SOLUTIONS AND THEIR PHYSICAL PROPERTIES

TYPES OF SOLUTIONS:

SOME TERMINOLOGY

A solution is a homogeneous mixture. It is homogeneous because its composition and properties are uniform, and it is a mixture because it contains two or more substances in proportions that can be varied. The **solvent** is the component that is present in the greatest quantity or that determines the state of matter in which a solution exists. A **solute** is a solution component present in lesser quantity than the solvent. A *concentrated* solution has a relatively large quantity of dissolved solute (s), and a *dilute* solution has only a small quantity. Consider solutions containing sucrose (cane sugar) as one their solutes in the solvent water: A pancake syrup is a concentrated solution, whereas a sweetened cup of coffee is much more dilute.

Although liquid solutions are not common, solutions can exist in the gaseous and solid states as well. For instance, the U.S. five-cent nickel is a solid solution of 75 % Cu and 25 % Ni. Solid solutions with a metal as the solvent are also called alloys.

SOLUTION CONCENTRATION

To describe a solution fully we must know its *concentration*, a measure of the quantity of the solute present in a given quantity of solvent (or solution). The unit we stressed there was molarity. In this section we describe several methods of expressing concentration, each of which serves a different purpose.

Mass Percent, Volume Percent, and Mass/ Volume Percent

If we dissolve 5.00 g NaCl in 95.00 g H_2O, we get 100.0 g of a solution that is 5.00 % NaCl, by *mass*. Mass percent is widely used in industrial chemical applications. Thus, we might read that the action of 78 % $H_2SO_4(aq)$ on phosphate rock $[3Ca_3(PO_4)_2 \cdot CaF_2]$ produces 46 % $H_3PO_4(aq)$.

Because liquid volumes are so easily measured, some solutions are prepared on a *volume* percent basis. For example, a handbook lists a freezing point of - 15.6 ^oC for a methyl alcohol- water antifreeze solution that is 25.0% CH_3OH, by volume. This solution is prepared by dissolving 25.0 ml CH_3OH in enough water to yield 100.0 ml of solution.

Another possibility is to express the mass of solute and volume of solution. An aqueous solution with 0.9 g NaCl in 100.0 ml of solution is said to be 0.9% NaCl (*mass/vol*). This unit is extensively used in medicine and pharmacy.

Mole Fraction and Mole Percent

To relate certain physical properties (such as vapour pressure) to solution concentration we need a concentration unit in which all solution components are expressed on a mole basis. This we can do with the mole fraction. The **mole fraction** of component ***i*** , designated X_i , is the fraction of all the molecules in a solution that are of type ***i***. The mole fraction of component ***j*** is X_j and so on. The sum of the mole fraction of all the solution components is 1. The mole fraction of a solution component is defined as

$$X_i = \frac{\text{amount of component } i \text{ (in moles)}}{\text{total amount of all soln : components (in moles)}}$$

The **mole percent** of a solution component is the percent of all the molecules in solution that are of a given type. Mole percents are mole fractions multiplied by 100% .

Molarity (M)

The concentration or molarity of a solution is defined as

$$\text{molarity} = \frac{\text{amount of solute (in moles)}}{\text{volume of solution(in liters)}}$$

The unit of molarity, mol (solute) / L (solution), is often replaced by the symbol M and called “ molar ”.

Molality (*m*)

Suppose we prepare a solution at 20 °C by using a volumetric flask calibrated at 20 °C. Then suppose we warm this solution to 25 °C. As the temperature increases from 20 to 25 °C, the amount of solute remains ***constant*** but the solution volume ***increases*** slightly (about 0.1%). The number of moles of solute per liter - the molality - ***decreases*** slightly (about 0.1%).

A concentration unit that is ***independent*** of temperature and also proportion to mol fraction in dilute solution is **molality**, the amount of solute (in moles) per kilogram of ***solvent*** (not of solution). A solution in which 1.00 mol of urea, $CO(NH_2)_2$, is dissolved in 1.00 kg of water is described as a 1.00 molal solution and designated as 1.00 ***m*** $CO(NH_2)_2$ unit . Molality is defined as:

$$\text{molality } (m) = \frac{\text{amount of solute (in moles)}}{\text{mass of solvent (in kilograms)}}$$

Example-1 : *Expressing a Solution Concentration in various Units.* An alcohol-water solution is prepared by dissolving 10 .00 ml of ethanol, C_2H_5OH (*d* = 0.789 g/ml), in a sufficient volume of water to produce 100.00ml of a solution with a density of 0.982g/ml. What is the concentration of ethanol in this solution, expressed as (a) volume percent; (b) mass percent ; (c) mass / volume percent; (d) mole fraction;(e)mole percent; (f) molarity; (g) molality?

a. Volume percent ethanol

$$\text{Volume percent ethanol} = \frac{10.00 \text{ ml ethanol}}{100.00 \text{ ml soln}} \text{ x } 100\% = 10.00\%$$

b. Mass percent ethanol

$$\text{mass ethanol} = 10.00\text{ml ethanol x } \frac{0.789 \text{ g ethanol}}{1 \text{ ml ethanol}}$$

$$= 7.89 \text{ g ethanol}$$

$$\text{mass soln} = 100.0 \text{ ml soln x } \frac{0.982 \text{ g soln}}{1 \text{ ml soln}} = 98.2 \text{ g soln}$$

$$\text{mass percent ethanol} = \frac{7.89 \text{ g ethanol}}{98.2 \text{ g soln}} \text{ x } 100\% = 8.03\%$$

c. Mass / volume percent ethanol

$$\text{Mass / volume percent ethanol} = \frac{7.89 \text{ g ethanol}}{100.0 \text{ ml soln}} \text{ x } 100\% = 7.89\%$$

d. Mole fraction of ethanol

Convert the mass of ethanol from part (b) to an amount in moles.

$$\text{? mol ethanol} = 7.89 \text{ g } C_2H_5OH \text{ x } \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH}$$

$$= 0.171 \text{ mol } C_2H_5OH$$

Determine the mass of water present in 100.0 ml of solution.

98.2 g soln - 7.89 g ethanol = 90.3 g water

convert the mass of water to an amount in moles.

$$\text{? mol } H_2O = 90.3 \text{ g } H_2O \text{ x } \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 5.o1 \text{ mol } H_2O$$

$$x\ C_2H_5OH = \frac{0.171 \text{ mol } C_2H_5OH}{0.171 \text{ mol } C_2H_5OH + 5.01 \text{ mol } H_2O} = \frac{0.171}{5.18} = 0.0330$$

e. Mole percent ethanol

$$\text{mol percent } C_2H_5OH = x\ C_2H_5OH \text{ x } 100\% = 0.0330 \text{ x } 100\% = 3.30\%$$

f. Molarity of ethanol

Divide the amount of ethanol from part (d) by the solution volume,

$$100.0\ \text{mL} = 0.1000\ \text{L}$$

$$\text{molarity} = \frac{0.171\ \text{mol}\ C_2H_5OH}{0.1000\ \text{L soln}} = 1.71\ \text{M}\ C_2H_5OH$$

g. Molality of ethanol

First, convert the mass of water percent in 100.0 mL of solution [from part (d)] to the unit kg.

$$?\ \text{kg}\ H_2O = 90.3\ \text{g}\ H_2O \times \frac{1\ \text{kg}\ H_2O}{1000\ \text{g}\ H_2O} = 0.0903\ \text{kg}\ H_2O$$

Use this result and the amount of C_2H_5OH from part (d) to establish the molality.

$$\text{molality} = \frac{0.171\ \text{mol}\ C_2H_5OH}{0.0903\ \text{kg}\ H_2O} = 1.89\ \text{m}\ C_2H_5OH$$

Example 2

Converting Molarity to Mole Fraction. Laboratory ammonia is 14.8 M NH_3 (aq) with a density of 0.8980 g/mL. What is X_{NH3} in this solution?

SOLUTION

No volume of solution is stated, and this suggests that our calculation can be based on any fixed volume of our choice. A convenient volume to work with is one liter. We need to determine the amount, in moles, of NH_3 and H_2O in one liter of the solution.

$$\text{amount of } NH_3 = 1.00\ \text{L} \times \frac{14.8\text{mol}\ NH_3}{1\text{L}} = 14.8\ \text{mol}\ NH_3$$

To get the amount of H_2O we can proceed as follows.

$$\text{mass of soln} = 1000.0\ \text{mL soln} \times \frac{0.8980\ \text{g soln}}{1\ \text{ml soln}} = 898.0\ \text{g soln}$$

$$\text{mass of } NH_3 = 14.8\ \text{mol}\ NH_3 \times \frac{17.03\ \text{g}\ NH_3}{1\ \text{mol}\ NH_3} = 252\ \text{g}\ NH_3$$

$$\text{mass of } H_2O = 898.0\ \text{g soln} - 252\ \text{g}\ NH_3 = 646\ \text{g}\ H_2O$$

$$\text{amount of } H_2O = 646\ \text{g}\ H_2O \times \frac{1\ \text{mol}\ H_2O}{18.02\ \text{g}\ H_2O} = 35.8\ \text{mol}\ H_2O$$

$$X_{NH3} = \frac{14.8\ \text{mol}\ NH_3}{14.8\ \text{mol}\ NH_3 + 35.8\ \text{mol}\ H_2O} = 0.292$$

PRACTICE EXAMPLE: A 16.00% by mass aqueous solution of glycerol. $C_3H_5(OH)_3$, has a density of 1.037 g/mL. What is the molality of $C_3H_5(OH)_3$ in this solution?

INTERMOLECULAR FORCES IN MIXTURES

The strengths of *three* kinds of intermolecular forces of attraction represent in Fig-1. Four possibilities for the relative strengths of these intermolecular forces are described in the discussion that follows:

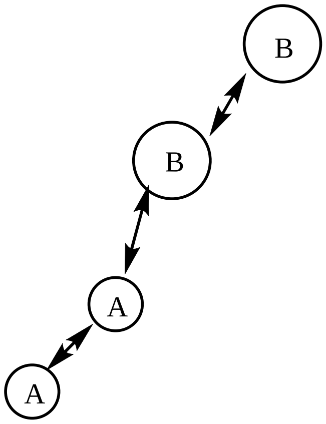


Fig - 1
Representing intermolecular forces in a slution

The intermolecular forces of attraction represented here are between: (1) solvent molecules A(↔), (2) solute molecules B (↔), and (3) solvent A and solute B (⟷).

If all intermolecular forces of attraction are of about equal strength, a random intermingling of molecules occurs. A homogeneous mixture or solution results. Because properties of solution of this type can generally be predicted from the properties of pure components, they are called **ideal solutions.** Many mixtures of liquid hydrocarbons fit this description. (see Fig-2)

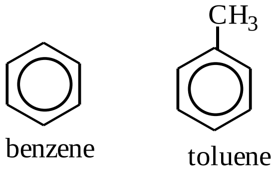
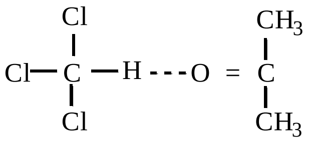


Fig -2
Two components of an ideal solution.

Think of the $-CH_3$ group in toluene as a small 'bump' on the planar benzene ring. Substances with similar molecular substances have similar intermolecular forces of attraction.

If forces of attraction between unlike molecules ***exceed*** those between like molecules, a solution also forms. However, the properties of such solutions generally cannot be predicted; they are ***nonideal*** solutions. Solutions of acetone and chloroform fit this type. As suggested by Fig-3, weak ***hydrogen bonding*** occurs between the two kinds of molecules, but the conditions for hydrogen bonding are not met in either of the pure liquids alone.



$Cl_3C{-}H\cdots O{=}C(CH_3)_2$

Fig -3
Intermolecular force between unlike molecules leading to a nonideal solution.
Hydrogen bonding between $CHCl_3$ (chloroform) and $(CH_3)_2CO$ (acetone) molecules causes forces of attraction between unlike molecules to exceed those between like molecules.

If forces of attraction between solute and solvent molecules are somewhat *smaller than* between molecules of the same kind, complete mixing may still occur, but the solution formed is *nonideal*. The solution has a higher enthalpy than the pure components, and the solution process is *endothermic*. This type of behavior is observed in mixtures of carbon disulfide (CS_2), a *nonpolar* liquid, and acetone, a polar liquid; In these mixtures the acetone molecules show a preference for other acetone molecules as neighbors, to which they are attracted by dipole-dipole interactions.

Finally, if forces of attraction between unlike molecules are much smaller than between like molecules, the components remain segregated in a *heterogeneous mixture*. Dissolving does not occur to any significant extent. In a mixture of water and octane (a constituent of gasoline) strong hydrogen bonds hold water molecules together in clusters. The nonpolar octane molecules are not able to exert a strong attractive force on the water molecules, and the two liquids do not mix. And so, we have an answer to the question of why water does not dissolve in gasoline posed at the beginning of this section.

As an oversimplified summary of the four cases described in the preceding paragraphs, we can say that "like dissolves like." That is, substances with similar molecular structures are likely to exhibit similar intermolecular forces of attraction and be soluble in one another. Those with dissimilar structures are likely not to form solutions. Of course, in many cases the structures may be similar in part and dissimilar in part. Then it is a matter of trying to establish which part is most important, a matter we explore in Example 3.

Example -3

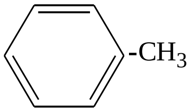
Using Intermolecular *Forces to Predict Solution Formation.* Predict whether you would except a solution to form in each of the following mixtures. If so, tell whether the solution is likely to be ideal. (a) ethyl alcohol, CH_3CH_2OH, and water (HOH); (b) the hydrocarbons hexane, $CH_3(CH_2)_4CH_3$,and octane, $CH_3(CH_2)_6CH_3$; (c) octyl alcohol, $CH_3(CH_2)_6CH_2OH$, and water (HOH).

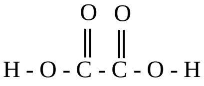
(a) If we think of water as H - OH, ethyl alcohol is similar to water. (Just substitute the group CH_3CH_2- for one of the H atoms in water.) Both molecules meet the requirements of hydrogen bonding as an important intermolecular force. However, the strengths of the hydrogen bonds between like and between unlike molecules are likely to differ. We should expect ethyl alcohol and water to form nonideal solutions.

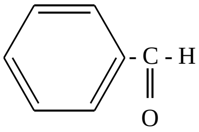
(b) In hexane the carbon chain is six atoms long and in octane, eight. Both substances are virtually nonpolar, and intermolecular attractive forces (of the dispersion type) in the solution and in the pure liquids should be quite similar. We expect a solution to form and for it to be nearly *ideal*.

(c) At first sight, this case may seem similar to (a), with the substitution of a hydrocarbon group for an H atom in H - OH. However, here the carbon chain is *eight* members long. This long carbon chain is much more important than the terminal -OH group in establishing the physical properties of octyl alcohol. Viewed from this perspective, octyl alcohol and water are quite dissimilar. We do not expect a solution to form.

PRACTICE EXAMPLE: Which of the following organic compounds do you think is most readily soluble in water? Explain.

(a) toluene, 

(b) oxalic acid, 
$H-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-H$

(c) benzaldehyde, 

SOLUTION FORMATION AND EQUILIBRIUM

In this section we describe solution formation in terms of phenomena that we can actually observe. We call this a ‘macroscopic’ view.

When a solute and solvent are mixed, at first only dissolving occurs, but soon the reverse process of precipitation becomes increasingly important, and some dissolved atoms, ions, or molecules return to the undissolved state. When dissolving and precipitation occur at the same rate, the quantity of dissolved solute remains constant with time, and the solution is said to be **saturated.** The concentration of the saturated solution is called the **solubility** of the solute in the given solvent.

If in preparing a solution we start with less solute than would be present in the saturated solution, the solute completely dissolves, and the solution is unsaturated. On the other hand, suppose we prepare a saturated solution at one temperature and then change the temperature to a value where the solubility is lower (generally this means a lower temperature). Usually the excess solute precipitates from solution, but occasionally all the solute may remain in solution. Because in these cases the quantity of solute is greater than in a normal saturated solution, the solution is said to be **supersaturated**. A supersaturated solution is unstable and if a few crystals of solute are added to serve as nuclei on which precipitation can occur, the excess solute precipitates.

Fractional Crystallization

The fact that the solubilities of most compounds increase with increased temperature is of practical use. Consider the problem of purifying a compound. Suppose both the compound and its impurities are soluble in a particular solvent and that we prepare a concentrated solution at a high temperature. Then we let the concentrated solution cool. At lower temperatures the solution becomes saturated in the desired compound. The exceed compound crystallizes from solution and the impurities remain in solution. This method of purifying a solid, called **fractional crystallization or recrystallization.**

The solubility of one liquid in another

When referring to a liquid, A , dissolving in another liquid, B , the term solute and solvent cause to have any useful meaning and it is more usual to refer to the extent to which A and B will mix. Many pairs of liquid will mix in all proportions, for example ethanol and water (both strongly polar) and carbon tetrachloride and benzene (both non-polar). Such pairs of liquid are said to be completely miscible. On the other hand, two liquids with very different intermolecular forces such as a polar and a non-polar liquid, may have only a very small solubility in each other and are therefore only partially miscible. If the two partially miscible liquids are mixed together, two layers may be formed. These two layers are both saturated solutions, i.e, the one liquid is saturated in the other. The solubility of one liquid in the other is dependent upon the temperature. Under constant temperature equilibrium may be attached between the two layers of liquid.

Distribution of a solute between partially miscible liquids

If a mixture of two partially miscible liquids, consisting of two layers, has a third material dissolved in it, then this material will dissolve in each layer to an extent related to its solubility in that layer. At any one temperature, the concentrations of this material in the two layers will therefore be in a constant ratio. This is known as the distribution law.

The law can be explained in the following way.

If a substance C is dissolved in a mixture of two immiscible liquids A and B, which are in equilibrium at a constant temperature then

$$\frac{\text{concentration of C in liquid A}}{\text{concentration of C in liquid B}} = \gamma$$

Where **γ** is a constant which depends only on the temperature, and not on the total amount of C present. **γ** is known as the distribution coefficient.

The solute C may be either a solid, a liquid or a gas. The value of the distribution coefficient can be found by analyzing the two liquid layers to find the concentration of the dissolved material, having first brought the system to equilibrium by keeping the mixture in a constant temperature bath for a time with frequent shaking. The mixture is finally allowed to separate completely into the two liquid layers, and samples of both layers are taken out with a pipette and analyzed. The result should be independent of the amounts of the two liquids, and of the solute that were taken.

The most common example of solvent extraction is the removal of an organic material from an aqueous solution, using an organic solvent which is almost immiscible with water (ether, benzene, carbon tetrachloride etc.). If the distribution coefficient is large, a high proportion of the material can be extracted with a reasonable amount of solvent.

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Suppose an aqueous solution to have a volume V_1 and to contain ‘m’ g of the material to be extracted. On shaking with a volume of V_2 of an organic solvent, a certain proportion of the material will finally be dissolved in the solvent layer, let this proportion be x. Then in the solvent layer;

$$\text{Mass of solute} = m\,x$$

$$\text{concentration of solute} = \frac{\text{mass}}{\text{volume}}$$

$$= \frac{m\,x}{V_2}$$

In the aqueous layer;

$$\text{Mass of solute} = m - m\,x$$

$$= m\,(1 - x)$$

$$\text{concentration of solute} = \frac{m\,(1 - x)}{V_1}$$

The distribution coefficient is given by:

$$\gamma = \frac{\text{concentration in solvent layer}}{\text{concentration in aqueous layer}}$$

$$\gamma = \frac{m\,x\,V_1}{m\,(1 - x)\,V_2}$$

$$\text{Hence} \quad x = \frac{\gamma\,V_2}{V_1 + \gamma\,V_2}$$

The proportion of material extracted is thus independent of the actual amount present, and is determined by the volume of solvent used relative to the volume of the aqueous solution, and the value of the distribution ratio. If successive extractions are made, using the same volume of solvent each time, the same proportion is removed in each extraction. It is more economical, when using a given volume of solvent, to make several extraction with small portions rather than one extraction with all the solvent at once. The following example illustrates this point.

Example 4

The distribution coefficient for ethyl acetate between benzene and water is 12.2 at 20^{o}C. If 1 dm^3 of an aqueous solution containing 10 g of ethyl acetate is extracted with a total of 300 cm^3 of benzene how much will be extracted (a) in a single extraction, (b) in three successive extractions of 100 cm^3 each?

(a) Using 300 cm^3 of solvent $V_2 = 300$ and $V_1 = 1000$

$$\text{Proportion extracted} = \frac{12.2 \times 100}{1000 + 12.2 \times 100}$$

$$= \frac{3600}{4660}$$

$$= 0.785$$

$$\text{Mass extracted} = 10 \times 0.785$$

$$= 7.85\,g \ (\text{i.e. } 78.5\ \%)$$

(b) In the first extraction, using 100 cm^3 of solvent, $V_2 = 100$ and $V_1 = 1000$

$$\text{Proportion extracted} = \frac{12.2 \times 100}{1000 + 12.2 \times 100}$$

$$= \frac{1220}{2220}$$

$$= 0.550$$

$$\text{Mass extracted} = 10 \times 0.550$$

$$= 5.50 \text{ g}$$

Mass left in aqueous layer = 10 - 5.50 = 4.50 g

The proportion extracted will be the same or all subsequence extractions if the volume of solvent used is the same as for the first:

Second extraction = 4.50 x 0.550

= 2.48 g

Mass left in aqueous layer = 4.50 - 2.48

= 2.02

Third extraction = 2.00 x 0.550

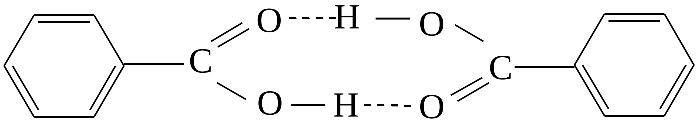
= 1.11 g

Total amount extraction = 5.50 + 2.48 + 1.11

= 9.09 g (i. e. 90.9 %)

The distribution law only applies to materials that are in the same molecular state in the two solutions, and so does not hold when the solute is largely dissociated or associated in one of the liquids.

In some cases, the law can be modified to allow for this, as in the case of carboxylic acid, which in benzene solution are almost entirely associated into double molecules owing to hydrogen bonding between the carboxylic groups.



In water, however, the benzoic acid is =solvated, that is, the molecules are associated with water molecules rather than with each other. If some benzoic acid is shaken up with a mixture of benzene and water until it has dissolved, it will be mostly in the form of single molecules in the water and double molecules in the benzene. It can be shown that the distribution law will now take the form.

$$\frac{\text{concentration of benzoic acid in water}}{\sqrt{\text{concentration of benzoic acid in benzene}}} = \text{constant}$$

SOLUBILITIES OF GASES

Why does a freshly opened can of cola " fizz", and why does the cola go "flat" after a time? To answer questions like these requires an understanding of the solubilities of gases. As we see in this section, the effect of temperature is generally opposite to what we find with solid solutes, and the pressure of a gas strongly affects its solubility.

Effect of Temperature

In a gas, the molecules are much farther apart than they will be in solution. We must think in terms of gas molecules being brought *closer together* before they dissolve. This is like saying that the gas must condense to a liquid before it dissolves in another liquid. Condensation is an *exothermic* process, and ΔH_{cond} is generally much greater than the energy needed to separate solvent molecules to make room for the solute. As a result the formation of solutions of *gaseous* solutes is an *exothermic* process, and the solubilities of gases *decrease* with increased temperature. We observe this behavior when we see bubbles of dissolved air escaping from heated water (see Figure 14-10).This observation also helps us to understand why many types of fish require cold water. There is not enough dissolved air (oxygen) in warm water.

Effect of Pressure

Pressure effects the solubility of a gas in a liquid much more than does temperature. The English chemist William Henry (1797-1836) found that the *solubility of a gas increases as the gas pressure is increased*. A mathematical statement of **Henry's law** is

$$\boldsymbol{C = k \cdot P_{gas}} \quad \text{---eq - 1}$$

We do not need to evaluate the proportionality constant *k* if we can treat a problem as a comparison of gas solubilities at two different pressures.

For example, the aqueous solubility of $N_2(g)$ at $0^{o}C$ and 1.00 atm is 23.54 ml N_2 per liter. Suppose we wish to increase the solubility of the $N_2(g)$ to a value of 100.0 ml N_2 per liter. Equation (1) suggests that to do so we must increase the pressure of $N_2(g)$ above the solution. That is,

$$k = \frac{C}{P_{gas}} = \frac{23.54\,\text{mL } N_2/L}{1.00\,\text{atm}} = \frac{100.0\,\text{ml } N_2/L}{P_{N_2}}$$

The required gas pressure, = (100/23.54) x 1.00 atm = 4.25 atm.

At times we are required to change the units used to express a gas solubility at the same time that the pressure is changed. This variation is illustrated in Example :

#Using Henry's Law. At 0°C and an O_2 pressure of 1.00 atm, the aqueous solubility of $O_{2(g)}$ is 48.9 ml O_2 per liter. What is the molarity of O_2 in a saturated water solution when the O_2 is under its normal partial pressure in air, 0.2095 atm?

Solution

Think of this as a two-part problem. (1) Determine the molarity of the saturated O_2 solution at 0°C and 1 atm. (2) Use Henry's law in the manner outlined above.

Determine the molarity of O_2 at 0°C when = 1 atm.

$$\text{molarity} = \frac{0.0489\,\text{L}\,O_2\,(\text{STP}) \times \dfrac{1\,\text{mol}\,O_2}{22.4\,\text{L}\,O_2\,(\text{STP})}}{1\,\text{L solution}} = 2.18 \times 10^{-3}\,\text{M}\,O_2$$

Apply Henry's law.

$$k = \frac{C}{P_{gas}} = \frac{2.18 \times 10^{-3}\,\text{M}\,O_2}{1.00\,\text{atm}} = \frac{C}{0.2095\text{atm}}$$

$C = (0.2095/1.00) \times 2.18 \times 10^{-3}\,\text{M}\,O_2 = 4.57 \times 10^{-4}\,\text{M}\,O_2$

PRACTICE EXAMPLE : A handbook lists the solubility of carbon monoxide in water at 0˚C and 1 atm pressure as 0.0354 mL CO/mL H_2O. What should be the pressure of $CO_{(g)}$ above the solution to obtain 0.0100 M CO ?

Here is how we can rationalize Henry's law: In a saturated solution the rate of evaporation of gas molecules from solution and the rate of condensation of gas molecules into the solution are equal. These rates both depend on the number of molecules per unit volume. As the number of molecules per unit volume increases in the gaseous state (through an increase in the gas pressure), the number of molecules per unit volume must also increase in the solution (through an increase in concentration).

We see a practical application of Henry's law in soft drinks. The dissolved gas is carbon dioxide, and the higher the gas pressure is maintained above the soda pop, the more CO_2 dissolves. When we open a can of pop, we release some gas. As the gas pressure above the solution drops, dissolved CO_2 is expelled, usually fast enough to cause fizzing. In sparkling wines the dissolved CO_2 is also under pressure, but the CO_2 is produced by a fermentation process within the bottle, rather than being added artificially as in soda pop.

Deep-sea diving provides us with still another example. Divers must carry a supply of air to breathe while underwater. If they are to stay submerged for any period of time, divers must breathe compressed air. However, high-pressure air is much more soluble in blood and other body fluids than is air at normal pressures. When a diver returns to the surface, excess dissolved $N_{2(g)}$ is released as tiny bubbles and can cause severe pain in the limbs and joints, probably by interfering with the nervous system. This dangerous condition, known as '**the bends**', can be avoided if the diver ascends very slowly or spends time in a decompression chamber. Another effective method is to substitute a helium-oxygen mixture for compressed air. Helium is less soluble in blood than is nitrogen.

Henry's law fails for gases at high pressure, and it also fails if the gas ionizes in water or reacts with water. For example, at 20^{o} C and with = 1 atm, a saturated solution of HCl (aq) is about 20M. But to prepare 10M HCl we do not need to maintain = 0.5 atm above the solution, nor is = 0.05 atm above 1 M HCl. We cannot even detect HCl (aq) above 1 M HCl by its odor. The reason we cannot is that HCl ionizes in aqueous solution, and in dilute solutions there are almost no molecules of HCl.

$$HCl_{(aq)} \longrightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

We only expect Henry's law to apply to eqilibrium between molecules of a gas and the same *molecules* in solution.

VAPOUR PRESSURE OF SOLUTIONS

We find the vapour pressures of solutions to be important when we want to devise a method of separating volatile liquid mixtures by distillation. Also they provide a springboard for dealing with other important solution properties, such as boiling points and osmotic pressures.

In our discussion we will consider solutions that contain only two components, a solvent A and a solute B. In the 1880s the French chemist F.M. Raoult found that a dissolved solute *lowers* the vapour pressure of the solvent. **Raoult's law** states that the partial pressure exerted by solvent vapour above at ideal solution; P_A, is the product of the mole fraction of solvent in the solution, X_A, and the vapour pressure of the pure solvent at the given temperature, .

$$P_A = X_A P_A^0 \quad \text{---eq - 2}$$

To see how above equation relates to Raoult's observation that a dissolved solute lowers the vapour pressure of the solvent, note that because $X_A + X_B = 1.00$, X_A must be less than 1.00, and P_A must be smaller than .

EXAMPLE - 5

Predicting vapour Pressure of Ideal Solutions. The vapour pressure of pure benzene and tolulene at 25^{0}C are 95.1 and 28.4 mmHg, respectively. A solution is prepared in which the mole fractions of benzene and toluene are both 0.500. What are the partial pressure of the benzene and toluene above this solution? What is the total vapour pressure?

SOLUTION

We saw that benzene-toluene solutions should be ideal. We expect Raoult's law to apply to both solution components.

$$P_{benz} = X_{benz}P^{0}_{benz} = 0.500 \text{ x } 95.1 \text{ mmHg} = 47.6 \text{ mmHg}$$
$$P_{tolu} = X_{tolu}P^{0}_{tolu} = 0.500 \text{ x } 28.4 \text{ mmHg} = 14.2 \text{ mmHg}$$
$$P_{total} = P_{benz} + P_{totu} = 47.6 \text{ mmHg} + 14.2 \text{ mmHg} = 61.8 \text{ mmHg}$$

PRACTIC EXAMPLE : Calculate the vapour pressure of benzene,'C_6H_6, and toluene, C_7H_8, and the tolal pressure at 25^0C above a solution with equal masses of the two liquids. (*Hint*: You may choose any amount of solution. How are mole fractions related to the mass? Use the vapour pressure deta given above.)

EXAMPLE - 6

Calculating the composition of vapor in Equilibrium with a Liquid Solution. What is the composition of the vapor in equilibrium with the benzene-toluene solution of above example?

Solution

The ratio of each partial pressure to the total pressure is the mole fraction of that component in the vapor. (This is another application of equation). The mole- fraction composition of the vapor is

$$X_{benz} = \frac{p_{benz}}{p_{total}} = \frac{47.6 \text{ mmHg}}{61.8 \text{ mmHg}} = 0.770$$

$$X_{totu} = \frac{p_{totu}}{p_{total}} = \frac{14.2 \text{ mmHg}}{61.8 \text{ mmHg}} = 0.230$$

ADDITIONAL CONSEQUENCES OF VAPOR PRESSURE LOWERING: OSMOTIC PRESSURE

In the preceding section we saw that freezing point depression and boiling point elevation are both associated with the vapor pressure lowering of a solvent in a solution. Another phenomenon related to vapor pressure lowering.

Two aqueous solutions of a nonvolatile solute are within the same enclosure. They are labeled A and B. The curved arrow indicates that water vaporizes from A and condenses into B. What is the driving force behind this? It must be that the vapor pressure of H_2O above A is greater than that above B. Solution A is more dilute; it has a higher mole fraction of H_2O. How long will this transfer of water continue? Solution A becomes more concentrated as it loses water and solution B becomes more dilute as it gains water. When the mole fraction of H_2O is the same in each solution, the transfer of H_2O stops.

A similar phenomenon occurs when $CaCl_2.6H_2O(s)$ is exposed to air. Water vapor from the air condenses on the solid, and the solid begins to dissolve, a phenomenon known as *deliquescence.** A practical application of deliquescence is seen in the spreading of $CaCl_2.6H_2O(s)$ on dirt roads to hold down dust.

Like the case just described the flow of solvent molecules. Here, however, the flow is not through the vapor phase.

An aqueous sucrose (sugar) solution in a long glass tube is separated from pure water by a semipermeable membrane (permeable to water only). Water molecules can pass through the membrane is either direction, and they do. But because the concentration of water molecules is *greater* in the pure water than in the solution, there is a net flow *from* the pure water *into* the solution. This net flow, called osmosis, causes the solution to rise up the tube. The more concentrated the sucrose solution, the higher the solution level rises. A 20 % solution would rise to about 150 meters!

Applying a pressure to the sucrose solution increases the tendency for water molecules to leaves the solution, thus slowing down the net flow of water into the solution. With a sufficiently high pressure the net influx of water can be stopped altogether. The necessary pressure to stop osmotic flow is called the **osmotic pressure** of the solution. For the 20 % sucrose solution this pressure is about 15 atm.

Osmotic pressure is a colligative property because its magnitude depends only on the *number* of solute particles per unit volume of solution. It does not depend on the identity of the solute. The expression written below works quite well for calculating osmotic pressure of *dilute* solutions of nonelectrolytes. The osmotic pressure is represented by the symbol , R is the gas constant (0.08206 L atm mol^{-1} K^{-1}); and temperature *T* is the Kelvin temperature. The term *n* represents the amount of solute (in moles) and *V* is the volume (in liters) of solution. The ratio,

n/V , then , is the *molarity* of the solution, represented by the symbol *c*.

$$\pi = \frac{n}{V} RT = c\,RT \quad \text{---eq - 5}$$

Example - 7

Calculating Osmotic Pressure. What is the osmotic pressure at 25°C of an aqueous solution that is 0.0010 M $C_{12}H_{22}O_{11}$ (sucrose)?

$$\pi = \frac{0.0010\ \text{mol x } 0.08206\ \text{L atm mol}^{-1}\text{K}^{-1}\ \text{x } 298\text{K}}{1\text{L}}$$

$$= 0.024\ \text{atm (18 mmHg)}$$

Practic Example: What mass of urea [$CO(NH_2)_2$] would you dissolve in 225 mL of solution to obtain an osmotic pressure of 0.015 atm at 25°C ? (*Hint;* What molarity solution has this osmotic pressure ?)

The 0.0010 M sucrose solution has a molarity of about 0.001 *m*. According to equation -3 we should expect a freezing point depression of about 0.00186º C for this solution. We would have a hard time measuring this small a temperature difference with any precision. On the other hand, the pressure difference of 18 mmHg we calculated in above example is easy to measure. (It corresponds to a solution height of about 25 cm!). From this we see that measuring osmotic pressure is an especially useful method for determining molar masses when we are dealing with very dilute solutions and / or solutes with high molar masses.

Example - 8

Establishing a Molar Mass from a Measurement of Osmotic Pressure. A 50.00 mL sample of an aqueous solution is prepared containing 1.08 g of a blood plasma protein, human serum albumin. The solution has an osmotic pressure of 5.85 mmHg at 298K. What is the molar mass of the albumin ?

Solution

First we need to express the osmotic pressure in atm.

$$?\ \text{atm} = 5.85\ \text{mmHg x } \frac{1\ \text{atm}}{760\ \text{mmHg}} = 7.70\ \text{x } 10^{-3}\ \text{atm}$$

Now, we can modify equation(5) slightly[i.e., with the number of moles of solute (n) represented by the mass of solute (m) divided by the molar mass M , and solve it for M.

$$\pi = \frac{(m/M)RT}{V} \quad \text{and} \quad M = \frac{mRT}{\pi V}$$

$$M = \frac{1.08\ \text{g x } 0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1}\ \text{x } 298\ \text{K}}{7.70\ \text{x}10^{-3}\ \text{atm x } 0.0500\ \text{l}} = 6.86\ \text{x } 10^{4}\ \text{gmol}^{-1}$$

Practice Example : What should be the osmotic pressure at 37.0°C if a 2.12 g sample of human serum albumin is present in 75.00 mL of aqueous solution? Use the molar mass determined above.

Practical Applications

Some of the best examples of osmosis are those associated with living organisms. For instance, consider red blood cells. If we place red blood cells in pure water, the cells expands and eventually burst as a result of water entering through osmosis. The osmotic pressure associated with the fluid inside the cell is equivalent to that of 0.9 % (mass /volume) NaCl(aq). Thus, if we place the cells in a sodium chloride (saline) solution of this concentration there will be no net flow of water through the cell walls and the cell will remain stable. A solution with the same osmotic pressure as body fluids is said to be *isotonic*. If we place cells in a solution with concentration greater than 0.9 % NaCl, water flows out of the cells and the cells shrink. The solution is *hypertonic*. If the NaCl concentration is less than 0.9 %, water flows into the cells and the solution is *hypotonic*. Fluids that are intravenously injected into patients to combat dehydration or to supply nutrients must be adjusted so that they are isotonic with blood. The osmotic pressure of the fluids must be the same as that 0f 0.9 % (mass / vol) NaCl.

One recent application of osmotic goes to the very definition of osmotic pressure. Suppose in the device show in <u>below figure</u> we apply a pressure to the right side (side B) that is *less than* the osmotic pressure of the salt water solution. The net flow of water molecules through the membrane will be from side A to side B. This is the process of *osmosis*. If we apply a pressure *greater than* the osmotic pressure to side B, we can cause a net flow of water in the *reverse* direction, from the salt solution into the pure water. This is the condition known as reverse osmosis. Reverse osmosis can be used in the *desalination* of seawater, to supply drinking water for emergency situation or as an actual source of municipal water. Another application of reverse osmosis is the removal of dissolved materials from industrial or municipal wastewater before it is discharged into the environment.

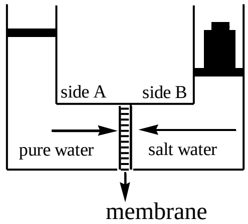


Fig - Desalination of salt water by reverse osmosis.

The membrane is permeable to water but not to ions. The normal flow of water is from side A to side B. If we exert a pressure on side B that exceeds the osmotic pressure of the salt water, a net flow of water occurs in the *reverse* direction- from the salt water to the pure water. The lengths of the arrows suggest the magnitudes of the flow of water molecules in each direction.

SOLUTION OF ELECTROLYTES

Our discussion of the electrical conductivities of solutions retraced some of the work done by the Swedish chemist Svante Arrhenius for his doctoral dissertation (1883). Prevailing opinion at the time was that ions form only with the passage of electric current. Arrhenius, however, reached the conclusion that in some cases ions exist in a solid substance and become dissociated from each other when the solid dissolves in water. Such is the case with NaCl, for example. In other cases as with HCl, ions are formed when the substance dissolves in water. In any event, electricity is not required to produce ions.

Although Arrhenius developed his theory of electrolytic dissociation to explain the electrical conductivities of solutions, he was able to apply it more widely. One of his first successes came in explaining certain anomalous values of colligative properties described by the Dutch chemist Jacobus Van't Hoff (1852-1911).

"Anomalous" Colligative Properties

Certain solute produce a greater effect on colligative properties than expected. For example, consider a 0.0100 m aqueous solution. The predicted freezing point depression of this solution is $T_f = K_f \times m = 1.86°Cm^{-1} \times 0.0100m = 0.0186°C$

We expect the solution to have a freezing point of -0.0186°C. If the 0.0100m solution is 0.0100m urea, the measured freezing point is just about -0.0186°C. However, if the solution is 0.0100m NaCl, the measured freezing point is -0.0361°C.

Van't Hoff defined the factor *i* as the ratio of the measured value of a colligative property to the expected value if the solute were a nonelectrolyte. For 0.0100m NaCl,

$$i = \frac{\text{measured } \Delta T_f}{\text{expected } \Delta T_f} = \frac{0.0361^\circ C}{1.86^\circ Cm^{-1} \times 0.0100m} = 1.94$$

Arrhenius's theory of electrolytic dissociation allows us to explain different values of the Van't Hoff factor *i* for different solutes. For solutes such as urea, glycerol, and sucrose-- all nonelectrolytes-- $i = 1$. For a strong electrolyte such as NaCl, which produces *two* moles of ions in solution per mole of solute dissolved, we should expect the effect on freezing point depression to be twice as great as for a nonelectrolyte. We should expect $i = 2$. Similarly, for $MgCl_2$ our exception would be that $i = 3$. For a weak acid $HC_2H_3O_2$(acetic acid), which is only slightly ionized in aqueous solution, we expect *i* to be slightly larger than I but not nearly equal to 2.

This discussion suggests that equations 1,2 and 3 should all be rewritten in the form

$$\Delta T_f = i \times K_f \times m$$
$$\Delta T_b = i \times K_b \times m$$
$$\pi = i \times c \times RT$$

If these equations are used for nonelectrolytes, simply substitute $i = 1$. For strong electrolytes, predict a value of i as suggested in the following example.

Example - 9

Predicting Colligative Properties for Electrolyte Solutions. Predict the freezing point of aqueous 0.00145 m $MgCl_2$.

Solution

First determine the value of i for $MgCl_2$. We can do this by writing an equation to represent the dissociation of $MgCl_2(aq)$.

$$MgCl_2(aq) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

Because *three* moles of ions are obtained per mole of formula units dissolved, we expect the value $i = 3$.

Now use the expression

$$\Delta T_f = i \times K_f \times m$$
$$\Delta T_f = 3 \times 1.68°\mathrm{C}\,\mathrm{m}^{-1} \times 0.00145\,\mathrm{m}$$
$$= 0.0081°\mathrm{C}$$

The freezing point is 0.0081°C below the normal freezing point of water, that is, the freezing point is -0.0081°C.

PRACTICE EXAMPLE: You wish to prepare an aqueous solution that has a freezing point of -0.100°C. What volume, in mL, of 12.0M HCl would you use to prepare 250 mL of such a solution? (*Hint*: what must be the molarity of the solution? Recall that in a dilute aqueous solution molarity and molarity are numerically equal.)

Colloidal Mixtures

Everybody known that in a mixture of sand and water the sand (silica, SiO_2) quickly settles to the bottom. Yet, mixtures can be prepared in which up to 40 % by mass of silica remains dispersed in water for many years. The silica is not present as dissolved ions or molecules in these mixtures. Rather, such mixtures consist of submicroscopic particles of SiO_2 suspended in water. The mixtures are said to be colloidal.

To be classified *colloidal,* a material must have one or more of its dimensions (length, width, or thickness) in the approximate range of 1 - 100 nm. If all the dimensions are smaller than 1 nm, the particles are of molecular size. If all the dimensions exceed

100nm, the particles are of ordinary or macroscopic size (even if they are only visible under a microscopic). The particles in colloidal silica have a spherical shape. Some colloidal particles are rod shaped, and some, like gamma globulin in human blood plasma, have a disclike shape. Thin films like an oil slick on water, are colloidal. And some colloids, such as cellulose fibers, are randomly coiled filaments.

One method of determining whether a mixture is a true solution or colloidal is illustrated. When light passes through a true solution, an observer viewing from a direction perpendicular to the light beam sees no light. In a colloidal dispersion light is scattered in many directions and if readily seen. This effect, first studied by Jhon Tyndall in 1869, is known as the *Tyndall effect*. A common example is the scattering of light by dust particles in a flashlight beam.

What keeps the SiO_2 particles suspended in colloidal silica? The most important factor is that the surfaces or the particles *adsorb* or attach to themselves ions from the solution, and they preferentially adsorb one type of ion over others. In the case of SiO_2 these preferred ions are OH^- , and as a result the particles acquire a net negative charge. Having like charges, the particles repel one another. These mutual repulsions overcome the force of gravity and the particles remain suspended indefinitely.

Although electrical charge can be important in stabilizing a colloid, a high concentration of ions can also bring about the *coagulation* or precipitation of a colloid. The ions responsible for the coagulation are those carrying a charge opposite to that on the colloidal particles themselves. *Dialysis,* a process similar to osmosis, can be used to remove excess ions from a colloidal mixture. Molecules of solvent and molecules or ions of solute pass through a semipermeable membrane, but the much larger colloidal particles do not. In some cases the process is more effective when carried out in an electric field. In *electrodialysis,* ions are attracted out of a colloidal mixture to an electrode carrying the opposite charge. A human kidney dialyzes blood, a colloidal mixture, to remove excess electrolytes produced in metabolism. In certain diseases the kidneys lose this ability, but a dialysis machine, external to the body, can function for the kidneys.

As so aptly put by Wilder Bancroft, an American pioneer in the field of colloid chemistry, "... colloid chemistry is essential to anyone who really wishes to understand ... oils, greases, soaps, ...glue, starch, adhesives, ... paints, varnishes, lacquers,...cream, butter, cheese, ... cooking, washing, dyeing, ... colloid chemistry is the chemistry of life."