5 Nonelectrolytes

Chapter Objectives

At the conclusion of this chapter the student should be able to:

1. Identify and describe the four colligative properties of nonelectrolytes in solution.
2. Understand the various types of pharmaceutical solutions.
3. Calculate molarity, normality, molality, mole fraction, and percentage expressions.
4. Calculate equivalent weights.
5. Define ideal and real solutions using Raoult's and Henry's laws.
6. Use Raoult's law to calculate partial and total vapor pressure.
7. Calculate vapor pressure lowering, boiling point elevation, freezing point lowering, and pressure for solutions of nonelectrolytes.
8. Use colligative properties to determine molecular weight.

Introduction

In this chapter, the student will begin to learn about pharmaceutical systems. In the pharmaceutical sciences, a *system* is generally considered to be a bounded space or an exact quantity of a material substance. Material substances can be mixed together to form a variety of pharmaceutical mixtures (or dispersions) such as true solutions, colloidal dispersions, and coarse dispersions. A *dispersion* consists of at least two phases with one or more dispersed (internal) phases contained in a single continuous (external) phase. The term *phase* is defined as a distinct homogeneous part of a system separated by definite boundaries from other parts of the system. Each phase may be consolidated into a contiguous mass or region, such as a single tea leaf floating in water. A *true solution* is defined as a mixture of two or more components that form a homogeneous molecular dispersion, in other words, a one-phase system. In a true solution, the suspended particles completely dissolve and are not large enough to scatter light but are small enough to be evenly dispersed resulting in a homogeneous appearance. The diameter of particles in *coarse dispersions* is greater than ~500 nm (0.5 μm). Two common pharmaceutical coarse dispersions are emulsions (liquid–liquid dispersions) and suspensions (solid–liquid dispersions). A colloidal dispersion represents a system having a particle size intermediate between that of a true solution and a coarse dispersion, roughly 1 to 500 nm. A colloidal dispersion may be considered as a two-phase (heterogeneous) system under some circumstances. However, it may also be considered as a one-phase system (homogeneous) under other circumstances. For example, liposomes or microspheres in an aqueous delivery vehicle are considered to be heterogeneous colloidal dispersions because they consist of distinct particles constituting a separate phase. On the other hand, a colloidal dispersion of acacia or sodium carboxymethylcellulose in water is homogeneous since it does not differ significantly from a solution of sucrose. Therefore, it may be considered as a single-phase system or true solution.[1] Another example of a homogeneous colloidal dispersion that is considered to be a true solution is drug-polymer conjugates since they can completely dissolve in water.

Key Concept

Pharmaceutical Dispersions

When two materials are mixed, one becomes dispersed in the other. To classify a pharmaceutical dispersion, only the size of the dispersed phase and not its composition is considered. The two components may become dispersed at the molecular level forming a true solution. In other words, the dispersed phase completely dissolves, cannot scatter light, and cannot be visualized using microscopy. If the dispersed phase is in the size range of 1 to 500 nm, it is considered to be a colloidal dispersion. Common examples of colloidal dispersions include blood, liposomes, and zinc oxide paste. If the particle size is greater than 500 nm (or 0.5 μm), it is considered to be a coarse dispersion. Two common examples of coarse dispersions are emulsions and suspensions.

This chapter focuses on molecular dispersions, which are also known as true solutions. A solution composed of only two substances is known as a *binary solution*, and the components or constituents are referred to as the *solvent* and the *solute*. Commonly, the terms *component* and *constituent* are used interchangeably to represent the pure chemical substances that make up a solution. The *number of components* has a definite significance in the phase rule. The constituent present in the greater amount in a binary solution is arbitrarily designated as the solvent and the constituent in the lesser amount as the solute. When a solid is dissolved in a liquid, however, the liquid is usually taken as the solvent and the solid as the solute, irrespective of the relative amounts of the constituents. When water is one of the constituents of a liquid mixture, it is usually considered the solvent. When dealing with mixtures of liquids that are miscible in all proportions, such as alcohol and water, it is less meaningful to classify the constituents as solute and solvent.

Physical Properties of Substances

The physical properties of substances can be classified as *colligative*, *additive*, and *constitutive*. Some of the constitutive and additive properties of molecules were considered in Chapter 4. In the field of thermodynamics, physical properties of systems are classified as *extensive* properties, which depend on the quantity of the matter in the system (e.g., mass and volume), and *intensive* properties, which are independent of the amount of the substances in the system (e.g., temperature, pressure, density, surface tension, and viscosity of a pure liquid).

Colligative properties depend mainly on the number of particles in a solution. The colligative properties of solutions are osmotic pressure, vapor pressure lowering, freezing point depression, and boiling point elevation. The values of the colligative properties are approximately the same for equal concentrations of different nonelectrolytes in solution regardless of the species or chemical nature of the constituents. In considering the colligative properties of solid-in-liquid solutions, it is assumed that the solute is nonvolatile and that the pressure of the vapor above the solution is provided entirely by the solvent.

Additive properties depend on the total contribution of the atoms in the molecule or on the sum of the properties of the constituents in a solution. An example of an additive property of a compound is the molecular weight, that is, the sum of the masses of the constituent atoms. The masses of the components of a solution are also additive, the total mass of the solution being the sum of the masses of the individual components.

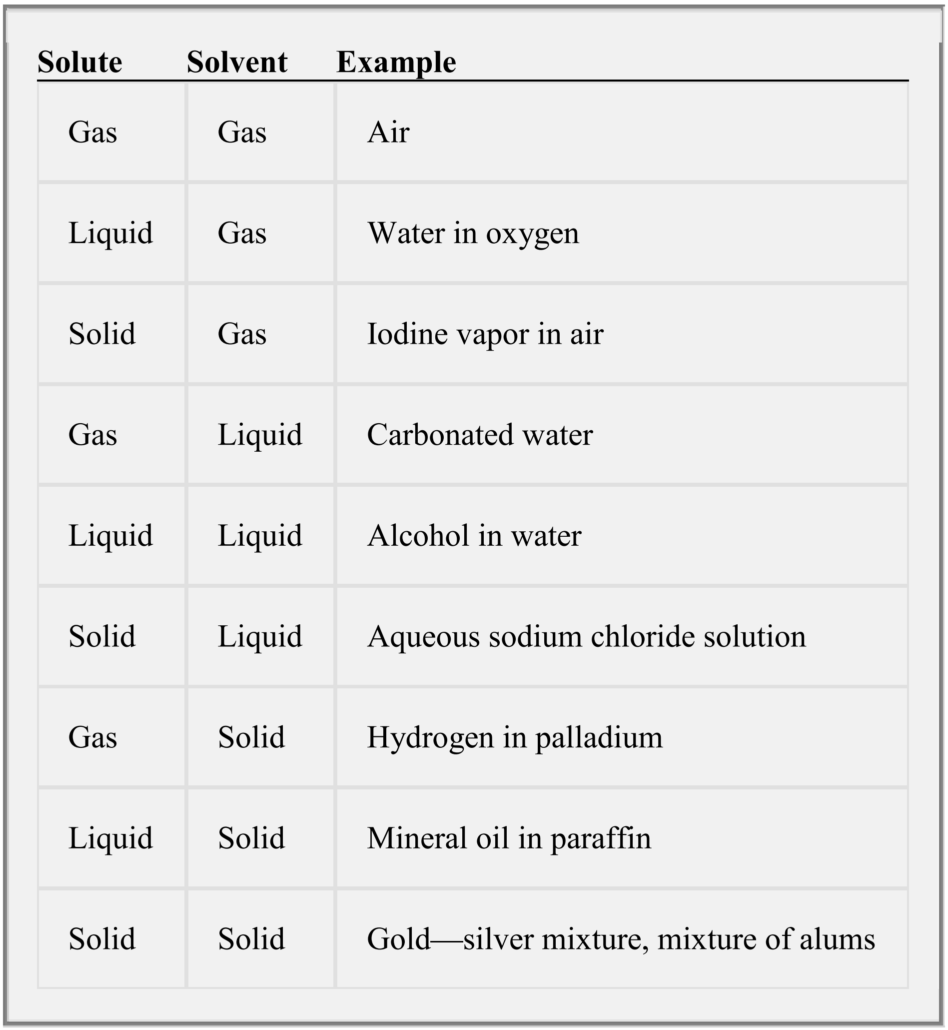
Constitutive properties depend on the arrangement and to a lesser extent on the number and kind of atoms within a molecule. These properties give clues to the constitution of individual compounds and groups of molecules in a system. Many physical properties may be partly additive and partly constitutive. The refraction of light, electric properties, surface and interfacial characteristics, and the solubility of drugs are at least in part constitutive and in part additive properties; these are considered in other sections of the book.

Types of Solutions

A solution can be classified according to the states in which the solute and solvent occur, and because three states of matter (gas, liquid, and crystalline solid) exist, nine types of homogeneous mixtures of solute and solvent are possible. These types, together with some examples, are given in Table 5-1.

When solids or liquids dissolve in a gas to form a gaseous solution, the molecules of the solute can be treated thermodynamically like a gas; similarly, when gases or solids dissolve in liquids, the gases and the solids can be considered to exist in the liquid state. In the formation of solid solutions, the atoms of the gas or liquid take up positions in the crystal lattice and behave like atoms or molecules of solids.

Table 5-1 Types of Solutions



Solute	Solvent	Example
Gas	Gas	Air
Liquid	Gas	Water in oxygen
Solid	Gas	Iodine vapor in air
Gas	Liquid	Carbonated water
Liquid	Liquid	Alcohol in water
Solid	Liquid	Aqueous sodium chloride solution
Gas	Solid	Hydrogen in palladium
Liquid	Solid	Mineral oil in paraffin
Solid	Solid	Gold—silver mixture, mixture of alums

The solutes (whether gases, liquids, or solids) are divided into two main classes: *nonelectrolytes* and *electrolytes*. Nonelectrolytes are substances that do not ionize when dissolved in water and therefore do not conduct an electric current through the solution. Examples of nonelectrolytes are sucrose, glycerin, naphthalene, and urea. The colligative properties of solutions of nonelectrolytes are fairly regular. A 0.1-molar (M) solution of a nonelectrolyte produces approximately the same colligative effect as any other nonelectrolytic solution of equal concentration. Electrolytes are substances that form ions in solution, conduct electric current, and show apparent “anomalous” colligative properties; that is, they produce a considerably greater freezing point depression and boiling point elevation than do nonelectrolytes of the same concentration. Examples of electrolytes are hydrochloric acid, sodium sulfate, ephedrine, and phenobarbital.

Electrolytes may be subdivided further into *strong electrolytes* and *weak electrolytes* depending on whether the substance is completely or only partly ionized in water. Hydrochloric acid and sodium sulfate are strong electrolytes, whereas ephedrine and phenobarbital are weak electrolytes. The classification of electrolytes according to Arrhenius and the discussion of the modern theories of electrolytes are given later in the book.

Concentration Expressions

The concentration of a solution can be expressed either in terms of the quantity of solute in a definite *volume of solution* or as the quantity of solute in a definite *mass of solvent or solution*. The various expressions are summarized in Table 5-2.

Molarity and Normality

Molarity and normality are the expressions commonly used in analytical work.[2] All solutions of the same molarity contain the same number of solute molecules in a definite volume of solution. When a solution contains more than one solute, it may have different molar concentrations with respect to the various solutes. For example, a solution can be 0.001 M with respect to phenobarbital and 0.1 M with respect to sodium chloride. One liter of such a solution is prepared by adding 0.001 mole of phenobarbital (0.001 mole × 232.32 g/mole = 0.2323 g) and 0.1 mole of sodium chloride (0.1 mole × 58.45 g/mole = 5.845 g) to enough water to make 1000 mL of solution.

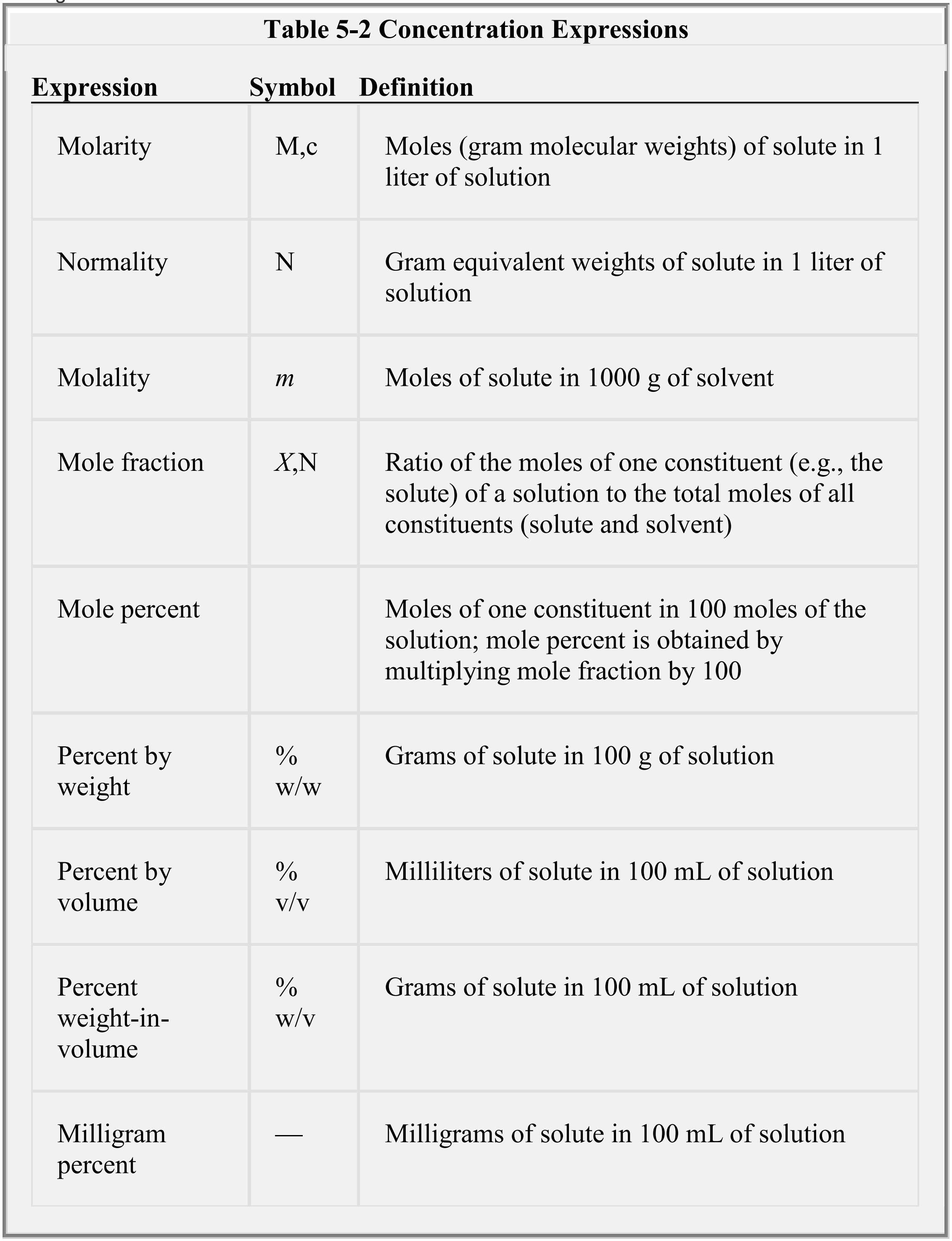


Table 5-2 Concentration Expressions

Expression	Symbol	Definition
Molarity	M,c	Moles (gram molecular weights) of solute in 1 liter of solution
Normality	N	Gram equivalent weights of solute in 1 liter of solution
Molality	*m*	Moles of solute in 1000 g of solvent
Mole fraction	*X*,N	Ratio of the moles of one constituent (e.g., the solute) of a solution to the total moles of all constituents (solute and solvent)
Mole percent		Moles of one constituent in 100 moles of the solution; mole percent is obtained by multiplying mole fraction by 100
Percent by weight	% w/w	Grams of solute in 100 g of solution
Percent by volume	% v/v	Milliliters of solute in 100 mL of solution
Percent weight-in-volume	% w/v	Grams of solute in 100 mL of solution
Milligram percent	—	Milligrams of solute in 100 mL of solution

Difficulties are sometimes encountered when one desires to express the molarity of an ion or radical in a solution. A molar solution of sodium chloride is 1 M with respect to both the sodium and the chloride ion, whereas a molar solution of Na_2CO_3 is 1 M with respect to the carbonate ion and 2 M with respect to the sodium ion because each mole of this salt contains 2 moles of sodium ions. A molar solution of sodium chloride is also 1 normal (1 N) with respect to both its ions; however, a molar solution of sodium carbonate is 2 N with respect to both the sodium and the carbonate ion.

Molar and normal solutions are popular in chemistry because they can be brought to a convenient volume; a volume aliquot of the solution, representing a known weight of solute, is easily obtained by the use of the burette or pipette.

Both molarity and normality have the disadvantage of changing value with temperature because of the expansion or contraction of liquids and should not be used when one wishes to study the properties of solutions at various temperatures. Another difficulty arises in the use of molar and normal solutions for the study of properties such as vapor pressure and osmotic pressure, which are related to the concentration of the solvent. The volume of the solvent in a molar or a normal solution is not usually known, and it varies for different solutions of the same concentration, depending upon the solute and solvent involved.

Molality

A molal solution is prepared in terms of weight units and does not have the disadvantages just discussed; therefore, molal concentration appears more frequently than molarity and normality in theoretical studies. It is possible to convert molality into molarity or normality if the final volume of the solution is observed or if the density is determined. In aqueous solutions more dilute than 0.1 M, it usually may be assumed for practical purposes that molality and molarity are equivalent. For example, a 1% solution by weight of sodium chloride with a specific gravity of 1.0053 is 0.170 M and 0.173 molal (0.173 *m*). The following difference between molar and molal solutions should also be noted. If another solute, containing neither sodium nor chloride ions, is added to a certain volume of a molal solution of sodium chloride, the solution remains 1 *m* in sodium chloride, although the total volume and the weight of the solution increase. Molarity, of course, *decreases* when another solute is added because of the increase in volume of the solution.

Molal solutions are prepared by adding the proper weight of solvent to a carefully weighed quantity of the solute. The volume of the solvent can be calculated from the specific gravity, and the solvent can then be measured from a burette rather than weighed.

Mole Fraction

Mole fraction is used frequently in experimentation involving theoretical considerations because it gives a measure of the relative proportion of moles of each constituent in a solution. It is expressed as

$$X_1 = \frac{n_1}{n_1 + n_2} \qquad (5\text{–}1)$$

$$X_2 = \frac{n_2}{n_1 + n_2} \qquad (5\text{–}2)$$

for a system of two constituents. Here X_1 is the mole fraction of constituent 1 (the subscript 1 is ordinarily used as the designation for the solvent), X_2 is the mole fraction of constituent 2 (usually the solute), and n_1 and n_2 are the numbers of moles of the respective constituents in the solution. The sum of the mole fractions of solute and solvent must equal

unity. Mole fraction is also expressed in percentage terms by multiplying X_1 or X_2 by 100. In a solution containing 0.01 mole of solute and 0.04 mole of solvent, the mole fraction of the solute is $X_2 = 0.01/(0.04 + 0.01) = 0.20$. Because the mole fractions of the two constituents must equal 1, the mole fraction of the solvent is 0.8. The mole percent of the solute is 20%; the mole percent of the solvent is 80%.

The manner in which mole fraction is defined allows one to express the relationship between the number of solute and solvent molecules in a simple, direct way. In the example just given, it is readily seen that 2 of every 10 molecules in the solution are solute molecules, and it will be observed later that many of the properties of solutes and solvents are directly related to their mole fraction in the solution. For example, the partial vapor pressure above a solution brought about by the presence of a volatile solute is equal to the vapor pressure of the pure solute multiplied by the mole fraction of the solute in the solution.

Percentage Expressions

The percentage method of expressing the concentration of pharmaceutical solutions is quite common. Percentage by weight signifies the number of grams of solute per 100 g of solution. A 10% by weight (% w/w) aqueous solution of glycerin contains 10 g of glycerin dissolved in enough water (90 g) to make 100 g of solution. Percentage by volume is expressed as the volume of solute in milliliters contained in 100 mL of the solution. Alcohol (United States Pharmacopeia) contains 92.3% by weight and 94.9% by volume of C_2H_5OH at 15.56°C; that is, it contains 92.3 g of C_2H_5OH in 100 g of solution or 94.9 mL of C_2H_5OH in 100 mL of solution.

Calculations Involving Concentration Expressions

The calculations involving the various concentration expressions are illustrated in the following example.

Example 5-1

Solutions of Ferrous Sulfate

An aqueous solution of exsiccated ferrous sulfate was prepared by adding 41.50 g of $FeSO_4$ to enough water to make 1000 mL of solution at 18°C. The density of the solution is 1.0375 and the molecular weight of $FeSO_4$ is 151.9. Calculate (*a*) the molarity; (*b*) the molality; (*c*) the mole fraction of $FeSO_4$, the mole fraction of water, and the mole percent of the two constituents; and (*d*) the percentage by weight of $FeSO_4$.

(*a*) Molarity:

$$\text{Moles of FeSO}_4 = \frac{\text{g of FeSO}_4}{\text{Molecular weight}}$$

$$= \frac{41.50}{151.9} = 0.2732$$

$$\text{Molarity} = \frac{\text{Moles of FeSO}_4}{\text{Liters of solution}} = \frac{0.2732}{1\ \text{liter}} = 0.2732\ \text{M}$$

(*b*) **Molality:**

$$\text{Grams of solution} = \text{Volume} \times \text{Density}$$

$$1000 \times 1.0375 = 1037.5\ \text{g}$$

$$\text{Grams of solvent} = \text{Grams of solution} - \text{Grams}$$

$$\text{of FeSO}_4 = 1037.5 - 41.5 = 996.0\ \text{g}$$

$$\text{Molality} = \frac{\text{Moles of FeSO}_4}{\text{kg of solvent}} = \frac{0.2732}{0.996} = 0.2743\, m$$

(*c*) **Mole fraction and mole percent:**

$$\text{Moles of water} = \frac{996}{18.02} = 55.27\ \text{moles}$$

Mole fraction of FeSO$_4$:

$$X_2 = \frac{\text{Moles of FeSO}_4}{\text{Moles of water} + \text{Moles of FeSO}_4}$$

$$= \frac{0.2732}{55.27 + 0.2732} = 0.0049$$

Mole fraction of water:

$$X_1 = \frac{55.27}{55.27 + 0.2732} = 0.9951$$

Notice that
$X_1 + X_2 = 0.9951 + 0.0049 = 1.0000$
Mole percent of FeSO$_4$ $= 0.0049 \times 100 = 0.49\%$
Mole percent of water $= 0.9951 \times 100 = 99.51\%$

(*d*) **Percentage by weight of FeSO$_4$:**

$$= \frac{\text{g of FeSO}_4}{\text{g of solution}} \times 100$$

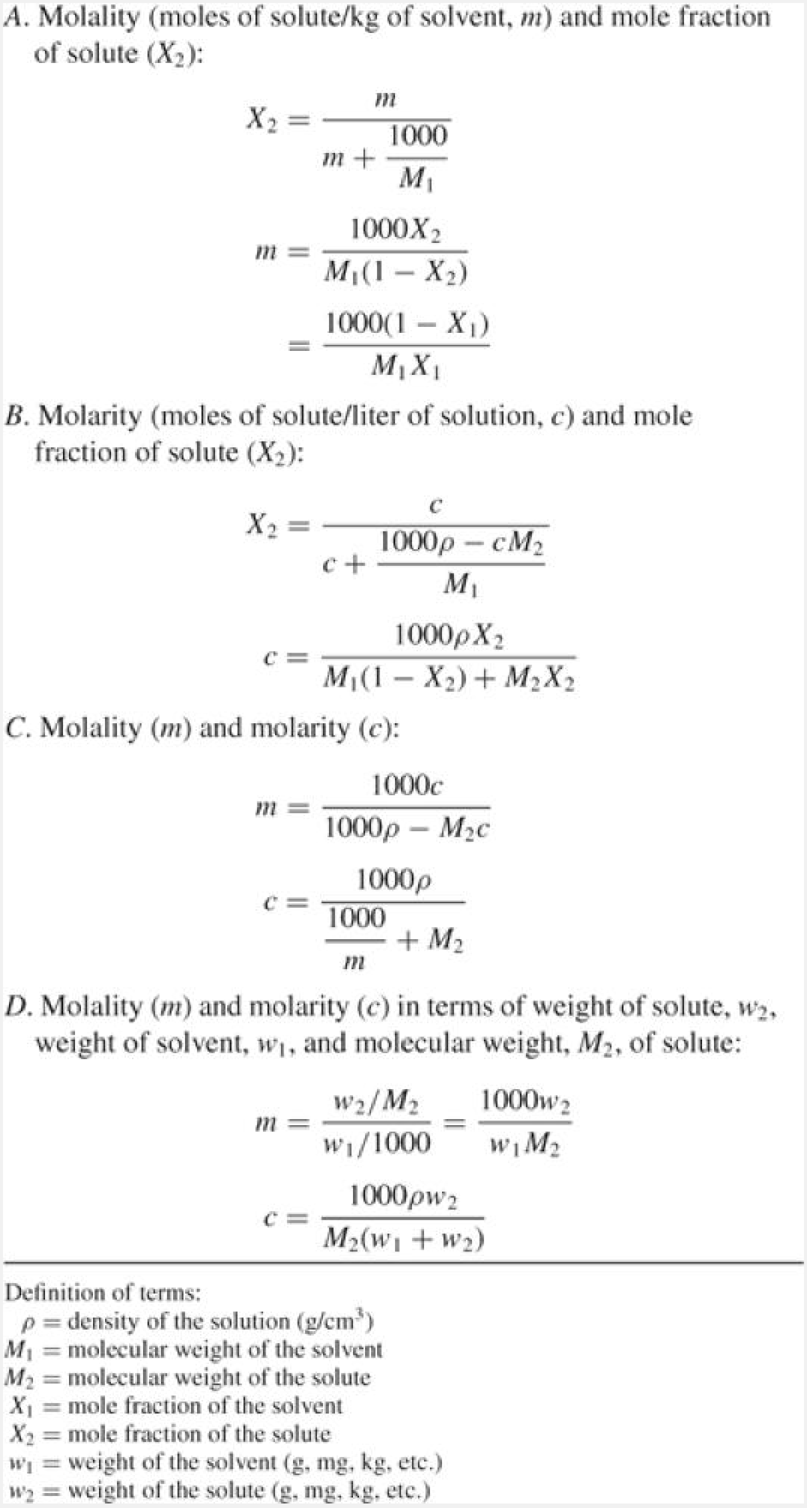
$$= \frac{41.50}{1037.5} \times 100 = 4.00\%$$

One can use the table of conversion equations, Table 5-3, to convert a concentration expression, say molality, into its value in molarity or mole fraction. Alternatively, knowing the weight, w_1, of a solvent, the weight, w_2, of the solute, and the molecular weight, M_2, of the solute, one can calculate the molarity, *c*, or the molality, *m*, of the solution. As an exercise, the reader should derive an expression relating X_1 to X_2 to the weights w_1 and w_2 and the solute's molecular weight, M_2. The data inExample 5-1 are useful for determining whether your derived equation is correct.

Equivalent Weights

One gram atom of hydrogen weighs 1.008 g and consists of 6.02×10^{23} atoms (Avogadro's number) of hydrogen. This gram atomic weight of hydrogen combines with 6.02×10^{23} atoms of fluorine and with half of 6.02×10^{23} atoms of oxygen. One gram atom of fluorine weighs 19 g, and 1 g atom of oxygen weighs 16 g. Therefore, 1.008 g of hydrogen combines with 19 g of fluorine and with half of 16 or 8 g of

oxygen. The quantities of fluorine and oxygen combining with 1.008 g of hydrogen are referred to as the equivalent weight of the combining atoms. One equivalent (Eq) of fluorine (19 g) combines with 1.008 g of hydrogen. One equivalent of oxygen (8 g) also combines with 1.008 g of hydrogen.



A. Molality (moles of solute/kg of solvent, m) and mole fraction of solute (X_2):

$$X_2 = \frac{m}{m + \dfrac{1000}{M_1}}$$

$$m = \frac{1000X_2}{M_1(1 - X_2)}$$

$$= \frac{1000(1 - X_1)}{M_1 X_1}$$

B. Molarity (moles of solute/liter of solution, c) and mole fraction of solute (X_2):

$$X_2 = \frac{c}{c + \dfrac{1000\rho - cM_2}{M_1}}$$

$$c = \frac{1000\rho X_2}{M_1(1 - X_2) + M_2X_2}$$

C. Molality (m) and molarity (c):

$$m = \frac{1000c}{1000\rho - M_2c}$$

$$c = \frac{1000\rho}{\dfrac{1000}{m} + M_2}$$

D. Molality (m) and molarity (c) in terms of weight of solute, w_2, weight of solvent, w_1, and molecular weight, M_2, of solute:

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000w_2}{w_1M_2}$$

$$c = \frac{1000\rho w_2}{M_2(w_1 + w_2)}$$

Definition of terms:

ρ = density of the solution (g/cm^3)
M_1 = molecular weight of the solvent
M_2 = molecular weight of the solute
X_1 = mole fraction of the solvent
X_2 = mole fraction of the solute
w_1 = weight of the solvent (g, mg, kg, etc.)
w_2 = weight of the solute (g, mg, kg, etc.)

Table 5-3 Conversion Equations for Concentration Terms

It is observed that 1 equivalent weight (19 g) of fluorine is identical with its atomic weight. Not so with oxygen; its gram equivalent weight (8 g) is equal to half its atomic weight. Stated otherwise, the atomic weight of fluorine contains 1 Eq of fluorine, whereas the atomic weight of oxygen contains 2 Eq. The equation relating these atomic quantities is as follows (the equation for molecules is quite similar to that for atoms, as seen in the next paragraph):

$$\text{Equivalent weight} = \frac{\text{Atomic weight}}{\text{Number of equivalents per atomic weight (valence)}} \qquad (5\text{–}3)$$

The number of equivalents per atomic weight, namely, 1 for fluorine and 2 for oxygen, is the common *valence* of these elements. Many elements may have more than one valence and hence several equivalent weights, depending on the reaction under consideration. Magnesium will combine with two atoms of fluorine, and each fluorine can combine with one atom of hydrogen. Therefore, the valence of magnesium is 2, and its equivalent weight, according to equation **(**5-3**)**, is one half of its atomic weight (24/2 = 12 g/Eq). Aluminum will combine with three atoms of fluorine; the valence of aluminum is therefore 3 and its equivalent weight is one third of its atomic weight, or 27/3 = 9 g/Eq.

The concept of equivalent weights not only applies to atoms but also extends to molecules. The equivalent weight of sodium chloride is identical to its molecular weight, 58.5 g/Eq; that is, the equivalent weight of sodium chloride is the sum of the equivalent weights of sodium (23 g) and chlorine (35.5 g), or 58.5 g/Eq. The equivalent weight of sodium chloride is identical to its molecular weight, 58.5 g, because the valence of sodium and chlorine is each 1 in the compound. The equivalent weight of Na_2CO_3 is numerically half of its molecular weight. The valence of the carbonate ion, CO_3^{2-}, is 2, and its equivalent weight is 60/2 = 30 g/Eq. Although the valence of sodium is 1, two atoms are present in Na_2CO_3, providing a weight of 2 × 23 g = 46 g; its equivalent weight is one half of this, or 23 g/Eq. The equivalent weight of Na_2CO_3 is therefore 30 + 23 = 53 g, which is one half the molecular weight. The relationship of equivalent weight to molecular weight for molecules such as NaCl and Na_2CO_3 is [compare equation **(**5-3**)** for atoms]

$$\text{Equivalent weight (g/Eq)} = \frac{\text{molecular weight (g/mole)}}{\text{equivalent/mole}} \qquad (5\text{–}4)$$

Example 5-2
Calculation of Equivalent Weight

(*a*) What is the number of equivalents per mole of K_3PO_4, and what is the equivalent weight of this salt? (*b*) What is the equivalent weight of KNO_3? (*c*) What is the number of equivalents per mole of $Ca_3(PO_4)_2$, and what is the equivalent weight of this salt?

a. K_3PO_4 represents 3 Eq/mole, and its equivalent weight is numerically equal to one third of its molecular weight, namely, (212 g/mole) ÷ (3 Eq/mole) = 70.7 g/Eq.
b. The equivalent weight of KNO_3 is also equal to its molecular weight, or 101 g/Eq.
c. The number of equivalents per mole for $Ca_3(PO_4)_2$ is 6 (i.e., three calcium ions each with a valence of 2 or two phosphate ions each with a valence of 3). The equivalent weight of $Ca_3(PO_4)_2$ is therefore one sixth of its molecular weight, or 310/6 = 51.7 g/Eq.

For a complex salt such as monobasic potassium phosphate (potassium acid phosphate), KH_2PO_4 (molecular weight, 136 g), the equivalent weight depends on how the compound is used. If it is used for its potassium content, the equivalent weight is identical to its molecular weight, or 136 g. When it is used as a buffer for its hydrogen content, the equivalent weight is one half of the molecular weight, 136/2 = 68 g, because two hydrogen atoms are present. When used for its phosphate content, the equivalent weight of KH_2PO_4 is one third of the molecular weight, 136/3 = 45.3 g, because the valence of phosphate is 3.

As defined in Table 5-2, the normality of a solution is the equivalent weight of the solute in 1 liter of solution. For NaF, KNO_3, and HCl, the number of equivalent weights equals the number of molecular weights, and normality is identical with molarity. For H_3PO_4, the equivalent weight is one third of the molecular weight, 98 g/3 = 32.67 g/Eq, assuming complete reaction, and a 1 N solution of H_3PO_4 is prepared by weighing 32.67 g of H_3PO_4 and bringing it to a volume of 1 liter with water. For a 1 N solution of sodium bisulfate (sodium acid sulfate), $NaHSO_4$ (molecular weight 120 g), the weight of salt needed depends on the species for which the salt is used. If used for sodium or hydrogen, the equivalent weight would equal the molecular weight, or 120 g/Eq. If the solution were used for its sulfate content, 120/2 = 60 g of $NaHSO_4$ would be weighed out and sufficient water added to make 1 liter of solution.

In electrolyte replacement therapy, solutions containing various electrolytes are injected into a patient to correct serious electrolyte imbalances. The concentrations are usually expressed as equivalents per liter or milliequivalents per liter. For example, the normal plasma concentration of sodium ions in humans is about 142 mEq/liter; the normal plasma concentration of bicarbonate ion, HCO_3^-, is 27 mEq/liter. Equation **(**5-4**)** is useful for calculating the quantity of salts needed to prepare electrolyte solutions in hospital practice. The moles in the numerator and denominator of equation **(**5-4**)** may be replaced with, say, liters to give

$$\text{Equivalent weight (in g/Eq)} = \frac{\text{Grams/liter}}{\text{Equivalents/liter}} \qquad (5\text{–}5)$$

or

$$\text{Equivalent weight (in mg/mEq)} = \frac{\text{Milligrams/liter}}{\text{Milliequivalents/liter}} \qquad (5\text{–}6)$$

Equivalent weight (analogous to molecular weight) is expressed in g/Eq, or what amounts to the same units, mg/mEq.

Example 5-3

Ca^{2+} in Human Plasma

Human plasma contains about 5 mEq/liter of calcium ions. How many milligrams of calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$ (molecular weight 147 g/mole), are required to prepare 750 mL of a solution equal in Ca^{2+} to human plasma? The equivalent weight of the dihydrate salt $CaCl_2 \cdot 2H_2O$ is half of its molecular weight, 147/2 = 73.5 g/Eq, or 73.5 mg/mEq. Using equation (5-6), we obtain

$$73.5\ \text{mg/mEq} = \frac{\text{mg/liter}}{5\ \text{mEq/liter}}$$

$$73.5\ \text{mg/mEq} \times 5\ \text{mEq/liter} = 367.\ 5\ \text{mg/liter}$$

$$\text{For } 750\ \text{cm}^3,\ 367.5 \times \frac{750\ \text{mL}}{1000\ \text{mL}} = 275.6\ \text{mg of } CaCl_2 \bullet 2H_2O$$

Example 5-4

Equivalent Weight and Molecular Weight

Calculate the number of equivalents per liter of potassium chloride, molecular weight 74.55 g/mole, present in a 1.15% w/v solution of KCl.

Using equation (5-5) and noting that the equivalent weight of KCl is identical to its molecular weight, we obtain

$$74.55\ \text{g/Eq} = \frac{11.5\ \text{g/liter}}{\text{Eq/liter}}$$

$$(11.5\ \text{g/liter})/(74.55\ \text{g/Eq}) = 0.154\ \text{Eq/liter (or 154 mEq/liter)}$$

Example 5-5

Sodium Content

What is the Na^+ content in mEq/liter of a solution containing 5.00 g of NaCl per liter of solution? The molecular weight and therefore the equivalent weight of NaCl is 58.5 g/Eq or 58.5 mg/mEq.

$$\text{mEq/liter} = \frac{\text{mg/liter}}{\text{Eq. wt.}} = \frac{5000\ \text{mg/liter}}{58.5\ \text{mg/mEq}}$$

$$= 85.47\ \text{mEq of } Na^+ \text{per liter}$$

Ideal and Real Solutions

As stated earlier, the colligative properties of nonelectrolytes are ordinarily regular; on the other hand, solutions of electrolytes show apparent deviations. The remainder of this chapter relates to solutions of nonelectrolytes, except where comparison with an electrolyte system is desirable for clarity. Solutions of electrolytes are dealt with in Chapter 6.

An ideal gas is defined in Chapter 2 as one in which there is no attraction between the molecules, and it is found desirable to establish an ideal gas equation to which the properties of real gases tend as the pressure approaches zero. Consequently, the ideal gas law is referred to as a *limiting law*. It is convenient to define an *ideal solution* as one in which there is no change in the properties of the components, other than dilution, when they are mixed to form the solution. No heat is evolved or absorbed during the mixing process, and the final volume of the solution represents an additive property of the individual constituents. Stated another way, no shrinkage or expansion occurs when the substances are mixed. The constitutive properties, for example, the vapor pressure, refractive index, surface tension, and viscosity of the solution, are the weighted averages of the properties of the pure individual constituents.

Key Concept

Ideality

Ideality in a gas implies the *complete absence* of attractive forces, and ideality in a solution means *complete uniformity* of attractive forces. Because a liquid is a highly condensed state, it cannot be expected to be devoid of attractive forces; nevertheless, if, in a mixture of A and B molecules, the forces between A and A, B and B, and A and B are all of the same order, the solution is considered to be ideal according to the definition just given.

Mixing substances with similar properties forms ideal solutions. For example, when 100 mL of methanol is mixed with 100 mL of ethanol, the final volume of the solution is 200 mL, and no heat is evolved or absorbed. The solution is nearly *ideal*.

When 100 mL of sulfuric acid is combined with 100 mL of water, however, the volume of the solution is about 180 mL at room temperature, and the mixing is attended by a considerable evolution of heat; the solution is said to be *nonideal*, or real. As with gases, some solutions are quite ideal in moderate concentrations, whereas others approach ideality only under extreme dilution.

*Escaping Tendency*3

Two bodies are in thermal equilibrium when their temperatures are the same. If one body is heated to a higher temperature than the other, heat will flow “downhill” from the hotter to the colder body until both bodies are again in thermal equilibrium. This process is described in another way by using the concept of *escaping tendency*, and say that the heat in the hotter body has a greater escaping tendency than that in the colder one. Temperature is a quantitative measure of the escaping tendency of heat, and at thermal equilibrium, when both bodies finally have the same temperature, the escaping tendency of each constituent is the same in all parts of the system.

A quantitative measure of the escaping tendencies of material substances undergoing physical and chemical transformations is *free energy*. For a pure substance, the free energy per mole, or the *molar free energy*, provides a measure of escaping tendency; for the constituent of a solution, it is the *partial molar free energy* or*chemical potential* that is used as an expression of escaping tendency. Chemical potential is discussed in Chapter 3. The free energy of 1 mole of ice is greater than that of liquid water at 1 atm above 0°C and is spontaneously converted into water because

$$\Delta G = G_{\text{liq}} - G_{\text{ice}} < 0$$

At 0°C, at which temperature the system is in equilibrium, the molar free energies of ice and water are identical and Δ*G* = 0. In terms of escaping tendencies, the escaping tendency of ice is greater than the escaping tendency of liquid water above 0°C, whereas at equilibrium, the escaping tendencies of water in both phases are identical.

Ideal Solutions and Raoult's Law

The vapor pressure of a solution is a particularly important property because it serves as a quantitative expression of escaping tendency. In 1887, Raoult recognized that, in an ideal solution, the partial vapor pressure of each volatile constituent is equal to the vapor pressure of the pure constituent multiplied by its mole fraction in the solution. Thus, for two constituents A and B,

$$p_A = p_A{}^{\circ} X_A \qquad (5\text{–}7)$$

$$p_B = p_B{}^{\circ} X_B \qquad (5\text{–}8)$$

where p_A and p_B are the partial vapor pressures of the constituents over the solution when the mole fraction concentrations are X_A and X_B, respectively. The vapor pressures of the pure components are $p_A{}^{\circ}$ and $p_B{}^{\circ}$, respectively. For example, if the vapor pressure of ethylene chloride in the pure state is 236 mm Hg at 50°C, then in a solution consisting of a mole fraction of 0.4 ethylene chloride and 0.6 benzene, the partial vapor pressure of ethylene chloride is 40% of 236 mm, or 94.4 mm. Thus, in an ideal solution, when liquid A is mixed with liquid B, the vapor pressure of A is reduced by dilution with B in a manner depending on the mole fractions of A and B present in the final solution. This will diminish the escaping tendency of each constituent, leading to a reduction in the rate of escape of the molecules of A and B from the surface of the liquid.

Example 5-6

Partial Vapor Pressure

What is the partial vapor pressure of benzene and of ethylene chloride in a solution at a mole fraction of benzene of 0.6? The vapor pressure of pure benzene at 50°C is 268 mm, and the corresponding $p_A{}^{\circ}$ for ethylene chloride is 236 mm. We have

$$p_B = 268 \times 0.6 = 160.8 \text{ mm}$$

$$p_A = 236 \times 0.4 = 94.4 \text{ mm}$$

If additional volatile components are present in the solution, each will produce a partial pressure above the solution, which can be calculated from Raoult's law. The total pressure is the sum of the partial pressures of all the constituents. In Example 5-6, the total vapor pressure P is calculated as follows:

$$P = p_A + p_B = 160.8 + 94.4 = 255.2 \text{ mm}$$

The vapor pressure–composition curve for the binary system benzene and ethylene chloride at 50°C is shown in Figure 5-1. The three lines represent the partial pressure of ethylene chloride, the partial pressure of benzene, and the total

pressure of the solution as a function of the mole fraction of the constituents.

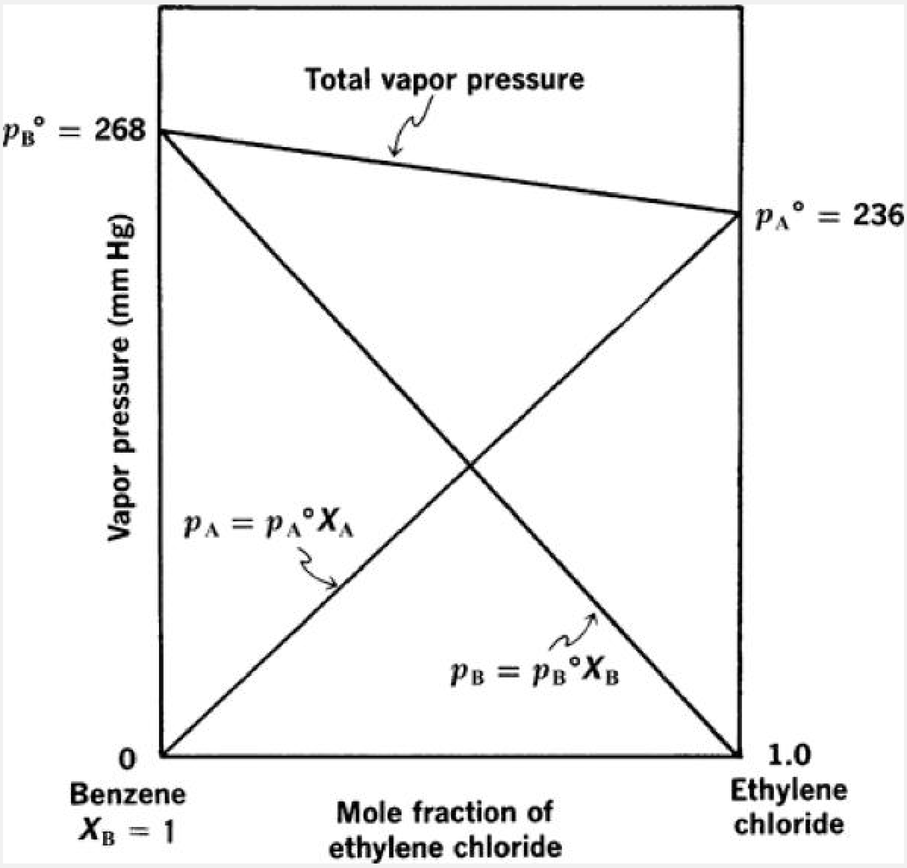


Fig. 5-1. Vapor pressure–composition curve for an ideal binary system.

Aerosols and Raoult's Law

Aerosol dispensers have been used to package some drugs since the early 1950s. An aerosol contains the drug concentrated in a solvent or carrier liquid and a propellant mixture of the proper vapor characteristics. Chlorofluorocarbons (CFCs) were very popular propellants in aerosols until about 1989. Since that time they have been replaced in nearly every country because of the negative effects that CFCs have on the Earth's ozone layer. Today, two volatile hydrocarbons are commonly used as propellants in metered dose inhalers for treating asthma, hydrofluoroalkane 134a (1,1,1,2,tetrafluoroethane) or hydrofluoroalkane 227 (1,1,1,2,3,3,3-heptafluoropropane) or combinations of the two. Early metered dose inhalers commonly used trichloromonofluoromethane (CFC propellant 11) and dichlorodifluoromethane (CFC propellant 12) as propellants. CFC 11 and CFC 12 were used in various proportions to yield the proper vapor pressure and density at room temperature. Although still used with drugs, these halogenated hydrocarbons are no longer used in cosmetic aerosols and have been replaced by nitrogen and unsubstituted hydrocarbons. Since propellants represent the vast majority (>99%) of the dose delivered by a metered dose inhaler, it must be nontoxic to the patient.

Example 5-7

Aerosol Vapor Pressure

The vapor pressure of pure CFC 11 (molecular weight 137.4) at 21°C is $p_{11}° = 13.4$ lb/in2 (psi) and that of CFC 12 (molecular weight 120.9) is $p_{12}° = 84.9$ psi. A 50:50 mixture by gram weight of the two propellants consists of 50 ÷ 137.4 g/mole = 0.364 mole of CFC 11 and 50 g ÷ 120.9 g/mole = 0.414 mole of CFC 12. What is the partial pressure of CFCs 11 and 12 in the 50:50 mixture, and what is the total vapor pressure of this mixture? We write

$$p_{11} = \frac{n_{11}}{n_{11} + n_{12}} p_{11}^{\circ} = \frac{0.364}{0.364 + 0.414}(13.4) = 6.27 \text{ psi}$$

$$p_{12} = \frac{n_{12}}{n_{11} + n_{12}} p_{12}^{\circ} = \frac{0.414}{0.364 + 0.414}(84.9) = 45.2 \text{ psi}$$

The total vapor pressure of the mixture is

$$6.27 + 45.2 = 51.5 \text{ psi}$$

To convert to gauge pressure (psig), one subtracts the atmospheric pressure of 14.7 psi:

$$51.5 - 14.7 = 36.8 \text{ psig}$$

The psi values just given are measured with respect to zero pressure rather than with respect to the atmosphere and are sometimes written psia to signify *absolute* pressure.

Real Solutions

Ideality in solutions presupposes complete uniformity of attractive forces. Many examples of solution pairs are known, however, in which the “cohesive” attraction of A for A exceeds the “adhesive” attraction existing between A and B. Similarly, the attractive forces between A and B may be greater than those between A and A or B and B. This may occur even though the liquids are miscible in all proportions. Such mixtures are *real* or *nonideal*; that is, they do not adhere to Raoult's law throughout the entire range of composition. Two types of deviation from Raoult's law are recognized, *negative deviation* and *positive deviation*.

When the “adhesive” attractions between molecules of different species exceed the “cohesive” attractions between like molecules, the vapor pressure of the solution is less than that expected from Raoult's ideal solution law, and *negative deviation* occurs. If the deviation is sufficiently great, the total vapor pressure curve shows a minimum, as observed in Figure 5-2, where A is chloroform and B is acetone.

The dilution of constituent A by addition of B normally would be expected to reduce the partial vapor pressure of A; this is the simple dilution effect embodied in Raoult's law. In the case of liquid pairs that show negative deviation from the law, however, the addition of B to A tends to reduce the vapor pressure of A to a greater extent than can be accounted for by the simple dilution effect. Chloroform and acetone manifest such an attraction for one another through the formation of a hydrogen bond, thus further reducing the escaping tendency of each constituent. This pair forms a weak compound,

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

that can be isolated and identified. Reactions between dipolar molecules, or between a dipolar and a nonpolar molecule, may also lead to negative deviations. The interaction in these cases, however, is usually so weak that no definite compound can be isolated.

When the interaction between A and B molecules is less than that between molecules of the pure constituents, the presence of B molecules reduces the interaction of the A molecules, and A molecules correspondingly reduce the B—B interaction. Accordingly, the dissimilarity of polarities or internal pressures of the constituents results in a greater escaping tendency of both the A and the B molecules. The partial vapor pressure of the constituents is greater than that expected from Raoult's law, and the system is said to exhibit *positive deviation*. The total vapor pressure often shows a maximum at one particular composition if the deviation is sufficiently large. An example of positive deviation is shown in Figure 5-3. Liquid pairs that demonstrate positive deviation are benzene and ethyl alcohol, carbon disulfide and acetone, and chloroform and ethyl alcohol.

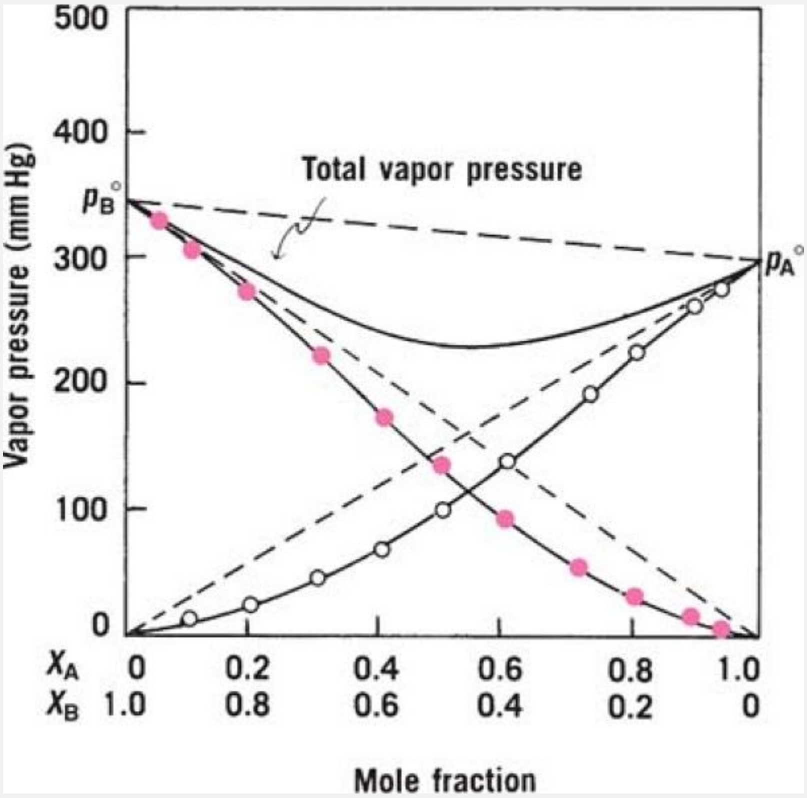


Fig. 5-2. Vapor pressure of a system showing negative deviation from Raoult's law.

Raoult's law does not apply over the entire concentration range in a nonideal solution. It describes the behavior of either component of a real liquid pair only when that substance is present in high concentration and thus is considered to be the solvent. Raoult's law can be expressed as

$$p_{\text{solvent}} = p^{\circ}_{\text{solvent}} X_{\text{solvent}} \qquad \textbf{(5–9)}$$

in such a situation, and it is valid only for the solvent of a nonideal solution that is sufficiently dilute with respect to the solute. It cannot hold for the component in low concentration, that is, the solute, in a dilute nonideal solution.

These statements will become clearer when one observes, in Figure 5-2, that the actual vapor pressure curve of chloroform (component A) approaches the ideal curve defined by Raoult's law as the solution composition approaches pure chloroform. Raoult's law can be used to describe the behavior of chloroform when it is present in high concentration (i.e., when it is the solvent). The ideal equation is not applicable to acetone (component B), however, which is present in low concentration in this region of the diagram, because the actual curve for acetone does not coincide with the ideal line. When one studies the left side of Figure 5-2, one observes that the conditions are reversed: Acetone is considered to be the solvent here, and its vapor pressure curve tends to coincide with the ideal curve. Chloroform is the solute in this range, and its curve does not approach the ideal line. Similar considerations apply to Figure 5-3.

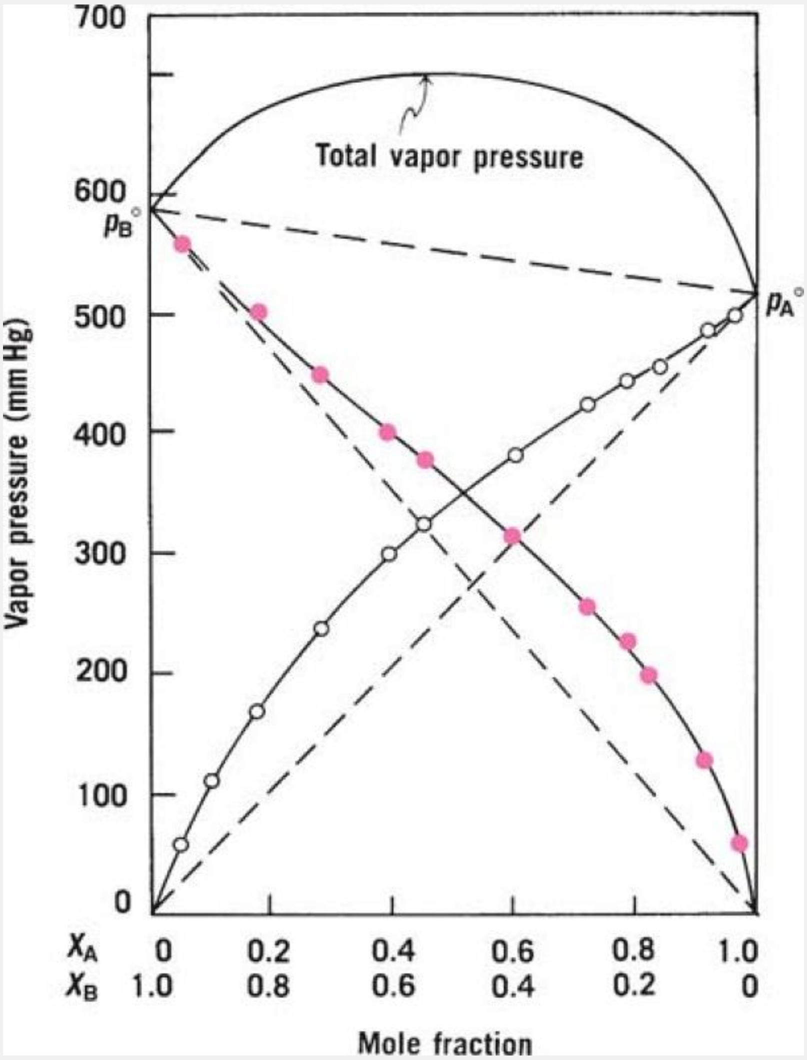


Fig. 5-3. Vapor pressure of a system showing positive deviation from Raoult's law.

Henry's Law

The vapor pressure curves for both acetone and chloroform as *solutes* are observed to lie considerably below the vapor pressure of an ideal mixture of this pair. The molecules of solute, being in relatively small number in the two regions of the diagram, are completely surrounded by molecules of solvent and so reside in a uniform environment. Therefore, the partial pressure or escaping tendency of chloroform at low concentration is in some way proportional to its mole fraction, but, as observed in Figure 5-2, the proportionality constant is not equal to the vapor pressure of the pure substance. The vapor pressure–composition relationship of the solute cannot be expressed by Raoult's law but instead by an equation known as *Henry's law*:

$$p_{\text{solute}} - k_{\text{solute}} X_{\text{solute}} \qquad \textbf{(5–10)}$$

where *k* for chloroform is less than p°_{CHCL3}. Henry's law applies to the solute and Raoult's law applies to the solvent in dilute solutions of real liquid pairs. Of course, Raoult's law also applies over the entire concentration range (to both solvent and solute) when the constituents are sufficiently similar to form an ideal solution. Under any circumstance, when the partial vapor pressures of both of the constituents are directly proportional to the mole fractions over the entire range, the solution is said to be ideal; Henry's law becomes identical with Raoult's law, and *k* becomes equal to *p*°. Henry's law is used for the study of gas solubilities discussed later in the book.

Distillation of Binary Mixtures

The relationship between vapor pressure (and hence boiling point) and composition of binary liquid phases is the underlying principle in distillation. In the case of miscible liquids, instead of plotting vapor pressure versus composition, it is more useful to plot the boiling points of the various mixtures, determined at atmospheric pressure, against composition.

The higher the vapor pressure of a liquid—that is, the more volatile it is—the lower is the boiling point. Because the vapor of a binary mixture is always richer in the more volatile constituent, the process of distillation can be used to separate the more volatile from the less volatile constituent. Figure 5-4 shows a mixture of a high-boiling liquid A and a low-boiling liquid B. A mixture of these substances having the composition *a* is distilled at the boiling point *b*. The composition of the vapor v_1 in equilibrium with the liquid at this temperature is *c*; this is also the composition of the distillate when it is condensed. The vapor is therefore richer in B than the liquid from which it was distilled. If a fractionating column is used, A and B can be completely separated. The vapor rising in the column is met by the condensed vapor or downward-flowing liquid. As the rising vapor is cooled by contact with the liquid, some of the lower-boiling fraction condenses, and the vapor contains more of the volatile component than it did when it left the retort. Therefore, as the vapor proceeds up the fractionating column, it becomes progressively richer in the more volatile component B, and the liquid returning to the distilling retort becomes richer in the less volatile component A.

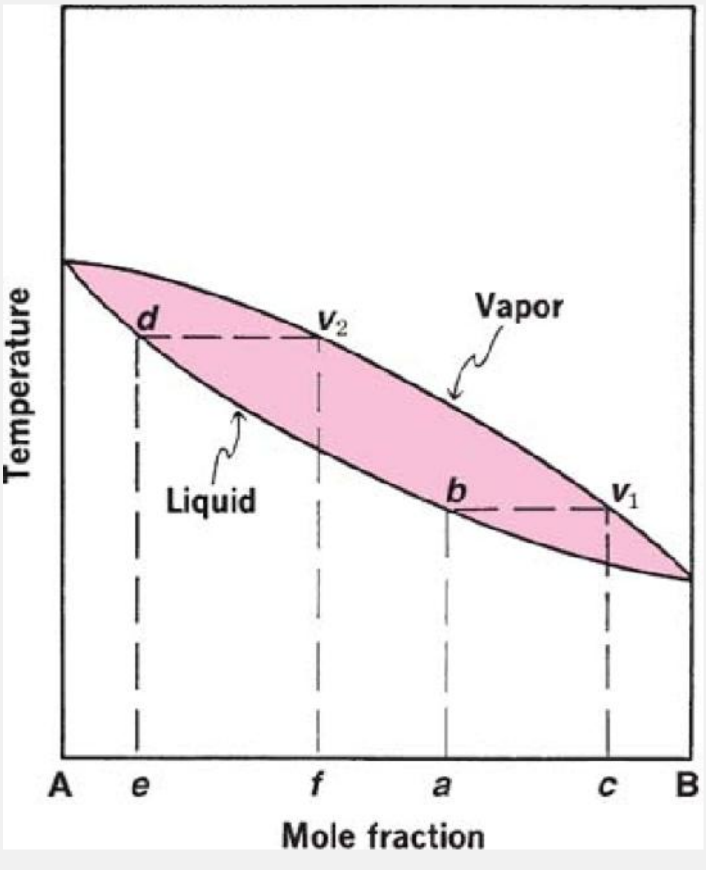


Fig. 5-4. Boiling point diagram of an ideal binary mixture.

Figure 5-4 shows the situation for a pair of miscible liquids exhibiting ideal behavior. Because vapor pressure curves can show maxima and minima (see Figs. 5-2and 5-3), it follows that boiling point curves will show corresponding minima and maxima, respectively. With these mixtures, distillation produces either pure A or pure B plus a mixture of constant composition and constant boiling point. This latter is known as an *azeotrope* (Greek: “boil unchanged”) or *azeotropic mixture*. It is not possible to separate such a mixture completely into two pure components by simple fractionation. If the vapor pressure curves show a minimum (i.e., negative deviation from Raoult's law), the azeotrope has the highest boiling point of all the mixtures possible; it is therefore least volatile and remains in the flask, whereas either pure A or pure B is distilled off. If the vapor pressure curve exhibits a maximum (showing a positive deviation from Raoult's law), the azeotrope has the lowest boiling point and forms the distillate. Either pure A or pure B then remains in the flask.

When a mixture of HCl and water is distilled at atmospheric pressure, an azeotrope is obtained that contains 20.22% by weight of HCl and that boils at 108.58°C. The composition of this mixture is accurate and reproducible enough that the solution can be used as a standard in analytic chemistry. Mixtures of water and acetic acid and of chloroform and acetone yield azeotropic mixtures with maxima in their boiling point curves and minima in their vapor pressure curves. Mixtures of ethanol and water and of methanol and benzene both show the reverse behavior, namely, minima in the boiling point curves and maxima in the vapor pressure curves.

When a mixture of two practically *immiscible* liquids is heated while being agitated to expose the surfaces of both liquids to the vapor phase, each constituent independently exerts its own vapor pressure as a function of temperature as though the other constituent were not present. Boiling begins, and distillation may be effected when the sum of the partial pressures of the two immiscible liquids just exceeds the atmospheric pressure. This principle is applied in *steam distillation*, whereby many organic compounds insoluble in water can be purified at a temperature well below the point at which decomposition occurs. Thus, bromobenzene alone boils at 156.2°C, whereas water boils at 100°C at a pressure of 760 mm Hg. A mixture of the two, however, in any proportion, boils at 95°C. Bromobenzene can thus be distilled at a temperature 61°C below its normal boiling point. Steam distillation is particularly useful for obtaining volatile oils from plant tissues without decomposing the oils.

Colligative Properties

When a *nonvolatile solute* is combined with a *volatile solvent*, the vapor above the solution is provided solely by the solvent. The solute reduces the escaping tendency of the solvent, and, on the basis of Raoult's law, the vapor pressure of a solution containing a nonvolatile solute is lowered proportional to the relative number.

Key Concept

Colligative Properties

The freezing point, boiling point, and osmotic pressure of a solution also depend on the relative proportion of the molecules of the solute and the solvent. These are called *colligative properties* (Greek: “collected together”) because they depend chiefly on the number rather than on the nature of the constituents.

Lowering of the Vapor Pressure

According to Raoult's law, the vapor pressure, p_1, of a solvent over a dilute solution is equal to the vapor pressure of the pure solvent, $p_1°$, times the mole fraction of solvent in the solution, X_1. Because the solute under discussion here is considered to be nonvolatile, the vapor pressure of the solvent, p_1, is identical to the total pressure of the solution, p.

It is more convenient to express the vapor pressure of the solution in terms of the concentration of the solute rather than the mole fraction of the solvent, and this may be accomplished in the following way. The sum of the mole fractions of the constituents in a solution is unity:

$$X_1 + X_2 = 1 \qquad (5\text{–}11)$$

Therefore,

$$X_1 = 1 - X_2 \qquad (5\text{–}12)$$

where X_1 is the mole fraction of the solvent and X_2 is the mole fraction of the solute. Raoult's equation can be modified by substituting equation **(**5-12**)** for X_1 to give

$$p = p_1{}^{\circ}(1 - X_2) \qquad (5\text{–}13)$$

$$p_1{}^{\circ} - p = p_1{}^{\circ} X_2 \qquad (5\text{–}14)$$

$$\frac{p_1{}^{\circ} - p}{p_1{}^{\circ}} = \frac{\Delta p}{p_1{}^{\circ}} = X_2 = \frac{n_2}{n_1 + n_2} \qquad (5\text{–}15)$$

In equation **(**5-15**)**, $\Delta p = p_1{}^{\circ} - p$ is the lowering of the vapor pressure and $\Delta p/p_1{}^{\circ}$ is the *relative vapor pressure lowering*. The relative vapor pressure lowering depends only on the mole fraction of the solute, X_2, that is, on the number of solute particles in a definite volume of solution. Therefore, the relative vapor pressure lowering is a *colligative property*.

Example 5-8

Relative Vapor Pressure Lowering of a Solution

Calculate the relative vapor pressure lowering at 20°C for a solution containing 171.2 g of sucrose (w_2) in 100 g (w_1) of water. The molecular weight of sucrose (M_2) is 342.3 and the molecular weight of water (M_1) is 18.02 g/mole. We have

$$\text{Moles of sucrose} = n_2 = \frac{w_2}{M_2} = \frac{171.2}{342.3} = 0.500$$

$$\text{Moles of water} = n_1 = \frac{w_1}{M_1} = 1000/18.02 = 55.5$$

$$\frac{\Delta p}{p_1{}^{\circ}} = X_2 = \frac{n_2}{n_1 + n_2}$$

$$\frac{\Delta p}{p_1{}^{\circ}} = \frac{0.50}{55.5 + 0.50} = 0.0089$$

Key Concept

Osmolality

In most solutions, changes in concentration are accompanied by linear and proportional changes in the cardinal colligative properties of the solvent—vapor pressure, freezing point, and boiling point. Measuring any of these properties provides an indirect indication of osmolality, but among them, only vapor pressure can be determined passively without a forced change in the sample's physical state.

Notice that in Example 5-8, the relative vapor pressure lowering is a dimensionless number, as would be expected from its definition. The result can also be stated as a percentage; the vapor pressure of the solution has been lowered 0.89% by the 0.5 mole of sucrose.

The mole fraction, $n_2/(n_1 + n_2)$, is nearly equal to, and may be replaced by, the mole ratio n_2/n_1 in a dilute solution such as this one. Then, the relative vapor pressure lowering can be expressed in terms of molal concentration of the solute by setting the weight of solvent w_1 equal to 1000 g. For an aqueous solution,

$$X_2 = \frac{\Delta P}{p_1{}^{\circ}} \cong \frac{n_2}{n_1} = \frac{w_2/M_2}{1000/M_1} = \frac{m}{55.5} = 0.018\,m \qquad (5\text{–}16)$$

Example 5-9

Calculation of the Vapor Pressure

Calculate the vapor pressure when 0.5 mole of sucrose is added to 1000 g of water at 20°C. The vapor pressure of water at 20°C is 17.54 mm Hg. The vapor pressure lowering of the solution is

$$\begin{aligned} \Delta p &= p_1{}^{\circ} X_2 \cong p_1{}^{\circ} \times 0.018 \times m \\ &= 17.54 \times 0.018 \times 0.5 \\ &= 0.158\ \text{mm} \cong 0.16\ \text{mm} \end{aligned}$$

The final vapor pressure is

$$17.54 - 0.16 = 17.38\ \text{mm}$$

Elevation of the Boiling Point

The normal boiling point is the temperature at which the vapor pressure of the liquid becomes equal to an external pressure of 760 mm Hg. A solution will boil at a higher temperature than will the pure solvent. This is the colligative property called boiling point elevation. As shown in Figure 5-5, the more of the solute that is dissolved, the greater is the effect. The boiling point of a solution of a nonvolatile solute is higher than that of the pure solvent owing to the fact that the solute lowers the vapor pressure of the solvent. This may be seen by referring to the curves in Figure 5-6. The vapor pressure curve for the solution lies below that of the pure solvent, and the temperature of the solution must be elevated to a value above that of the solvent in order to reach the normal boiling point. The elevation of the boiling point is shown in the figure as $T - T_o = \Delta T_b$. The ratio of the elevation of the boiling point, ΔT_b, to the vapor pressure lowering, $\Delta p = p° - p$, at 100°C is approximately a constant at this temperature; it is written as

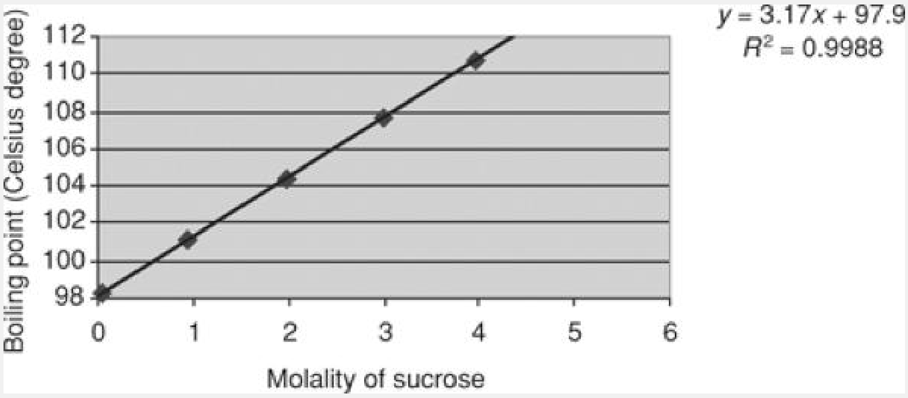


Fig. 5-5. Theoretical plot of the normal boiling point for water (solvent) as a function of molality in solutions containing sucrose (a nonvolatile solute) in increasing concentrations. Note that the normal boiling point of water increases as the concentration of sucrose increases. This is known as boiling point elevation.

$$\frac{\Delta T_b}{\Delta p} = k' \qquad \textbf{(5–17)}$$

or

$$\Delta T_b = k' \Delta p \qquad \textbf{(5–18)}$$

Moreover, because $p°$ is a constant, the boiling point elevation may be considered proportional to $\Delta p/p°$, the relative lowering of vapor pressure. By Raoult's law, however, the relative vapor pressure lowering is equal to the mole fraction of the solute; therefore,

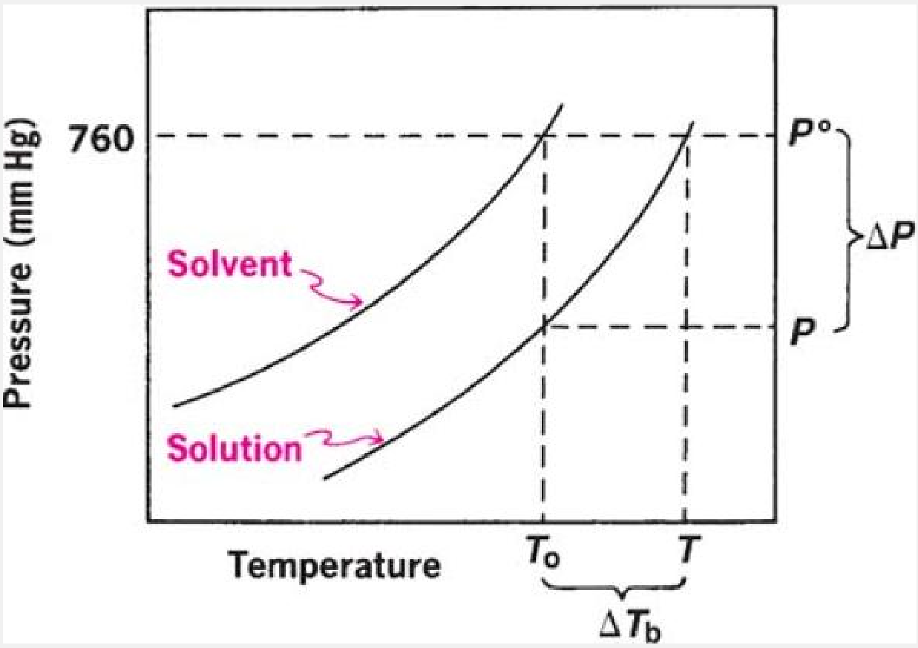


Fig. 5-6. Boiling point elevation of the solvent due to addition of a solute (not to scale).

Table 5-4 Ebullioscopic (K_b) and Cryoscopic (K_f) Constants for Various Solvents

Substance	Boiling Point (°C)	K_b	Freezing Point (°C)	K_f
Acetic acid	118.0	2.93	16.7	3.9
Acetone	56.0	1.71	-94.82*	2.40*
Benzene	80.1	2.53	5.5	5.12
Camphor	208.3	5.95	178.4	37.7
Chloroform	61.2	3.54	-63.5	4.96
Ethyl alcohol	78.4	1.22	-114.49*	3*
Ethyl ether	34.6	2.02	-116.3	1.79*
Phenol	181.4	3.56	42.0	7.27

Water	100.0	0.51	0.00	1.86

*From G. Kortum and J. O'M. Bockris, *Textbook of Electrochemistry*, Vol. II, Elsevier, New York, 1951, pp. 618, 620.

$$\Delta T_b = kX_2 \qquad (5\text{–}19)$$

Because the boiling point elevation depends only on the mole fraction of the solute, it is a colligative property.

In dilute solutions, X_2 is equal approximately to $m/(1000/M_1)$ [equation **(**5-16**)**], and equation **(**5-19**)** can be written as

$$\Delta T_b = \frac{kM_1}{1000}m \qquad (5\text{–}20)$$

or

$$\Delta T_b = K_b m \qquad (5\text{–}21)$$

where ΔT_b is known as the *boiling point elevation* and K_b is called the *molal elevation constant* or the *ebullioscopic constant*. K_b has a characteristic value for each solvent, as seen in Table 5-4. It may be considered as the boiling point elevation for an ideal 1 *m* solution. Stated another way, K_b is the ratio of the boiling point elevation to the molal concentration in an extremely dilute solution in which the system is approximately ideal.

The preceding discussion constitutes a plausible argument leading to the equation for boiling point elevation. A more satisfactory derivation of equation **(**5-21**)**, however, involves the application of the Clapeyron equation, which is written as

$$\frac{\Delta T_b}{\Delta p} = T_b \frac{V_v - V_1}{\Delta H_v} \qquad (5\text{–}22)$$

where V_v and V_1 are the molar volume of the gas and the molar volume of the liquid, respectively, T_b is the boiling point of the solvent, and ΔH_v is the molar heat of vaporization. Because V_1 is negligible compared to V_v, the equation becomes

$$\frac{\Delta T_b}{\Delta p} = T_b \frac{V_v}{\Delta H_v} \qquad (5\text{–}23)$$

and V_v, the volume of 1 mole of gas, is replaced by $RT_b/p°$ to give

$$\frac{\Delta T_b}{\Delta p} = \frac{RT_b^2}{p°\Delta H_v} \qquad (5\text{–}24)$$

or

$$\Delta T_b = \frac{RT_b^2}{\Delta H_v}\frac{\Delta p}{p°} \qquad (5\text{–}25)$$

From equation **(**5-16**)**, $\Delta p/p_1° = X_2$, and equation **(**5-25**)** can be written as

$$\Delta T_b = \frac{RT_b^2}{\Delta H_v} X_2 = kX_2 \qquad (5\text{–}26)$$

which provides a more exact equation with which to calculate ΔT_b.

Replacing the relative vapor pressure lowering $\Delta p/p_1°$ by $m/(1000/M_1)$ according to the approximate expression **(**5-16**)**, in which $w_2/M_2 = m$ and $w_1 = 1000$ s, we obtain the formula

$$\Delta T_b = \frac{RT_b^2 M_1}{1000\,\Delta H_v} m = k_b m \qquad (5\text{–}27)$$

Equation **(**5-27**)** provides a less exact expression with which to calculate ΔT_b.

For water at 100°C, we have $T_b = 373.2$ K, $\Delta H_v = 9720$ cal/mole, $M_1 = 18.02$ g/mole, and $R = 1.987$ cal/mole deg.

Example 5-10

Calculation of the Elevation Constant

A 0.200 *m* aqueous solution of a drug gave a boiling point elevation of 0.103°C. Calculate the approximate molal elevation constant for the solvent, water. Substituting into equation (5-21) yields

$$K_b = \frac{\Delta T_b}{m} = \frac{0.103}{0.200} = 0.515 \text{ deg kg/mole}$$

The proportionality between ΔT_b and the molality is exact only at infinite dilution, at which the properties of real and ideal solutions coincide. The ebullioscopic constant, K_b, of a solvent can be obtained experimentally by measuring ΔT_b at various molal concentrations and extrapolating to infinite dilution ($m = 0$), as seen inFigure 5-7.

Depression of the Freezing Point

The normal freezing point or melting point of a pure compound is the temperature at which the solid and the liquid phases are in equilibrium under a pressure of 1 atm. Equilibrium here means that the tendency for the solid to pass into the liquid state is the same as the tendency for the reverse process to occur, because both the liquid and the solid have the same escaping tendency. The value T_0, shown in Figure 5-8, for water saturated with air at this pressure is arbitrarily assigned a temperature of 0°C. The *triple point* of air-free water, at which solid, liquid, and vapor are in equilibrium, lies at a pressure of 4.58 mm Hg and a temperature of 0.0098°C. It is not identical with the ordinary freezing point of water at atmospheric pressure but is rather the freezing point of water under the pressure of its own vapor. We shall use the triple point in the following argument because the depression ΔT_f here does not differ significantly from ΔT_f at a pressure of 1 atm. The two freezing point depressions referred to are illustrated in Figure 5-7. The ΔT_b of Figure 5-6 is also shown in the diagram.

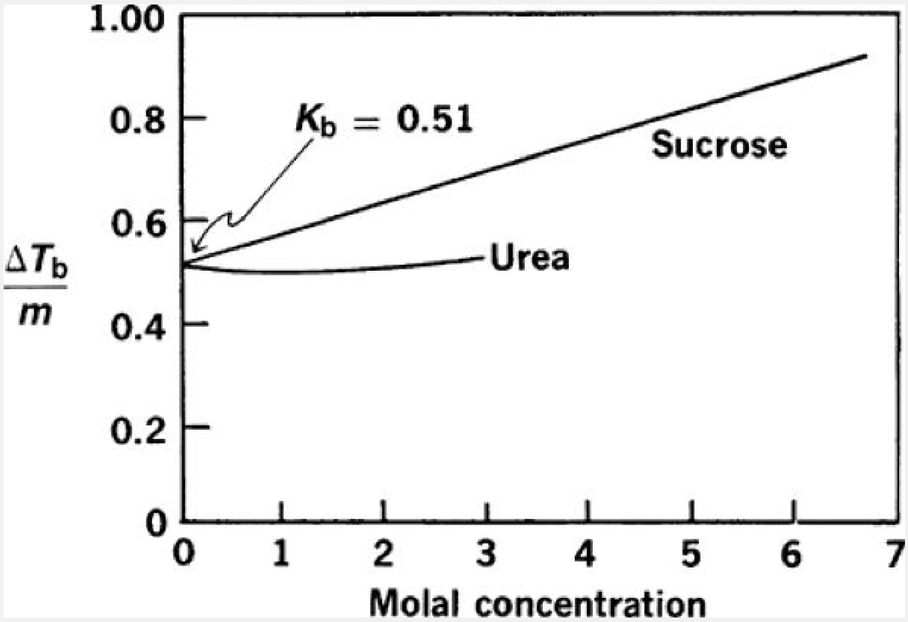


Fig. 5-7. The influence of concentration on the ebullioscopic constant.

If a solute is dissolved in the liquid at the triple point, the escaping tendency or vapor pressure of the liquid solvent is lowered below that of the pure solid solvent. The temperature must drop to reestablish equilibrium between the liquid and the solid. Because of this fact, the freezing point of a solution is always lower than that of the pure solvent. It is assumed that the solvent freezes out in the pure state rather than as a *solid solution* containing some of the solute. When such a complication does arise, special calculations, not considered here, must be used.

The more concentrated the solution, the farther apart are the solvent and the solution curves in the diagram (see Fig. 5-8) and the greater is the freezing point depression. Accordingly, a situation exists analogous to that described for the boiling point elevation, and the freezing point depression is proportional to the molal concentration of the solute. The equation is

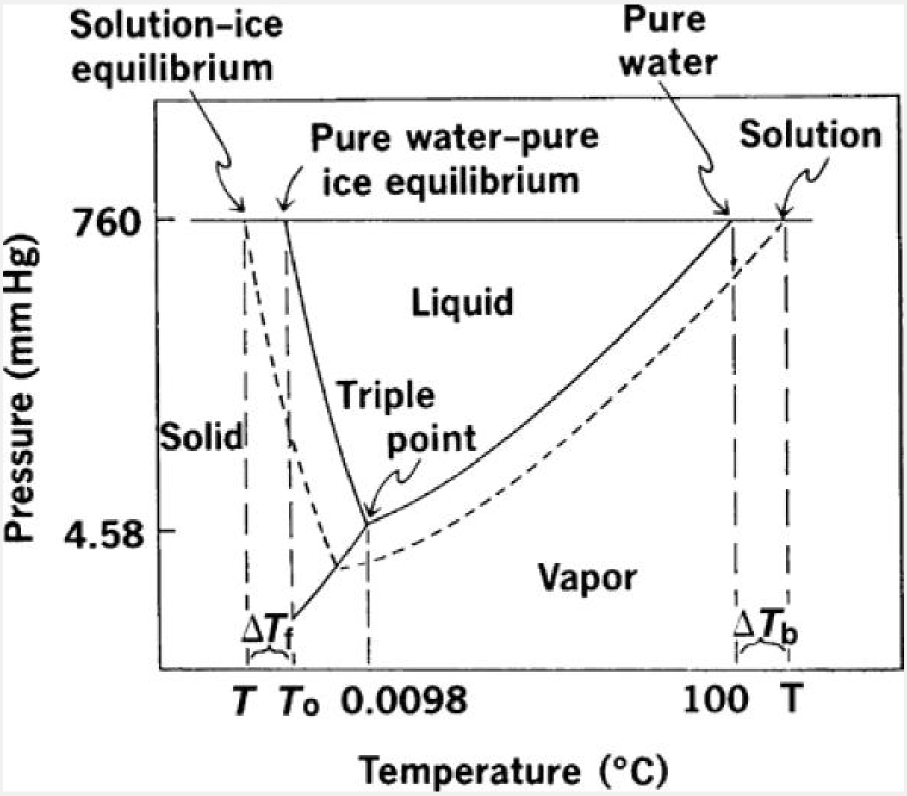


Fig. 5-8. Depression of the freezing point of the solvent, water, by a solute (not to scale).

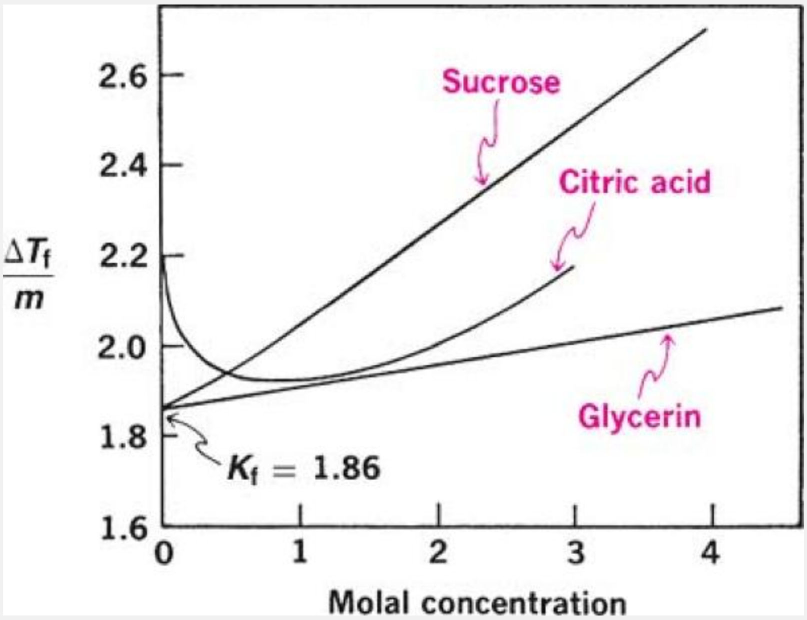


Fig. 5-9. The influence of concentration on the cryoscopic constant for water.

$$\Delta T_f = K_f m \qquad (5\text{–}28)$$

or

$$\Delta T_f = K_f \frac{1000 w_2}{w_1 M_2} \qquad (5\text{–}29)$$

ΔT_f is the *freezing point depression*, and K_f is the *molal depression constant* or the *cryoscopic constant*, which depends on the physical and chemical properties of the solvent.

The freezing point depression of a solvent is a function only of the number of particles in the solution, and for this reason it is referred to as a *colligative* property. The depression of the freezing point, like the boiling point elevation, is a direct result of the lowering of the vapor pressure of the solvent. The value of K_f for water is 1.86. It can be determined experimentally by measuring $\Delta T_f/m$ at several molal concentrations and extrapolating to zero concentration. As seen in Figure 5-9, $K_f$approaches the value of 1.86 for water solutions of sucrose and glycerin as the concentrations tend toward zero, and equation (5-28) is valid only in very dilute solutions. The apparent cryoscopic constant for higher concentrations can be obtained from Figure 5-9. For work in pharmacy and biology, the K_f value of 1.86 can be rounded off to 1.9, which is good approximation for practical use with aqueous solutions, where concentrations are usually lower than 0.1 M. The value of K_f for the solvent in a solution of citric acid is observed not to approach 1.86. This abnormal behavior is to be expected when dealing with solutions of electrolytes. Their irrationality will be explained in Chapter 6, and proper steps will be taken to correct the difficulty.

K_f can also be derived from Raoult's law and the Clapeyron equation. For water at its freezing point, T_f = 273.2 K, ΔH_f is 1437 cal/mole, and

$$K_f = \frac{1.987 \times (273.2)^2 \times 18.02}{1000 \times 1437} = 1.86 \text{ deg kg/mole}$$

The cryoscopic constants, together with the ebullioscopic constants, for some solvents at infinite dilution are given in Table 5-4.

Example 5-11

Calculation of Freezing Point

What is the freezing point of a solution containing 3.42 g of sucrose and 500 g of water? The molecular weight of sucrose is 342. In this relatively dilute solution, K_f is approximately equal to 1.86. We have

$$\Delta T_f = K_f m = K_f \frac{1000\, w_2}{w_1 M_2}$$

$$\Delta T_f = 1.86 \times \frac{1000 \times 3.42}{500 \times 342}$$

$$\Delta T_f = 0.037°\text{C}$$

Therefore, the freezing point of the aqueous solution is -0.037°C.

Example 5-12

Freezing Point Depression

What is the freezing point depression of a 1.3 *m* solution of sucrose in water?

From the graph in Figure 5-8, one observes that the cryoscopic constant at this concentration is about 2.1 rather than 1.86. Thus, the calculation becomes

$$\Delta T_f = K_f \times m = 2.1 \times 1.3 = 2.73°\text{C}$$

Osmotic Pressure

If cobalt chloride is placed in a parchment sac and suspended in a beaker of water, the water gradually becomes red as the solute diffuses throughout the vessel. In this process of *diffusion*, both the solvent and the solute molecules migrate freely. On the other hand, if the solution is confined in a membrane permeable only to the solvent molecules, the phenomenon known as *osmosis* (Greek: “a push or impulse”)4 occurs, and the barrier that permits only the molecules of one of the components (usually water) to pass through is known as a *semipermeable membrane*. A thistle tube over the wide opening of which is stretched a piece of untreated cellophane can be used to demonstrate the principle, as shown in Figure 5-10. The tube is partly filled with a concentrated solution of sucrose, and the apparatus is lowered into a beaker of water. The passage of water through the semipermeable membrane into the solution eventually creates enough pressure to drive the sugar solution up the tube until the hydrostatic pressure of the column of liquid equals the pressure causing the water to pass through the membrane and enter the thistle tube. When this occurs, the solution ceases to rise in the tube. Osmosis is therefore defined as the passage of the solvent into a solution through a semipermeable membrane. This process tends to equalize the escaping tendency of the solvent on both sides of the membrane. Escaping tendency can be measured in terms of vapor pressure or the closely related colligative property *osmotic pressure*. It should be evident that osmosis can also

take place when a concentrated solution is separated from a less concentrated solution by a semipermeable membrane.

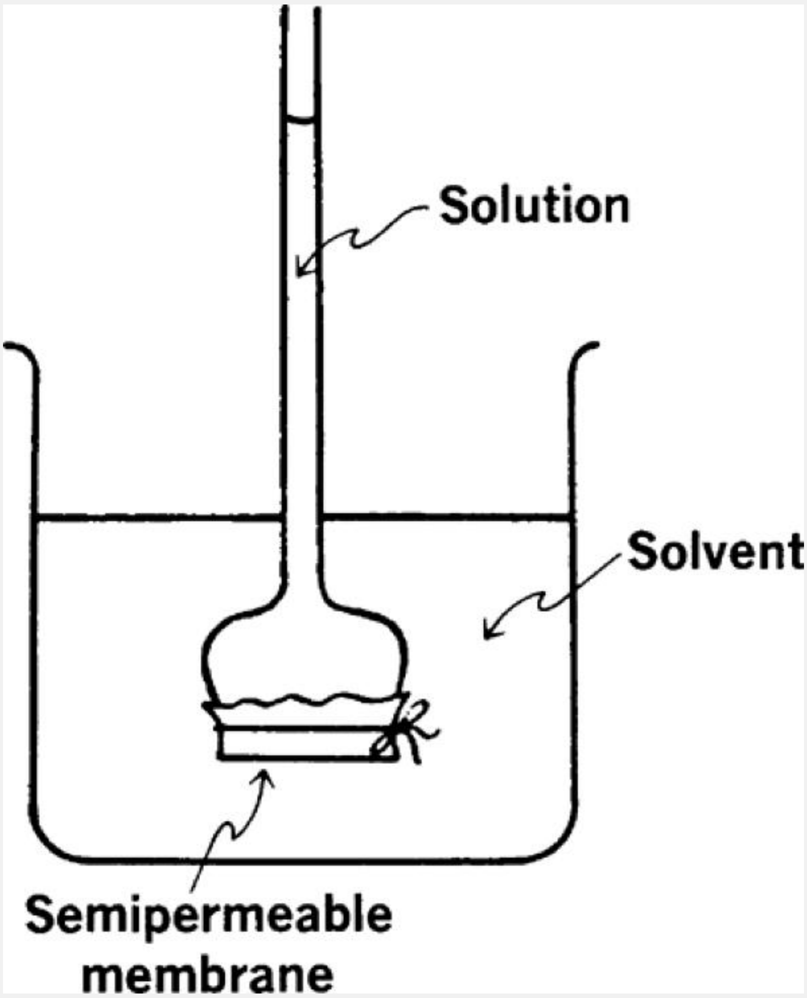


Fig. 5-10. Apparatus for demonstrating osmosis.

Osmosis in some cases is believed to involve the passage of solvent through the membrane by a distillation process or by dissolving in the material of the membrane in which the solute is insoluble. In other cases, the membrane may act as a sieve, having a pore size sufficiently large to allow passage of solvent but not of solute molecules.

In either case, the phenomenon of osmosis depends on the fact that the chemical potential (a thermodynamic expression of escaping tendency) of a solvent molecule in solution is less than exists in the pure solvent. Solvent therefore passes spontaneously into the solution until the chemical potentials of solvent and solution are equal. The system is then at equilibrium. It may be advantageous for the student to consider osmosis in terms of the following sequence of events. (*a*) The addition of a nonvolatile solute to the solvent forms a solution in which the vapor pressure of the solvent is reduced (see Raoult's law). (*b*) If pure solvent is now placed adjacent to the solution but separated from it by a semipermeable membrane, solvent molecules will pass through the membrane into the solution in an attempt to dilute out the solute and raise the vapor pressure back to its original value (namely, that of the original solvent). (*c*) The osmotic pressure that is set up as a result of this passage of solvent molecules can be determined either by measuring the hydrostatic head appearing in the solution or by applying a known pressure that just balances the osmotic pressure and prevents any net movement of solvent molecules into the solution. The latter is the preferred technique. The osmotic pressure thus obtained is proportional to the reduction in vapor pressure brought about by the concentration of solute present. Because this is a function of the molecular weight of the solute, osmotic pressure is a colligative property and can be used to determine molecule weights.

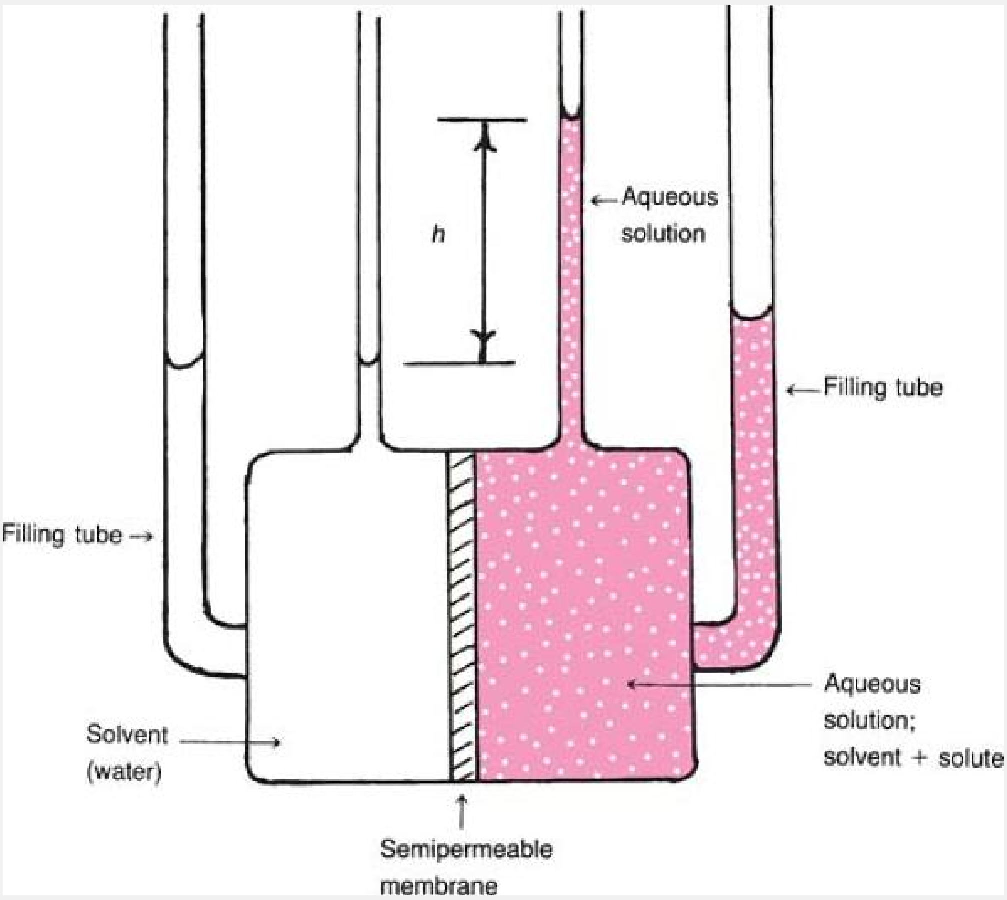


Fig. 5-11. Osmotic pressure osmometer.

An *osmotic pressure* osmometer (Fig. 5-11) is based on the same principle as the thistle tube apparatus shown in Figure 5-10. Once equilibrium has been attained, the height of the solution in the capillary tube on the solution side of the membrane is greater by the amount *h* than the height in

the capillary tube on the solvent (water) side. The hydrostatic head, *h*, is related to the osmotic pressure through the expression osmotic pressure π (atm) = Height h× Solution density ρ × Gravity acceleration. The two tubes of large bore are for filling and discharging the liquids from the compartments of the apparatus. The height of liquid in these two large tubes does not enter into the calculation of osmotic pressure. The determination of osmotic pressure is discussed in some detail in the next section.

Measurement of Osmotic Pressure

The osmotic pressure of the sucrose solution referred to in the last section is not measured conveniently by observing the height that the solution attains in the tube at equilibrium. The concentration of the final solution is not known because the passage of water into the solution dilutes it and alters the concentration. A more exact measure of the osmotic pressure of the undiluted solution is obtained by determining the excess pressure on the solution side that just prevents the passage of solvent through the membrane. Osmotic pressure is defined as the excess pressure, or pressure greater than that above the pure solvent, that must be applied to the solution to prevent the passage of the solvent through a perfect semipermeable membrane. In this definition, it is assumed that a semipermeable sac containing the solution is immersed in the *pure* solvent.

In 1877, the botanist Wilhelm Pfeffer measured the osmotic pressure of sugar solutions, using a porous cup impregnated with a deposit of cupric ferrocyanide, $Cu_2Fe(CN)_6$, as the semipermeable membrane. The apparatus was provided with a manometer to measure the pressure. Although many improvements have been made through the years, including the attachment of sensitive pressure transducers to the membrane that can be electronically amplified to produce a signal,5 the direct measurement of osmotic pressure remains difficult and inconvenient. Nevertheless, osmotic pressure is the colligative property best suited to the determination of the molecular weight of polymers such as proteins.

van't Hoff and Morse Equations for Osmotic Pressure

In 1886, Jacobus van't Hoff recognized in Pfeffer's data proportionality between osmotic pressure, concentration, and temperature, suggested a relationship that corresponded to the equation for an ideal gas. van't Hoff concluded that there was an apparent analogy between solutions and gases and that the osmotic pressure in a dilute solution was equal to the pressure that the solute would exert if it were a gas occupying the same volume. The equation is

$$\pi V = nRT \qquad (5\text{–}30)$$

where π is the osmotic pressure in atm, *V* is the volume of the solution in liters, *n* is the number of moles of solute, *R* is the gas constant, equal to 0.082 liter atm/mole deg, and *T* is the absolute temperature. The student should be cautioned not to take van't Hoff's analogy too literally, for it leads to the belief that the solute molecules “produce” the osmotic pressure by exerting pressure on the membrane, just as gas molecules create a pressure by striking the walls of a vessel. It is more correct, however, to consider the osmotic pressure as resulting from the relative escaping tendencies of the *solvent* molecules on the two sides of the membrane. Actually, equation **(**5-30**)** is a limiting law applying to dilute solutions, and it simplifies into this form from a more exact expression [equation **(**5-36**)**] only after introducing a number of assumptions that are not valid for real solutions.

Example 5-13

Calculating the Osmotic Pressure of a Sucrose Solution

One gram of sucrose, molecular weight 342, is dissolved in 100 mL of solution at 25°C. What is the osmotic pressure of the solution? We have

$$\text{Moles of sucrose} = \frac{1.0}{342} = 0.0029$$

$$\pi \times 0.10 = 0.0029 \times 0.082 \times 298$$

$$\pi = 0.71\ \text{atm}$$

Equation **(**5-30**)**, the van't Hoff equation, can be expressed as

$$\pi = \frac{n}{V}RT = cRT \qquad (5\text{–}31)$$

where *c* is the concentration of the solute in moles/liter (molarity). Morse and others have shown that when the concentration is expressed in molality rather than in molarity, the results compare more nearly with the experimental findings. The Morse equation is

$$\pi = RTm \qquad (5\text{–}32)$$

Thermodynamics of Osmotic Pressure and Vapor Pressure Lowering

Osmotic pressure and the lowering of vapor pressure, both colligative properties, are inextricably related, and this relationship can be obtained from certain thermodynamic considerations.
We begin by considering a sucrose solution in the right-hand compartment of the apparatus shown in Figure 5-12 and the pure solvent—water—in the left-hand compartment. A semipermeable membrane through which water molecules, but not sucrose molecules, can pass separates the two compartments. It is assumed that the gate in the air space connecting the solutions can be shut during osmosis. The external pressure, say 1 atm, above the pure solvent is P_o and the pressure on the solution, provided by the piston in Figure 5-12 and needed to maintain equilibrium, is P. The difference between the two pressures at equilibrium, $P - P_o$, or the excess pressure on the solution just required to prevent passage of water into the solution is the osmotic pressure π.

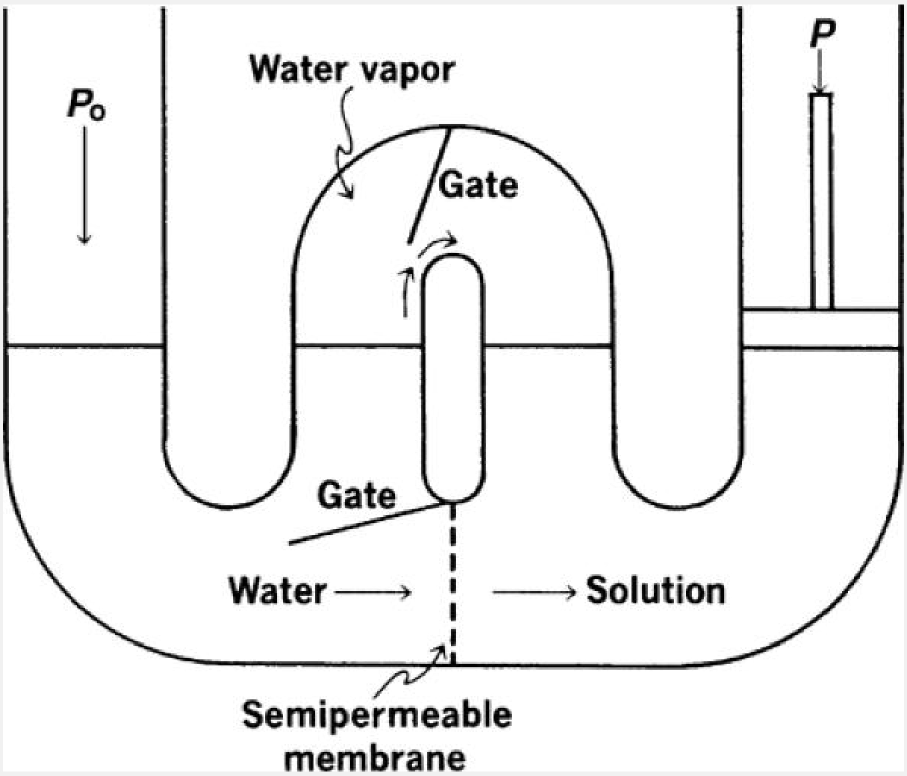


Fig. 5-12. Apparatus for demonstrating the relationship between osmotic pressure and vapor pressure lowering.

Let us now consider the alternative transport of water through the air space above the liquids. Should the membrane be closed off and the gate in the air space opened, water molecules would pass from the pure solvent to the solution by way of the vapor state by a distillation process. The space above the liquids actually serves as a “semipermeable membrane,” just as does the real membrane at the lower part of the apparatus. The vapor pressure $p°$ of water in the pure solvent under the influence of the atmospheric pressure P_o is greater than the vapor pressure p of water in the solution by an amount $p° - p = \Delta p$. To bring about equilibrium, a pressure P must be exerted by the piston on the solution to increase the vapor pressure of the solution until it is equal to that of the pure solvent, $p°$. The excess pressure that must be applied, $P - P_o$, is again the osmotic pressure π. The operation of such an apparatus thus demonstrates the relationship between osmotic pressure and vapor pressure lowering.

By following this analysis further, it should be possible to obtain an equation relating osmotic pressure and vapor pressure. Observe that both the osmosis and the distillation process are based on the principle that the escaping tendency of water in the pure solvent is greater than that in the solution. By application of an excess pressure, $P - P_o = \pi$, on the solution side of the apparatus, it is possible to make the escaping tendencies of water in the solvent and solution identical. A state of equilibrium is produced; thus, the free energy of solvent on both sides of the membrane or on both sides of the air space is made equal, and $\Delta G = 0$.

To relate vapor pressure lowering and osmotic pressure, we must obtain the free energy changes involved in (*a*) transferring 1 mole of solvent from solvent to solution by a distillation process through the vapor phase and (*b*) transferring 1 mole of solvent from solvent to solution by osmosis. We have

(*a*)

$$\Delta G = RT \quad \ln \frac{p}{p^\circ} \qquad \textbf{(5–33)}$$

as the increase in free energy at constant temperature for the passage of 1 mole of water to the solution through the vapor phase, and

(*b*)

$$\Delta G = -V_1(P - P_o) = -V_1\pi \qquad \textbf{(5–34)}$$

as the increase in free energy at a definite temperature for the passage of 1 mole of water into the solution by osmosis. In equation (5-34), V_1 is the volume of 1 mole of solvent, or, more correctly, it is the *partial molar volume*, that is, the change in volume of the solution on the addition of 1 mole of solvent to a large quantity of solution.

Setting equations (5-33) and (5-34) equal gives

$$-\pi V_1 = RT \quad \ln \frac{p}{p^\circ} \qquad \textbf{(5–35)}$$

and eliminating the minus sign by inverting the logarithmic term yields

$$\pi = \frac{RT}{V_1} \ln \frac{p^\circ}{p} \qquad \textbf{(5–36)}$$

Equation (5-36) is a more exact expression for osmotic pressure than are equations (5-31) and (5-32), and it applies to concentrated as well as dilute solutions, provided that the vapor follows the ideal gas laws.

The simpler equation (5-32) for osmotic pressure can be obtained from equation (5-36), assuming that the solution obeys Raoult's law,

$$p = p^\circ X_1 \qquad \textbf{(5–37)}$$

$$\frac{p}{p^\circ} = X_1 = 1 - X_2 \qquad \textbf{(5–38)}$$

Equation (5-36) can thus be written

$$\pi V_1 = -RT \quad \ln(1 - X_2) \qquad \textbf{(5–39)}$$

and $\ln(1 - X_2)$ can be expanded into a series,

$$\ln(1 - X_2) = -X_2 - \frac{X_2^2}{2} - \frac{X_2^3}{3} \cdots - \frac{X_2^n}{2} \qquad \textbf{(5–40)}$$

When X_2 is small, that is, when the solution is dilute, all terms in the expansion beyond the first may be neglected, and

$$\ln(1 - X_2) \cong -X_2 \qquad \textbf{(5–41)}$$

so that

$$\pi V_1 = RTX_2 \qquad \textbf{(5–42)}$$

For a dilute solution, X_2 equals approximately the mole ratio n_2/n_1, and equation (5-42) becomes

$$\pi \cong \frac{n_2}{n_1 V_1} RT \qquad \textbf{(5–43)}$$

where n_1V_1, the number of moles of solvent multiplied by the volume of 1 mole, is equal to the total volume of solvent V in liters. For a dilute aqueous solution, the equation becomes

$$\pi = \frac{n_2}{V} RT = RTm \qquad \textbf{(5–44)}$$

which is Morse's expression, equation (5-32).

Example 5-14

Compute π

Compute π for a 1 *m* aqueous solution of sucrose using both equation (5-32) and the more exact thermodynamic equation (5-36). The vapor pressure of the solution is 31.207 mm Hg and the vapor pressure of water is 31.824 mm Hg at 30.0°C. The molar volume of water at this temperature is 18.1 cm^3/mole, or 0.0181 liter/mole.

a. By the Morse equation,

$$\pi = RTm = 0.082 \times 303 \times 1$$
$$\pi = 24.8\text{atm}$$

b. By the thermodynamic equation,

$$\pi = \frac{RT}{V_1} \ln \frac{p^\circ}{p}$$
$$\pi = \frac{0.082 \times 303}{0.0181} \times 2.303 \log \frac{31.824}{31.207}$$
$$= 27.0 \text{ atm}$$

The experimental value for the osmotic pressure of a 1 *m* solution of sucrose at 30°C is 27.2 atm.

Molecular Weight Determination

The four colligative properties that have been discussed in this chapter—vapor pressure lowering, freezing point lowering, boiling point elevation, and osmotic pressure—can be used to calculate the molecular weights of nonelectrolytes present as solutes. Thus, the lowering of the vapor pressure of a solution containing a nonvolatile solute depends only on the mole fraction of the solute. This allows the molecular weight of the solute to be calculated in the following manner.

Because the mole fraction of solvent, $n_1 = w_1/M_1$, and the mole fraction of solute, $n_2 = w_2/M_2$, in which w_1 and w_2 are the weights of solvent and solute of molecular weights M_1 and M_2 respectively, equation **(**5-15**)** can be expressed as

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1 + n_2} = \frac{w_2/M_2}{(w_1/M_1) + (w_2/M_2)} \quad \textbf{(5–45)}$$

In dilute solutions in which w_2/M_2 is negligible compared with w_1/M_1, the former term may be omitted from the denominator, and the equation simplifies to

$$\frac{\Delta p}{p_1^\circ} = \frac{w_2/M_2}{w_1/M_1} \quad \textbf{(5–46)}$$

The molecular weight of the solute M_2 is obtained by rearranging equation **(**5-46**)** to

$$M_2 = \frac{w_2 M_1 p_1^\circ}{w_1 \Delta p} \quad \textbf{(5–47)}$$

The molecular weight of a nonvolatile solute can similarly be determined from the boiling point elevation of the solution. Knowing K_b, the molal elevation constant, for the solvent and determining T_b, the boiling point elevation, one can calculate the molecular weight of a nonelectrolyte. Because $1000w_2/w_1$ is the weight of solute per kilogram of solvent, molality (moles/kilogram of solvent) can be expressed as

$$m = \frac{w_2/M_2}{w_1} \times 1000 = \frac{1000w_2}{w_1 M_2} \quad \textbf{(5–48)}$$

and

$$\Delta T_b = K_b m \quad \textbf{(5–49)}$$

Then,

$$\Delta T_b = K_b \frac{1000 w_2}{w_1 M_2} \qquad (5\text{–}50)$$

or

$$M_2 = K_b \frac{1000 w_2}{w_1 \Delta T_b} \qquad (5\text{–}51)$$

Example 5-15

Determination of the Molecular Weight of Sucrose by Boiling Point Elevation

A solution containing 10.0 g of sucrose dissolved in 100 g of water has a boiling point of 100.149°C. What is the molecular weight of sucrose? We write

$$\begin{aligned} M_2 &= 0.51 \times \frac{1000 \times 10.0}{100 \times 0.149} \\ &= 342 \text{ g/mole} \end{aligned}$$

As shown in Figure 5-8, the lowering of vapor pressure arising from the addition of a nonvolatile solute to a solvent results in a depression of the freezing point. By rearranging equation **(**5-29**)**, we obtain

$$M_2 = K_f \frac{1000 w_2}{\Delta T_f w_1} \qquad (5\text{–}52)$$

where w_2 is the number of grams of solute dissolved in w_1 grams of solvent. It is thus possible to calculate the molecular weight of the solute from cryoscopic data of this type.

Example 5-16

Calculating Molecular Weight Using Freezing Point Depression

The freezing point depression of a solution of 2.000 g of 1,3-dinitrobenzene in 100.0 g of benzene was determined by the equilibrium method and was found to be 0.6095°C. Calculate the molecular weight of 1,3-dinitrobenzene. We write

$$M_2 = 5.12 \times \frac{1000 \times 2.000}{0.6095 \times 100.0} = 168.0 \text{ g/mole}$$

The van't Hoff and Morse equations can be used to calculate the molecular weight of solutes from osmotic pressure data, provided the solution is sufficiently dilute and ideal. The manner in which osmotic pressure is used to calculate the molecular weight of colloidal materials is discussed in Chapter 17.

Example 5-17

Determining Molecular Weight by Osmotic Pressure

Fifteen grams of a new drug dissolved in water to yield 1000 mL of solution at 25°C was found to produce an osmotic pressure of 0.6 atm. What is the molecular weight of the solute? We write

$$\pi = cRT = \frac{c_g RT}{M_2} \qquad (5\text{–}53)$$

where c_g is in g/liter of solution. Thus,

$$\pi = \frac{15 \times 0.0821 \times 298}{M_2}$$

or

$$M_2 = \frac{15 \times 24.45}{0.6} = 612 \text{ g/mole}$$

Choice of Colligative Properties

Each of the colligative properties seems to have certain advantages and disadvantages for the determination of molecular weights. The boiling point method can be used only when the solute is nonvolatile and when the substance is not decomposed at boiling temperatures. The freezing point method is satisfactory for solutions containing volatile solutes, such as alcohol, because the freezing point of a solution depends on the vapor pressure of the solvent alone. The freezing point method is easily executed and yields results of high accuracy for solutions of small molecules. It is sometimes inconvenient to use freezing point or boiling point methods, however, because they must be carried out at definite temperatures. Osmotic pressure measurements do not have this disadvantage, and yet the difficulties inherent in this method preclude its wide use. In summary, it may be said that the cryoscopic and newer vapor pressure techniques are the methods of choice, except for high polymers, in which instance the osmotic pressure method is used.

Because the colligative properties are interrelated, it should be possible to determine the value of one property from knowledge of any other. The relationship between vapor pressure lowering and osmotic pressure has already been shown. Freezing point depression and osmotic pressure can be related approximately as follows. The molality from the equation $m = \Delta T_f/K_f$ is substituted in the osmotic pressure equation, $\pi = RTm$, to give, at 0°C,

$$\pi = RT\frac{\Delta T_f}{K_f} = \frac{22.4}{1.86}\Delta T_f \qquad (5\text{–}54)$$

or

$$\pi \cong 12\Delta T_f \qquad (5\text{–}55)$$

Lewis6 suggested the equation

$$\pi = 12.06\,\Delta T_f - 0.021\,\Delta T_f^2 \qquad (5\text{–}56)$$

which gives accurate results.

Colligative Property	Expression	Proportionality Constant in Aqueous Solution
Vapor pressure lowering	$\Delta p = 0.018\,p_1{}^\circ m$	$0.018\,p_1{}^\circ = 0.43$ at 25°C $= 0.083$ at 0°C
Boiling point elevation	$\Delta T_b = K_b m$	$K_b = 0.51$
Freezing point depression	$\Delta T_f = K_f m$	$K_f = 1.86$
Osmotic pressure	$\pi = RTm$	$RT = 24.4$ at 25°C $= 22.4$ at 0°C

Table 5-5 Approximate Expressions for the Colligative Properties

Example 5-18

Osmotic Pressure of Human Blood Serum

A sample of human blood serum has a freezing point of -0.53°C. What is the approximate osmotic pressure of this sample at 0°C? What is its more accurate value as given by the Lewis equation? We write

$$\pi = 12 \times 0.53 = 6.36 \text{ atm}$$

$$\pi = 12.06 \times 0.53 - 0.021(0.53)^2 = 6.39 \text{ atm}$$

Table 5-5 presents the equations and their constants in summary form. All equations are approximate and are useful only for dilute solutions in which the volume occupied by the solute is negligible with respect to that of the solvent.

Chapter Summary

This chapter focused on an important pharmaceutical mixture known as a molecular dispersion or true solution. Nine types of solutions, classified according to the states in which the solute and solvent occur, were defined. The concentration of a solution was expressed in two ways: either in terms of the quantity of solute in a definite volume of solution or as the quantity of solute in a definite mass of solvent or solution. You should be able to calculate molarity, normality, molality, mole fraction, and percentage expressions. Ideal and real solutions were described using Raoult's and Henry's laws. Finally, the colligative properties of solutions (osmotic pressure, vapor pressure lowering, freezing point depression, and boiling point elevation) were described. Colligative properties depend mainly on the number of particles in a solution and are approximately the same for equal concentrations of different nonelectrolytes in solution regardless of the species or chemical nature of the constituents.

Practice problems for this chapter can be found at thePoint.lww.com/Sinko6e.

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Recommended Readings

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Chapter Legacy

Fifth Edition: published as Chapter 5. Updated by Patrick Sinko.

Sixth Edition: published as Chapter 5. Updated by Patrick Sinko.