known as solution, is a mixture that is uniform in its properties throughout a given sample. When sodium chloride is dissolved in water, you obtain a homogeneous mixture, or solution. Air is a gaseous solution, principally of two elementary substances, nitrogen and oxygen, which are physically mixed but not chemically combined.

There are various practical reasons for preparing solutions. For instance, most chemical reactions are run in solution. Solutions have specific useful properties. For example, when gold is used for making jewellery, it is mixed, or alloyed with a small amount of silver. Gold-silver alloys are not only harder than pure gold, but they also melt at lower temperatures and are therefore easier to cast.

In this unit, you will study the dependence of solubility (*the amount of substance that dissolves in another*) on temperature and (in some cases) on pressure; the ways of expressing the concentration of a solution. You will also study about the colligative properties of solutions.

1.1   HOMOGENEOUS AND HETEROGENEOUS MIXTURES

At the end of this section, you should be able to:

- define the terms mixture, homogeneous and heterogeneous mixture, solute, solvent, solution;

- distinguish between homogeneous and heterogeneous mixtures;
- describe suspensions and colloids.

1.1.1 Some Basic Definitions

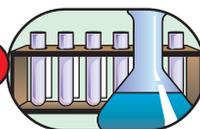*How do you distinguish homogeneous and heterogeneous mixtures?*

Mixtures are combinations of two or more substances in which each substance retains its own chemical identity and hence its own properties. A sample of clean air, for example, consists of many elements and compounds physically mixed together, including oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), noble gases, and water vapour (H_2O). *Can you give more examples of mixtures?* There are two broad classes of mixtures, homogeneous and heterogeneous mixtures.

A **homogeneous mixture** is a mixture in which the composition of the mixture is the same throughout. i.e., it has no visible boundaries because the components are mixed as individual atoms, ions and molecules. For example, when a spoonful of sugar dissolves in water you obtain a homogeneous mixture.

A **heterogeneous mixture** has one or more visible boundaries between the components. Thus, its composition is not uniform. In this type of mixture, each component's particles can be detected by the naked eye or with a magnifying glass. If sand is mixed with iron filings, the sand grains and the iron filings remain separate. This is an example of a heterogeneous mixture.

A typical solution consists of at least two substances; a substance in smaller amount called the solute, dissolved in a larger amount of another substance, known as the solvent. The solvent is often but not always present in excess. For example, the physical state of a solution containing 40 g of table sugar and 30 g of water is liquid. In this case, though water is present in small amount, it is present as solvent.

Experiment 1.1

Distinction between homogeneous and heterogeneous mixtures

Objective: To distinguish between homogeneous and heterogeneous mixtures.
Apparatus: Beakers, test tubes, watch glass, stirrer.
Chemicals: Table salt, water, iron filings, sulphur powder, oil, alcohol.
Procedure:
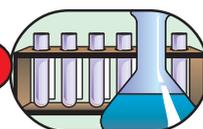Prepare mixtures of the following pairs in suitable apparatus.
  a   Table salt and water

b   Iron filings and sulphur powder

c   Oil and water

d   Water and alcohol

Use either naked eye or hand lens to observe each mixture. Classify the mixtures you prepared as homogeneous and heterogeneous. Give reason for your classification.

1.1.2 Suspension and Colloids

Experiment 1.2

Investigating properties of some mixtures

Objective: To see the difference between suspensions, solutions and colloids.

Apparatus: Three 100 mL beakers.

Chemicals: Sand, gentian violet and bile.

Procedure:

1. Label the beakers as A, B, and C; add sand to beaker A, gentian violet to beaker B, and bile to beaker C.

2. Add about 50 mL water to each beaker and stir the contents.

3. Leave the beakers undisturbed for about 30 minutes and see if they become clear on standing.

4. Pass a beam of light through each beaker.

Observations and analysis:

a   In which beaker the contents separate in two layers on standing?

b   Which beaker scatters light without separating the contents on standing?

c   Which beaker contains a solution and which beaker contains a colloid?

d   What do you conclude from this experiment?

Exercise 1.1

Define each of the following terms and give examples for each.

a   homogeneous mixture   c   solute   e   colloid

b   heterogeneous mixture   d   solvent   f   suspension

What is the difference between suspensions and solutions?

We are all familiar with suspensions such as a mixture of mud and water or flour and water. Sometimes we prepare and use a suspension of paint in water. These suspensions are heterogeneous mixtures composed of particles that are visible *to the naked eye or that can be seen with a magnifying glass*. The suspended particles appear cloudy, and settle down in due course of time. When $Mg(OH)_2$ (called milk of magnesia) is shaken with water, it forms a suspension. In contrast, when we make a solution, we prepare a homogeneous mixture in which the dissolved species are molecules or ions. A solution may be coloured, but it is transparent; the dissolved molecules or ions are invisible, and they do not settle out on standing. Figure 1.1a and Figure 1.1b show a solution and a suspension, respectively.

Figure 1.1 a) Solution   b) Suspension

There is another group, called colloids that exhibit properties intermediate between those of suspensions and solutions. The particles in a colloid are larger than most simple molecules. However, colloidal particles are small enough and do not settle down. Although colloid particles may be so small that the dispersion appears uniform, even under a microscope, they are large enough to scatter light very effectively (see Figure 1.2). Consequently, most colloids appear cloudy or opaque unless they are very dilute. Like solutions, colloids can be gaseous, liquid or solid. Clouds are colloidal mixtures composed of air and water droplets that are small enough that they do not settle out.

Figure 1.2   The light beam is not visible as it passes through a true solution (left), but it is clearly visible as it passes through colloidal mixture (right).

1.2   TYPES OF SOLUTIONS

At the end of this section, you should be able to:

- explain different types of solutions;
- give examples for each type of solution;
- after a visit to nearby gold smith, present a report to class on how jewellery gold is made.

Solutions may exist in any of the three states of matter.

Activity 1.1

Form groups and discuss the following points. Report the result of your discussion in tabular form.

1. Mention the types of solutions.

2. What are the possible physical states of solutes and solvents in each type of solution?

3. Give at least one example to each type of solution.

4. Explain briefly how solid solutions are formed?

5. Copy the given table in your note book and write your answers in it:

State of solute	State of solvent	State of solution	Type of solution	Examples

PROJECT

Do you know how jewellery gold is made?

Your teacher will arrange a visit to the nearby goldsmith. Ask the following questions during your visit to the goldsmith:

How is jewellery made from gold? What are the possible components, other than gold present in the jewellery? Which component is present in large quantity? What is the advantage of mixing gold with other materials? Can you separate the components present in the jewellery? How is purity of gold assessed and what is the unit of measuring the purity? Write a report about what you have observed during your visit and present it to the class.

Exercise 1.2

1. Give two examples of
   a   gas-gas solution
   b   gas-liquid solution
   c   liquid-liquid solution
   d   solid-liquid solution
   e   solid-solid solution
2. What are the possible physical states of solutes and solvents in
   a   gaseous solutions?
   b   liquid solutions?
   c   solid solutions?

1.3 THE SOLUTION PROCESS

At the end of this section, you should be able to:

- explain how the "like dissolves like" rule depends on inter-particle forces of interactions and predict relative solubility;
- define rate of dissolution;

- define heat of solution, solvation energy and hydration energy;
- apply the concept of heat of solution to a solution of ammonium nitrate and sodium hydroxide crystals;
- explain how heat of solution is influenced by the inter-particle interaction forces.

Activity 1.2

Try to mix the following substances with water.

a oil   b benzene   c ethanol

What did you observe? Which of the substances is completely miscible with water and which of them is immiscible? Discuss your observations with your classmates, and report your possible reasons to the class.

1.3.1 Liquid Solutions and Interparticle Forces of Attractions

What are the major factors that affect the solubility of substances in liquid solvents?

When a solute dissolves in a solvent, particles of the solute disperse throughout the solvent. The solute particles occupy positions that are normally taken by solvent molecules i.e., particles of the solute mix with particles of the solvent. The tendency to mix is affected by the relative strengths of three types of interaction. These are

* *Solvent-solvent interaction*

* *Solute-solute interaction*

* *Solvent-solute interaction*

Strong forces of attraction between solute particles (*solute-solute interactions*) or between solvent particles (*solvent-solvent interactions*) tend to keep like particles close together and reduce the solubility of solute in the solvent. On the other hand, strong attraction forces between solute and solvent particles (*solute-solvent interactions)* makes dissolving easier and helps to keep particles in solution. For simplicity, we can imagine the solution process taking place in three distinct steps (Figure 1.3).
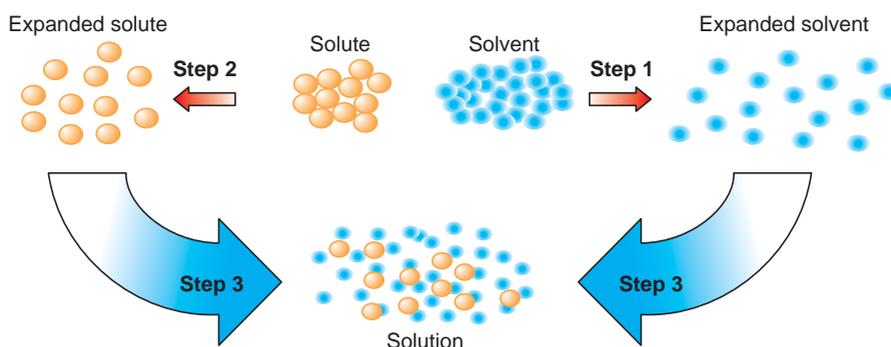
Figure 1.3   A molecular view of the solution process, portrayed as taking place in three steps.

Step 1 – is the separation of solvent molecules from each other to "make room" for the incoming solute particles and **step 2** – is the separation of solute molecules. These two steps require energy input to break attractive intermolecular forces. Therefore, they are endothermic. In **step 3** – the solvent and solute molecules mix. This process can be exothermic or endothermic.

Solution of liquids in liquids

Ethanol mixes with water but oil does not. Why? Solubility is a measure of how much solute will dissolve in a solvent at a specific temperature. Do you know the principle "like dissolves like"? The "like dissolves like" principle is helpful in predicting the solubility of a substance in a given solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other.

For example, in a solution formed between benzene (C_6H_6) and carbon tetrachloride (CCl_4), both species are non-polar and experience only relatively weak London forces. When these two liquids are mixed, they readily dissolve in each other because the attraction between CCl_4 and C_6H_6 molecules is comparable in magnitude to the forces between CCl_4 molecules and between C_6H_6 molecules. Two liquids are said to be miscible if they are completely soluble in each other in all proportions. *What can you say about the solubility of C_6H_6 and CCl_4?*

Water is the most prominent solvent because it is so common and dissolves so many ionic and polar substances. Water molecules are strongly associated with each other through hydrogen bonding. Compounds that form hydrogen bonding tend to be soluble in water. For example, alcohols such as methanol, ethanol and 1, 2-ethylene glycol are miscible in water because they can form hydrogen bonding with water molecules.
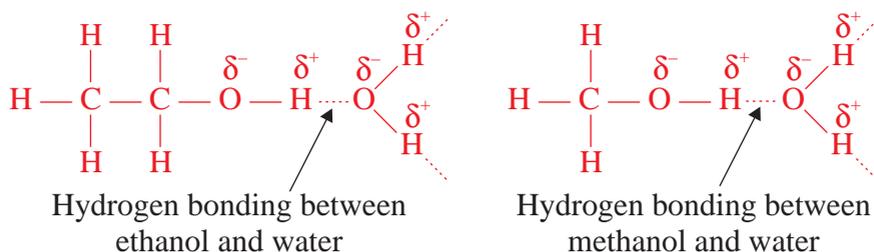
Figure 1.4   Solubility of ethanol and methanol in water through hydrogen bonding.

What happens if octane, a typical hydrocarbon, is added to water? Water molecules are held in contact by hydrogen bonding, while octane molecules are held in contact by London or dispersion forces. When the two liquids are mixed, the attraction between the octane molecules and the water molecules is not strong enough to overcome the hydrogen bonding between the water molecules. The relatively strong hydrogen bonding keep the water molecules clustered together, and no mixing occurs.

Solutions of Solids in Liquids

Activity 1.3

Take two containers and add water to both. Put table salt in the first container and table sugar in the second container and stir. What did you observe? Did both solids dissolve in water? Repeat the same procedure using oil instead of water.

What did you observe? Did both solids dissolve in oil? Discuss your observations with your classmates. Can you make generalization from your observation?

Solids composed of polar molecules or ions, are insoluble in non-polar solvents. The weak solute-solvent interaction, compared with the strong attractions within the crystal, is not sufficient to tear apart the lattice. This is why sugar, which consists of molecules lightly bound to each other by hydrogen bonding, is insoluble in solvents like oil. However, sugar is soluble in water, because this solvent attracts sugar molecules in the same way that sugar molecules attract each other.

Solids whose crystals are held together by London forces are able to dissolve to appreciable extents in non-polar solvents. However, they are not soluble to any great

degree in polar solvents, for the same reason that non-polar liquids are insoluble in polar solvents.

Can you give an example of a solid non-polar compound that dissolves in benzene but not in water? Water and other polar molecules are attracted to ions. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water (Figure 1.5).
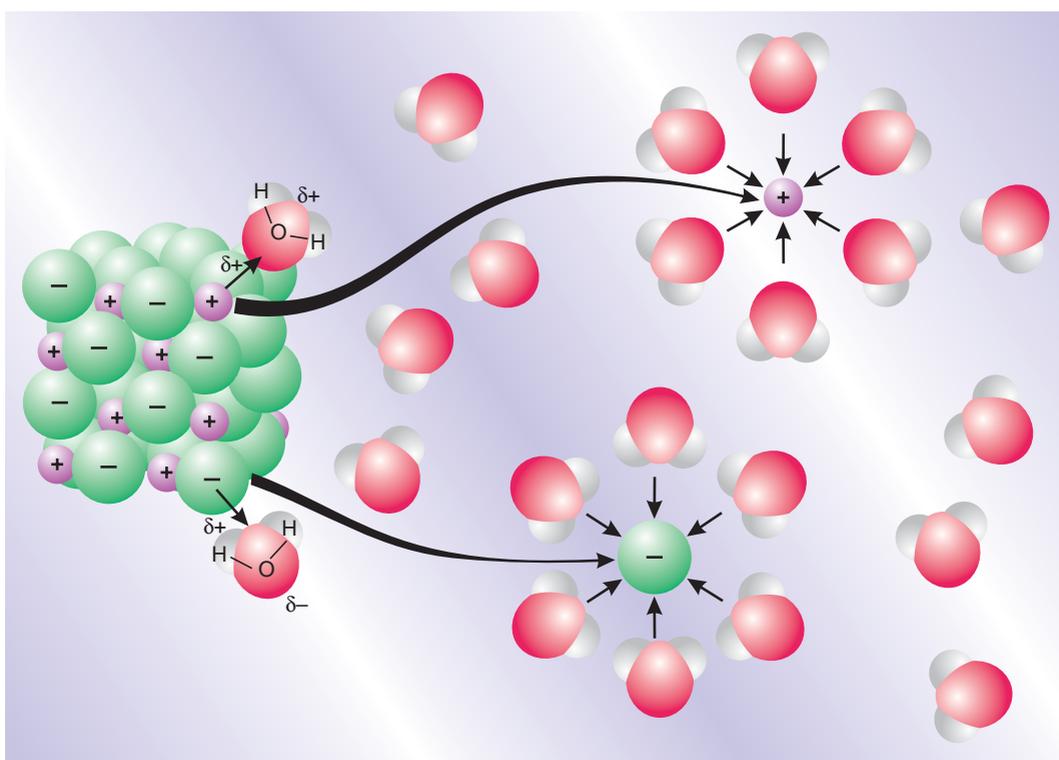

Figure 1.5 Ion-dipole force in dissolving an ionic crystal.

What happens when ionic compounds dissolve in water?

When ionic compounds, such as KCl, dissolve in water, (Figure 1.6), the ions in the solid separate because water molecules surround and solvate the ions. When potassium chloride is added to water, the ion-dipole forces attract the positive (*hydrogen*) end of the polar water molecules to the negative chloride ion at the surface of the solid, and they attract the negative (*oxygen*) end to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong inter-ionic

forces that bind the ions together. This reduction allows them to move off into solution as hydrated ions. In general, when a solute particle becomes surrounded by solvent molecules, we say that it is solvated. When the solvent is water the process is called hydration.
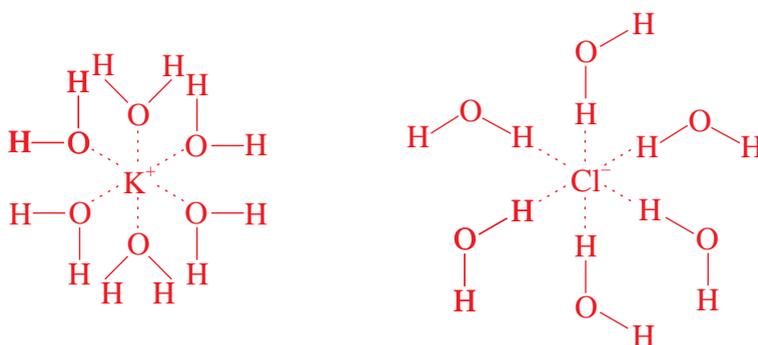
Figure 1.6   K$^+$ and Cl$^-$ surrounded by H$_2$O molecules.

In Grade 11 Chemistry, you learned about the cleansing action of soap, which work on the principle of "like dissolves like". Non-polar tails of soap dissolve in oil and grease globules. The polar heads keep the particle suspended in water in which they can be washed away.

1.3.2 The Rate of Dissolution

What are the major factors that affect the rate of dissolution?

The rate of dissolution is the speed with which a solute goes into solution. This largely depends upon the inter-particle forces and, to a lesser extent, on conditions such as the surface area of the solid solute, and the temperature and the pressure of the system.

Inter-particle force is the extent to which solvent molecules interact with particles of the solute. When the solvent-solute interactions are stronger than those between solute-solute and solvent-solvent particles, the dissolution process becomes easier.

Increasing surface area will increase the rate of dissolution because it increases the number of solute particles in contact with the solvent.

1.3.3 Energy Changes in the Solution Process

Heat of Solution

Experiment 1.3
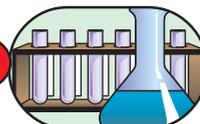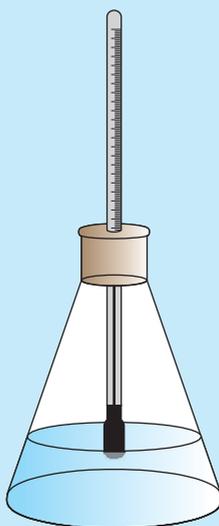
Investigation of Heat of Solution

Objective: To investigate the heat of solution of sodium hydroxide and ammonium nitrate.

Apparatus: Erlenmeyer flask, thermometer, cork.

Chemicals: Sodium hydroxide, ammonium nitrate and water.

Procedure:

1. Pour 50 ml of water into Erlenmeyer flask and place a thermometer as shown in Figure 1.7.

Figure 1.7 Apparatus to measure the heat of solution of sodium hydroxide.

2. Record the initial temperature of the water.

3. Remove the cork, along with the thermometer, and add 4 g of sodium hydroxide pellets.

4. Replace the cork gently, stir the contents, and note the highest temperature reading.

5. Determine the heat of the solution of sodium hydroxide.

6. Repeat the experiment, using 4 g of ammonium nitrate.

7. Copy and complete the following table.

Chemical	Initial temperature of the solvent	Maximum temperature of the solution	Heat of solution
NaOH			
NH_4NO_3			

8. Write down your conclusion.

9. Present your findings.

What are the three major interactions that are observed in the solution process?

You have learned that the solution process has three steps. The amount of energy that is absorbed or released when one mole of a substance enters solution is called *the heat of solution* and is given the symbol $\Delta H°_{Sol}$, which is the sum of the enthalpies associated with the three steps in the solution process (Figure 1.3).

* The separation of solute particles is endothermic because energy is required to overcome the forces holding the solute particles together. For gases, this step is ignored because their molecules are already widely separated.

* The separation of solvent particles is also endothermic because energy is required to overcome the forces holding the solvent molecules together.

* Each solute particle is surrounded by a layer or "cage" of solvent molecules that is attracted to it by *intermolecular forces*. This step can be endothermic or exothermic, and is referred to as solvation.

The heat of solution $\Delta H°_{Sol}$

$$\Delta H°_{Sol} = \Delta H_1° + \Delta H_2° + \Delta H_3° = \Delta H°_{Hydration} + \Delta H°_{Latice\ energy}$$

where $\Delta H_1°$ and $\Delta H_2°$ are enthalpies required to separate solute particles and solvent molecules, respectively, and $\Delta H_3°$ is the enthalpy of solvation. If the solute-solvent attraction is stronger than both the solvent-solvent attraction and the solute-solute attraction, the solution process is favourable, or exothermic ($\Delta H°_{Sol} < 0$). If the solute-solvent interaction

is weaker than the solvent-solvent and solute-solute interactions, then the solution process is endothermic ($\Delta H^o{}_{Sol} > 0$).

Hydration of Ionic Solids in Water

What is lattice energy? How can it affect the solubility of ionic solids?

Hydration of ions favours the dissolution of an ionic solid in water. The ions in an ionic crystal are very strongly attracted to one another. Therefore, the solubility of an ionic solid depends not only on the energy of the hydration of ions, but also on lattice energy, which are the energy holding ions together in the crystal lattice. Lattice energy works against the solution process, so an ionic solid with relatively large lattice energy is usually insoluble.

Lattice energies depend on the charge on the ions and also the distance between the centres of the neighbouring positive and negative ions. As the magnitude of the charge on the ions increases the lattice energy also increases. For this reason, you can expect substances with single charged ions to be more comparatively soluble, and those with multiple charged ions to be less soluble in water.

Activity 1.4

Take 1 g of KNO_3, NH_4Cl, and Na_2CO_3 each and dissolve them in water in different test tubes. What did you observe? Which of these chemicals dissolves faster? Is there any change in temperature before and after mixing? Which solution becomes hot and which becomes cold, when solute and solvents are mixed? Discuss your observations with your classmates.

Activity 1.5

Discuss the following questions and write a report. Present your report to the class.

1. How do you compare the hydration of the ions of Group I metals with that of Group II metals? Give reasons.

2. Compare the solubility of $Mg(OH)_2$ with $Ba(OH)_2$, $MgSO_4$ with $BaSO_4$. Justify your answers in terms of lattice energy and hydration energy.

Exercise 1.3

1. Define each of the following.
   a rate of dissolution
   b heat of solution
   c solvation
   d hydration energy
   e lattice energy
   f ideal solution

2. Indicate the type of solute-solvent interaction that should be most important in each of the following solutions:
   a KBr in water
   b Toluene, C_7H_8, in cyclohexane, C_6H_{12}
   c NaOH in water

3. Sodium carbonate is soluble in water, while calcium carbonate is insoluble. Why?

1.4 SOLUBILITY AS AN EQUILIBRIUM PROCESS

At the end of this section, you should be able to:
- describe the distinctions among unsaturated, saturated and supersaturated solutions;
- prepare a supersaturated solution of sodium phosphate;
- explain the equilibrium nature of a saturated solutions;
- define solubility and describe the factors that affect the solubility of substances;
- investigate the effect of temperature on the solubility of sodium sulphate in water;
- conduct an experiment to determine the solubility of table salt and sugar in water;
- state Henry's law;
- use Henry's law to calculate the concentration of gaseous solute in a solution.

Activity 1.6

Form a group and perform the following activity.
1. Pour 50 mL water in a beaker.
2. Add some crystal of Na_2SO_4 into the water using spatula and stir until it dissolves.
   a What do you call this type of solution?
3. Continue adding more and more Na_2SO_4 stirring to dissolve.
   b What do you observe after addition of large amount of solute?
4. Filter the undissolved solute. Collect the filtrate or the solution.
   c Why does the solute remains undissolved?
   d What is the name of such a solution?
5. Add some more solute to the filtrate and stir.
   e Does the additional solute dissolve?

Discuss your findings with rest of the class.

Experiment 1.4
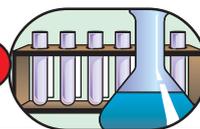
Investigating the solubility of NaCl

Objective: To determine the solubility of sodium chloride in water.

Apparatus: Beaker, evaporating dish, measuring cylinder, glass rod, filter paper, analytical balance, and Bunsen burner.

Chemicals: Sodium chloride and water.

Figure 1.8 Experimental set-up for the determination of the solubility.

Procedure:

1. Take an evaporating dish and weigh it.
2. Take 100 mL of water in a beaker and add sodium chloride to it. Stirr the solution vigorously with a glass rod, until undissolved sodium chloride is left in the beaker.
3. Take 50 mL of the supernatant saturated solution (assume that 50 mL of solution is equal to 50 mL of the solvent) and transfer it to an evaporating dish.
4. Heat the solution in the evaporating dish as shown in the Figure 1.8, till all the water has evaporated and dry sodium chloride is left in the evaporating dish.
5. Cool the evaporating dish containing dry sodium chloride to room temperature and weigh it again.

Observations and analysis:

1. Volume of the NaCl solution   ……………………..
2. Weight of the empty evaporating dish   ……………………..
3. Weight of the evaporating dish + NaCl collected after evaporating the solvent ....
4. Calculate the solubility of NaCl in water and express the results in grams of NaCl/ 100 g of water.

When an ionic solid dissolves, ions leave the solid and become dispersed in the solvent. Occasionally some dissolved ions collide with the undissolved solute and crystallize. As long as the rate of dissolution is greater than the rate of crystallization, the concentration of ions in the solution rises. Eventually, ions from the solid are dissolved at the same rate as the ions in the solution are crystallized. At this point, even though dissolution and crystallization continue, there is no further change in the concentration over time. The system has reached equilibrium. That is, excess undissolved solute is in equilibrium with the dissolved solute.

$$\text{Solid (solute)} \underset{\text{Crystallization}}{\overset{\text{Dissolution}}{\rightleftharpoons}} \text{Dissolved ions}$$

After equilibrium is established, no more solid dissolves. *Why?* Such a solution is said to be saturated. A saturated solution is a solution in which the dissolved and undissolved solutes are in dynamic equilibrium see Figure 1.9.
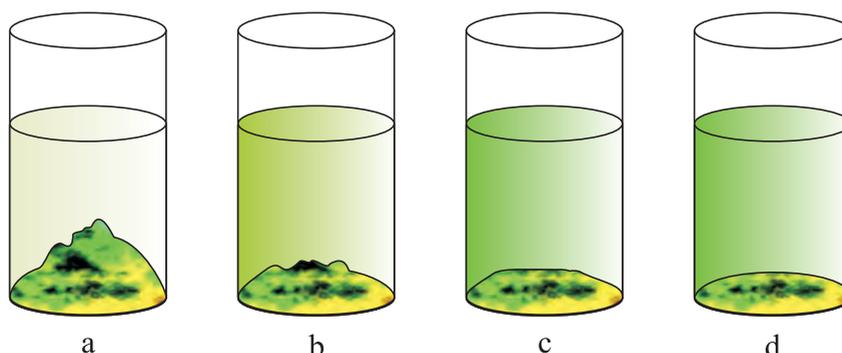
Figure 1.9   Formation of a saturated solution.

a   A coloured solid solute is added to water.

b   After a few minutes, the solution is coloured, due to the dissolved solute, and there is less undissolved solute than in (a).

c   After more time passes, the solution's colour has intensified and there is less undissolved solute. Therefore, the solution in (b) must have been unsaturated.

d   Still later, the solution colour and the quantity of undissolved solute appear to be the same as that in (c). Dynamic equilibrium must have been attained in (c) and persists in (d). The solution is saturated.

Before equilibrium is reached, the solution is said to be unsaturated. An unsaturated solution is a solution that can dissolve more solute at a given temperature.

Activity 1.7

Prepare a saturated solution of sodium thiosulphate ($Na_2S_2O_3$) in beaker containing 50 mL water. Heat the solution so that extra amount of solute dissolves.

Filter and divide the solution into two parts in two different beakers. Keep both the solutions to cool slowly undisturbed. After cooling stir one of the solutions and observe what happens.

Drop a small grain of crystal in the second one and observe the result.

a What is the name of such a solution that is made by cooling concentrated solution?

b What happens when the solution was stirred?

c What about the solution to which a crystal grain is dropped? Why?

d What did you understand from the activity?

The solubility of many ionic solids in water increases as temperature increases. They form supersaturated solutions, which actually contain larger amounts of solute than in saturated solutions. Supersaturated solutions can sometimes be prepared by saturating a solution at a high temperature. Honey is an example of naturally occurring supersaturated solution. It contains glucose, as a solute, and water, as a solvent. If honey is left to stand, the glucose eventually crystallizes.

Supersaturated solutions are unstable, and addition of a "seed" crystal of solute will generally cause all of the excess solute to suddenly crystallize see Figure 1.10.

A Hot supersaturated solution before seeding.

B Cold and undisturbed supersaturated solution without seeding.

C Cold supersaturated solution after seeding.

Figure 1.10 Seeding a supersaturated solution.

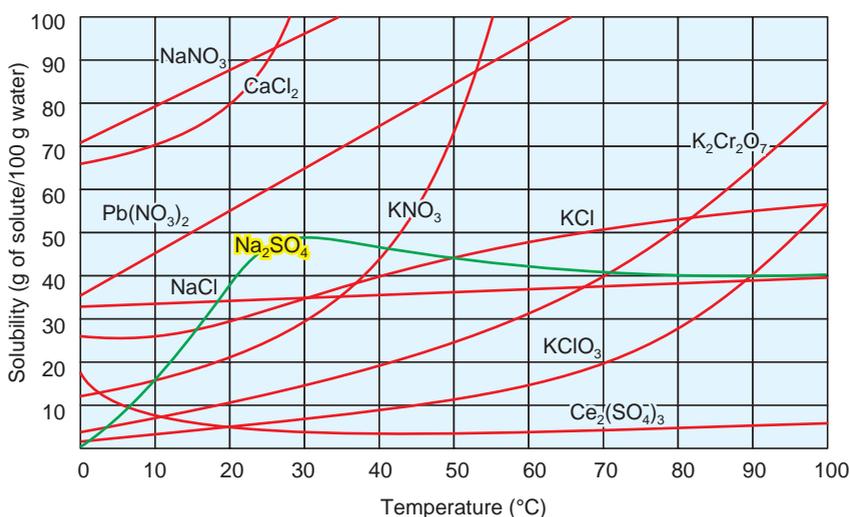## 1.4.1 Effect of Temperature on Solubility of Solute

Activity 1.8

1. Prepare a saturated solution of Na_2SO_4 at room temperature.
2. Heat the solution on a tripod with wire gauze and add some crystal of Na_2SO_4.
3. What happens to the solute?
4. If the solute dissolves add more and continue heating.
5. What is the effect of temperature on solubility of this solute?
6. After all the additional solute dissolves remove the beaker from the tripod and add cold water on the side of the beaker.
7. What do you observe?
8. What is the effect of cooling the solution?
9. Why do we always mention temperature when we report solubility of substances?

Temperature affects the solubility of most substances. When a solid dissolves in a liquid, the solute particles must separate, so energy must be added. Thus, for a solid, $\Delta H^\circ_{Solute} > 0$. In contrast, gas particles are already separated, so $\Delta H^\circ_{Solute} \approx 0$. Because the hydration step is exothermic ($\Delta H^\circ_{Hydra} < 0$), the sum of these two terms must be negative. Thus, for all gases in water, $\Delta H^\circ_{Sol} < 0$.

$$\text{Solute(g)} \quad + \quad \text{Water(l)} \quad \rightarrow \quad \text{Saturated solution(aq)} \quad + \quad \text{Heat}$$

This equation means that solubility of gases in water decreases with rising temperature. In most (*but certainly not all*) cases, the solubility of a solid substance increases with increase in temperature. The magnitude of the increase in solubility varies from one substance to another. The solubility of sodium chloride in water increases by only about 10% from 35.7 g/100 g to 39.8 g/100 g, when the temperature is raised from 0 °C to 100 °C. The solubility of silver nitrate, however, increases by over 700% from 122 g /100 g to 951 g/100 g, over the same temperature range.

A few solids such as sodium sulphate have unusual solubility characteristics in water. The solubility of sodium sulphate rises between 0 °C to 32.4 °C, where it reaches a maximum of 49.7 g Na_2SO_4 per 100 g water. Further, the solubility of sodium sulphate, decreases by about 19.23%, changing from 49.7 g/100 g at 32.4 °C, to 42 g/100 g at 100 °C. Thus some ionic compounds show mixed solubility behaviour. Figure 1.11 shows the solubility of some ionic compounds in water, as a function of temperature.

Figure 1.11 Approximate variation of solubility with temperature for some ionic salts in water.

1.4.2 The Effect of Pressure on Solubility

Why pressure significantly affect only the solubility of gases? Since liquids and solids are almost incompressible, pressure has little effect on their solubility, but it has a major effect on gas solubility. The solubility of gases always increases with increasing pressure. The effect of increased pressure on solubility has long been used in the beverage industry, where carbonated beverages such as champagne, beer and many soft drinks are bottled under CO_2 pressure, up to 4 Pa.

The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution.

The quantitative relationship between gas solubility and pressure is given by Henry's law, which states that

"at a given temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution".

$$C_g = k_H P_g$$

where C_g is the molar concentration (mol/L) of the dissolved gas, P_g is the pressure (in atm) of the gas over the solution and k_H is Henry's law constant, which is expressed in mol/L atm.

Consider the piston-cylinder assembly in Figure 1.12, in which gas is above a saturated aqueous solution of the same gas. At a given pressure, P_1, the same number of gas molecules enters and leave the solution per unit time. i.e., the system is at equilibrium.

Gas + Solvent → Saturated solution

If you push down the piston (*increasing pressure to* P_2), the gas volume decreases and gas particles collide with the liquid surface more often. Thus, more gas particles enter the solution per unit time. Higher gas pressure disturbs the balance of equilibrium, so more gas dissolves to reduce this disturbance until the equilibrium is established in the system.

a   b
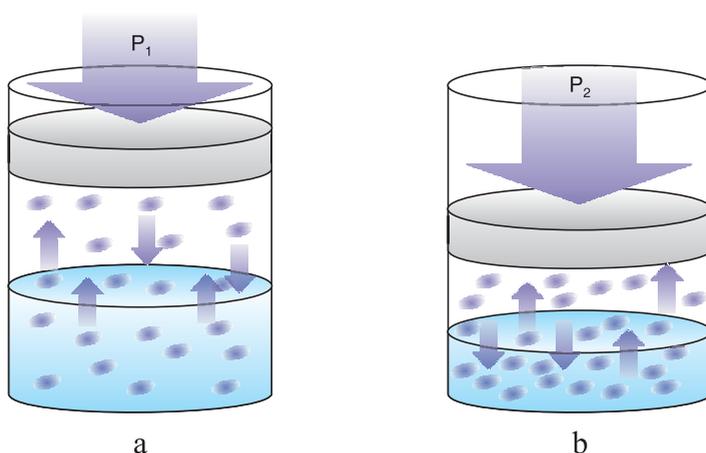
a) *A saturated solution of a gas is in equilibrium at pressure* P_1

b) *If the pressure is increased to* P_2, *the volume of the gas decreases. As a result, the collisions with the surface increases, and more gas molecules enter the solution when equilibrium is re–established.*

Figure 1.12 The effect of pressure on gas solubility:

Table 1.1 Henry's Law constants for some gases in water at 20°C.

Gas	k_H (mol/L. atm)
Air	7.9×10^{-4}
Argon	1.5×10^{-3}
Carbon dioxide	3.3×10^{-2}
Helium	3.7×10^{-4}
Neon	5.0×10^{-4}
Hydrogen	8.5×10^{-4}
Nitrogen	7.0×10^{-4}
Oxygen	1.23×10^{-3}

Example 1.1

The partial pressure of carbon dioxide gas inside a bottle of mineral water is 4 atm at 25°C. What is the solubility of CO_2?

Solution:

Given:

$P_{CO_2} = 4$ atm

$k_H = 3.3 \times 10^{-2}$ mol/L atm

Required:

$C_{CO_2} = ?$

$$C_{CO_2} = k_H \cdot P_{CO_2}$$

$$= 3.3 \times 10^{-2} \text{ mol/L. } \cancel{atm} \times 4 \cancel{atm}$$

$$= 0.1 \text{ mol/L}$$

$$C_{CO_2} = 0.1 \text{ mol/L}$$

Exercise 1.4

1. If air contains 78% N_2 by volume, what is the solubility of nitrogen in water at 25°C?

2. Calculate the concentration of CO_2 in a soft drink after the bottle is opened at 25 °C under a CO_2 partial pressure of 3.0×10^{-4} atm.

1.5 WAYS OF EXPRESSING CONCENTRATIONS OF SOLUTION

At the end of this section, you should be able to:

- define terms like solution, concentration, mass percentages, ppm and ppb of a solute in a solution;

- calculate the mass percentage, ppm and ppb of a solute in a solution from given set of information;

- define mole fraction, molarity, equivalent mass, number of equivalents, normality and molality;

- calculate mole fraction, molarity, normality and molality of a solution from given set of information; and

- interconvert various concentration expressions.

What does concentration mean? How do you determine it?

The concentration of a solution is the amount of solute present in a given quantity of solvent or solution. The concentration of a solution can be expressed either qualitatively or quantitatively. The terms dilute and concentrated are used to describe a solution qualitatively. A solution with a relatively small amount of solute is said to be dilute. One with a large amount of the solutes is said to be concentrated.

The knowledge of concentration can be very useful in everyday life. For example, human beings estimate the quantity of solutes such as sugar and salt, in beverages and other food solutions by tasting. However, sometimes tasting a substance is not safe and, in general, this is not an accurate method of estimating the concentration of solute in a solution. *Why?*

Several quantitative expressions of concentration are used in chemistry. Here you are going to learn mass percentage, ppm and ppb, mole fraction, molarity, normality and molality of a solution.

1.5.1 Mass Percentage, ppm and ppb of Solute

What does mass percent mean? How do you convert it to ppm and ppb?

Percent by mass: The percent by mass, also called percent by weight or weight percent, is the ratio of the mass of a solute to the mass of the solution, multiplied by 100.

$$\text{Percent by mass of solute} = \frac{\text{Mass of solute}}{\text{Mass of solute} + \text{Mass of solvent}} \times 100$$

or

$$\text{Percent by mass of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

The percent by mass has no unit because it is the ratio of two similar quantities.

Example 1.2

A solution is made by dissolving 13.5 g of glucose, $C_6H_{12}O_6$, in 0.100 kg of water. What is the mass percentage of solute in this solution?

Solution:

Given:	**Required:**
Mass of solute $= 13.5$ g	% by mass of solute?
Mass of solvent $= 0.100$ kg $= 100$ g	

$$\text{\% by mass of glucose} = \frac{\text{Mass of glucose}}{\text{Mass of solution}} \times 100$$

$$= \frac{13.5 \text{ g}}{13.5 \text{ g} + 100 \text{ g}} \times 100 = 11.9\%$$

Parts per million (ppm): When the mass of solute in the solution is very small, a widely used expression is parts per million (ppm).

$$\text{ppm of component} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

or

$$\text{ppm} = \text{Mass percentage of solute} \times 10^4$$

Example 1.3

A 2.5 g sample of ground water was found to contain 5.4 µg of Zn^{2+}. What is the concentration of Zn^{2+}, in parts per million?

Solution:

Because 1 µg is 1×10^{-6} g, 5.4 µg $= 5.4 \times 10^{-6}$ g

Thus, ppm $= \dfrac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6 = \dfrac{5.4 \times 10^{-6}\,g}{2.5\ g} \times 10^6 = 2.16$ ppm

Example 1.4

Express 5% (m/m) solution of NaCl in ppm.

Solution:

ppm $= $ Mass percentage $\times 10^4$

$\qquad = 5 \times 10^4$

For solutions that are even more dilute, parts per billion (ppb) is used. A concentration of 1 ppb represents 1 g of solute per billion (10^9) grams of solution.

$$\text{ppb} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^9$$

Exercise 1.5

1. A sample of 0.892 g of potassium chloride, KCl, is dissolved in 54.6 g of water. What is the percent, by mass, of KCl in the solution?

2. a If 150 g of orange juice contains 120 mg of ascorbic acid (Vitamin C), what is the concentration of ascorbic acid, expressed in ppm?

   b Express the concentration of ascorbic acid given in (a) in ppb.

1.5.2 Mole Fraction (X)

What is the difference between mole fraction of non-electrolytes and mole-fraction of electrolytes?

The mole fraction (X) of a solute is the ratio of the number of moles of solute divided by the total number of moles of a solution (*moles of solute + moles of solvent*).

Mole fraction for a non-electrolyte (X) =

$$\frac{\text{Number of moles of solute}}{\text{Number of moles of solute} + \text{Number of moles of solvent}}$$

or $\quad X_{\text{Solute}} = \dfrac{n_{\text{Solute}}}{n_{\text{Solute}} + n_{\text{Solvent}}}$; $\quad X_{\text{Solvent}} = \dfrac{n_{\text{Solvent}}}{n_{\text{Solvent}} + n_{\text{Solute}}}$

A useful relation between X_{solute} and X_{solvent} is:

$$X_{\text{Solvent}} + X_{\text{Solute}} = \frac{n_{\text{Solvent}}}{n_{\text{Solvent}} + n_{\text{Solute}}} + \frac{n_{\text{Solute}}}{n_{\text{Solute}} + n_{\text{Solvent}}} = 1$$

For an electrolyte solution, the mole fraction is calculated by treating the cations and anions as individual particles; hence,

$$X_{\text{Cations}} = \frac{n_{\text{Cations}}}{n_{\text{Cations}} + n_{\text{Anions}} + n_{\text{Solvent}}}$$

A similar expression can be written for X_{Anions}.

Example 1.5

What is the mole fraction of I_2 in a solution containing 30 g of I_2 in 400 g of CCl_4?

Solution:

First find the number of moles of I_2 and the number of moles of CCl_4

$$\text{Number of moles of } I_2 = \frac{\text{Mass of } I_2}{\text{Molar mass of } I_2} = \frac{30\text{ g}}{254\text{ g/mol}} = 0.12\text{ mol } I_2$$

$$\text{Number of moles of } CCl_4 = \frac{\text{Mass of } CCl_4}{\text{Molar mass of } CCl_4} = \frac{400\text{ g}}{254\text{ g/mol}} = 2.6\text{ mol } CCl_4$$

$$X_{I_2} = \frac{n_{I_2}}{n_{I_2} + n_{CCl_4}} = \frac{0.12\text{ mol}}{0.12\text{ mol} + 2.6\text{ mol}} = 0.044$$

Exercise 1.6

1. 1 mole of alcohol is mixed with 3 moles of water. Calculate the mole fraction of alcohol and water.

2. Determine the mole fraction of the substances in a solution containing 36 g of water and 46 g of glycerine, $C_3H_5(OH)_3$.

3. 0.1 mole of NaCl is dissolved in 10 moles of water. Calculate the mole fraction of Na^+ ions and Cl^- ions.

1.5.3 Molarity (M)

Molarity or molar concentration is the number of moles of solute in 1 L of solution. Molarity is determined by the equation

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume (L) of solution}}$$

But, $\text{Number of moles of solute} = \dfrac{\text{Mass of solute}}{\text{Molar mass of solute}}$

Therefore,

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{Volume (L) of solution}}$$

Example 1.6

What is the molar concentration of a solution containing 16.0 g of CH_3OH in 200 mL of solution?

Solution:

Given: **Required:**

Mass of solute $(CH_3OH) = 16$ g Molarity = ?

Volume of solution $= 200$ mL $= 0.20$ L

Molar mass of $CH_3OH = 32$ g/mol

$$\text{Molarity} = \frac{\text{Mass of } CH_3OH}{\text{Molar mass of } CH_3OH \times \text{Volume (L) of Solution}}$$

$$= \frac{16 \text{ g}}{32 \text{ g/mol} \times 0.20 \text{ L}} = 2.50 \text{ mol/L} = 2.50 \text{ M}$$

Example 1.7

How many grams of potassium dichromate ($K_2Cr_2O_7$) are required to prepare 250 mL of solution whose concentration is 2.16 M?

Solution:

Given: **Required:**

Volume of solution $= 250\,mL = 0.250\,L$ Mass of $K_2Cr_2O_7 = ?$

Molarity (M) of solution $= 2.16\,M$

Molar mass of $K_2Cr_2O_7 = 294$ g/mol

$$\text{Molarity} = \frac{\text{Mass of } K_2Cr_2O_7}{\text{Molar mass of } K_2Cr_2O_7 \times \text{Volume(L) of Solution}}$$

$$\text{Mass of } K_2Cr_2O_7 = \text{Molarity} \times \text{Molar mass of } K_2Cr_2O_7 \times \text{Volume (L) of solution}$$

$$= 2.16 \text{ mol/L} \times 294 \text{ g/mol} \times 0.250 \text{ L}$$

$$= 159 \text{ g } K_2Cr_2O_7$$

Exercise 1.7

1. 5.85 g of sodium chloride (NaCl) is dissolved in 250 mL of solution. Calculate

   a   the molarity of the solution.

   b   the mass percentage of the solute.

2. How would 250 ml of 0.15 M KNO_3 solution be prepared?

1.5.4 Normality (N)

What are number of equivalents and equivalent mass? How are they used in calculating the normality of a solution?

The normality of a solution (N) is the number of equivalents of the solute contained in one litre of solution.

$$\text{Normality } (N) = \frac{\text{Number of equivalents of solute}}{\text{Volume (L) of solution}}$$

The number of equivalents can be determined from the equivalent mass.

* The equivalent mass of an acid is obtained by dividing its molar mass by the number of H^+ ions furnished by one formula unit of the acid, or by the number of hydroxide ions with which one formula unit of the acid reacts.

  The equivalent mass of HCl, for example, is the same as its molar mass, since it contains one acidic hydrogen per molecule. The equivalent mass of sulphuric acid, H_2SO_4, is usually half its molar mass, since both hydrogen are replaceable in most reactions of dilute sulphuric acid. An equivalent of phosphoric acid may be 1 mol, 1/2 mol or 1/3 mol, depending on whether one, two or three hydrogen atoms per molecule are replaced, respectively, in a particular reaction.

* The equivalent mass of a base is obtained by dividing its molar mass by the number of OH^- ions furnished by one formula unit of a base or the number of H^+ ions with which one formula unit of the base reacts. The equivalent mass of NaOH, for example, is equal to its molar mass, since one mole furnishes only one mole of OH^- ion.

* The equivalent mass of an oxidizing agent or a reducing agent for a particular reaction is equal to its molar mass divided by the total number of moles of electrons gained or lost when the redox reaction occurs. For example, the equivalent mass of $KMnO_4$ in the reaction

  $$KMnO_4 \ + \ KI \ + \ H_2SO_4 \ \rightarrow \ K_2SO_4 \ + \ MnSO_4 \ + \ I_2 \ + \ H_2O$$

  is determined as follows.

The oxidation number of Mn ion is $(+7)$ in $KMnO_4$, and is changed to $(+2)$ in $MnSO_4$. This shows that it is a 5-electron transfer reaction.

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molar mass of } KMnO_4}{\text{Number of Electrons gained}}$$

$$= \frac{158 \text{ g/mol}}{5 \text{ eq/mol}} = 31.6 \text{ g/eq}$$

* The equivalent mass of a salt is equal to its molar mass divided by number of total positive charges (*total positive valency*).

$$\text{Normality } (N) = \frac{\text{Number of equivalents of solute}}{\text{Volume (L) of solution}}$$

or   Normality $(N) = \dfrac{\text{Mass of solute}}{\text{Equivalent mass of solute} \times \text{Volume (L) of Solution}}$

Notice that normality is molarity times n. It is always equal to or greater than molarity.

$N = M \times n$

Where n is

* number of ionisable hydrogen ions and hydroxide ions per molecule for acids and bases, respectively.

* total number of positive charges for salts.

* total number of electrons lost or gained in redox reactions.

Example 1.8

Calculate the number of equivalents present in 0.50 mol H_3PO_4 if the acid is

a completely neutralized to give PO_4^{3-}

b converted to $H_2PO_4^-$

c converted to HPO_4^{2-}

Solution:

a Since it is completely neutralized, a balanced equation is written as

$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$

From the reaction, one mole of H_3PO_4 produces three moles of H^+ ions. Therefore,

Number of equivalents $= \text{Moles of } H_3PO_4 \times 3$

$= 0.5 \times 3 = 1.5$ equivalents

b The reaction for the formation of $H_2PO_4^-$ is

$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$

One mole of H_3PO_4 produces one mole of H^+. Therefore,

Number of equivalents $= \text{moles of } H_3PO_4 \times 1$

$= 0.5 \times 1 = 0.5$ equivalents

c $H_3PO_4 \rightarrow 2H^+ + HPO_4^{2-}$

One mole of H_3PO_4 produces two moles H^+. Therefore,

Number of equivalents $= \text{moles of } H_3PO_4 \times 2$

$= 0.5 \times 2 = 1$ equivalent

Example 1.9

Calculate the:

a normality   b molarity

of 49 g of H_2SO_4 in 500 mL of solution?

Solution:

Given:

$V = 500$ mL $= 0.5$ L

Mass of $H_2SO_4 = 49$ g

a Normality $= \dfrac{\text{Number of equivalents}}{\text{Volume (L) of solution}}$

Number of equivalents $= \dfrac{\text{Given mass}}{\text{Equivalent mass}}$

Equivalent mass $= \dfrac{\text{Molar mass}}{n}$

Since H_2SO_4 furnishes 2 moles of H^+ ions, n equals 2.

$\Rightarrow$ Equivalent mass $= \dfrac{\text{Molar mass of } H_2SO_4}{n}$

$= \dfrac{98 \text{ g / mol}}{2 \text{ eq / mol}} = 49$ g/eq

Number of equivalents $= \dfrac{\text{Given mass}}{\text{Equivalent mass}} = \dfrac{49 \text{ g}}{49 \text{ g / eq}} = 1$ eq

Normality $= \dfrac{\text{Number of equivalents}}{\text{Volume (L) of solution}} = \dfrac{1 \text{ eq}}{0.5 \text{ L}} = 2$ N

b To find molarity, use the relation

$N = n \times M$, where $n = 2$ for H_2SO_4

$M = \dfrac{N}{n} = \dfrac{2}{2} = 1$ M

Example 1.10

Given the unbalanced equation

$KMnO_4 + KI + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + I_2 + H_2O$

a How many grams of $KMnO_4$ are needed to make 500 mL of 0.250 N solution?

b How many grams of KI are needed to make 25 mL of 0.36 N solution?

Solution:

a In the example given in the note above, we have seen that the equivalent mass of $KMnO_4$ is

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molar mass}}{\text{Number of electron gained per mole}}$$

$$= \frac{158 \text{ g/mol}}{5 \text{ eq/mol}} = 31.6$$

$$\text{Normality (N)} = \frac{\text{Mass of } KMnO_4}{\text{Equivalent mass of } KMnO_4 \times \text{Volume (L) of solution}}$$

Mass of $KMnO_4$ = Normality (N) × Equivalent mass of $KMnO_4$ × Volume (L) solution

$$= 0.250 \text{ eq/L} \times 31.6 \text{ g/eq} \times 0.50 \text{ L} = 3.95 \text{ g } KMnO_4$$

b In the given reaction, the oxidation state of iodine is changed from –1 in KI to 0 in I_2.

$$\text{Hence, equivalent mass of KI} = \frac{\text{Molar mass of KI}}{\text{Number of electrons lost per mole}}$$

$$= \frac{166 \text{ g/mol}}{1 \text{ eq/mol}}$$

Mass of KI = Normality (N) × Equivalent mass of KI × Volume (L) of solution

$$= 0.36 \text{ eq/L} \times 166 \text{ g/eq} \times 0.025 \text{ L}$$

$$= 1.49 \text{ g KI}$$

Example 1.11

What is the normality of a solution that contains 2.94 g of $K_2Cr_2O_7$ in 100 mL of solution? What is its molarity? $K_2Cr_2O_7$ is used as a salt.

Solution:

Given: **Required:**

Mass of $K_2Cr_2O_7$ = 2.94 g   Normality (N) = ?

Volume of solution $= 100\,mL = 0.10\,L$

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{\text{Mass of } K_2Cr_2O_7}{\text{Total positive valance per mole}}$$

$$= \frac{294\,g/mol}{2\,g/eq} = 147\,g/eq$$

$$\text{Normality (N)} = \frac{\text{Mass of } K_2Cr_2O_7}{\text{Equivalent mass of } K_2Cr_2O_7 \times \text{Volume(L) of solution}}$$

$$= \frac{2.94\,g}{147g/eq \times 0.10\,L} = 0.2\,N$$

$$\text{Molarity} = \frac{\text{Normality}}{n} = \frac{0.2N}{2} = 0.1\,M$$

Exercise 1.8

1. How many equivalents of solute are contained in
   a 1 L of 2 N solution?
   b 1 L of 0.5 N solution?
   c 0.5 L of 0.2 N solution?
2. Calculate the mass of $Al_2(SO_4)_3$ in 250 mL of solution if the concentration is 0.48 N.
3. Calculate the molarity and normality of a solution that contains 16.2 g of the salt $Fe_2(SO_4)_3$ in 200 mL of solution.

1.5.5 Molality (m)

What is the difference between molarity and molality?

The molality of a solution is the number of moles of solute per kilogram of solvent contained in a solution.

Note that molal solutions are prepared by measuring masses of solute and solvent, not volumes of solvent or solution.

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass (kg) of solvent}}, \quad \text{or}$$

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{Mass (kg) of solvent}}$$

Example 1.12

Calculate the molality of a solution prepared by dissolving 32.0 g of $CaCl_2$ in 271 g of water.

Solution:

Given: **Required:**

Mass of $CaCl_2$ = 32.0 g   Molality (m) =?

Mass of H_2O = 271 g = 0.271 kg

$$\text{Molality } (m) = \frac{\text{Mass of } CaCl_2}{\text{Molar mass of } CaCl_2 \times \text{Mass (kg) of } H_2O}$$

$$= \frac{32.0 \text{ g}}{111 \text{ g / mol} \times 0.271 \text{ kg}} = 1.06 \ m \ CaCl_2$$

Exercise 1.9

A solution of hydrochloric acid contains 36 percent HCl, by mass

a   Calculate the mole fraction of HCl in the solution.

b   Calculate the molality of HCl in the solution.

c   What additional information would you need to calculate the molarity of the solution?

1.5.6   Conversion of Concentration Units

All the terms we just discussed represent different ways of expressing concentration. *How can you convert one concentration unit to another?* Observe the following guidelines when you convert one concentration unit to another.

* If the density and mass of a solution are given, you can determine the volume of the solution. Similarly, if the density and volume of a solution are given, you can calculate the mass of the solution.

* Molality involves quantity of solvent, whereas the other concentration units involve quantity of solution.

Example 1.13

Hydrogen peroxide is a powerful oxidizing agent used in concentrated solution in rocket fuels and, in dilute solution, in hair bleach. An aqueous solution of H_2O_2 is 30% by mass and has a density of 1.11 g/mL. Calculate the:

a   molality of the solution

b   mole fraction of H_2O_2

c   molarity of the solution

Solution:

a   For molality, we need the number of moles of solute and the mass (kg) of solvent. If we assume 100 g of H_2O_2 solution, we can express the mass percentage directly as mass of substance. We subtract the mass of H_2O_2 to obtain the mass of solvent. To find molality, we convert mass of H_2O_2 to moles and divide by mass of solvent.

Mass of solvent (H_2O) = Mass of solution – Mass of solute

$$= 100.0 \text{ g} - 30.0 \text{ g} = 70.0 \text{ g}$$

$$\text{Moles of } H_2O_2 = \frac{30.0 \text{ g}}{34 \text{ g / mol}} = 0.882 \text{ mol } H_2O_2$$

$$\text{Molality } (m) = \frac{\text{moles of } H_2O_2}{\text{Mass (kg) of solvent}} = \frac{0.882 \text{ mol}}{0.070 \text{ kg}}$$

$$= 12.6 \text{ } m \text{ } H_2O_2 \text{ solution}$$

b   To find the mole fraction, you use the number of moles of H_2O_2 from part a and convert the mass of H_2O to moles.

Number of moles of $H_2O_2 = 0.882$ mol H_2O_2

$$\text{Number of moles of } H_2O = \frac{70.0 \text{ g}}{18 \text{ g / mol}} = 3.88 \text{ mol of } H_2O$$

$$X_{H_2O_2} = \frac{\text{moles of } H_2O_2}{\text{moles of } H_2O_2 + \text{moles of } H_2O} = \frac{0.882}{0.822 + 3.88} = 0.185$$

c   To find molarity, we assume 100.0 g of solution and use the given solution density to find the volume.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$

$$= \frac{100.0 \text{ g}}{1.11 \text{ g/mL}}$$

$$= 90.1 \text{ mL}$$

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume (L) of solution}}$$

$$= \frac{0.882 \text{ mol}}{0.090 \text{ L}} = 9.79 \text{ M } H_2O_2 \text{ solution}$$

Exercise 1.10

1. A sample of commercial concentrated hydrochloric acid is 11.8 M HCl and has a density of 1.190 g/mL. Calculate

   a the mass % of HCl

   b the molality of HCl

   c the mole fraction of HCl

2. The mole fraction of ethanol in water is 0.3. Calculate

   a the molality of the solution

   b the mass percent of ethanol

1.6 PREPARATION OF SOLUTIONS

At the end of this section, you will be able to:

- Prepare molar solutions, normal solutions and molal solutions of different substances;

- Explain dilution process and calculate the volume or concentration changes during the dilution of solutions; and

- Prepare a dilute solution from a concentrated solution.

Experiment 1.5
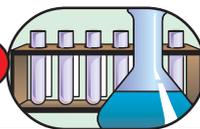
Preparation of Solutions of Known Concentrations

Objective: To prepare a 1 molar NaCl solution and a 1 molar table-sugar solution.

Apparatus and Chemicals: 200 mL volumetric flasks, stirrers, beakers, measuring cylinders, balance, sodium chloride, sugar, and water.

Procedure 1:

1. Weigh 11.7 g of sodium chloride, using a balance, and add to a beaker.
2. Add about 50 mL of water to the beaker containing the sodium chloride and dissolve it by stirring.
3. Using a funnel, transfer the solution to the volumetric flask.
4. Slowly add more water to the volumetric flask until the solution reaches the volume mark.

Observations and analysis:

a How many moles of sodium chloride did you use to prepare the solution?

b What are the molarity and normality of the solution?

Procedure 2:

1. Weigh a beaker and record its mass. Then add 50 g of water. Perform the measurement and calculations:

   Mass of beaker _____

   Mass of beaker + mass of water _____

   Mass of water _____

2. Weigh 17.1 g of table sugar. _____
3. Dissolve the 17.1 g of table sugar in the beaker containing 50 g of water, by stirring.

Observations and analysis:

Calculate:

a mass percent of the solution.

b mole fraction of the solution.

c molality of the solution.

How do you prepare a solution of known concentration?

A common task in school, medical, industrial and other chemical laboratories is the preparation of solutions of known concentrations. For aqueous solutions, distilled, de-mineralized or de-ionized water is used. Other solvents can also be used, depending on the solution

specified. Solutions are usually prepared from solutes of liquids or solids. Occasionally they are prepared from gases. First, the solute is accurately weighed and transferred to a volumetric flask, then water is added through a funnel (Figure 1.13 a). Next, the solid is slowly dissolved by gently swirling the flask (Figure 1.13 b). After all the solid has dissolved, more water is slowly added to bring the level of solution exactly to the volume mark (Figure 1.13 c). Knowing the volume of the solution in the flask and the quantity of compound (*the number of moles*), you can calculate the molarity of the solution using the formula of molarity.

— Marker showing known volume of solution

— Meniscus

a
b
c
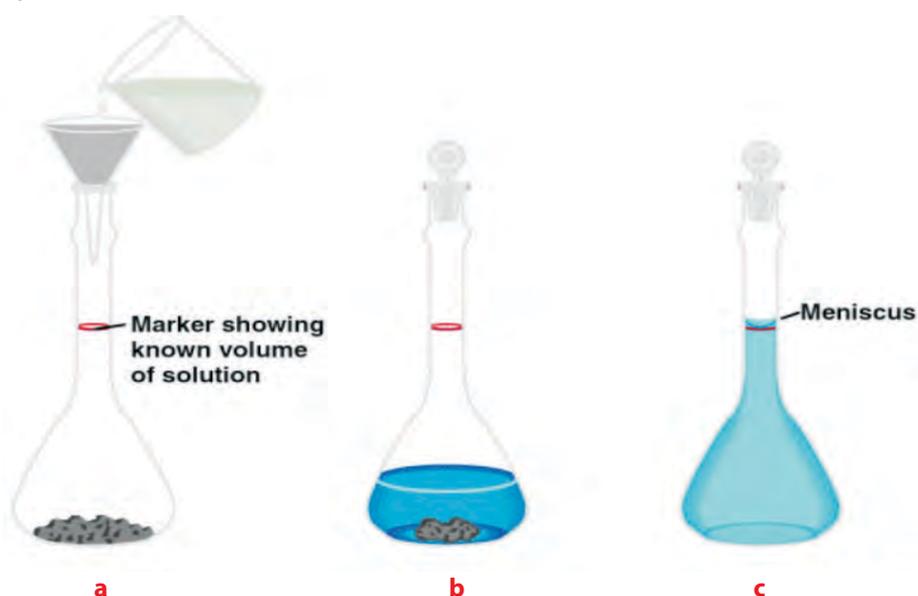
Figure 1.13 Preparation of a solution of known molarity.

A one-molar solution of NaCl can be prepared by dissolving 58.5 g of NaCl in water until the solution becomes one litre.

Activity 1.9

Dissolve 1g each of NaCl, $CuSO_4$, and $KMnO_4$ in different 50 mL measuring flasks. Note the colour intensity of the solutions.

Take 25 mL of solution from each flask and further dilute each solution to 50 mL.

Note the colour intensity again.

What did you observe? Can you correlate the colour intensity with the concentration of the solution? Does this analogy works for colourless solution also? Discuss your observations with your classmates.

Diluting Solutions

Concentrated solutions are often stored in the laboratory as "stock" solutions for use as needed. Frequently we dilute this stock solution before working with them.

Dilution is the procedure for preparing a less-concentrated solution from a more-concentrated one.

In carrying out a dilution process, it is useful to remember that adding more solvent to a given amount of the stock solution changes (*decreases*) the concentration of the solution without changing the number of moles of solute present in the solution. In other words,

Number of moles of solute before dilution = Number of moles of solute after dilution

Since number of moles of solute = molarity × volume of solution,

$$= M \times V$$

Number of of moles of solute before dilution $= M_i V_i$

Number of moles of solute after dilution $= M_f V_f$

Therefore, dilution can be expressed as

$$M_i V_i = M_f V_f$$

or, more generally,

$$C_i V_i = C_f V_f$$

Where C_i is initial concentration, C_f is final concentration, V_i is initial volume and V_f is final volume.

Example 1.14

Describe how you would prepare 5.00×10^2 mL of a 1.75 M H_2SO_4 solution, starting with an 8.61 M stock solution of H_2SO_4.

Solution:

Because the concentration of the final solution is less than that of the original one, this is a dilution process.

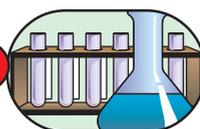**Given:** **Required:**

$M_i = 8.61$ M $V_i = ?$

$M_f = 1.75$ M

$V_f = 5.00 \times 10^2 \ \text{mL}$

$M_i V_i = M_f V_f$

$V_i = \dfrac{M_f \times V_f}{M_i} = \dfrac{1.75 \ M \ \times 5.0 \times 10^2 \ mL}{8.61 \ M} = 102 \ \text{mL}$

Thus, we must dilute 102 mL of 8.61 M H_2SO_4 solution with sufficient water to give a final volume of 5.0×10^2 mL.

Experiment 1.6

Preparation of Solution of Lower Concentration from Standard Stock Solution

Objective: To prepare diluted solution of H_2SO_4

Apparatus: burette, beaker, stirrer, funnel, stand with clamp

Chemicals: 18 M H_2SO_4, distilled water.

Procedure:

1. Carefully add the concentrated acid into the burette.
2. Slowly add with stirring 10.0 mL of the acid into a beaker containing 50 mL of distilled water.
3. Transfer the new solution into a volumetric flask (1 L) and add water up to the mark.

Observations and analysis:

From Procedure 1 and 2:

a Why are acid added to the water not the water to the acid?

b Explain whether volume, mass or number of moles of the solute is changed or not in the process.

c What is the new concentration of the H_2SO_4?

From Procedure 3:

d Calculate concentration of the new solution.

Exercise 1.11

a   How do you prepare 60.0 mL of 0.2 M HNO_3 from a stock solution of 4 M HNO_3?

b   You have 100 mL of a 0.5 M HCl solution, and you want to dilute it to exactly 0.1 M. How much water should you add?

1.7   SOLUTION STOICHIOMETRY

At the end of this section, you should be able to:

- Use stoichiometerically equivalent molar ratios to calculate the amounts of reactants and products in a reaction of pure and dissolved substances.

Activity 1.10

In Grade 9 Chemistry, you learned the stoichiometry of pure substances. What does stoichiometry mean? How can you apply it to solutions? Form a group and discuss these questions.

Since many environmental reactions and almost all biochemical reactions occur in solution, an understanding of reactions in solution is extremely important in chemistry and related sciences.

Solution stoichiometry differs from pure-substances stoichiometry in that the amount of a pure substance can be obtained by converting its mass into moles. For substances in solution, we must know the concentration to find the volume that contains a given number of moles. Thus, the concept of molarity is very important in solution stoichiometry.

You can think of molarity as a conversion factor. We use it to convert the volume of a solution to the number of moles of a solute. From the result, we can find the mass or the number of particles of a solute.

Mole-Mass Problems

The relationship between the mass of a substance and the corresponding number of moles is governed by the molar mass of the substance. But, for problems involving substances in solution, we need to know the concentration of the solution before we can find the number of moles.

Mole of a substance = Concentration × Volume

Example 1.15

What volume of 1.40 M H_2SO_4 solution is needed to react exactly with 100 g of Al? The balanced molecular equation for the reaction is

$$2Al \ + \ 2H_2SO_4 \ \rightarrow \ Al_2(SO_4)_2 \ + \ 2H_2$$

Solution:

We use the mole-mass method:

Number of moles of Al $= \dfrac{100 \text{ g}}{27.0 \text{ g/mol}} = 3.70 \text{ mol}$

From the balanced equation, 2 moles of Al reacts with 2 moles of H_2SO_4. To find the number of moles of H_2SO_4 that reacts with 3.70 moles of Al, we proceed as follows: 2 moles of Al needs 2 moles of H_2SO_4

3.7 moles Al needs X moles of H_2SO_4, therefore

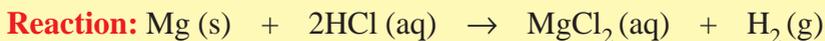$$X = \dfrac{3.7 \text{ mol Al} \times 2 \text{ mol } H_2SO_4}{2 \text{ mol Al}}$$

$X = 3.7 \text{ mol } H_2SO_4$
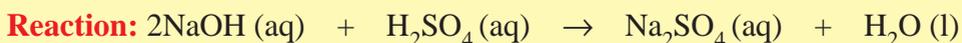
Volume of 1.40 M H_2SO_4 containing 3.70 mol

$$\dfrac{\text{Number of moles of } H_2SO_4}{\text{molarity}} = \dfrac{3.70 \text{ mol}}{1.40 \text{ mol L}^{-1}} = 2.64 \text{ L}$$

Exercise 1.12

1. What volume of 1M HCl solution is required to react with 6 g of magnesium?

    Reaction: Mg (s) $+$ 2HCl (aq) $\rightarrow$ $MgCl_2$ (aq) $+$ H_2 (g)

2. What volume of 0.25 M NaOH solution is needed to react with 50 mL of 0.125 M H_2SO_4?

    Reaction: 2NaOH (aq) $+$ H_2SO_4 (aq) $\rightarrow$ Na_2SO_4 (aq) $+$ H_2O (l)

3. Calcium hydroxide is sometimes used in water treatment plants to purify water for residential use. Calculate the volume of 0.0250 M calcium hydroxide solution that can react completely with 25.0 mL of 0.125 mol L^{-1} aluminium sulphate solution.

   **Reaction:** $Al_2(SO_4)_3$(aq) $+$ 3Ca(OH)$_2$(aq) $\rightarrow$ 2Al(OH)$_3$(aq) $+$ 3CaSO$_4$(s)
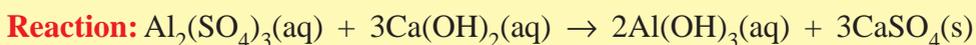
Mole-Volume Problems

In this type of problem, the concentration of the solution is given, and you are asked to determine the volume of the solution that contains a required number of moles or *vice versa*.

Example 1.16

Ammonium sulphate is manufactured by reacting sulphuric acid with ammonia. What concentration of sulphuric acid is needed to react with 24.4 mL of a 2.20 mol L^{-1} ammonia solution, if 50.0 mL of sulphuric acid is used?

$$H_2SO_4\,(aq) \quad + \quad 2NH_3\,(aq) \quad \rightarrow \quad (NH_4)_2SO_4\,(aq)$$
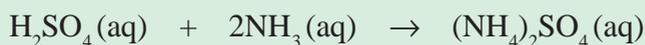
Solution:

First, we calculate the number of moles of H_2SO_4 that react with the given amount of ammonia. To do this, we need to know the number of moles of NH_3.

Number of moles of NH_3 = Molarity of NH_3 × Volume (L) of solution

$$= 2.20 \text{ mol L}^{-1} \times 0.0244 \text{ L}$$

$$= 0.0537 \text{ mol}$$

From the balanced equation above, 2 mol NH_3 reacts with 1 mol H_2SO_4. Therefore, the number of moles of H_2SO_4 that reacts with 0.0537 moles of NH_3 is

$$\frac{0.0537 \text{ mol } NH_3 \times 1 \text{ mol } H_2SO_4}{2 \text{ mol } NH_3} = 0.0268 \text{ mol } H_2SO_4$$

$$\text{Concentration (molarity of } H_2SO_4) = \frac{0.0268 \text{ mol}}{0.05 \text{ L}} = 0.536 \text{ M}$$

Mole-Number of Particles Problems

How do you relate number of moles and number of particles?

Example 1.17

What volume of 0.5 M glucose ($C_6H_{12}O_6$) contains 3.01×10^{22} molecules of glucose?

Solution:

We first change 3.01×10^{22} molecules of glucose to moles of glucose. 1 mole of glucose contains 6.02×10^{23} molecules.

Therefore, 3.01×10^{22} molecules of glucose will be

$$\frac{1 \text{ mol} \times 3.01 \times 10^{22} \text{ molecule}}{6.02 \times 10^{23} \text{ molecule}} = 0.05 \text{ mol}$$

Since,

Number of moles = Concentration $\times$ Volume

$$\text{Volume} = \frac{\text{Number of moles}}{\text{Concentration}} = \frac{0.05 \text{ mol}}{0.500 \text{ mol L}^{-1}} = 0.1 \text{ L} = 100 \text{ mL}$$

1.8   DESCRIBING REACTIONS IN SOLUTION

At the end of this section, you should able to:

- explain the relationship between reacting ions, spectator ions, precipitation and solubility;
- write net ionic equations.

What is the difference between molecular equations and ionic equations? What are spectator ions?

We use chemical equations to help us describe reactions. Reaction involving ions can be presented with different types of chemical equations. The one we use depends on the kind of information we want to convey. We can represent such a reaction by a molecular equation or an ionic equation.

1.8.1   Molecular Equation

A molecular equation is a chemical equation in which the reactants and the products are written as if they were molecular substances, even though they may actually exist in solution as ions. Molecular equations are useful because they are explicit about what the *reactants* are and what *products* you obtain.

Consider the reaction between calcium chloride, $CaCl_2$, and sodium carbonate, Na_2CO_3, in aqueous solution to give solid calcium carbonate and aqueous sodium chloride. The equation for this reaction may be written as:

$$CaCl_2 (aq) + Na_2CO_3 (aq) \longrightarrow CaCO_3 (s) + 2NaCl (aq)$$
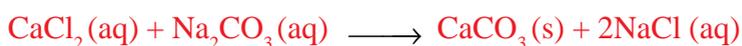
The molecular equation closely describes what is actually done in the laboratory or in an industrial process.

1.8.2 Ionic Equation

Although a molecular equation is useful in describing the actual reactants and products, it does not give any information about what is happening at the level of ions. Since this kind of information is very useful, you often need to write the molecular equation as an ionic equation.

Consider the reaction of calcium chloride and sodium carbonate. Both are soluble ionic substances and are strong electrolytes. When they dissolve in water, they go into solution as ions. Each formula unit of $CaCl_2$ forms one Ca^{2+} ion and two Cl^- ions in solution. So, instead of $CaCl_2(aq)$, it would be better to write $Ca^{2+}(aq) + 2Cl^-(aq)$. Similarly, each formula unit of Na_2CO_3 forms two Na^+ ions and one CO_3^{2-} ion in solution, and this can be written as $2Na^+(aq) + CO_3^{2-} (aq)$ instead of $Na_2CO_3(aq)$. The reactant side of the reaction becomes

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-} (aq)$$

On the product side of the equation, $CaCO_3(s)$ is an ionic compound, but the ions are held together in particular sites in the crystalline solid. We leave the formula as $CaCO_3(s)$ to convey this information in the equation. On the other hand, $NaCl$ is a soluble ionic compound and is a strong electrolyte. Also it dissolves in aqueous solution to give freely moving ions. Therefore, we can write it as $Na^+(aq) + Cl^-(aq)$.

The complete equation is

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-} (aq) \rightarrow CaCO_3(s) + 2Na^+(aq) + 2Cl^-(aq)$$
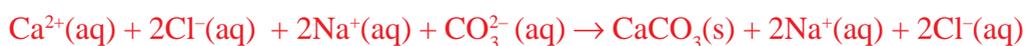
The ions appearing on both sides of the equation (Na^+ and Cl^-) are called spectator ions, as they do not take part in the reaction and they can be cancelled on both sides to express the essential reaction that occurs.

$$Ca^{2+}(aq) + 2\cancel{Cl^-}(aq) + 2\cancel{Na^+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) + 2\cancel{Na^+}(aq) + 2\cancel{Cl^-}(aq)$$
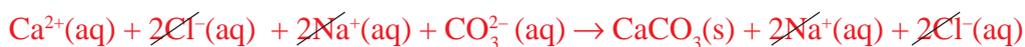
The resulting equation is:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$
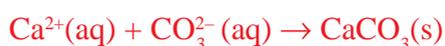
This net ionic equation, is without spectator ions and the reaction that actually occurs at an ionic level is between calcium ions and carbonate ions which form solid calcium carbonate.

Activity 1.11

Form a group and discuss the following:

1. How are sodium carbonate and calcium hydroxide found in water solution? Write dissociation reaction for each of them.

2. Write the ionic equation for the reaction between sodium carbonate and calcium hydroxide. Are the products formed soluble in water?

3. Write the soluble product in ionic form. Are there the same ions in the reactant and product side?

4. Write the net ionic equation.

Exercise 1.13

For each of the following molecular equations, write ionic equation, write a net ionic equation, and identify the spectator ions:

a $2AgNO_3(aq) + Na_2CrO_4(aq) \rightarrow Ag_2CrO_4(s) + 2NaNO_3(aq)$

b $2HClO_4(aq) + Ca(OH)_2(aq) \rightarrow Ca(ClO_4)_2(aq) + 2H_2O(l)$

c $2HNO_3(aq) + Mg(OH)_2(s) \rightarrow 2H_2O(l) + Mg(NO_3)_2(aq)$

d $Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$

1.9 COLLIGATIVE PROPERTIES OF SOLUTION

At the end of this section, you should be able to:

- define colligative properties:
- list the important properties of solvents that are affected by the formation of a solution;
- state Raoult's law;

- explain the change in the colligative properties of solvent when a certain solute is added;

- describe the Van't Hoff's factor;

- calculate the vapour pressure, boiling point, and freezing point of a solvent after a given amount of solute is dissolved in it;

- define osmosis and osmotic pressure of a solution;

- calculate the osmotic pressure of a solution; and

- compare and contrast change in colligative properties of electrolytic and non electrolytic solution.

What is meant by colligative? Why does the addition of ethylene glycol lower the freezing point and raise the boiling point of water? Discuss this question with your classmates.

Certain physical properties of solutions differ in important ways from those of pure solvents. For example, pure water at 1 atm pressure freezes at 0°C, while an aqueous solutions at 1 atm pressure freezes at a lower temperature. Ethylene glycol is added to water in radiators of cars as antifreeze to lower the freezing point of the solution. This also raises the boiling point of the solution above that of pure water, permitting operation of engines at higher temperatures.

The lowering of the freezing point and the raising of the boiling point are examples of the physical properties of solutions that depend on the quantity (*concentration*) of the solute but not on the kind of solute particle. Properties that depend on the number of particles or concentration of the solute in the given amount of solvent and not on their nature are called colligative properties. (*Colligative* is a Latin word that means "*depending on the collection*".)

There are four important properties of a solution that are affected by the addition of a non-volatile solute to a solvent. These are:

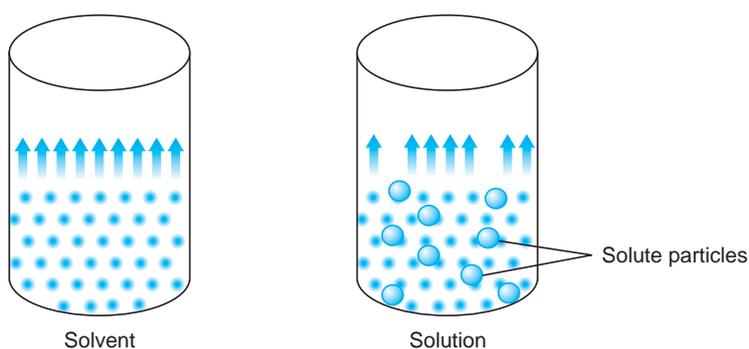1. Vapour pressure lowering
2. Boiling point elevation
3. Freezing point depression
4. Osmotic pressure

1.9.1 Vapour Pressure Lowering

How do non-volatile solutes affect the vapour pressure of the solvent?

If a solute is non-volatile i.e., it does not have a measurable vapour pressure, the vapour pressure of its solution is always less than that of the pure solvent. Vapour pressure lowering

is the lowering of the vapour pressure of the solvents that results when a non-volatile solute is added to form a solution. The solute prevents (*blanket*) the tendency of the solvent to escape and it also lowers the vapour pressure of the solvent (Figure 1.14). Thus, the relationship between solution vapour pressure and solvent vapour pressure depends on the concentration of the solute in the solution.

Solute particles

Solvent   Solution

Figure 1.14   shows the lowering of the rate of vaporization of a solvent when a non-volatile solute is added.

The relationship between solution vapour pressure and solvent vapour pressure is expressed by Raoult's law. This law states that "the partial pressure of a solvent over a solution, P_1, is given by the vapour pressure of the pure solvent, times the mole fraction of the solvent in the solution, x_1, at constant temperature".

$$P_1 = x_1 P_1^\circ$$
$$\Delta P = P_1^\circ - P_1$$

where ΔP = Change in vapour pressure (vapour pressure lowering)

P° = Vapour pressure of pure solvent

P_1 = Vapour pressure of solvent in solution

Note that the vapour pressure of a solvent is not a colligative property. Only the change in vapour pressure, ΔP, which occurs when a solute is added to the solvent, is a colligative property. It can be defined as the difference between the vapour pressure of the pure solvent and the vapour pressure of solvent in the solution.

In a solution containing only one solute, $x_1 = 1 - x_2$, where x_2 is the mole fraction of the solute. Inserting this into the Raoult's-law equation gives:

$$P_1 = (1 - x_2)\, P_1^\circ$$
$$P_1 = P_1^\circ - P_1^\circ\, x_2$$

$$P_1^\circ - P_1 = P_1^\circ \, x_2$$
$$\Delta P = P_1^\circ \, x_2$$

Example 1.18

Calculate the vapour pressure of water at 90 °C in a solution containing 5.0 g of glucose ($C_6H_{12}O_6$) in 100 g of water. The *vapour pressure* of pure water at 90 °C is 525.8 Pa.

Solution:

Given:

Mass of $C_6H_{12}O_6 = 5.0$ g

Mass of water $= 100$ g

Vapour pressure of pure water at 90ºC $= 525.8$ Pa

Required:

Vapour pressure of water in a solution $P_1 = ?$

First, we find mole fractions of both solute and solvent. To do this, we must find the number of moles of glucose and water.

$$\text{Number of moles of } C_6H_{12}O_6 = \frac{\text{Mass of } C_6H_{12}O_6}{\text{Molar mass of } C_6H_{12}O_6} = \frac{5.0 \text{ g}}{180 \text{ g/mol}}$$
$$= 0.028 \text{ mol}$$

$$\text{Number of moles of } H_2O = \frac{100 \text{ g}}{18 \text{ g/mol}} = 5.56 \text{ mol}$$

$$x_{C_6H_{12}O_6} = \frac{0.028 \text{ mol}}{0.028 \text{ mol} + 5.56 \text{ mol}} = 0.005$$

$$x_{H_2O} = \frac{5.56 \text{ mol}}{5.56 \text{ mol} + 0.028 \text{ mol}} = 0.995$$

$$P_1 = x_{H_2O} \, P_1^\circ$$
$$= 0.995 \times 525.8 \text{ Pa} = 523.17 \text{ Pa}$$
$$\Delta P = P^\circ - P$$
$$= 525.8 \text{ Pa} - 523.17 \text{ Pa} = 2.63 \text{ Pa}$$

Example 1.19

Calculate the vapour pressure of a solution made by dissolving 218 g of glucose in 460 mL of water at 30 °C. What is the vapour pressure lowering? (*Assume that the density of water is* 1.00 g/mL). Vapour pressure of water at 30 °C is 31.82 torr.

Solution:

Given:

Mass of solute $(C_6H_{12}O_6) = 218$ g

Volume of water $= 460$ mL $= 0.46$ L

Required:

P_1 (vapour pressure of solution) $= ?$

ΔP (lowering in vapour pressure) $= ?$

From Raoult's law

$$P_1 = x_1 \, P_1^\circ$$

To determine the number of moles of H_2O, its density is used.

$$1\,\text{mL} \rightarrow 1\,\text{g} \qquad \frac{460\ \cancel{\text{mL}} \times 1\,\text{g}}{1\ \cancel{\text{mL}}} = 460\,\text{g}$$

$460\,\text{mL} \rightarrow ?$

$$\text{Number of moles of } H_2O = \frac{460\,\text{g}}{18\ \text{g/mol}} = 25.56\,\text{mol}$$

$$\text{Number of mole of } C_6H_{12}O_6 = \frac{218\,\text{g}}{180\ \text{g/mol}} = 1.21\,\text{mol}$$

$$x_{H_2O} = \frac{25.56\,\text{mol}}{25.56\,\text{mol} + 1.21\,\text{mol}} = 0.955$$

$$x_{C_6H_{12}O_6} = \frac{1.2\,\text{mol}}{1.21\,\text{mol} + 25.56\,\text{mol}} = 0.045$$

$$P_1 = x_1 \, P_1^\circ$$

P_1° is the vapour pressure of water at 30°C, which is equal to 31.82 torr.

$$P_1 = 0.955 \times 31.82\,\text{torr}$$

$$= 30.4\,\text{torr}$$

$$\Delta P = P^\circ - P$$

$$= 31.82\,\text{torr} - 30.4\,\text{torr}$$

$$= 1.42\,\text{torr}$$

Exercise 1.14

1. Why is the vapour pressure of a solution less than that of the pure solvent?

2. The vapour pressure of pure water at 110°C is 1070 torr. A solution of ethylene glycol in water has a vapour pressure of 1.00 atm at 110°C. Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in water?

3. Calculate the vapour pressure lowering, ΔP, when 10.0 mL of glycerol ($C_3H_8O_3$) is added to 500.0 mL of water at 50°C. At this temperature, the vapour pressure of pure water is 92.5 torr and its density is 0.988 g/mol. The density of glycerol is 1.26 g/mL.

Solutions that obey Raoult's law are said to be ideal solutions. If both components of a solution are volatile, i.e., have measurable vapour pressure, the vapour pressure of the solution is the sum of the individual partial vapour pressures. Thus, for two volatile components, A and B, the vapour pressure of each component above the solution is proportional to its mole fraction in the solution.

$$P_A = x_A P_A^\circ$$

$$P_B = x_B P_B^\circ$$

According to Dalton's law of partial pressure, at constant temperature, the pressure of a mixture of gases is equal to the sum of the partial pressures of all of the constituent gases. The total pressure, is:

$$P_T = P_A + P_B = x_A P_A^\circ + x_B P_B^\circ$$

This can be shown graphically as in Figure 1.15, assuming that A is more volatile than B.
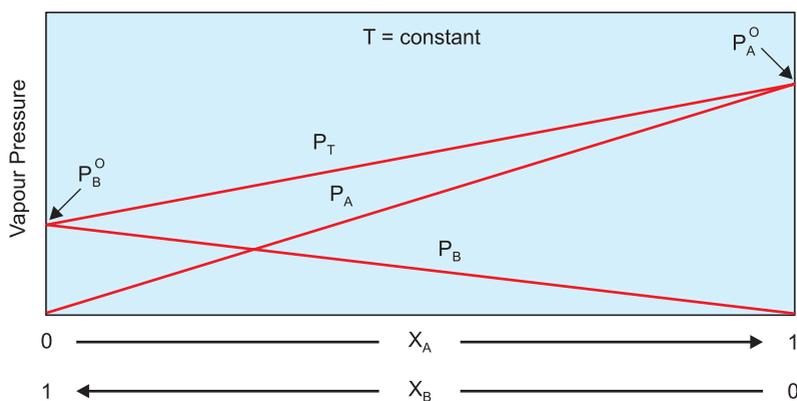
Figure 1.15   Vapour pressure versus mole fraction for an ideal solution.

Ideal solutions are characterized by the following properties:

i) The volume of an ideal solution is the sum of the volumes of its pure components. i.e., there is no expansion or contraction on mixing.

ii) The heat of a solution is zero. i.e., mixing is neither exothermic nor endothermic. Intermolecular forces between solute-solute and solute-solvent molecules are equal, as are those between solvent-solvent molecules and solute-solvent molecules.

iii) The vapour pressure above the solution is equal to the sum of the individual partial vapour pressures.

iv) The components have similarity in their chemical structures.

v) The solutions obey Raoult's law.

Can you give examples of an ideal solution?

Many solutions do not behave ideally. They deviate from Raoult's law and are said to be non-ideal. Here, we can consider the following two cases.

Case 1: If the intermolecular forces between A and B molecules are weaker than those between A and A molecules and those between B and B molecules, then there is a greater tendency for A-B molecules to leave the solution, compared to the case of an ideal solution. Consequently, the vapour pressure of the solution is greater than the sum of the vapour pressures that would be predicted by Raoult's law for the same concentration.

This behaviour exemplifies the positive deviation from Raoult's law (Figure 1.16 a). In this case, the heat of mixing is an endothermic process.

Case 2: If A molecules attract B molecules more strongly than they do their own kind, then the escaping tendency decreases and the vapour pressure of the solution is less than the sum of the vapour pressures as predicted by Raoult's law.

Here, we have a negative deviation from Raoult's law, and mixing is an exothermic process (Figure 1.16 b).
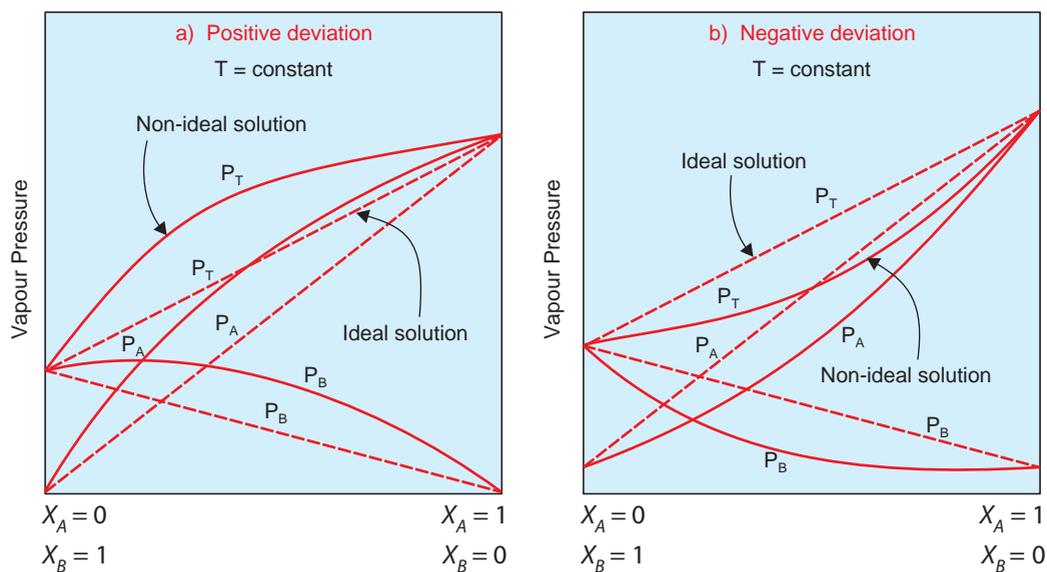
(Dotted lines show the expected values and the solid lines show the observed values).

Figure 1.16 Vapour pressure versus mole fraction for real solutions.

1.9.2 Boiling Point Elevation

Which do you think has a higher boiling point, a pure solvent or a solution containing a non-volatile solute? Why?

The boiling point of a liquid is the temperature at which its vapour pressure equals the atmospheric pressure. If a non-volatile solute is added to a solvent, the solution's boiling point will be increased. This is due to the fact that the vapour pressure of a solvent at a given temperature is lowered by the presence of a non-volatile solute in it, because less number of solvent molecules are available on the surface exposed to atmosphere in presence of solute molecules, as shown in Figure 1.14. Therefore, such a solution must be heated to a higher temperature than the pure solvent in order for its vapour pressure to be equal to the atmospheric pressure.

The boiling-point elevation (ΔT_b) is defined as the boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b°).

$$\Delta T_b = T_b - T_b^\circ$$

The elevation in boiling point (ΔT_b) is directly proportional to the molality of the solution. That is:

$$\Delta T_b \ \alpha \ m$$
$$\Delta T_b = K_b m$$

where m is the molality of the solution, and K_b is the molal boiling point elevation constant for the solvent.

Table 1.2 Boiling points, molal boiling point elevation constants, freezing points and molal freezing point depression constants of some solvents at 1 atm pressure.

Solvent	Boiling point (°C)	K_b (°C/m)	Freezing point (°C)	K_f (°C/m)
Acetic acid ($C_2H_4O_2$)	118.10	3.07	16.60	3.90
Benzene (C_6H_6)	80.10	2.53	5.50	5.12
Camphor ($C_{10}H_{16}O$)	208.00	5.95	179.00	39.70
Carbon disulfide (CS_2)	46.30	2.34	– 111.50	3.83
Chloroform ($CHCl_3$)	61.26	3.63	– 63.50	4.70
Cyclohexane (C_6H_{12})	80.70	2.79	6.60	20.00
Nitrobenzene ($C_6H_5NO_2$)	210.88	5.24	5.70	7.00
Phenol (C_6H_5OH)	182.00	3.56	43.00	7.40
Water (H_2O)	100.00	0.51	0.00	1.86

Example 1.20

Calculate the boiling point of a 0.33 m solution of a solute in benzene. ($K_b = 2.53°C /m$).

Solution:

Given:

Molality $= 0.33$ m

$K_b = 2.53°C /m$

$\Delta T_b = K_b m,$

$\Delta T_b = 2.53°C /m \times 0.33\ m = 0.83°C$

Required:

Boiling point of the solution?

Therefore, the boiling point of the solution is determined from the boiling point of the pure solvent benzene (Table 1.2) and the change, in boiling point, ΔT_b.

Boiling point of the solution $= 80.1°C + 0.83°C$

$\qquad\qquad = 80.93°C$

Example 1.21

Calculate the boiling point of a solution that contains 200 g of sucrose, $C_{12}H_{22}O_{11}$, in 500 g of water.

Solution:

From the given masses of solute and solvent, we can find the molality of the solution.

$$\text{Molality (m)} = \frac{\text{Mass of sucrose}}{\text{Molar mass of sucrose} \times \text{Mass of } H_2O \text{ in kg}}$$

$$= \frac{200 \text{ g}}{342 \text{ g}/\text{mol} \times 0.5 \text{ kg}} = 1.17 \text{ m}$$

$\Delta T_b = K_b m$, from Table 1.2, K_b for H_2O is 0.512°C /m

Therefore, $\Delta T_b = 0.512°C/m \times 1.17 \text{ m} = 0.6°C$

Since the normal boiling point of water is 100°C, the boiling point of the solution will be equal to $100°C + 0.6°C = 100.6°C$.

Exercise 1.15

1. What is the boiling point of 1.93 m solution of a non-volatile solute in nitrobenzene?

2. Automotive antifreeze consists of ethylene glycol, $C_2H_6O_2$, a non-volatile non-electrolyte solute. Calculate the boiling point of a 25.0 mass percent solution of ethylene glycol in water.

1.9.3 Freezing Point Depression

Activity 1.12

Discuss in group and account for the following processes. Report your idea to the class.

1. In countries with extremely cold conditions, anti-freezing substances like ethylene glycol ($C_2H_6O_2$) are used in the cooling system of the automobiles.

2. Salts such as NaCl or $CaCl_2$ can be used to prepare ice cream or to de-ice the roads.

When a solution begins to freeze, the component that crystalize out first is almost pure.

Pure ice, for example, crystallizes out of a solution of salt and water. Solute particles, because of their different size and shape, do not fit into the crystal lattice of the frozen solvent. They tend to concentrate in the remaining liquid, and they interfere with the freezing process by getting in the way of solvent molecules looking for lattice sites. This interference causes the solution to freeze at lower temperature than the pure solvent. The greater the concentration of the solution, the greater the interference and therefore, the lower the freezing point of the solution.

The freezing point depression (ΔT_f) is defined as the freezing point of the pure solvent (T) minus the freezing point of the solution (T_f).

$$\Delta T_f = T - T_f$$

The freezing point depression (ΔT_f) of solutions of nonelectrolytes has been found to be equal to the molality of the solution times a proportionality constant. This constant is the molal freezing point depression constant, K_f, of the solvent.

$$\Delta T_f = K_f m$$

Example 1.22

The freezing point of pure camphor ($C_{10}H_{16}O$), T_f°, is 179.0°C, and its K_f is 39.70°C kg/mol. Find the freezing point of a solution containing 1.50 g of a compound of molecular mass 125, dissolved in 35 g camphor (*solvent*).

Solution:

First we find number of moles of the compound

$$\text{Number of moles} = \frac{1.5 \text{ g}}{125 \text{ g/mol}} = 0.012 \text{ mol}$$

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight (kg) of solvent}} = \frac{0.012 \text{ mol}}{0.035 \text{ kg}} = 0.343 \text{ mol/kg}$$

$$\Delta T_f = K_f m = 39.7°C \text{ kg/mol} \times 0.343 \text{ mol/kg}$$
$$= 13.6°C$$

The normal freezing point of camphor is lowered by 13.6°C. Therefore, the freezing point of the solution, T_f, will be:

$$\Delta T_f = T - T_f = 179.0°C - 13.6°C = 165.4°C$$

Exercise 1.16

1. Calculate the freezing point of a solution that contains 60.0 g of urea, N_2H_4CO, in 500.0 g of water.

2. Calculate the molecular mass of sulphur if 35.5 g of sulphur dissolves in 100.0 g of CS_2 to produce a solution that has a boiling point of 49.48°C.

1.9.3 Osmosis and Osmotic Pressure

How do you calculate osmotic pressure?

Osmosis is the selective passage of solvent molecules through a porous (*semi- permeable*) membrane from a dilute to a more concentrated solution or from the solvent side into the solution side.

Figure 1.17 shows two solutions on equal level, separated by a semi-permeable membrane. Solvent molecules move through the membrane from left to right. As a result, the liquid levels in the two arms become uneven. Eventually, the pressure difference resulting from the unequal heights of the liquid in the two arms becomes so large that the net flow of solvent ceases. Alternatively, we may apply pressure to the right arm of the apparatus, as shown in Figure 1.17 b, to stop the net flow of solvent either way.

The pressure required to prevent osmosis is known as the osmotic pressure, π, of the solution.

a) A pure solvent and its solution are separated by a semi-permable membrane through which solvent molecules can pass but solute molecules cannot.

$P = \pi$

b) The system at equilibrium, where the rate of solvent transfer is the same in both direction.
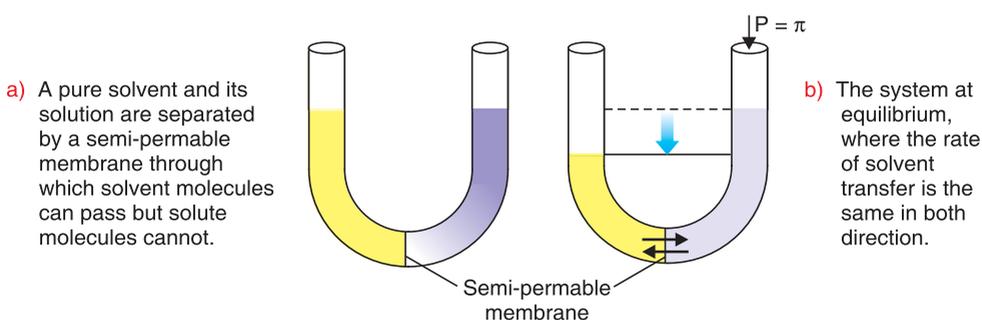
Semi-permable membrane

Figure 1.17   Apparatus for measuring osmotic pressure.

Jacobus Henricus Van't Hoff found that the osmotic pressure obeys a law similar to the ideal gas law, $PV = nRT$,

where V is the volume of the solution, n is the number of moles of solute, R is the ideal gas constant, and T is the temperature on the Kelvin scale. From the equation, we can write:

$$\pi = P = \left(\frac{n}{V}\right)RT = MRT$$

where M is the molarity of the solution.

Like other colligative properties, osmotic pressure can be used to determine the molar mass of solute. Especially osmotic pressure is used in biological laboratories to determine molecular masses of huge molecules like proteins and nucleic acids.

Example 1.23

What is the osmotic pressure at 17°C of 150 mL aqueous solution containing 1.75 g of sucrose ($C_{12}H_{22}O_{11}$) per 150 mL of solution?

Solution:

First we calculate the molarity (M) of the solution

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume (L) of solution}}$$

$$= \frac{1.75 \ \cancel{g} / \left(342 \ \cancel{g} / \text{mol}\right)}{0.150 \ \text{L}} = 0.034 \ \text{mol/L}$$

$$\pi = MRT$$

$$= 0.0851 \ \cancel{mol}/\cancel{L}\left(0.0821 \frac{\cancel{L} \ \text{atm}}{\cancel{mol} \ \cancel{K}}\right)(290 \ \cancel{K}) = 0.812 \ \text{atm}$$

Example 1.24

In an experiment to measure the molar mass of polyethylene, 2.20 g of polyethylene plastic was dissolved in enough toluene to produce a 100 mL solution. Its osmotic pressure at 25°C was measured as 1.10×10^{-2} atm. Calculate the molar mass of polyethylene.

Solution:

From the equation, $\pi = MRT \Rightarrow M = \dfrac{\pi}{RT}$

$$M = \frac{1.10 \times 10^{-2} \ \text{atm}}{\left(0.0821 \dfrac{\text{L.atm}}{\text{mol.K}}\right)(298 \ \text{K})} = 4.5 \times 10^{-4} \ \text{mol/L}$$

That is, 1 L solution contains 4.5×10^{-4} mole of polyethylene. The amount of polyethylene in 100 mL of the solution is therefore

$$1 \ \text{L} \rightarrow 4.5 \times 10^{-4} \ \text{mol}$$

$$0.10 \ \text{L} \rightarrow \ ?$$

$$\text{Amount of polyethylene (mol)} = \frac{0.10\,\text{L} \times 4.5 \times 10^{-4}\,\text{mol}}{1\,\text{L}}$$

$$= 4.5 \times 10^{-5}\,\text{mol}$$

$$\text{Molar mass of polyethylene (g/mol)} = \frac{2.20\,\text{g}}{4.5 \times 10^{-5}\,\text{mol}}$$

$$= 4.89 \times 10^{4}\,\text{g/mol}$$

Activity 1.13

Take 5%,10% and 20% solutions of sucrose in water.

Take 3 potatoes of almost equal size and make one cubic hole in each potato of equal dimensions.

Fill the holes with water and keep these potatoes in different solutions of sucrose.

Observe the change in the water level at different time intervals.

Discuss your observations with your teacher as well as classmates.

Exercise 1.17

1. A sample of 2.05 g of polystyrene plastic was dissolved in enough toluene to form 100 mL of solution. The osmotic pressure of this solution was found to be 1.21 kPa at 25°C. Calculate the molar mass of polystyrene.

2. What is the osmotic pressure, in atm, of a 0.30 M solution of glucose in water that is used for intravenous infusion at body temperature, 37°C?

1.9.4 Colligative Properties of Electrolytic Solutions

Activity 1.14

Form groups and discuss the following. Present the result of your discussion to the class as a report.

1. What is the difference between electrolytes and non-electrolytes?

2. How do the effects of the presence of electrolyte solute on the properties of pure solvent differ from the effect of the presence of non-electrolyte solvent? Justify your answer by giving example.

The effective number of moles of ions produced by one mole of a solute is expressed in terms of the Van't Hoff factor (i).

$$i = \frac{\text{Measured value for electrolyte solution}}{\text{Expected value for nonelectrolyte solution}}$$

Thus, i is 1 for all solutions of nonelectrolytes, but is greater than 1 for solutions of electrolytes. Therefore, the colligative-property relationship should be modified to account for dissociation of electrolyte solutes. Consequently,

$$\Delta P = i \, x_2 P_1^{\circ}$$

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

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

$$\pi = i \, MRT$$

Table 1.3 Experimental values of the Van't Hoff factor for some substances.

Compound	0.100 m	0.001 m
HCl	1.9	2.0
NaCl	1.87	1.97
$MgSO_4$	1.21	1.82
K_2SO_4	2.32	2.84
KBr	1.88	1.97

As can be seen in Table 1.3 the experimental Van't Hoff factors are less than the theoretical prediction. This is mainly due to the cation-anion interaction in the solution of the electrolytes that prevents complete dissociation.

Example 1.25

If a 0.10 m $MgSO_4$ solution causes an elevation of 0.062°C in the boiling point of water, what is:

a   the Van't Hoff Factor (i)?

b   the boiling point of this solution?

Solution:

a   First, we find i by applying the modified colligative-property relationship for ΔT_b.

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

Given:

$\Delta T_b = 0.062°C$

$K_{b, H_2O} = 0.512°C/m$

$m = 0.1\ m$

$0.062°C = i \times 0.512°C\ /m \times 0.1\ m$

$i = 1.21$. What does this indicate?

b Recall that $\Delta T_b = T_b - T_b^\circ$

$0.062°C = T_b - 100°C$

$T_b = 100°C + 0.062°C = 100.062°C$

Exercise 1.18

A 0.0622 m solution of iron (III) chloride, $FeCl_3$, in water freezes at $-0.412°C$.

Determine the Van't Hoff's factor of $FeCl_3$ in this solution.

Unit Summary

- *Solutions are homogeneous mixtures of two or more substances.*

- *Solubility depends on the relative magnitude of solute-solute, solute-solvent, and solvent-solvent attractive forces.*

- *The relative amounts of solute and solvent in a solution can be described quantitatively in terms of mass percentage, parts per million, parts per billion, mole fraction, molarity, molality and normality.*

- *Increasing the temperature usually increases the solubility of solids in water and liquids in water while it decreases the solubility of gases in water.*

- *Raoult's law states that the partial vapour pressure of substance A over a solution is equal to the mole fraction of A, X_A, times the vapour pressure of pure solvent. An ideal solution obeys Raoult's law over the entire range of concentration. Non ideal solutions show positive or negative deviation from Raoult's law.*

- *Some physical properties of solutions are colligative, that is, they depend on the concentration of the solute particles that are present in a given amount*

of solvent and not on their chemical identity. These are vapour pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

• The Van't Hoff factor provides a measure of the extent of dissociation of electrolyte in solution.

Check List

Key terms of the unit

• Boiling point elevation

• Colligative properties

• Electrolyte solution

• Freezing point depression

• Henry's law

• Heterogeneous solution

• Homogeneous solution

• Ideal solution

• Lowering of vapor pressure

• Mass percentage

• Miscible

• Molality

• Molarity

• Mole fraction

• Negative deviation from Raoult's law

• Nonelectrolyte

• Nonideal solution

• Normality

• Osmosis

• Osmotic pressure

• Parts per billion

• Parts per million

• Positive deviation from Raoult's law

• Raoult's law

• Solvation

• Van't Hoff factor

REVIEW EXERCISE FOR UNIT 1

Part I: Multiple Choice Questions

1. A solution is a:

    a heterogeneous mixture

    b homogeneous mixture

    c suspension

    d colloid

2. Soda water is an example of:

   a liquid-liquid solution   c gas-liquid solution

   b solid-liquid solution   d gas-gas solution

3. Which of the following substances are not readily miscible within each other?

   a C_6H_6 and CCl_4 c C_2H_5OH and H_2O

   b C_2H_5OH and CCl_4 d CH_3OH and H_2O

4. Rate of dissolution is largely dependent upon:

   a the inter-particle forces

   b the surface area of solid solute

   c the temperature of the system

   d the pressure of the system

5. Which of the following statements is not correct?

   a pressure has little effect on the solubility of liquids and solids

   b the solubility of most solids increases with increasing temperature

   c the solubility of gases in water increases with increasing temperature.

   d none of the above

6. The quantitative relationship between gas solubility and pressure is given by:

   a Raoult's law   c Hess's law

   b Henry's law   d Dalton's law

7. When a non-volatile solute is added to a pure solvent the:

   a vapour pressure of the solvent decreases.

   b vapour pressure of the solvent increases.

   c boiling point of the solution decreases.

   d freezing point of the solution increases.

8. Which of the following is not true about ideal solutions?

   a the volume of an ideal solution is the sum of the volume of its pure components

   b there is no expansion or contraction on mixing

   c the heat of solution is zero

   d they deviate from Raoult's law

9. The ratio of the number of moles of solute divided by the total number of moles gives:

   a the mole fraction of the solute

   b the molarity of the solution

   c the molality of the solution

   d the normality of the solution

10. Which of the following liquid pairs shows a positive deviation from Raoult's law?

   a octane, chloroform

   b ethanol, water

   c benzene, methanol

   d water, nitric acid

11. Which of the following is not a colligative property?

   a Osmotic pressure

   b Vapour pressure

   c Boiling point elevation

   d Freezing point depression

12. The addition of a non-volatile solute to a solvent results in the lowering of:

   a boiling point as well as freezing point

   b freezing point as well as vapour pressure

   c vapour pressure as well as density

   d boiling point as well as vapour pressure

13. Phosphoric acid reacts with calcium hydroxide to form calcium hydrogen phosphate and water. The equivalent mass of phosphoric acid in this reaction will be:

   a 98 g/eq

   b 32.6 g/eq

   c 49 g/eq

   d 14 g/eq

14. A non-volatile electrolyte dissolved in an aqueous solution with the same molal proportion as a nonelectrolyte produces:

   a the same colligative effect

   b lower colligative effect

   c higher colligative effect

   d no colligative effect

15. According to Raoult's law, the relative lowering of vapour pressure of a solution by a non-volatile solute is:

   a equal to the mole fraction of solvent

   b equal to the mole fraction of solute

c   directly proportional to mole fraction of solute

d   equal to normality of solution

Part II: Short Answer Questions

16. Distinguish between solutions and colloids. Give an example of each.

17. Explain the principle "like dissolves like".

18. Explain how soaps and detergents remove dirt from clothing.

19. Indicate the type of solute-solvent interaction that is most important in each of the following solutions:

    a   KBr in water

    b   hexane, C_6H_{14}, in gasoline

    c   ammonia in water

20. Consider the following solutions. In each case, predict whether the solubility of the solute should be high or low. Justify your answer.

    a   KCl in H_2O d H_2O in CH_3OH

    b   HF in H_2O e NH_4Cl in C_5H_{12}

    c   KCl in CCl_4 f CCl_4 in H_2O

21. Calculate the molarity of each of the following solutions:

    a   10.5 g NaCl in 350.0 mL of solution

    b   40.7 g $LiClO_4 \cdot 3H_2O$ in 125 mL of solution

22. The concentrated sulfuric acid we use in the laboratory is 98.0% H_2SO_4, by mass. Calculate the molality and molarity of the acid solution. The density of the solution is 1.83 g/mL.

23. Calculate the approximate volume of water that must be added to 250 mL of 1.25 N solution to make it 0.500 N.

24. a   What is meant by the terms saturated and unsaturated solutions?

    b   Explain how supersaturated solution can be formed.

25. State Raoult's law and explain it on a molecular basis.

26. Use the example of a solution of benzene in toluene to explain what is meant by an ideal solution.

27. What characteristic of a solution determines its colligative properties?

28. The vapour pressure of ethanol (C_2H_5OH) and 1-propanol (C_3H_7OH) at 35°C are 100 mmHg and 37.6 mmHg, respectively. Assuming ideal behaviour, calculate the partial vapour pressures of ethanol and 1-propanol over a solution, in which the mole fraction of ethanol is 0.3.

29. A solution was made by dissolving 3.75 g of a pure non-volatile solute in 95 g of acetone. The boiling point of pure acetone was observed to be 55.95°C, and that of the solution was 56.50°C. If the molar boiling point elevation constant (K_b) of acetone is 1.71°C kg/mol, what is the approximate molar mass of the solute?

30. Urea ($NH_2)_2CO$ is the product of protein metabolism in mammals. What is the osmotic pressure of an aqueous solution containing 1.10 g of urea in 100 mL of solution at 20°C?

31. Calculate the freezing point of a solution of 3.46 g of a compound, X, in 160 g of benzene. When a separate sample of X was vaporised, its density was found to be 3.27 g/L at 116°C and 773 torr. The freezing point of pure benzene is 5.45°C, and K_f is 5.12°C kg/mol.

32. Why attention given to the colligative properties of electrolyte solutions than that of nonelectrolyte solutions?

33. Pure benzene freezes at 5.45°C. A solution containing 7.24 g of $C_2Cl_4H_4$ in 115.3 g of benzene was observed to freeze at 3.55°C. From these data, calculate the molal freezing point depression constant of benzene.

34. The osmotic pressure of a 0.010 M aqueous solution of $CaCl_2$ is found to be 0.674 atm at 25°C. Calculate Van't Hoff's factor, i, for the solution.

35. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g of the protein in 125 mL of water. At 4°C, a 2.6 mmHg osmotic-pressure rise of the solution was observed. The solution had a density of 1.00 g/mL. Determine the molar mass of the protein.