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Materials may be mixed together to form a true solution, a colloidal solution, or a coarse dispersion. 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, the composition of which can vary over a wide range. The terms in this definition warrant further comment, and an attempt at clarification is made in the following paragraphs.

A *system* is a bounded space or a definite quantity of substance that is under observation and experimentation. Under some circumstances, the system may consist only of radiant energy or an electric field, containing no material substances. The term *phase* has already been defined in Chapter 2 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 piece of ice floating in water, or it may be distributed as small particles throughout the system, such as oil droplets in an emulsion or solid particles in a pharmaceutical suspension.

These latter two are examples of *coarse dispersions*, the diameter of the particles in emulsions and suspensions for the most part being larger than $0.1\ \mu\text{m}$ ($100\ \text{\AA}$ or $10^{-5}\ \text{cm}$). A *colloidal dispersion* represents a system having a particle size intermediate between that of a true solution and a coarse dispersion, roughly 10 to 5000 \AA . A colloidal dispersion may be considered as a two-phase system (heterogeneous) under certain circumstances and as a one-phase system (homogeneous) under others. A colloidal dispersion of silver proteinate in water is heterogeneous since it consists of distinct particles constituting a separate phase. A colloidal dispersion of acacia or sodium carboxymethylcellulose in water, on the other hand, is homogeneous. It does not differ significantly from a solution of sucrose and

may be considered as a single-phase system or true solution.¹

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*. We use the terms *component* and *constituent* interchangeably here, as do other authors, to represent the pure chemical substances that make up a solution. The *number of components* has a definite significance in the phase rule, as explained on p. 37. 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.

Properties of Solutions. The physical properties of substances may 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, depending 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 eleva-

tion. 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 molecules 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 may be classified according to the states in which the solute and solvent occur, and since 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.

The solutes (whether gases, liquids, or solids) are divided into two main classes: *nonelectrolytes* and *electrolytes*. Nonelectrolytes are substances that do not yield ions 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 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 the 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 found in Chapter 6.

CONCENTRATION EXPRESSIONS

The concentration of a solution may 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.² Molarity and normality are the expressions commonly used in analytical work. 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 molar (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 \times 232.32 g/mole = 0.2323 g) and 0.1 mole of sodium chloride (0.1 mole \times 58.45 g/mole = 5.845 g) to enough water to make 1000 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, since 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 since they may be brought to a convenient volume; a

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

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

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 theoretic 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 the carefully weighed quantity of the solute. The volume of the solvent can be calculated from the specific gravity, and the solvent may then be measured from a burette rather than weighed.

Mole Fraction. Mole fraction is used frequently in experimentation involving theoretical considerations since it gives a measure of the relative proportion

of moles of each constituent in a solution. It is expressed as

$$X_1 = \frac{n_1}{n_1 + n_2} \quad (5-1)$$

$$X_2 = \frac{n_2}{n_1 + n_2} \quad (5-2)$$

for a system of two constituents.

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 number of moles of the 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 $X_2 = 0.01/(0.04 + 0.01) = 0.20$. Since 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 two out 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.

Percent Expressions. The percentage method of expressing the concentration of pharmaceutical solutions is quite common. Percent by weight signifies the number of grams of solute per 100 grams 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. Percent by volume is expressed as the volume of solute in milliliters con-

tained in 100 mL of the solution. Alcohol (USP) contains 92.3% by weight and 94.9% by volume of C_2H_5OH at 15.56° , 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. 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 $18^\circ C$. 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 percent by weight of $FeSO_4$.

(a) Molarity

$$\begin{aligned} \text{Moles of } FeSO_4 &= \frac{\text{g of } FeSO_4}{\text{molecular weight}} \\ &= \frac{41.50}{151.9} = 0.2732 \end{aligned}$$

$$\text{Molarity} = \frac{\text{moles of } FeSO_4}{\text{liters of solution}} = \frac{0.2732}{1 \text{ liter}} = 0.2732 M$$

(b) Molality

$$\begin{aligned} \text{Grams of solution} &= \text{volume} \times \text{density}; \\ 1000 \times 1.0375 &= 1037.5 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Grams of solvent} &= \text{grams of solution} - \text{grams} \\ \text{of } FeSO_4 &= 1037.5 - 41.5 = 996.0 \text{ g} \end{aligned}$$

$$\text{Molality} = \frac{\text{moles of } FeSO_4}{\text{kg of solvent}} = \frac{0.2732}{0.996} = 0.2743 m$$

(c) Mole fraction and mole percent

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

Mole fraction of $FeSO_4$,

$$X_2 = \frac{\text{moles of } FeSO_4}{\text{moles water} + \text{moles } FeSO_4} = \frac{0.2732}{55.27 + 0.2732} = 0.0049$$

Mole fraction of water,

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

$$\text{Notice that } X_1 + X_2 = 0.9951 + 0.0049 = 1.0000$$

$$\text{Mole percent of } FeSO_4 = 0.0049 \times 100 = 0.49\%$$

$$\text{Mole percent of water} = 0.9951 \times 100 = 99.51\%$$

(d) Percent by weight

Percent by weight of $FeSO_4$

$$\begin{aligned} &= \frac{\text{g of } FeSO_4}{\text{g of solution}} \times 100 \\ &= \frac{41.50}{1037.5} \times 100 = 4.00\% \end{aligned}$$

One may use the table of conversion equations, Table 5-3, to convert concentration expressions, say molality, into its value in molarity or mole fraction. Or, 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 in

TABLE 5-3. Conversion Equations for Concentration Terms

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

$$\begin{aligned} X_2 &= \frac{m}{m + \frac{1000}{M_1}} \\ m &= \frac{1000 X_2}{M_1(1 - X_2)} \\ &= \frac{1000(1 - X_1)}{M_1 X_1} \end{aligned}$$

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

$$\begin{aligned} X_2 &= \frac{c}{c + \frac{1000\rho - cM_2}{M_1}} \\ c &= \frac{1000\rho X_2}{M_1(1 - X_2) + M_2 X_2} \end{aligned}$$

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

$$\begin{aligned} m &= \frac{1000 c}{1000\rho - M_2 c} \\ c &= \frac{1000\rho}{m + M_2} \end{aligned}$$

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.

$$\begin{aligned} m &= \frac{w_2/M_2}{w_1/1000} = \frac{1000 w_2}{w_1 M_2} \\ c &= \frac{1000 \rho w_2}{M_2(w_1 + w_2)} \end{aligned}$$

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.)

Example 5-1 are useful to determine whether your derived equation is correct.

EQUIVALENT WEIGHTS²

A 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 one gram atom of oxygen weighs 16 g. Therefore, 1.008 g of hydrogen combines with 19 grams of fluorine and with half of 16 or 8 grams 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

lent of oxygen (8 g) also combines with 1.008 g of hydrogen.

We observe 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 equivalent of fluorine, while the atomic weight of oxygen contains two equivalents. The equation relating these atomic quantities is as follows (the equation relating these atomic quantities is quite similar to that for atoms, as seen in the next paragraph):

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

The number of equivalents per atomic weight, namely 1 for fluorine and 2 for oxygen, are the common *valences* 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 its atomic weight ($24/2 = 12$ g/equivalent). Aluminum will combine with three atoms of fluorine; the valence of aluminum is therefore 3 and its equivalent weight is one third its atomic weight, or $27/3 = 9$ g/equivalent.

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, since the valence of sodium and chlorine are 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 unity, two atoms are present in Na_2CO_3 , providing a weight of $2 \times 23 \text{ g} = 46 \text{ g}$; 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 equations [5-3] for atoms):

$$\begin{aligned} \text{Equivalent weight (g/Eq)} \\ = \frac{\text{molecular weight (g/mole)}}{\text{equivalent/mole}} \end{aligned} \quad (5-4)$$

Example 5-2. (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 $\text{Ca}_3(\text{PO}_4)_2$, and what is the equivalent weight of this salt?

(a) K_3PO_4 represents 3 equivalents per mole, and its equivalent weight is numerically equal to one third its molecular weight—namely, $212 \text{ g/mole} \div 3 \text{ Eq/mole} = 70.7 \text{ g/Eq}$.

(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 $\text{Ca}_3(\text{PO}_4)_2$ 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 $\text{Ca}_3(\text{PO}_4)_2$ is therefore one sixth its molecular weight, or $310/6 = 51.7 \text{ g/Eq}$.

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 used as a buffer for its hydrogen content, the equivalent weight is one half the molecular weight, $136/2 = 68$ g, since two hydrogen atoms are present. When used for its phosphate content, the equivalent weight of KH_2PO_4 is one third the molecular weight, $136/3 = 45.3$ g, since 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 the molecular weight, $98 \text{ g}/3 = 32.67 \text{ g/Eq}$, 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 a liter of solution.

In electrolyte replacement therapy in the hospital, solutions containing various electrolytes are injected into the body to correct serious electrolytes 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 ions, 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

$$\text{Equivalent weight (in g/Eq)} = \frac{\text{grams/liter}}{\text{equivalents/liter}} \quad (5-5)$$

or

$$\begin{aligned} \text{Equivalent weight (in mg/mEq)} \\ = \frac{\text{milligrams/liter}}{\text{milliequivalents/liter}} \end{aligned} \quad (5-6)$$

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

Example 5-3. Human plasma contains about 5 mEq/liter of calcium ions. How many milligrams of calcium chloride dihydrate, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (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 $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is half its molecular weight, $147/2 = 73.5 \text{ g/Eq}$, or 73.5 mg/mEq . Using equation (5-6),

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

$$73.5 \text{ mg/mEq} \times 5 \text{ mEq/liter} = 367.5 \text{ mg/liter}$$

$$\text{For } 750 \text{ cm}^3, 367.5 \times \frac{750 \text{ mL}}{1000 \text{ mL}} = 275.6 \text{ mg of } \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$$

Example 5-4. 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,

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

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

Example 5-5. 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.

$$\text{mEq/liter} = \frac{\text{mg/liter}}{\text{Eq. wt.}} = \frac{5000 \text{ mg/liter}}{58.5 \text{ mg/mEq}} = 85.47 \text{ mEq of } \text{Na}^+ \text{ per liter}$$

SOLUTIONS OF NONELECTROLYTES

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

IDEAL AND REAL SOLUTIONS

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.

Ideal solutions are formed by mixing substances with similar properties. 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, while others approach ideality only under extreme dilution.

To summarize, whereas ideality in a gas implies the *complete absence* of attractive forces, ideality in a solution means *complete uniformity* of attractive forces. Since 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.

Escaping Tendency.³ It is common knowledge that 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. We can describe this process 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 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 a mole of ice is greater than that of liquid water at 1 atm above 0° C and is spontaneously converted into water, since

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

At 0° C, at which temperature the system is in equilibrium, the molar free energies of ice and water are identical and $\Delta G = 0$. In terms of escaping tendencies, we can say that above 0° C, the escaping tendency of ice is greater than the escaping tendency of liquid water, 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 since 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:

$$p_A = p_A^\circ X_A \quad (5-7)$$

$$p_B = p_B^\circ X_B \quad (5-8)$$

in which 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° and p_B° . 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 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. 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° for ethylene chloride is 236 mm.

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

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

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.

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. Trichloromonofluoromethane (designated as propellant 11) and dichlorodifluoromethane (designated as propellant 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

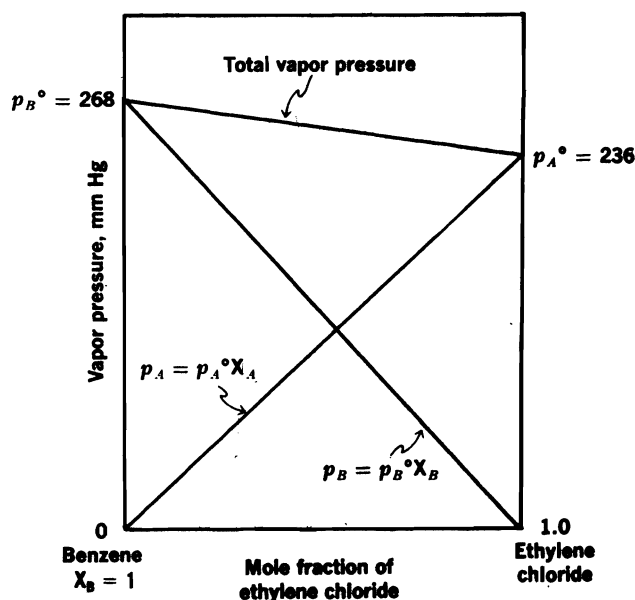


Fig. 5-1. Vapor pressure-composition curve for an ideal binary system.

by nitrogen and unsubstituted hydrocarbons (see *Problem 5-9*).

Example 5-7. The vapor pressure of pure propellant 11 (MW 137.4) at 21° C is $p_{11}^\circ = 13.4$ pounds/square inch (psi) and that of propellant 12 (MW 120.9) is $p_{12}^\circ = 84.9$ psi. A 50:50 mixture by gram weight of the two propellants consists of $50 \text{ g} \div 137.4 \text{ g mole}^{-1} = 0.364$ mole of propellant 11, and $50 \text{ g} / 120.9 \text{ g mole}^{-1} = 0.414$ mole of propellant 12. What is the partial pressure of propellants 11 and 12 in the 50:50 mixture, and what is the total vapor pressure of this mixture?

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

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

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 (p. 106). 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*.

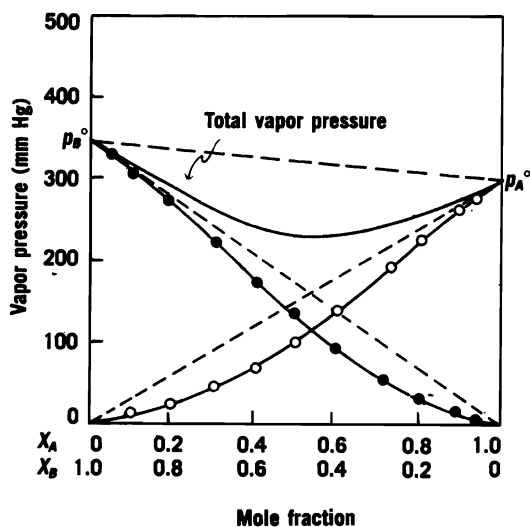


Fig. 5-2. Vapor pressure of a system showing negative deviation from Raoult's law.

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 additions 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,



which may 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.

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 may be expressed as

$$p_{\text{solvent}} = p^{\circ}_{\text{solvent}} X_{\text{solvent}} \quad (5-9)$$

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, since the actual curve for acetone does not coincide with the ideal

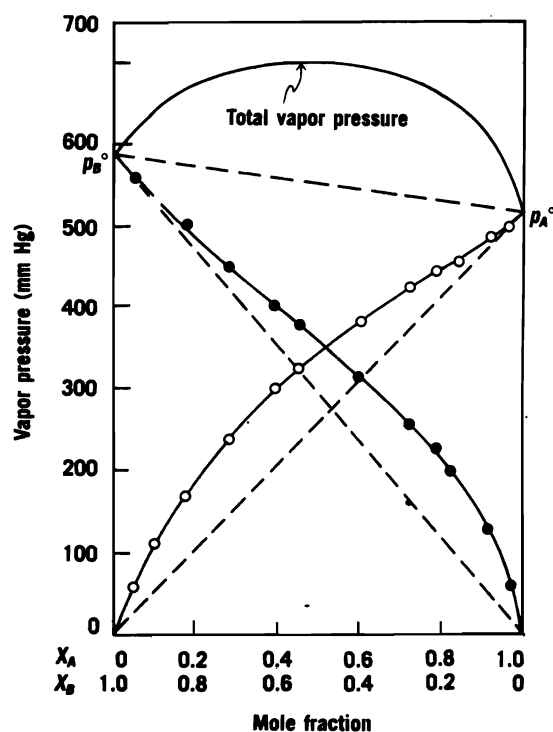


Fig. 5-3. Vapor pressure of a system showing positive deviation from Raoult's law.

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.

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*:

$$p_{\text{solute}} = k_{\text{solute}}X_{\text{solute}} \quad (5-10)$$

in which k for chloroform is less than $p^{\circ}_{\text{CHCl}_3}$. 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 and will be discussed in Chapter 10.

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 the boiling point. Since 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

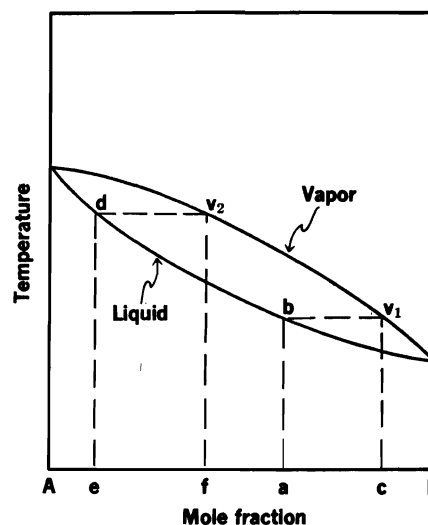


Fig. 5-4. Boiling point diagram of an ideal binary mixture.

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 .

Figure 5-4 shows the situation for a pair of miscible liquids exhibiting ideal behavior. Since vapor pressure curves can show maxima and minima (see Figs. 5-2 and 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, while 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, while 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 may 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 (rather than the weight concentration) of the solute molecules. 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) since 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 . Since 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:

$$X_1 + X_2 = 1 \quad (5-11)$$

Therefore,

$$X_1 = 1 - X_2 \quad (5-12)$$

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

$$p = p_1^\circ(1 - X_2) \quad (5-13)$$

$$p_1^\circ - p = p_1^\circ X_2 \quad (5-14)$$

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

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. Calculate the relative vapor pressure lowering at 20° C for a solution containing 171.2 g of sucrose (w_2) in 1000 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.

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

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

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

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

Notice that in *Example 5-8*, the relative vapor pressure lowering is a dimensionless number, as would be expected from its definition. The result may 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 grams. For an aqueous solution,

$$X_2 = \frac{\Delta p}{p_1^\circ} \cong \frac{n_2}{n_1} = \frac{w_2/M_2}{1000/M_1} = \frac{m}{55.5} = 0.018 \, m \quad (5-16)$$

Example 5-9. 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

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

Determination of the Vapor Pressure of Solutions. The vapor pressure of a solution may be determined directly by means of a manometer, and the vapor pressure lowering is then obtained by subtracting the vapor pressure of the solution from the vapor pressure of the pure solvent. For dilute aqueous solutions, however, the vapor pressure lowering, as seen in *Example 5-9*, is so slight as to produce a serious error in the measurement. Accurate differential manometers have been developed and are available for measuring small differences in vapor pressure.⁴

The *isopiestic method* is used frequently for the precise determination of vapor pressures. The solution whose vapor pressure is to be determined and a solution containing a standard solute, for example, potassium chloride, are placed in separate dishes in a closed container, as shown in Figure 5-5. The vapor of the solution with the higher pressure passes to the one with the lower pressure until the vapor pressures of the two solutions are the same, that is, *isopiestic* (Greek: equal pressure). When there is no further change in weight, the solutions are analyzed to determine their concentrations. The vapor pressures of potassium chloride solutions of various concentrations have been determined accurately, and tables of these values are available in the literature. The vapor pressure of the test solution, which is isopiestic with the potassium chloride solution, is thus readily obtained. Knowing the vapor pressure of water at this temperature, it is a simple matter to calculate the vapor pressure lowering of the solution. Robinson and Sinclair and Scatchard et al.⁵ discuss the details of the method.

Hill and Baldes⁶ described an apparatus consisting essentially of a combination of various wires of different alloys formed into two loops and connected to a galvanometer, as shown in Figure 5-6, for determining the relative vapor pressures of small amounts of liquids. This thermoelectric method depends on measuring the change in potential as a solution of known vapor pressure and an unknown evaporate in a chamber

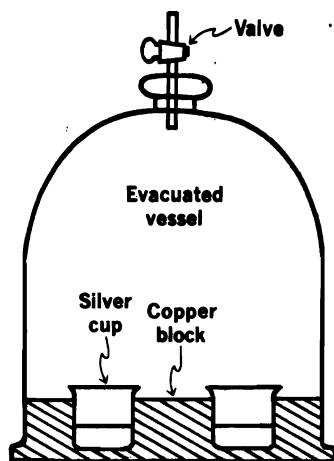


Fig. 5-5. Apparatus for the isopiestic method.

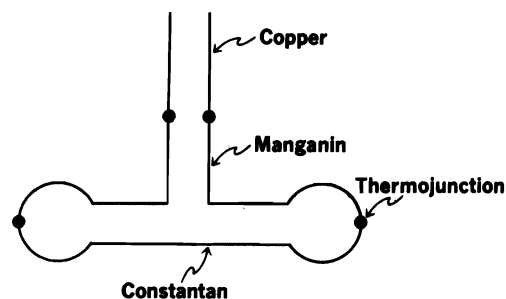


Fig. 5-6. Hill-Baldes apparatus for the thermoelectric determination of vapor pressure. (After E. J. Baldes, *J. Sci. Instr.* 11, 223, 1934.)

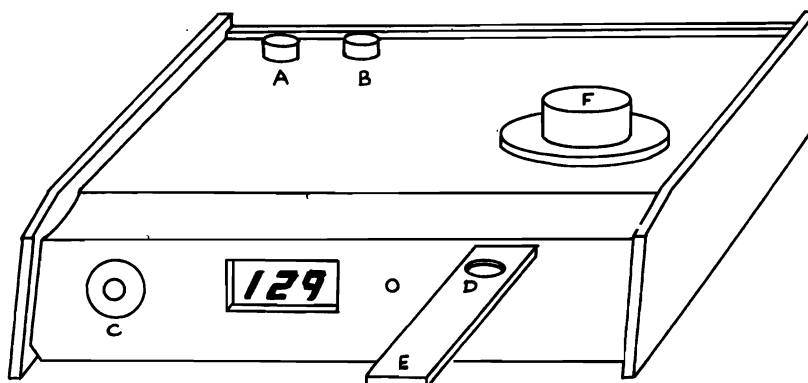
maintained at a constant humidity. The vapor pressure lowering of the solution is then obtained from a standard curve of vapor pressure versus galvanometer readings of potential. This method has been used to study the colligative properties of ophthalmic solutions.⁷

A modern variation of the thermoelectric method for determining vapor pressure lowering is embodied in the Wescor vapor pressure "osmometer" shown in Figure 5-7. In this instrument, the test solution, which is typically on the order of less than 10 microliters, is absorbed onto a filter paper disk. The disk is placed in a sealed chamber near the thermocouple, which is cooled below the dew point of the solution. The thermocouple is then equilibrated to the dew point of the solution, whereupon its potential is recorded. By electronically zeroing the instrument at the ambient temperature before the dew point reading, the potential determined is proportional to the vapor pressure lowering. Reference standard solutions are used to calibrate the potential readings against known vapor pressures at the ambient temperature. This instrument has been applied to monitoring diuretic therapy,⁸ quantitating sodium in isotonic solutions,⁹ and studying the colligative properties of parenteral solutions.¹⁰

Describing this instrument as an "osmometer" is inappropriate. Various thermoelectric vapor pressure and freezing point instruments have been termed "osmometers," even though no membrane diffusion is involved in their operation. It would perhaps be more appropriate to call these instruments "vapor pressure differentiators." UIC, Inc., of Joliet, Ill., manufactures vapor pressure osmometers, membrane osmometers, and a colloidal/oncotic osmometer for the automatic analysis of blood and biologic fluids.

Thermoelectric vapor pressure instruments have also been described that use separate chambers for the reference and sample and use thermistors instead of thermocouples as detectors.¹¹ The thermistor "osmometers" measure changes in resistance and are reported to have a sensitivity of 1×10^{-4} molal concentration, based on a sucrose solution standard. Studies of the colligative properties of nucleosides have been reported using such an instrument.¹²

Fig. 5-7. Vapor pressure osmometer (Wescor Inc., Logan, Utah). Dial A is used to calibrate the instrument within the range of 200 to 2000 milliosmolality (mOsm/kg) using a standard solution of known osmolality (see p. 137 for a discussion on milliosmolality). The control B is used to calibrate the instrument in the range of 0 to 200 mOsm/kg. C is the off-on power switch, D the sample holder, and E the sample slide. F is a chamber-sealing knob that is tightened after the sample slide is pushed fully in to center the sample holder in the chamber. A drop of sample solution placed in the holder comes to equilibrium in the chamber, and a thermocouple hygrometer provides an accurate readout of mOsm/kg in the display window.



Elevation of the Boiling Point. As stated in Chapter 2, 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. 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 5-8. 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 $T - T_0 = \Delta T_b$. The ratio of the elevation of the boiling point, ΔT_b , to the vapor pressure lowering, $\Delta p = p^\circ - p$, at 100°C is approximately a constant at this temperature; it is written as

$$\frac{\Delta T_b}{\Delta p} = k' \quad (5-17)$$

or

$$\Delta T_b = k' \Delta p \quad (5-18)$$

Moreover, since p° is a constant, the boiling point elevation may be considered proportional to $\Delta p/p^\circ$, 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,

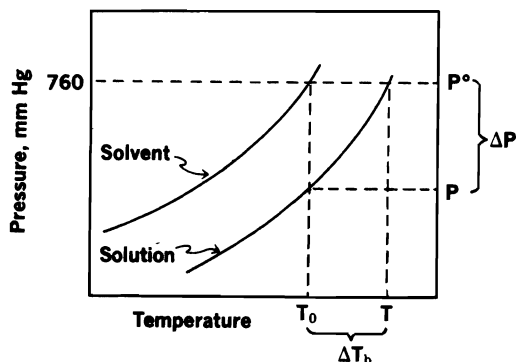


Fig. 5-8. Boiling point elevation of the solvent due to addition of a solute (not to scale).

$$\Delta T_b = kX_2 \quad (5-19)$$

Since 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) may be written as

$$\Delta T_b = \frac{kM_1}{1000} m \quad (5-20)$$

or

$$\Delta T_b = K_b m \quad (5-21)$$

in which 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 (pp. 31, 68), which is written as

TABLE 5-4. Ebullioscopic and Cryoscopic 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.

$$\frac{\Delta T_b}{\Delta p} = T_b \frac{V_v - V_l}{\Delta H_v} \quad (5-22)$$

V_v and V_l 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 the molar heat of vaporization. Since V_l is negligible compared to V_v , the equation becomes

$$\frac{\Delta T_b}{\Delta p} = T_b \frac{V_v}{\Delta H_v} \quad (5-23)$$

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

$$\frac{\Delta T_b}{\Delta p} = \frac{RT_b^2}{p^\circ \Delta H_v} \quad (5-24)$$

or

$$\Delta T_b = \frac{RT_b^2}{\Delta H_v} \frac{\Delta p}{p^\circ} \quad (5-25)$$

From equation (5-16), $\Delta p/p_1^\circ = X_2$, and equation (5-25) may be written

$$\Delta T_b = \frac{RT_b^2}{\Delta H_v} X_2 = kX_2 \quad (5-26)$$

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

Replacing the relative vapor pressure lowering $\Delta p/p_1^\circ$ by $m/(1000/M_1)$ according to the approximate expression (equation [5-16]), in which $w_2/M_2 = m$ and $w_1 = 1000$, the formula becomes

$$\Delta T_b = \frac{RT_b^2 M_1}{1000 \Delta H_v} m = K_b m \quad (5-27)$$

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

For water at 100°C , $T_b = 373.2^\circ\text{K}$, $\Delta H_v = 9720$ cal/mole, $M_1 = 18.02$ g/mole, and $R = 1.987$ cal/mole deg.

$$K_b = \frac{1.987 \times (373.2)^2 \times 18.02}{1000 \times 9720} = 0.513 \text{ deg kg/mole}$$

Example 5-10. 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 in Figure 5-9.

Determination of Boiling Point Elevation. Boiling point elevation is determined experimentally by placing a

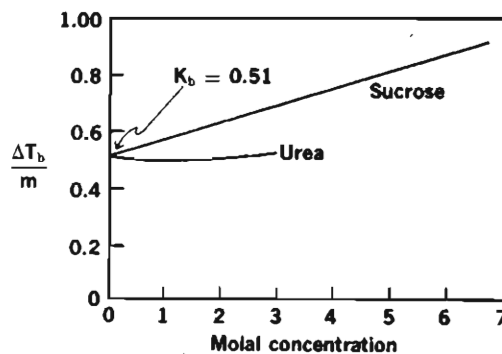


Fig. 5-9. The influence of concentration on the ebullioscopic constant.

weighed amount of the solute and the solvent in a glass vessel provided with a thermometer and a reflux condenser. In the *Cottrell boiling point apparatus*, the vapor and the boiling solvent are pumped by the force of ebullition through a glass tube and sprayed over the thermometer bulb to obtain an invariant equilibrium temperature. The boiling point of the pure solvent is determined in the same apparatus.

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, since both the liquid and the solid have the same escaping tendency. The value T_0 , observed in Figure 5-10, 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, as explained on page 38, 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, since the depression ΔT_f here does

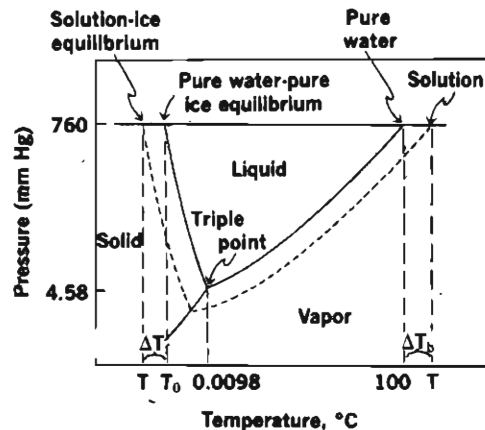


Fig. 5-10. Depression of the freezing point of the solvent, water, by a solute (not to scale).

not differ significantly from ΔT_f at a pressure of 1 atm. The two freezing point depressions referred to are illustrated in Figure 5-10. ΔT_b of Figure 5-8 is also shown in the diagram.

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 in order 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. 5-10) 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

$$\Delta T_f = K_f m \quad (5-28)$$

or

$$\Delta T_f = K_f \frac{1000 w_2}{w_1 M_2} \quad (5-29)$$

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 may be determined experimentally by measuring $\Delta T_f/m$ at several molal concentrations and extrapolating to zero concentration. As seen in Figure 5-11, K_f approaches the value of 1.86 for water

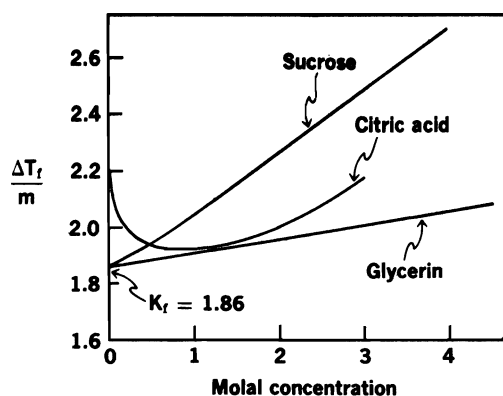


Fig. 5-11. The influence of concentration on the cryoscopic constant for water.

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 may be obtained from Figure 5-11. For work in pharmacy and biology, the K_f value 1.86 may 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 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 may also be derived from Raoult's law and the Clapeyron equation. For water at its freezing point, $T_f = 273.2^\circ \text{K}$, 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. 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.

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

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

$$\Delta T_f = 0.037^\circ \text{C}$$

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

Example 5-12. What is the freezing point depression of a 1.3-m solution of sucrose in water?

From the graph (see Fig. 5-11), one observes that the cryoscopic constant at this concentration is about 2.1 rather than 1.86. Thus, the calculation becomes

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

Determination of Freezing Point Lowering. Several methods are available for the determination of freezing point lowering. They include (a) the Beckmann method and (b) the equilibrium method.

The apparatus for the determination of the freezing point of a solution using the Beckmann method is seen in Figure 5-12. It consists of a jacketed tube with a sidearm through which the test material may be introduced. A Beckmann thermometer* is supported in the tube and extends into the test solution. A glass stirrer passes through a tube in the stopper and is operated manually or by means of a motor as shown in Figure 5-12. The tube and jacket are supported in a vessel containing a cooling mixture of salt and ice.

*The Beckmann thermometer is of the differential type that may be set arbitrarily to function within a 5° temperature range between -10° and $+140^\circ \text{C}$ and is graduated in 0.01 divisions. The temperature can be estimated to within about $\pm 0.005^\circ \text{C}$.

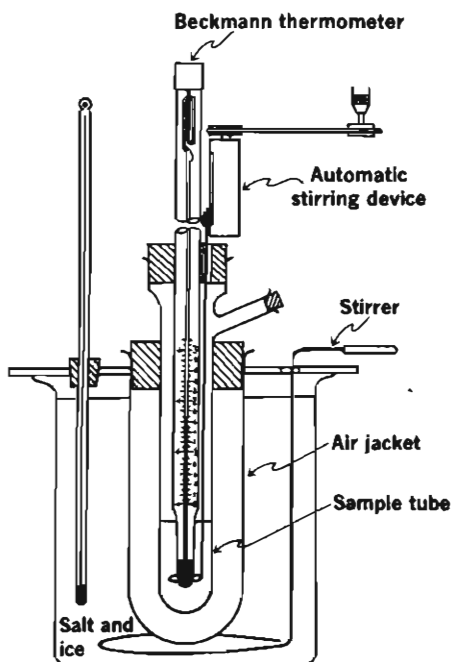


Fig. 5-12. Beckmann freezing point apparatus.

In carrying out a determination, the temperature is read on the Beckmann differential thermometer at the freezing point of the pure solvent, water. A known weight of the solute is introduced into the apparatus, containing a given weight of solvent, and the freezing point of the solution is read and recorded.

Example 5-13. The freezing point of water on the scale of the Beckmann thermometer is 1.112°C and the value for an aqueous solution of the solute is 0.120°C . What is the apparent K_f value if the concentration of the solution is 0.50 m ?

$$K_f = \frac{\Delta T_f}{m} = \frac{(1.112 - 0.120)}{0.50} = \frac{0.992}{0.50} = 1.98$$

Johlin¹³ described a semimicro apparatus for the determination of the freezing point of small quantities of physiologic solutions. Results may be obtained with as little as 1 mL of solution. The apparatus is now available commercially as the Osmette S, Model 400Z, from Precision Systems, Waltham, Mass., and the Advanced Digimatic Osmometer, Model 3DII, Advanced Instruments, Inc., Needham Heights, Mass. A schematic of the freezing point osmometer is shown in Figure 5-13.

The equilibrium method¹⁴ is the most accurate procedure for obtaining freezing point data. The freezing point of the pure solvent is determined accurately by intimately mixing the solid and liquid solvent (ice and water) in a jacketed tube or Dewar flask. When equilibrium is established, the temperature of the mixture is read with a Beckmann thermometer or with a multijunction thermocouple and a potentiometer. According to Ballard and Goyan,¹⁵ a thermistor may be used instead of a thermocouple. The solution, mixed

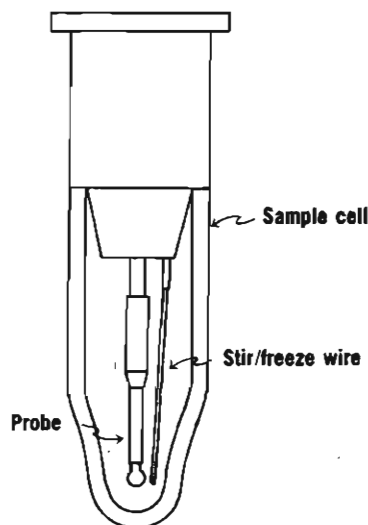


Fig. 5-13. Sensing unit of a freezing point "osmometer." The other parts of the osmometer, not shown, include a stirring motor, refrigeration unit, calibration dials, on-off switch, and a window that displays the freezing point value at equilibrium. The solution in the sample cell is supercooled several degrees below its freezing point; the tip of the stir/freeze wire then vibrates to form ice crystals. The temperature of the sample solution rises to its freezing point with the liberation of heat of fusion. The probe senses the equilibrium temperature, and it is read out in the display window (Advanced Digimatic osmometer, Model 3DII, Advanced Instruments, Inc., Needham Heights, MA).

with ice frozen from the pure solvent, is then placed in the flask, and when equilibrium is again attained, the temperature is recorded. A sample of the liquid phase is removed and analyzed at the time of measurement to determine accurately the concentration of the solution. The accuracy of the method can be improved by simultaneously placing the two ends of the thermocouple into two vacuum jacketed flasks, one containing the pure liquid in equilibrium with solid solvent and the other containing the solution in equilibrium with solid solvent. The difference in freezing points of the two systems can be determined to within $\pm 0.00002^{\circ}\text{C}$.

Ethylene glycol is the common antifreeze used in automobile cooling systems, air conditioners, freeze-drying apparatus, and so on. It has a high boiling point and may be retained in a car's radiator for as long as a year or more. It is therefore known as a *permanent* antifreeze. The same freezing point depression equation (5-28) that we have already used—namely, $\Delta T_f = K_f m$ —is used to estimate the effectiveness of an antifreeze to lower the freezing point of water in a car's cooling system. We see from the equation that the property of reducing the freezing point of water varies only with the molality of an antifreeze and not with the chemical characteristic of the agent. Methanol, denatured ethanol, propylene glycol, glycerol, and even sugars and honey have been used as antifreezes. However, ethylene glycol's high boiling point makes it particularly attractive. An automobile antifreeze is now used year-round; it raises the boiling point of water,

just as it lowers the freezing point, and thus prevents the loss of fluid through evaporation in the summer.

A more exact expression for freezing point depression is

$$\Delta T_f = \frac{RT_f T}{\Delta H_f} \ln X_1 \quad (5-30)$$

For a very dilute solution we can make the approximation that

$$\ln X_1 \approx \ln(1 - X_2) \approx -X_2 \quad (5-31)$$

Therefore, equation (5-30) becomes

$$\Delta T_f = \frac{RT_f T}{\Delta H_f} X_2 \quad (5-32)$$

in which T_f is the freezing point of the solvent, T is the freezing point of the solution, and ΔH_f is the heat of fusion of the solvent.

Example 5-14. How many liters of ethylene glycol (Caution, Poisonous!) must be added to a car's cooling system, which holds 12 kg of fluid, to protect the car from freezing at a temperature of +10° F? The molecular weight of ethylene glycol is 62.07 g/mole and its density $d_4^0 = 1.1274$ g/cm³. The heat of fusion of water is 1436 cal/mole. Use equation (5-32) and compare your result with that obtained from equation (5-28) on page 114.

We use the equation on the front leaf of the book to convert 10° F to -12.22° C, which is a lowering of the freezing point of water, 0° C, to -12.22° C, or $\Delta T_f = +12.22$

From equation (5-32),

$$X_2 = \frac{\Delta T_f \cdot \Delta H_f}{RT_f T} = \frac{(12.22)(1436)}{(1.9872)(273.2)(260.8)} = 0.1239$$

The quantity $X_2 = 0.1239$ is now expressed in molality; that is, in moles/kg water, and from moles/kg water to grams/kg water, then to mL/kg water, and finally to liters per 12 kg of fluid in the car's cooling system.

$$\begin{aligned} \text{molality, } * m, &= \frac{1000 X_2}{M_1(1 - X_2)} = \frac{1000 \times 0.1239}{18.015(1 - 0.1239)} \\ &= 7.850 \text{ moles/kg water} \end{aligned}$$

$$7.850 \text{ moles/kg water} \times 62.07 \text{ g/mole} = 487.25 \text{ g/kg water}$$

$$487.25 \text{ g/kg water} \div 1.1274 \text{ g/mL} = 432.19 \text{ mL/kg water}$$

$$432.19 \text{ mL/kg water} \times 12 \text{ kg fluid} = 5186.3 \text{ mL} = 5.19 \text{ liters}$$

Using the more approximate equation (5-28),

$\Delta T_f = K_f m$ in which $K_f = 1.86$ deg kg/mole, $\Delta T_f = 12.22$ deg, and molality, m , is

$$m = \Delta T_f / K_f = 12.22 / 1.86 = 6.570 \text{ mole/kg water}$$

$$\frac{6.570 \times 62.07}{1.1274} \times 12 \text{ kg fluid} = 4340.5 \text{ mL} = 4.34 \text{ liters}$$

A fair comparison—5.19 liters versus 4.34 liters—is obtained using the more exact equation (5-32) and the less exact equation (5-28).

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)¹⁶ 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 5-14. 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 (p. 106) 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.

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 really depends on the fact that the chemical potential (a thermodynamic expression of escaping tendency, discussed on page 106), of a solvent molecule in solution is less than exists in the pure solvent. Solvent therefore

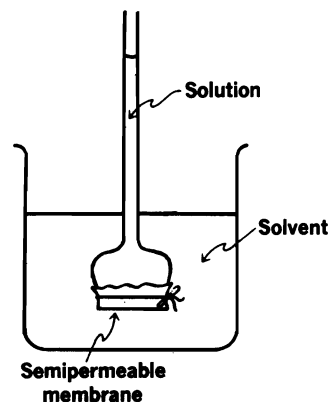


Fig. 5-14. Apparatus for demonstrating osmosis.

*See Table 5-3, page 104 for conversion equations used to change from one concentration unit to another. Note that in this example, an excess number of significant figures are retained until the final step, when they are rounded off. This is an acceptable procedure, particularly when using a hand calculator or computer.

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. (1) 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). (2) 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). (3) The osmotic pressure that is set up as a result of this passage of solvent molecules may 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. Since this is a function of the molecular weight of the solute, osmotic pressure is a colligative property and may be used to determine molecule weights.

As contrasted to the *freezing point* osmometer (Fig. 5-13), an *osmotic pressure* osmometer (Fig. 5-15) is based on the same principle as the thistle tube apparatus shown in Figure 5-14. 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 $h \times$ solution density $\rho \times$ 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 since 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 Pfeffer measured the osmotic pressure of sugar solutions, using a porous cup impreg-

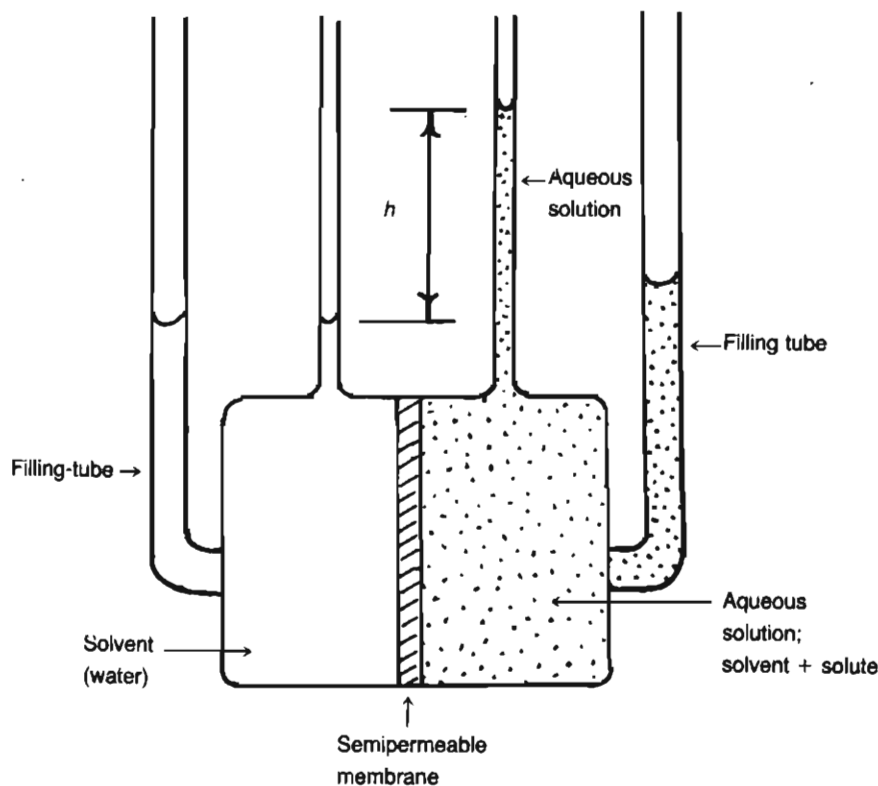


Fig. 5-15. Osmotic pressure osmometer.

nated with a deposit of cupric ferrocyanide ($\text{Cu}_2\text{Fe}(\text{CN})_6$) 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 signal¹⁷ 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, van't Hoff recognized in Pfeffer's data a proportionality between osmotic pressure, concentration, and temperature and 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

$$\pi V = nRT \quad (5-33)$$

in which 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 (5-33) is a limiting law applying to dilute solutions, and it simplifies into this form from a more exact expression (equation [5-39]) only after introducing a number of assumptions that are not valid for real solutions.

Example 5-15. 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?

$$\begin{aligned} \text{Moles of sucrose} &= \frac{1.0}{342} = 0.0029 \\ \pi \times 0.10 &= 0.0029 \times 0.082 \times 298 \\ \pi &= 0.71 \text{ atm} \end{aligned}$$

Equation (5-33), the van't Hoff equation, can be expressed as

$$\pi = \frac{n}{V} RT = cRT \quad (5-34)$$

in which c is the concentration of the solute in moles per liter (molarity). Morse and others have shown that when the concentration is expressed in molality rather

than molarity, the results compare more nearly with the experimental findings. The Morse equation is

$$\pi = RTm \quad (5-35)$$

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 may be obtained from certain thermodynamic considerations.

We begin by considering a sucrose solution in the right-hand compartment of the apparatus shown in Figure 5-16, and the pure solvent—water—in the left-hand compartment. The two compartments are separated by a semipermeable membrane through which water molecules, but not sucrose molecules, can pass. It is assumed that the gate in the air space connecting the solutions can be shut during osmosis. The external pressure, say 1 atmosphere, above the pure solvent is P_o , while the pressure on the solution, provided by the piston in Figure 5-16 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 .

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 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 $p^\circ - p = \Delta p$. 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

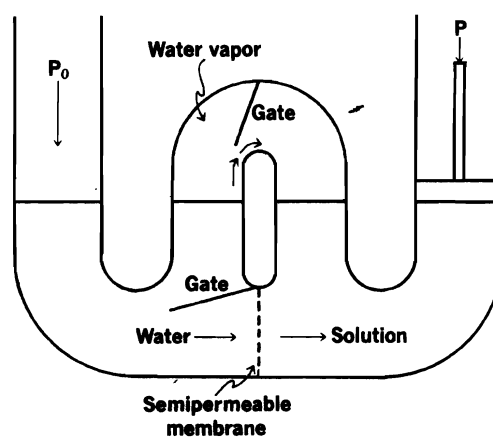


Fig. 5-16. Apparatus for demonstrating the relationship between osmotic pressure and vapor pressure lowering.

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 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 a mole of solvent from solvent to solution by a distillation process through the vapor phase and (b) transferring a mole of solvent from solvent to solution by osmosis.

$$(a) \quad \Delta G = RT \ln \frac{p}{p^\circ} \quad (5-36)$$

is the increase in free energy at a definite temperature for the passage of 1 mole of water to the solution through the vapor phase;

$$(b) \quad \Delta G = -V_1(P - P_o) = -V_1\pi \quad (5-37)$$

is the increase in free energy at constant temperature for the passage of 1 mole of water into the solution by osmosis. In equation (5-37), 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.

Equating equations (5-36) and (5-37) gives

$$-\pi V_1 = RT \ln \frac{p}{p^\circ} \quad (5-38)$$

and eliminating the minus sign by inverting the logarithmic term yields

$$\pi = \frac{RT}{V_1} \ln \frac{p^\circ}{p} \quad (5-39)$$

Equation (5-39) is a more exact expression for osmotic pressure than are equations (5-34) and (5-35), and it applies to concentrated as well as dilute solutions, provided that the vapor follows the ideal gas laws.

The simpler equation (5-35) for osmotic pressure may be obtained from equation (5-39), assuming that the solution obeys Raoult's law,

$$p = p^\circ X_1 \quad (5-40)$$

$$\frac{p}{p^\circ} = X_1 = 1 - X_2 \quad (5-41)$$

Equation (5-39) can thus be written

$$\pi V_1 = -RT \ln (1 - X_2) \quad (5-42)$$

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

$$\ln (1 - X_2) = -X_2 - \frac{X_2^2}{2} - \frac{X_2^3}{3} \dots - \frac{X_2^n}{n} \quad (5-43)$$

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

$$\ln (1 - X_2) \cong -X_2 \quad (5-44)$$

so that

$$\pi V_1 = RTX_2 \quad (5-45)$$

For a dilute solution, X_2 equals approximately the mole ratio n_2/n_1 , and equation (5-45) becomes

$$\pi \cong \frac{n_2}{n_1 V_1} RT \quad (5-46)$$

in which $n_1 V_1$, 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

$$\pi = \frac{n_2}{V} RT = RTm \quad (5-47)$$

which is Morse's expression, equation (5-35).

Example 5-16. Compute π for a 1-*m* aqueous solution of sucrose using both equation (5-35) and the more exact thermodynamic equation (5-39). 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 cm³/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—may 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.

Since 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 weight M_1 and M_2 respectively, equation (5-15) can be expressed as

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1 + n_2} = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2} \quad (5-48)$$

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

$$\frac{\Delta p}{p_1^\circ} = \frac{w_2/M_2}{w_1/M_1} \quad (5-49)$$

The molecular weight of the solute M_2 is obtained by rearranging equation (5-49) to

$$M_2 = \frac{w_2 M_1 p_1^\circ}{w_1 \Delta p} \quad (5-50)$$

Mason and Gardner¹⁸ have used the isopiestic method, outlined previously (p. 111), for the determination of molecular weights by vapor pressure lowering.

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. Since 1000 w_2/w_1 is the weight of solute per kilogram of solvent, molality (moles/kilogram of solvent) can be expressed as

$$m = \frac{w_2/M_2}{w_1} \times 1000 = \frac{1000w_2}{w_1 M_2} \quad (5-51)$$

and

$$\Delta T_b = K_b m \quad (5-52)$$

then

$$\Delta T_b = K_b \frac{1000w_2}{w_1 M_2} \quad (5-53)$$

or

$$M_2 = K_b \frac{1000w_2}{w_1 \Delta T_b} \quad (5-54)$$

Example 5-17. 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?

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

As was shown in Figure (5-10), the lowering of vapor pressure arising from the addition of a nonvola-

tile solute to a solvent results in a depression of the freezing point. By rearranging equation (5-29).

$$M_2 = K_f \frac{1000w_2}{\Delta T_f w_1} \quad (5-55)$$

in which 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 5-18. 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.

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

The van't Hoff and Morse equations may 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 15.

Example 5-19. 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?

$$\pi = cRT = \frac{c_p RT}{M_2} \quad (5-56)$$

in which c_p 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, since 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, since 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 (pp. 401-402).

Since the colligative properties are interrelated, it should be possible to determine the value of one

property from a 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,

$$\pi = RT \frac{\Delta T_f}{K_f} = \frac{22.4}{1.86} \Delta T_f \quad (5-57)$$

or

$$\pi \cong 12\Delta T_f \quad (5-58)$$

Lewis¹⁹ suggested an equation:

$$\pi = 12.06 \Delta T_f - 0.021 \Delta T_f^2 \quad (5-59)$$

which gives accurate results.

Example 5-20. 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?

$$\begin{aligned} \pi &= 12 \times 0.53 = 6.36 \text{ atm} \\ \pi &= 12.06 \times 0.53 - 0.021(0.53)^2 = 6.39 \text{ atm} \end{aligned}$$

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.

Example 5-21. In your laboratory you wish to study the applicability of various colligative property methods for determining the molecular weights of small and large molecules. You begin by comparing the freezing point depression method and the osmotic pressure method. To obtain freezing point depressions and osmotic pressures, you decide to use the following hypothetical data for both large and small drug molecules, and then compare the relative precision of the two methods. Let $M_2 = 250$ g/mole (small drug); $M_2 = 1,000,000$ g/mole (macromolecule). The concentration is 1% (w/v) or 10 g/1000 cm³ for both macromolecular and small-drug aqueous solutions. The density of both aqueous solutions is 1.010 g/cm³ and the temperature is 298° K.

Use the equations on page 120 for freezing point depression and osmotic pressure with $K_f = 1.86$ and $R = 0.0821$ liter atm deg⁻¹ mol⁻¹.

The weight of the solutions is

$$1000 \text{ cm}^3 \times 1.010 \text{ g/cm}^3 = 1010 \text{ g solution}$$

For the small-drug solution, equation (5-55),

$$\Delta T_f = K_f \frac{1000 w_2}{w_1 M_2} = 1.86 \times \frac{1000 \times 10}{(1010 - 10)250} = 0.0744 \text{ deg}$$

Osmotic pressure may be calculated using either the van't Hoff (equation [5-33]) or the Morse (equation [5-35]) expression. Beginning with the van't Hoff equation (5-33), we have equation (5-56):

$$\begin{aligned} \pi &= c_p RT/M_2 = (10 \times 0.0821 \times 298)/250 = 0.979 \text{ atm} \\ 0.979 \text{ atm} \times 760 \text{ mm Hg/atm} &= 744 \text{ mm Hg} \end{aligned}$$

Use of the Morse equation (5-35) proceeds as follows for the small drug:

$$\pi = RTm$$

where $m = 1000 w_2/w_1 M_2$ (equation [5-51]).

Therefore,

$$\begin{aligned} \pi &= (RT) \frac{1000 w_2}{w_1} \frac{1}{M_2} \\ &= (0.0821 \times 298) \frac{1000 \times 10}{(1010 - 10) 250} = 0.979 \text{ atm} \end{aligned}$$

Changing to mm Hg,

$$0.979 \text{ atm} \times 760 \text{ mm Hg/atm} = 743.8 \text{ mm Hg}$$

In actual experimental work, the capillary tube of the osmometer contains an aqueous solution and not mercury (see Fig. 5-15). Therefore, the height in the capillary calculated as mm Hg is converted into millimeters of solution. This is done using the conversion factor:

$$\text{mm aqueous solution} = \text{mm Hg} \times \frac{13.534 \text{ g/cm}^3 \text{ for Hg at } 25^\circ \text{ C}}{\text{density of solution (g/cm}^3\text{) at } 25^\circ \text{ C}}$$

The van't Hoff and the Morse equations yielded an osmotic pressure of 743.8 mm Hg as seen above. This value is then changed to mm aqueous solution:

$$743.8 \text{ mm Hg} \times \frac{13.534}{1.010} = 9967 \text{ mm solution}$$

for the small-drug molecule of molecular weight 250 g/mole.

For the freezing point depression of the macromolecular solution, $M_2 = 10^6$ g/mole,

$$\Delta T_f = (1.86) \frac{1000 \times 10}{(1010 - 10) 10^6} = 1.860 \times 10^{-6} \text{ deg}$$

Applying the Morse equation to obtain the osmotic pressure of the large molecule gives

$$\pi = (0.0821 \times 298) \frac{1000 \times 10}{(1010 - 10) 10^6} = 2.45 \times 10^{-4} \text{ atm}$$

Changing to mm Hg and then to mm aqueous solution:

$$2.45 \times 10^{-4} \text{ atm} \times 760 \text{ mm Hg/atm} = 0.186 \text{ mm Hg}$$

$$0.186 \text{ mm Hg} \times \frac{13.534}{1.010} = 2.492 \text{ mm solution}$$

This analysis shows that the freezing point depression method (*cryoscopic method*) is quite adequate for small-molecular-weight determinations, a 1% solution giving $\Delta T_f \cong 0.07$ deg, which is easily read on a Beckmann thermometer. Not so for a large polymeric

TABLE 5-5. Approximate Expressions for the Colligative Properties

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

drug molecule. The cryoscopic method yields $\Delta T_f = 1.8 \times 10^{-5}$ deg, which cannot be read accurately by any thermometric device readily available in the laboratory. The values given above are differences in degrees and may be expressed as either Kelvin or centigrade degrees. When we turn to osmometry, the situation brightens for the large-molecule analysis. Although it is

slower and more tedious than freezing point depression work, and need not be used for small molecules, which are easily analyzed by cryoscopy, osmometry provides values that are easily read on the millimeter scale for polymeric molecules of molecular weights as large as several millions.

A summary of the comparative results is as follows:

Cryoscopy			
Molecular Size	Molecular Weight	ΔT_f	
Small molecule, 1% (w/v)	250 g/mole	0.074 deg	
Large molecule, 1% (w/v)	10^6 g/mole	1.860×10^{-5} deg	
Osmometry			
Molecular Size	Molecular Weight	π	
		van't Hoff	Morse
Small molecule, 1% (w/v)	250 g/mole	9967 mm sol.	9967 mm sol.
Large molecule, 1% (w/v)	10^6 g/mole	2.492 mm sol.	2.492 mm sol.

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Problems

5-1. A solution of sucrose (molecular weight 342) is prepared by dissolving 0.5 g in 100 g of water. Compute (a) the weight percent, (b) the molal concentration, and (c) the mole fraction of sucrose and of water in the solution.

Answers: (a) 0.498% by weight; (b) 0.0146 m; (c) 0.00026 mole fraction of sucrose; 0.99974 mole fraction of water

5-2. An aqueous solution of glycerin, 7.00% by weight, is prepared. The solution is found to have a density of 1.0149 g/cm^3 at 20°C . The molecular weight of glycerin is 92.0473 and its density is 1.2609 g/cm^3 at 20°C . What is the molarity, molality, and percent by volume?

Answer: 0.7718 M, 0.8177 m, 5.63% v/v

5-3. What is the normality of a 25.0-mL solution of hydrochloric acid, that neutralizes 20.0-mL of a 0.50-N sodium hydroxide solution?

Answer: 0.40 N

5-4. How many grams of Na_2SO_4 (molecular weight 142) are required to make 1.2 liters of a 0.5-N solution?

Answer: 42.6 g

5-5. (a) Give the number of equivalents per mole of HCl, H_3PO_4 , and $\text{Ba}(\text{OH})_2$. (b) What is the equivalent weight of each of these compounds?

Answers: (a) The number of equivalents is 1, 3, and 2, respectively. (b) The equivalent weights of these compounds are 36.5 g/Eq, 32.7 g/Eq, and 85.7 g/Eq, respectively.

5-6. What is the equivalent weight of anhydrous $\text{NaAl}(\text{SO}_4)_2$ (molecular weight 242) when used for its sodium, aluminum, and sulfate content, respectively?

Answer: 242 g/Eq, 80.7 g/Eq, and 60.5 g/Eq, respectively

5-7. If normal human plasma contains about 3 mEq/liter of the hydrogen phosphate ion HPO_4^{2-} , how many milligrams of dibasic potassium phosphate, K_2HPO_4 (molecular weight 174), are required to supply the needed HPO_4^{2-} for an electrolyte replacement in the hospital?

Answer: 261 mg/liter

5-8. How many grams of $\text{Ca}_3(\text{PO}_4)_2$ are required to prepare 170 mL of a 0.67-N solution? The molecular weight of $\text{Ca}_3(\text{PO}_4)_2$ is 310.

Answer: 5.88 g

5-9. The vapor pressure p_B^0 of pure butane is 2.3966 atm at 25°C and that of n-pentane p_P^0 is 0.6999 atm at 25°C . Using Raoult's law, calculate the partial vapor pressure of n-butane (molecular weight 58.12) and n-pentane (molecular weight 72.15) in a mixture of 50 g of each of these two vapors at 25°C in atm and in pounds/in.².

Answer: 1.327 atm and 0.312 atm. To convert atm to pounds/in.², multiply by 14.70.

5-10. The vapor pressures of pure "Freon 11" and pure "Freon 12" at 25°C are 15 lb/in.² and 85 lb/in.² respectively. In the preparation of a pharmaceutical aerosol these two propellants were mixed together in the mole ratio of 0.6 to 0.4.

(a) What are the partial vapor pressures of "Freon 11" and "Freon

12" in a mixture having a mole ratio of 0.6 to 0.4, assuming that the mixture follows Raoult's law?

(b) What is the total vapor pressure of this mixture at 25° C?

(c) An aerosol can safely be packaged in a glass container protected with a plastic coating as long as the pressure does not exceed about 35 lb/in.² (20 lb/in.² in gauge pressure) at room temperature. Can such a container be used for the preparation described in this example? Can freons be used today in pharmaceutical aerosols?

Answers: (a) $p_{11} = 9 \text{ lb/in.}^2$; $p_{12} = 34 \text{ lb/in.}^2$; (b) $P = 43 \text{ lb/in.}^2$

5-11. (a) State Henry's law and discuss its relationship to Raoult's law. (b) How is Henry's law used in the study of gases in solution?

Answers: (a) See the sections on Raoult's law and Henry's law (pp. 107-109). (b) See Problems 5-12 and 5-13 in this chapter, and Problems 10-3 through 10-6 in Chapter 10.

5-12.* One may wonder how a fish breathes oxygen when the oxygen is dissolved in water. It is the peculiar gill system of a fish that allows it to take up the oxygen into its body directly from water. The solubility of oxygen in the air dissolved in water is calculated using Henry's law, $p_{O_2} = kX_{O_2}$. The partial pressure p_{O_2} of O_2 in the air at 25° C is 0.20 atm and that of N_2 is 0.80 atm. The Henry law constants at 25° C are given in the table.

Data for Problem 5-12

Gas	mm Hg per mole fraction of gas	atmospheres per mole fraction of gas
O_2	3.30×10^7	4.34×10^4
N_2	6.51×10^7	8.57×10^4

(a) Calculate X_{O_2} , the mole fraction of oxygen and X_{N_2} , the mole fraction of nitrogen gas in air at 25° C.

(b) What is the total mole fraction concentration of these two gases in water at 25° C?

(c) In air, oxygen constitutes 20% or one fifth of the total pressure (see above). What fractional contribution does oxygen make to the concentration of the two gases in water?

(d) Is the dissolved air a fish breathes in water proportionately greater in oxygen than the air we land animals breathe?

Answers: (a) $X_{O_2} = 4.61 \times 10^{-6}$; $X_{N_2} = 9.33 \times 10^{-6}$; (b) total mole fraction concentration = 13.94×10^{-6} ; (c) in water, oxygen constitutes one third of the pressure; (d) yes: one third is greater than one fifth

5-13. The partial vapor pressure of oxygen dissolved in water in equilibrium with the atmosphere at 25° C is 200 mm, and the Henry's law constant k is 3.3×10^7 mm Hg/mole fraction of O_2 . What is the concentration of oxygen in water expressed in mole fraction?

Answer: 6.06×10^{-6}

5-14. The freezing point lowering of a solution containing 1.00 gram of a new drug and 100 grams of water is 0.573° C at 25° C. (a) What is the molecular weight of the compound? (b) What is the boiling point of the solution? (c) What is the osmotic pressure of the solution?

Answers: (a) 32.46 g/mole; (b) b.p. 100.157° C; (c) 7.54 atm. Using equation (5-35), $\pi = 6.87$ atm.

5-15. (a) Derive an equation relating osmotic pressure and the lowering of the vapor pressure of a solution at 25° C. Refer to Table 5-5 for equations relating π to Δp .

(b) Give an explanation for the manner in which an osmotic membrane functions. Use a diagram of the cell and membrane to show the flow of the component liquids and the production of osmotic pressure.

Partial Answer: (a) At 25° C, $\pi = 56.93 \Delta p$.

5-16. A 105-g sample of polyethylene glycol 400 (PEG 400) was dissolved in 500 g of water, and the vapor pressure of the solution was found to be 122.6 torr at 56.0° C. The boiling point elevation of this solution over that of pure water (100° C at 1 atm) was determined to be 0.271° C. The vapor pressure of pure water, p_1^0 , at 56° C is 123.80 torr. Calculate the molecular weight of this sample of PEG 400 using vapor pressure lowering, boiling point elevation, and osmotic pressure. The "400" of PEG means that the molecular weight of this polymer is approximately 400 g/mole. The density of water at 56° C is 0.985 g/cm³. Experimentally, π was obtained as 0.0138 atm.

Answers: From vapor pressure lowering, $M_2 = 390$ g/mole. From boiling point elevation, $M_2 = 395$ g/mole. From osmotic pressure, $M_2 = 411$ g/mole.

5-17. Determine the boiling point elevation constant K_b for carbon tetrachloride. You can obtain the molecular weight and boiling point of CCl_4 from the *Merck Index*. To obtain the heat of vaporization ΔH_v at the boiling point, you will need to consult the *CRC Handbook of Chemistry and Physics* or other sources that give ΔH_v for CCl_4 at various temperatures. CRC gives ΔH_v values in units of BTU/lb or cal/g and temperatures in Fahrenheit or Celsius degrees, up to 120° F (48.89° C).

(a) Plot the ΔH_v values versus temperature and extrapolate the line (by eye) to 76.7° C, the boiling point of CCl_4 . The molecular weight of CCl_4 is 153.84 g/mole. Convert ΔH_v in cal/g to cal/mole and degrees C to degrees Kelvin, then square the temperature for use in the cryoscopic constant equation, $K_b = RT_b^2 M_1 / (1000 \cdot \Delta H_v)$ (p. 113).

(b) You may care to use linear, quadratic, or cubic regression of ΔH_v against temperature on a hand calculator or personal computer to obtain the best fit of the data and the most satisfactory extrapolation to give ΔH_v at the boiling point of carbon tetrachloride.

Answers: (a) $K_b = 5.0$ to 5.2 depending on the method of extrapolation used. (b) Using cubic regression, $K_b = 5.13$.

5-18. A solution of drug is prepared by dissolving 15.0 g in 100 g of water, and is subjected to ebullioscopic analysis. The boiling point elevation is 0.28° C. Compute the molecular weight of the drug.

Answer: 275 g/mole

5-19. In the summer the vaporization of the cooling fluid of a car is retarded by the presence of ethylene glycol, which acts by increasing the boiling point of water. (a) For the ethylene glycol-in-water solution discussed in *Example 5-14* calculate the boiling point elevation of water in degrees Fahrenheit using equation (5-26). The heat of vaporization of water is 9720 cal/mole. The mole fraction X_2 of ethylene glycol in the aqueous solution is 0.1239. (b) Compare the result with that obtained by using the less exact expression, $\Delta T_b = K_b m$.

Answers: (a) Using the mole fraction equation one obtains the boiling point elevation of water, ΔT_b , in Fahrenheit degrees as 6.35° F. (b) $\Delta T_b = 7.20$ ° F

5-20. (a) What is the boiling point rise for a 0.437 molal solution of anthracene in chloroform? Use equation 5-52, page 120. (b) The molecular weight of anthracene is 178.2 g/mole. Using equation (5-53), page 120, check your result in (a); i.e., calculate ΔT_b .

Answers: (a) $\Delta T_b = 1.586$ ° C; (b) $\Delta T_b = 1.586$ ° C

5-21. A solution containing 0.2223 grams of benzanthine penicillin G in 1000 grams of benzene has a freezing point of 0.00124° below that of the pure solvent (5.5° C for benzene). What is the molecular weight of benzanthine penicillin G?

Answer: 918 g/mole (actual mol. wt. = 909 g/mole)

5-22. Five grams of a new drug (a nonelectrolyte) are dissolved in 250 g of water, and the solution is subjected to a cryoscopic analysis to obtain the molecular weight. The freezing point depression is found to be 0.120° C. Compute the molecular weight.

Answer: 310 g/mole

5-23. (a) Compute the freezing point depression of 1 g of methylcellulose (molecular weight 26,000 g/mole) dissolved in 100 g of water.

(b) Using the Morse equation, compute the osmotic pressure of this solution at 20° C. Express the result in cm of solution. To convert mm

*Problem 5-12 is modified from J. W. Moncrief and W. H. Jones, *Elements of Physical Chemistry*, Addison-Wesley, Reading, Mass., 1977. p. 115.

of mercury to mm solution, mm solution = mm Hg $\times \frac{\rho_{\text{Hg}}}{\rho_{\text{solution}}}$. The density of mercury at 20° C is 13.5462 g/mL. Assume that the density of the solution is 1 g/mL.

(c) Assume that you have a thermometer in which you are able to accurately read 0.05° C and estimate the value to 0.005° C. Can you use freezing point depression of the methylcellulose solution to determine the molecular weight of this polymer? Can you use osmotic pressure to obtain the molecular weight?

Answers: (a) $\Delta T_f = 0.0007^\circ \text{C}$; (b) $\pi = 9.9 \text{ cm}$; (c) the freezing point depression is too small to read on most thermometers. You should use osmotic pressure to determine the molecular weight of methylcellulose.

5-24. (a) Calculate the cryoscopic constant of benzene. The heat of fusion, ΔH_f , is 2360 cal/mole, and the melting point of benzene is 5.5° C. Its molecular weight is 78.11 g/mole.

(b) Calculate the ebullioscopic constant of phenol. Its heat of vaporization is 9730 cal/mole and its boiling temperature is 181.4° C. The molecular weight of phenol is 94.11 g/mole. Compare your results with those found in Table 5-4.

Answers: (a) K_f (benzene) = 5.10 deg kg/mole; (b) K_b (phenol) = 3.97 deg kg/mole

5-25. Compute the freezing point depression of a 0.20% w/v glucose solution. The molecular weight of glucose is 180 gram/mole.

Answer: $\Delta T_f = 0.02^\circ$

5-26. What concentration of ethylene glycol is required to protect a car's cooling system from freezing down to -20° F? Express the concentration in grams of antifreeze per 100 grams of fluid in the system. The molecular weight of ethylene glycol is 62.07 g/mole.

Answer: 96.6 grams of ethylene glycol per 100 grams of fluid

5-27. It is winter and you are caught in your home at night in a severe winter storm of snow and ice; the temperature is -20° F. Your child is sick and you must get to the village pharmacy 10 miles away in the morning to have the child's prescription filled. You just brought home a new car but you forgot to have it serviced with antifreeze. You have a 5-pound bag of sucrose in the house and you know that the volume of the car's coolant system is 9 quarts (1 quart = 0.9463 liters).

(a) How far can the temperature drop overnight in your driveway (no garage) before the coolant system would freeze if you added 5 pounds of sugar to the water in the radiator and were sure that it dissolved completely? The molecular weight of sucrose is 342 g/mole and 1 lb (avoirdupois) = 0.4536 kg.

(b) All means of transportation, including taxis, buses, and emergency vehicles, are tied up because of the storm. The demands on the pharmacy, grocery and other stores are such that they cannot deliver. What other solutions might you arrive at to handle this emergency, should the addition of sucrose not protect the car's coolant system?

Answers: (a) $\Delta T_f = 1.09^\circ \text{C}$ or 1.96°F . These results show that the

use of sucrose will be of little help. (b) Discuss with your classmates other possibilities to deal with this emergency.

5-28. What is the osmotic pressure of a solution of urea (molecular weight 60) containing 0.30 g of the drug in 50 mL of water at 20° C? Use the van't Hoff equation.

Answer: 2.4 atm

5-29. Compute the osmotic pressure of a 0.60-m aqueous mannitol solution using (a) equation (5-35) and (b) equation (5-39). The vapor pressure of the solution p at 20° C is 17.349 mm Hg and the vapor pressure of water p° at the same temperature is 17.535 mm Hg. The molar volume of water at 20° C is 0.0181 liter/mole.

Answers: (a) 14.4 atm; (b) 14.3 atm

5-30. If the freezing point of blood is -0.52° C, what is its osmotic pressure at 25° C? What is the vapor pressure lowering of blood at this temperature?

Answer: $\pi = 6.84 \text{ atm}$; $\Delta p = 0.12 \text{ mm Hg}$

5-31. A new alkaloid, guayusine, was isolated from a South American plant, *Guayusa multiflora*. A solution containing 0.473 g of the alkaloid per 500 mL of aqueous solution produced an osmotic pressure of 0.060 atm (i.e., 45.6 mm of Hg or 619 mm of solution) at 25° C. The drug does not associate or dissociate in aqueous solution. Calculate the approximate molecular weight of guayusine.

Answer: 386 g/mole

5-32. The freezing point depression of 2.0 grams of antigesic, a new antipyretic and analgesic, in 100 mL of aqueous solution was found to be 0.198° C. (a) Compute the osmotic pressure of the solution. (b) Compute the molecular weight of antigesic from its osmotic pressure. ΔT_f and π are related through the equations $\Delta T_f = K_f c_g$ and $\pi = RTc_g$ where RT is taken as 22.43 at 0° C and c_g is concentration in g/liter. The drug behaves almost ideally in dilute aqueous solution. It does not dissociate or associate in water; therefore, equation (5-57) is adequate to yield an approximate molecular weight.

Answer: (a) $\pi = 2.39 \text{ atm}$; (b) $M_2 = 188 \text{ g/mole}$

5-33. A new polypeptide drug has been synthesized and its molecular weight is estimated to be in the range of 10,000 daltons (1 dalton = 1 g/mole). Which colligative property method would be best for accurately determining its molecular weight? The question is answered by calculating ΔT_b , ΔT_f , Δp , and π at 20° C for a 1% solution of the drug in water. The vapor pressure p_1° of water at 20° C is 17.54 mm Hg. The density of the solution is 1.015 g/mL, and the density of mercury needed to convert mm Hg to mm solution is 13.5462 g/mL at 20° C.

Answer: $\pi = 243 \text{ mm of solution}$; $\Delta T_b = 5.07 \times 10^{-4} \text{ deg}$; $\Delta T_f = 1.85 \times 10^{-3} \text{ deg}$; $\Delta p = 3.14 \times 10^{-3} \text{ mm Hg}$. The best colligative property to determine the molecular weight of this macromolecule is osmotic pressure, for the easiest to measure is $\pi = 243 \text{ mm solution}$. The other values are too small to measure accurately. The determination of the molecular weights of macromolecules is discussed in Chapter 15.