

CHEMISTRY 1102 NOTES
ZUMDAHL CHAPTER 11 - PROPERTIES OF SOLUTIONS

This chapter focuses on liquid solutions, especially those in water but there are a number of other types. Solutions are homogeneous mixtures of two or more pure substances. The solvent is taken as the major component (if there is one) and the solutes are the minor components

TABLE 11.1 Various Types of Solutions

Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas	Gas	Gas
Vodka in water, antifreeze	Liquid	Liquid	Liquid
Brass	Solid	Solid	Solid
Carbonated water (soda)	Liquid	Gas	Liquid
Seawater, sugar solution	Liquid	Solid	Liquid
Hydrogen in platinum	Solid	Gas	Solid

1. Solution Composition

This section defines various ways of expressing the composition of solutions:

- *Mass Percent* - often called *weight percent* is given by:

$$\text{Mass Percent} = (\text{mass of solute}) / (\text{mass of solution}) \times 100\%$$

(There are also percentage compositions based on volume percent (v/v) and even weight for volume percent (w/v). Be very careful to be certain which you are dealing with in measuring quantities in the lab.)

- *Molarity* - you already know about this from the section on stoichiometry of solution reactions in Chapter 4. It is expressed as:

$$\text{Molarity (M)} = (\text{moles of solute}) / (\text{litres of solution})$$

The problem with it, for certain applications, is that it is not temperature independent.

- *Molality* - is based on mass of solvent and is therefore temperature independent. It is defined as:

$$\text{Molality (m)} = (\text{moles of solute}) / (\text{kilogrammes of solvent})$$

- *Normality* - Fortunately not much used anymore, normality is based on the number of *equivalents* per litre of solution. An *equivalent* (or *equivalent*

weight) is the number of moles that supply one mole of protons or neutralize one mole of protons in acid/base reactions or involve 1 mole of electrons in redox processes:

○ *Mole Fraction* - this is defined as:

$$\text{Mole fraction of component A } (\chi_A) = n_A / (n_A + n_B + \dots)$$

Example (11.2)

The electrolyte used in automobile batteries is 3.75 M sulphuric acid solution with a density of 1.230 g/mL. Calculate the mass percent, molality, mole fraction and normality (assuming dibasic behaviour) of the acid.

1 L of acid weighs 1230 g and contains 3.75 mol of H₂SO₄, molecular weight 98.1 g/mol

ie $3.75 \times 98.1 = 368 \text{ g}$

Therefore the litre contains $1230 - 368 = 862 \text{ g H}_2\text{O}$ or $862 / 18.0 = 47.9 \text{ mol}$.

The mass percent of H₂SO₄ = $(368 / 1230) \times 100\% = 29.9\%$

The mass percent of H₂O = $862 / 1230 \times 100\% = 70.1$

Note: $29.9 + 70.1 = 100\%$

The mole fraction $\chi(\text{H}_2\text{SO}_4) = 3.75 / (3.75 + 47.9) = 0.0726$

The mole fraction $\chi(\text{H}_2\text{O}) = 47.9 / (3.75 + 47.9) = 0.9274$

Note: $0.0726 + 0.9274 = 1$

The molality = $3.75 \times 1000 / 862 = 4.35 \text{ m}$

The normality would be $2 \times 3.75 = 7.50 \text{ N}$

2. The Energetics of Solution Formation

The basic trend is that *like dissolves like*

(**Figures 11.1 and 11.2**) There are three basic processes each of which have associated energy costs or payoffs. They are shown in the figure:

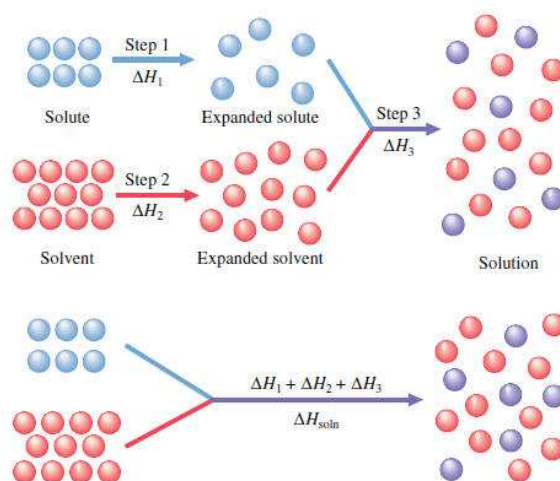


FIGURE 11.1
The formation of a liquid solution can be divided into three steps: (1) expanding the solute, (2) expanding the solvent, and (3) combining the expanded solute and solvent to form the solution.

- Expanding the solute which is naturally endothermic (ΔH_1).
- Expanding the solvent which is naturally endothermic (ΔH_2).
- "Allowing" the solute and solvent to associate which is normally more or less exothermic (ΔH_3).

(Note. The right-hand side of this diagram shows a representation of the species in the solution which is rather less densely packed than it should be, that is, the spacing is similar to the "separated" solute and solvent representations.)

$$\text{The Heat of solution, } \Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

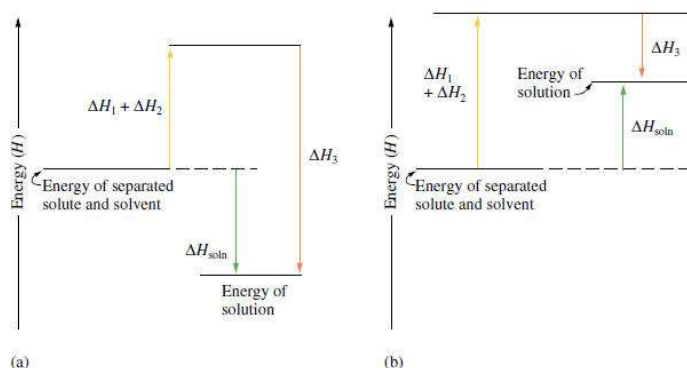


FIGURE 11.2
The heat of solution (a) ΔH_{soln} has a negative sign (the process is exothermic) if step 3 releases more energy than that required by steps 1 and 2. (b) ΔH_{soln} has a positive sign (the process is endothermic) if steps 1 and 2 require more energy than is released in step 3. (If the energy changes for steps 1 and 2 equal that for step 3, then ΔH_{soln} is zero.)

Note

The driving force for chemical processes whether actual reactions or just the dissolution of one compound in another is actually only partly a negative ΔH . The real determining quantity is ΔG , the change in (Gibbs') free energy which is given by the equation:

$$\Delta G = \Delta H - T.\Delta S$$

The quantity ΔS is the entropy change. Entropy is related to disorder. A change towards greater disorder is associated with a *positive* entropy

change, and hence a *negative* contribution to ΔG . In situations where the enthalpy of mixing is small, it is the greater disorder which is attained on mixing, which is the main driving force. More information about ΔG and ΔS can be found in Chapter 16 of Zumdahl.

TABLE 11.3 The Energy Terms for Various Types of Solutes and Solvents

	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar solute, polar solvent	Large	Large	Large, negative	Small	Solution forms
Nonpolar solute, polar solvent	Small	Large	Small	Large, positive	No solution forms
Nonpolar solute, nonpolar solvent	Small	Small	Small	Small	Solution forms
Polar solute, nonpolar solvent	Large	Small	Small	Large, positive	No solution forms

3. Factors Affecting Solubility :

Structure Effects

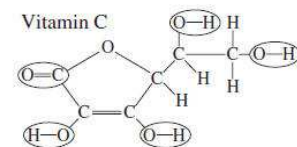
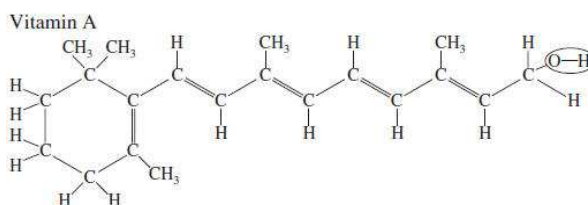
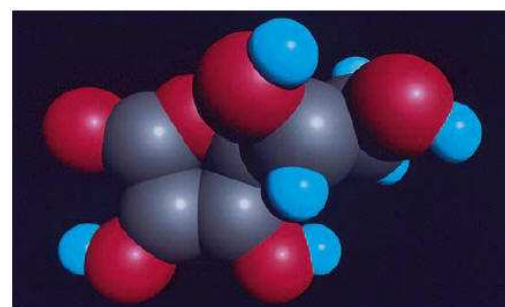
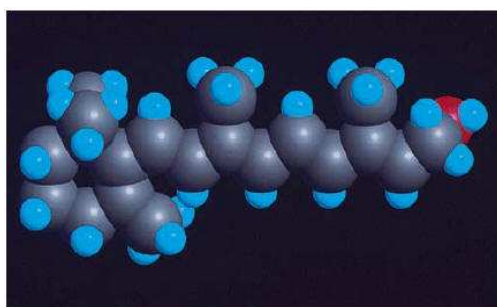


FIGURE 11.4

The molecular structures of (a) vitamin A (nonpolar, fat-soluble) and (b) vitamin C (polar, water-soluble). The circles in the structural formulas indicate polar bonds. Note that vitamin C contains far more polar bonds than vitamin A.

Vitamins (Figure 11.4), which illustrate the trend very well, can be categorized as fat-soluble (*hydrophobic*) such as A, D, E and K and water-soluble (*hydrophilic*) such as B and C. In general organic compounds with few or no polar groups are not water soluble. Then there are micelles...

Pressure Effects

Gases become more soluble at higher pressure according to *Henry's Law*:

$$P = kC$$

It applies to gases which dissolve without dissociation, e.g. oxygen or argon, but not to gases which react with water, for example HCl or NH₃.

Example (11.4):

The Henry's law constant for CO₂ in water is 32 L.atm/mol at 25°C. CO₂ in a soft drink is at 5 atm in the bottle at 25 °C. Assuming the partial pressure of CO₂ in the atmosphere is 4.0x10⁻⁴ atm, calculate the concentration of CO₂ in the "pop" before opening, and after it has gone flat:

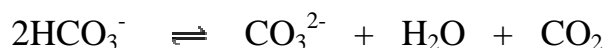
In the bottle: $[CO_2] = P(CO_2) / k(CO_2) = 5.0 / 32 = 0.16 \text{ M}$

When it is flat: $[CO_2] = 4.0 \times 10^{-4} / 32 = 1.2 \times 10^{-5} \text{ M}$

Temperature Effects (for Aqueous Solutions)

While *solid* substances dissolve more rapidly at higher temperatures (a kinetic effect) they are not always more soluble at the higher temperature (though usually they are) (Figures 11.6). Predicting the exceptions is not easy because of the complexity of the factors that influence solubility.

Gases are always less soluble in hot water (Figure 11.7). Boiler scale is created by the lowered solubility of CO₂ in hot water causing precipitation of CaCO₃ from Ca(HCO₃)₂.



4. The Vapour Pressure of Solutions

Figures 11.9, 11.10 illustrate *Raoult's Law* (for involatile solutes):

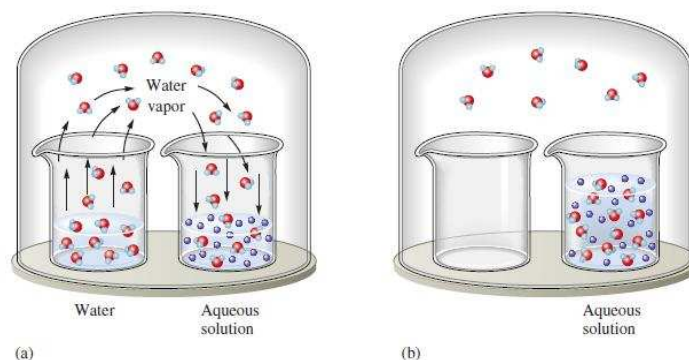


FIGURE 11.9
An aqueous solution and pure water in a closed environment. (a) Initial stage. (b) After a period of time, the water is transferred to the solution.

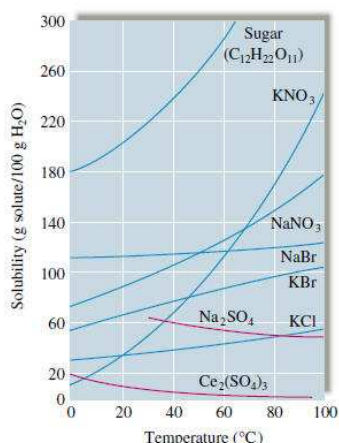


FIGURE 11.6
The solubilities of several solids as a function of temperature. Note that while most substances become more soluble in water with increasing temperature, sodium sulfate and cerium sulfate become less soluble.

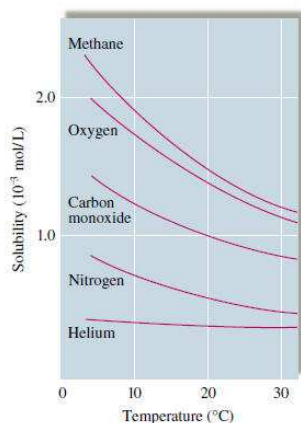
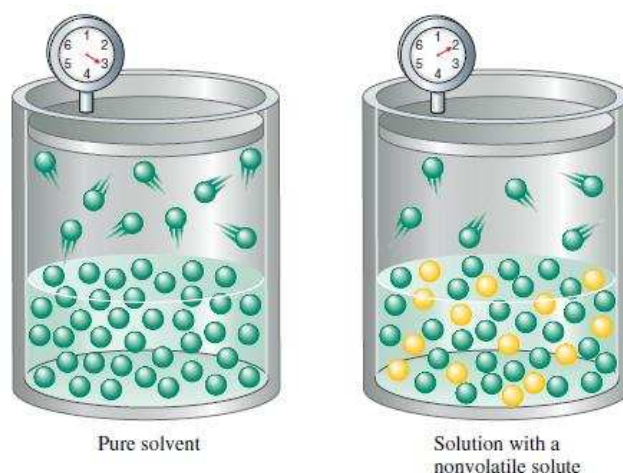


FIGURE 11.7
The solubilities of several gases in water as a function of temperature at a constant pressure of 1 atm of gas above the solution.

FIGURE 11.10

The presence of a nonvolatile solute inhibits the escape of solvent molecules from the liquid and so lowers the vapor pressure of the solvent.



$$P_{\text{solution}} = \chi_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$$

Example (11.6):

Calculate the vapour pressure of a solution of 35.0 g solid Na_2SO_4 (molecular mass = 142 g/mol) in 175 g of water at 25°C at which the vapour pressure of pure water is 23.76 torr.

$$\text{Moles of H}_2\text{O} = 175 / 18.0 = 9.72$$

$$\text{Moles of Na}_2\text{SO}_4 = 35.0 / 142 = 0.246$$

BUT this gives 0.246 moles of SO_4^{2-} and 0.492 moles of Na^+ ie 0.738 in total.

$$\text{Mole fraction } \chi(\text{H}_2\text{O}) = 9.72 / (9.72 + 0.738) = 0.929$$

$$P_{\text{solution}} = \chi(\text{H}_2\text{O}) \times P^{\circ}(\text{H}_2\text{O}) = 0.929 \times 23.76 = 22.1 \text{ torr}$$

While vapour pressure measurements could be used to measure molecular masses, they rarely are except by the method of allowing two solutions, one containing a known amount of solute to equilibrate with another containing the unknown.

Non-ideal Solutions

When the solution involves two (or more) components which are volatile and are *ideal* Raoult's Law becomes:

$$P_{\text{total}} = P_a + P_b + \dots = \chi_a \cdot P_a^{\circ} + \chi_b \cdot P_b^{\circ} + \dots$$

This behaviour and deviations from Raoult's law are depicted in **Figure 11.13**. The book gives acetone-water as an example of an exothermic mixing which results in lowered vapour pressure relative to the ideal and ethanol-hexane as an example of endothermic mixing and increase vapour pressures over the expected ideal.

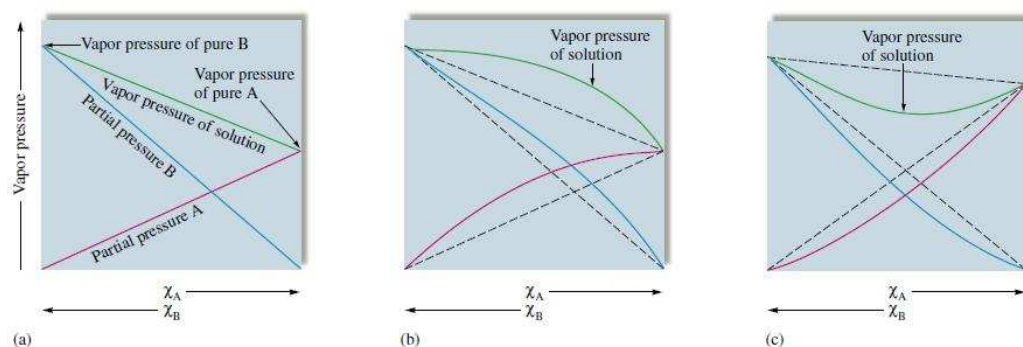


FIGURE 11.13
 Vapor pressure for a solution of two volatile liquids. (a) The behavior predicted for an ideal liquid–liquid solution by Raoult's law. (b) A solution for which P_{TOTAL} is larger than the value calculated from Raoult's law. This solution shows a positive deviation from Raoult's law. (c) A solution for which P_{TOTAL} is smaller than the value calculated from Raoult's law. This solution shows a negative deviation from Raoult's law.

1. **Exercise 11.7:**

A solution is prepared by mixing 15.0 g acetone (molar mass = 58.1 g/mol) with 20.0 g of chloroform (molar mass = 119.4 g/mol). At 35°C this mixture has a vapour pressure of 287 torr. Is this an ideal solution? If it is assumed to be ideal, what are the mole fractions of acetone and chloroform in the vapour? (The vapor pressures of pure acetone and pure chloroform respectively are 345 and 293 torr.)

First calculate the number of moles of each component

$$\text{Moles of acetone} = 15.0 / 58.1 = 0.2582$$

$$\text{Moles of chloroform} = 20.0 / 119 = 0.1681$$

Therefore the mole fractions are:

$$\chi_{\text{acetone}} = 0.2528 / (0.2528 + 0.1681) = 0.6057$$

$$\chi_{\text{chloroform}} = 0.1681 / (0.2528 + 0.1681) = 0.3943 (= 1 - 0.6057)$$

$$\text{Ideal } P_{\text{total}} = 0.6057 \times 345 + 0.2943 \times 293 = 209.0 + 115.5 = 325 \text{ torr}$$

Since the experimental value is 293 torr, the solution is non-ideal and the vapour pressures are lower than they would be if Raoult's law was perfectly obeyed. This indicates attractive interactions between the molecules, which is not surprising since they are both polar.

To calculate the composition of the vapour we need to use the ideal gas equation:

$$PV = nRT \quad \text{or} \quad n = PV/RT$$

where P = partial pressure, V = volume, n = number of moles, R = gas

constant, T absolute temperature.

In the vapour phase above the mixture:

$$\chi_{\text{acetone}} = (209.0 \times V/RT) / (209.0 \times V/RT + 115.5 \times V/RT) = 209.0 / (209.0 + 115.5) = 0.644$$

$$\chi_{\text{chloroform}} = 1 - 0.644 = 0.356$$

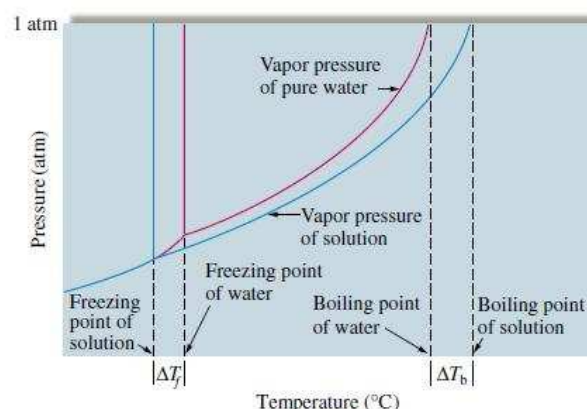
Notice that the concentration of acetone in the vapour is higher than it is in the liquid. This is why it is possible to separate the two components by distillation.

2. Boiling Point Elevation and Freezing Point Depression

These together with osmotic pressure are the *colligative properties* and the effects depend only on the number of solute particles. These properties are used for measuring molecular masses or apparent molecular masses which can give other information.

Both effects fp and bp are illustrated on [Figure 11.14](#).

FIGURE 11.14
Phase diagrams for pure water (red lines) and for an aqueous solution containing a nonvolatile solute (blue lines). Note that the boiling point of the solution is higher than that of pure water. Conversely, the freezing point of the solution is lower than that of pure water. The effect of a non-volatile solute is to extend the liquid range of a solvent.



Boiling Point Elevation

The vapour pressure of the solvent is depressed by the presence of an involatile solute so it must be heated to a higher temperature to make the vapour pressure equal 1 atm

The key formula is:

$$\Delta T = K_b \times m_{\text{solute}}$$

K_b is the *molal boiling point elevation constant*. Some are collected in [Table 11.5](#)

Example (11.8):

A solution was prepared by dissolving 18.00 g glucose (empirical formula CH_2O) in 150 g of water. The resulting solution was found to have a boiling point of 100.34°C (at 1 atm). Calculate the molar mass of glucose and deduce the molecular formula. $K_b = 0.51^\circ\text{C kg mol}^{-1}$.

$$\Delta T = 100.34 - 100.00$$

$$K_b = 0.51^\circ\text{C.kg/mol } m_{\text{solute}} = \Delta T/K_b = 0.34/0,51 = 0.67 \text{ mol/kg}$$

The solution contained 0.150 kg water so moles of glucose = $0.67 \times 0.150 = 0.10 \text{ mol}$

The molecular mass of glucose is therefore $18.0/0.10 = 180 \text{ g/mol}$

The mass of the empirical formula unit (CH_2O) is $12 + 2 \times 1 + 16 = 30$.

If the molecular formula is $(\text{CH}_2\text{O})_n$, then $30 \times n = 180$, or $n = 6$.

The molecular formula is $\text{C}_6\text{H}_{12}\text{O}_6$. Note that in real life, the numbers are never this exact!

Freezing Point Depression

In an ice - pure water equilibrium the vapour pressure of the ice and of the water is equal at 0°C . Addition of a solute will depress the vapour pressure of the liquid water. Since the vapour pressure of ice decreases more slowly than that of liquid water, the equilibrium where the vapour pressures are equal can be reestablished at a lower temperature.

The key formula is:

$$\Delta T = K_f \times m_{\text{solute}}$$

K_f is the *molal freezing point depression constant*. Some are collected in **Table 11.5**. Calculations are the same as for boiling point elevation.

TABLE 11.5 Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point ($^\circ\text{C}$)	K_b ($^\circ\text{C} \cdot \text{kg/mol}$)	Freezing Point ($^\circ\text{C}$)	K_f ($^\circ\text{C} \cdot \text{kg/mol}$)
Water (H_2O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl_4)	76.5	5.03	-22.99	30.
Chloroform (CHCl_3)	61.2	3.63	-63.5	4.70
Benzene (C_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	-111.5	3.83
Ethyl ether ($\text{C}_4\text{H}_{10}\text{O}$)	34.5	2.02	-116.2	1.79
Camphor ($\text{C}_{10}\text{H}_{16}\text{O}$)	208.0	5.95	179.8	40.

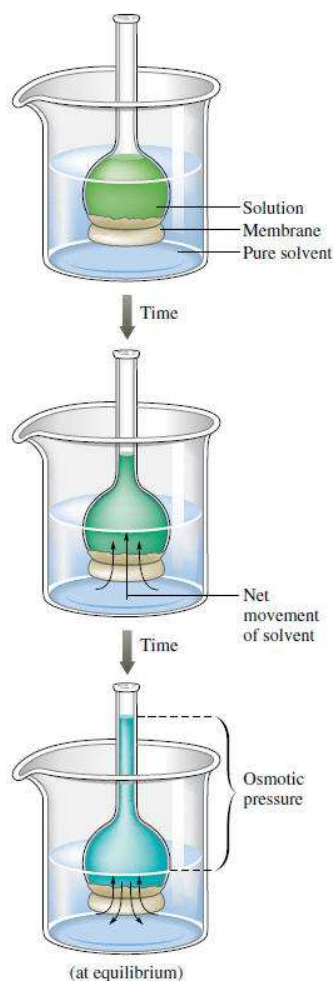


FIGURE 11.16
A tube with a bulb on the end that is covered by a semipermeable membrane. The solution is inside the tube and is bathed in the pure solvent. There is a net transfer of solvent molecules into the solution until the hydrostatic pressure equalizes the solvent flow in both directions.

Osmotic Pressure

When a solution and a solvent are separated by a *semipermeable membrane*, there is a tendency for the solvent to try to dilute the solution by flowing through the membrane (through which the solute cannot pass). This process is called osmosis. See **Figure 11.16** which illustrates a thistle funnel with a membrane over the mouth, upturned, partly filled with a solution and dipped in the solvent. The osmosis will persist until the hydrostatic pressure in the stem of the funnel resists further flow. This is not useful apparatus practically because it would take too long to establish equilibrium.

To measure osmotic pressure and use the effect notable to measure molecular masses specially of large protein molecules) apparatus as in **Figures 11.17, 11.18** is used. Pressure is applied to resist the osmotic flow from a solution of known composition.

The osmotic pressure $\pi = M.R.T$

M is molarity, R is the gas constant and T is the absolute temperature.

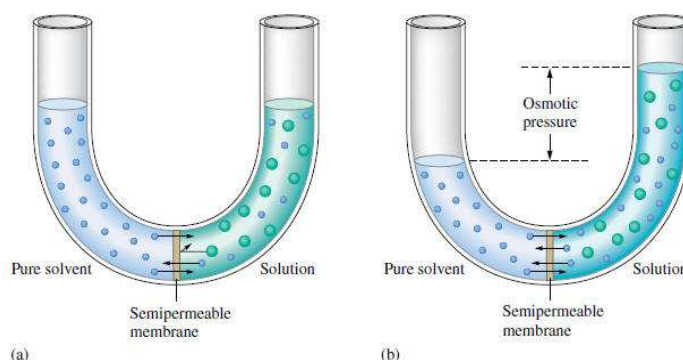


FIGURE 11.18
(a) A pure solvent and its solution (containing a nonvolatile solute) are separated by a semipermeable membrane through which solvent molecules (blue) can pass but solute molecules (green) cannot. The rate of solvent transfer is greater from solvent to solution than from solution to solvent. (b) The system at equilibrium, where the rate of solvent transfer is the same in both directions.

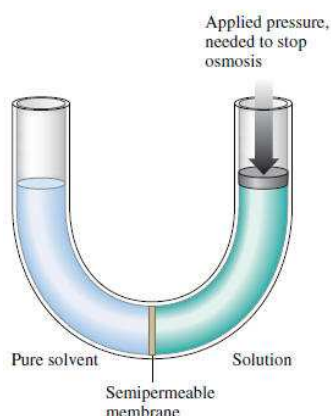
1. Example (11.11):

To determine the molar mass of a certain protein, 1.00×10^{-3} g of it are dissolved in 1.00 mL of solution. (Note the small quantities.) The osmotic pressure of this solution was found to be 1.12 torr at 25°C . Calculate the molar mass of the protein.

$$M = \pi / (R.T) = (1.12 \text{ torr} \times 1/760 \text{ atm/torr}) / (0.08206 \text{ L.atm/K/mol} \times (25 + 273) \text{ K})$$

$$= 6.01 \times 10^{-5} \text{ mol/L}$$

Now $0.001(\text{g/mL}) \times 1000(\text{mL/L}) = 1.00 \text{ g/L}$ of the protein, so 1 g is



$$6.01 \times 10^{-5} \text{ mol}$$

or the molecular mass is $1(\text{g/L})/6.01(\text{mol/L}) = 1.66 \times 10^4 \text{ g/mol}$.

FIGURE 11.17

The normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. The minimum pressure required to stop the osmosis is equal to the osmotic pressure of the solution.

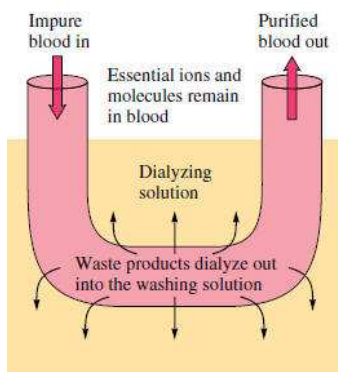


FIGURE 11.19

Representation of the functioning of an artificial kidney.

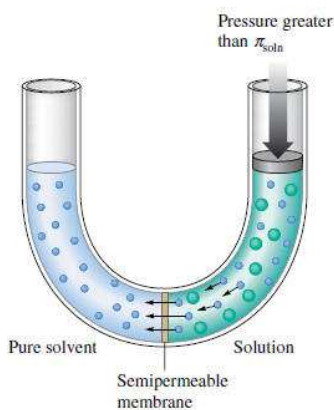


FIGURE 11.20

Reverse osmosis. A pressure greater than the osmotic pressure of the solution is applied, which causes a net flow of solvent molecules (blue) from the solution to the pure solvent. The solute molecules (green) remain behind.

Dialysis

This is a process where the semipermeable membrane allows the passage of solvent *and other small molecules*. It occurs naturally through cell walls which are highly specialized and selective, and is also done in artificial kidney machines.

Blood is passed through a tube shaped semipermeable membrane surrounded by a solution of all the salts etc which are supposed to be in the blood at the appropriate concentrations. The membrane is impermeable to blood cells (for example), but will allow small "waste" molecules to pass out. The desirable substances in clean blood pass equally in both directions. **Figure 11.19** shows the dialysis machine.

It is very important in giving transfusions that the fluids used be isotonic with blood cell fluids. If not the cells will either collapse (crenation) or explode (hemolysis).

The salting of foods is effectively the deliberate crenation of bacteria.

Reverse Osmosis

This is the forcing of a solution through a semipermeable membrane to "filter" out the solutes. The principal use is for desalination of sea-water. (**Figure 11.20**)

2. Colligative Properties of Electrolyte Solutions

The colligative properties of solutions depend on the numbers of solute particles and not their nature. Consider two 0.1M molar solutions, one of sugar and the other of sodium chloride. If the NaCl were completely dissociated, its effects should be exactly double those of sugar. This is not necessarily the case because of ion-pairing in salts and possible partial dissociation, for example for weak acid or bases.

The situation is quantified using the *van't Hoff factor*: $i = \text{moles of particles in solution}/\text{moles of solute}$

The van't Hoff factor is simply included as necessary in the equations for the colligative properties:

$$\Delta T = imK_b \quad \Delta T = imK_f \quad \text{and} \quad \pi = iMRT$$

The expected value and the observed value are a valuable probe for the actual nature of the solution.

TABLE 11.6 Expected and Observed Values of the van't Hoff Factor for 0.05 m Solutions of Several Electrolytes

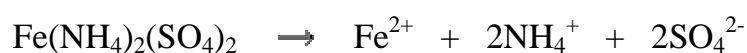
Electrolyte	<i>i</i> (expected)	<i>i</i> (observed)
NaCl	2.0	1.9
MgCl ₂	3.0	2.7
MgSO ₄	2.0	1.3
FeCl ₃	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

*A nonelectrolyte shown for comparison.

1. Example (11.13):

The observed osmotic pressure for a 0.1 M solution of Fe(NH₄)₂(SO₄)₂ at 25°C is 10.8 atm. Compare the expected and the observed van't Hoff factors.

Ferrous ammonium sulphate might be expected to ionize to give 5 ions:



$$i = \pi / (MRT) = 10.8 / (0.10 \times 0.08206 \times 298) = 4.4$$

2. Colloids

Not covered (Winter 2002)

