solution has been lowered 0.89% by the 0.5 mole of sucrose.

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

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

Example 5-9

Calculation of the Vapor Pressure

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

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

The final vapor pressure is

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

Elevation of the Boiling Point

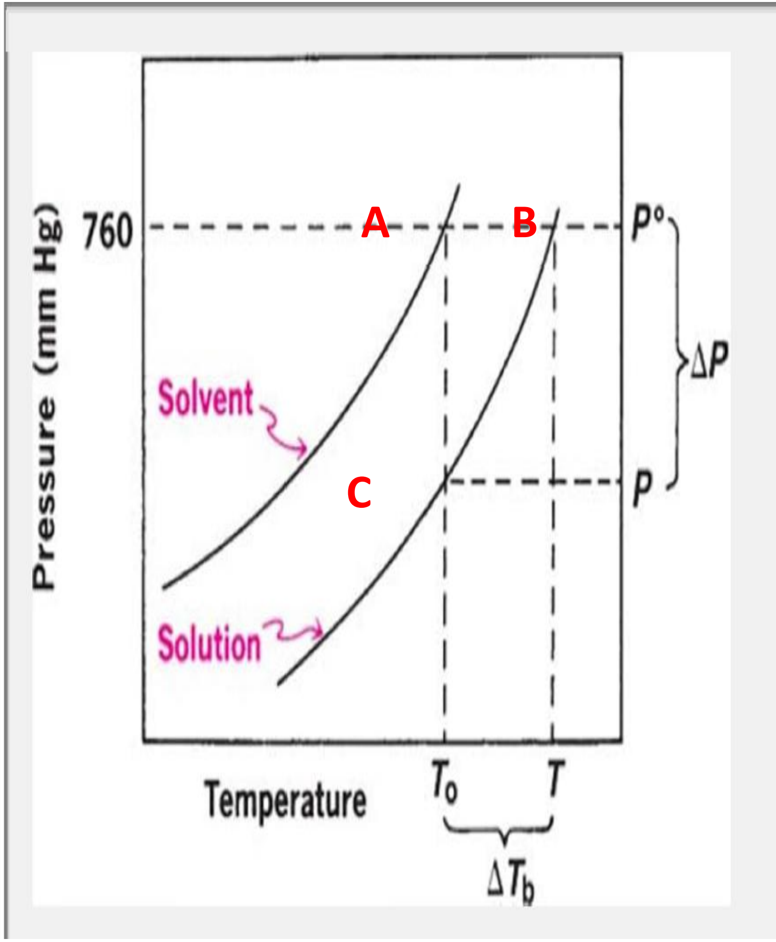
Elevation of boiling point (ΔT_b)

- When the solute dissolved in a solvent, the solute will be lowers the V.P. of the pure solvent.
- The V.P. curve for solution lies below that pure solvent.
- The ratio of ΔTb and ΔP at 100 ^{0}C is approximately constant

AC= lower V.P=$\Delta P = P^0 - P$

AB= Elevation $T_b = \Delta T = T_b - T^0$

$\Delta T_b / \Delta P = K'$



$\Delta T_b = K'\Delta P * P^0/P^0 \longrightarrow \Delta T_b = K'P^0 \, \Delta P/P^0 \longrightarrow$

$\Delta T_b = K \, X_2$ ....$K = K'P^0$ = constant and $\Delta P/P^0 = X_2$

$X_2 = m * Mw1/1000$

$\Delta T_b = K \, m * Mw1/1000$

$\Delta T_b = K_b \, m$ .... $K_b = K \, Mw_1/1000$ = constant

K_b: ***molal elevation constant*** (*ebullioscopic constant*) *it is characteristic value for each solvent*

- From clapyron equation, $K = RT_b^2/\Delta H\boldsymbol{v}$
- $K_b = RT_b^2 \, Mw_1/1000 \, \Delta H\boldsymbol{v}$ ***(constant)***

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

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

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

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

Example 5-10

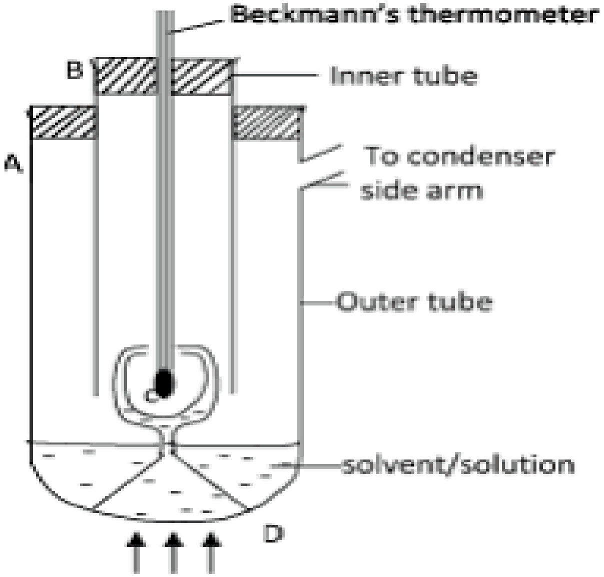
Calculation of the Elevation Constant

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

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

The proportionality between ΔT_b and the molality is exact only at infinite dilution, at which the properties

The T_b determined by Cottell's boiling apparatus

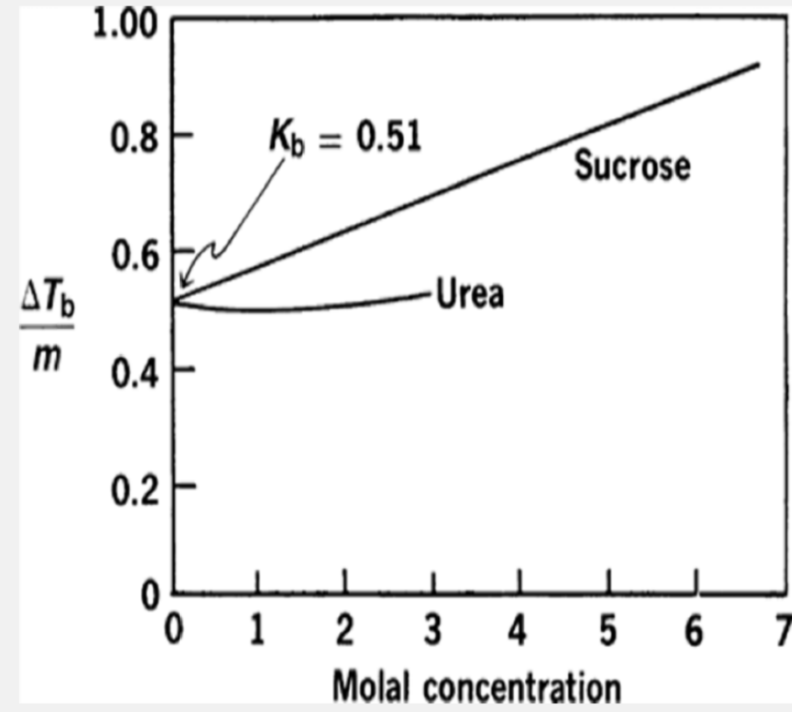


$K_b = \Delta T_b / m$

at very dilute concentration C→0 and when $\Delta T_b / m$ plotted against m, so k_b will be equal the intercept of $\Delta T_b / m$ axis

K_b= **0.51** for water solvent (aqueous solution)

$\Delta T_b = 0.51 * m$ for aqueous solutions



3- Freezing point depression

$S \overset{Tm}{\underset{Tf}{\longleftrightarrow}} L$

At the equilibrium S and L are identical escaping tendency. (such as transfer heat to cold)

The P,T curve for pure solvent and ΔT_f is proportional to the **m**

A > B

$\Delta T_f = T^0 - T_f = K_f \mathbf{m}$

Where Kf is the molal depression constant (cryoscopic constant)

Depend on the chemical and physical Properties of solvent.

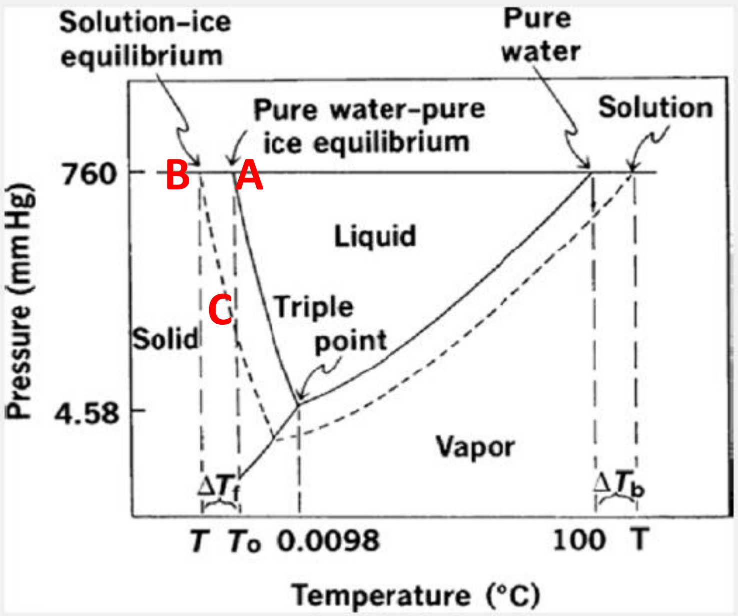


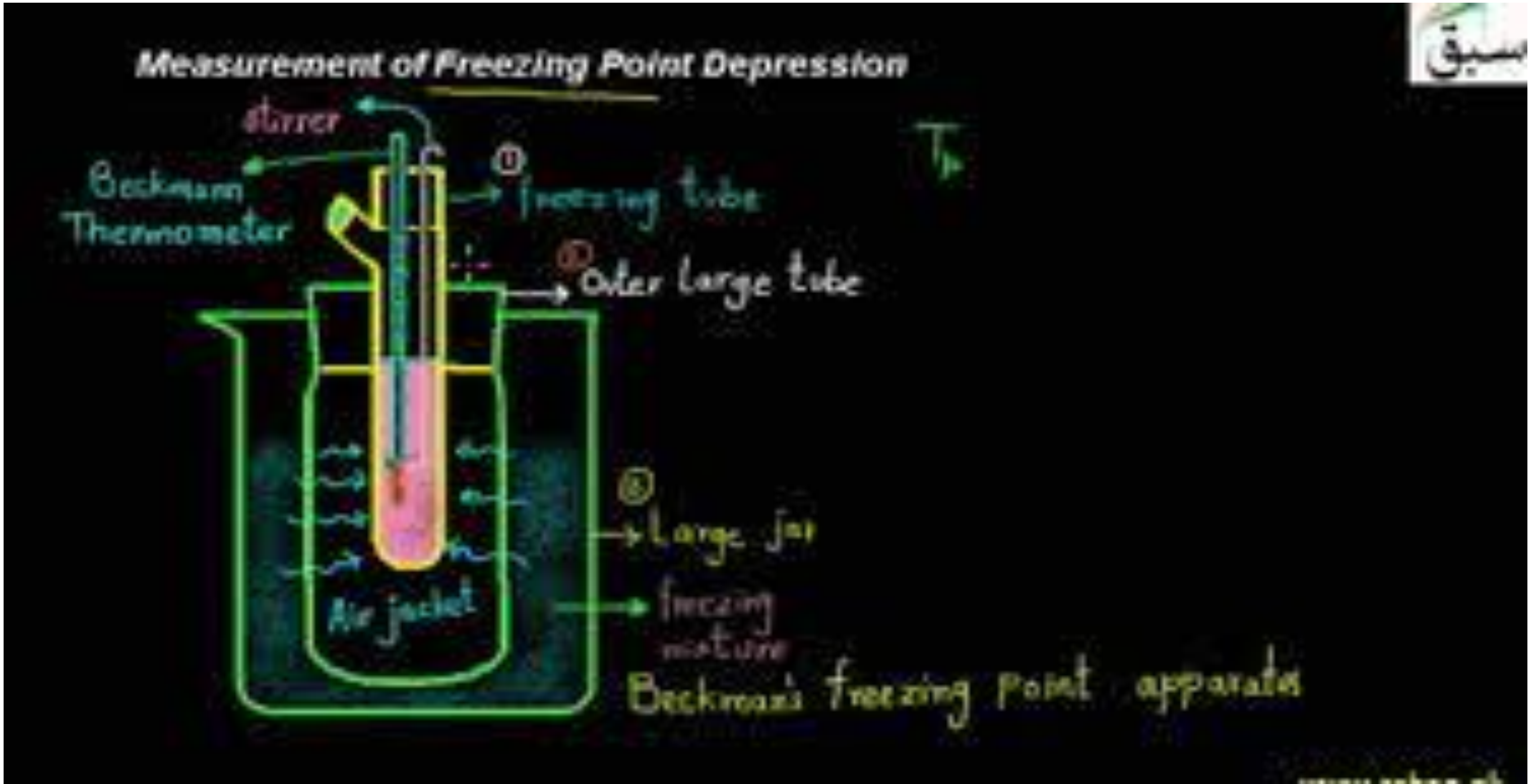
Fig. 5-8. Depression of the freezing point of the solvent, water, by a solute (not to scale).

From Clapyron equation

$K_f = RT_f^2\ Mw_1/1000\ \Delta H_f$

K_f for water=1.86 deg.kg.mol^{-1}

the T_f determination by Beckman freezing point apparatus



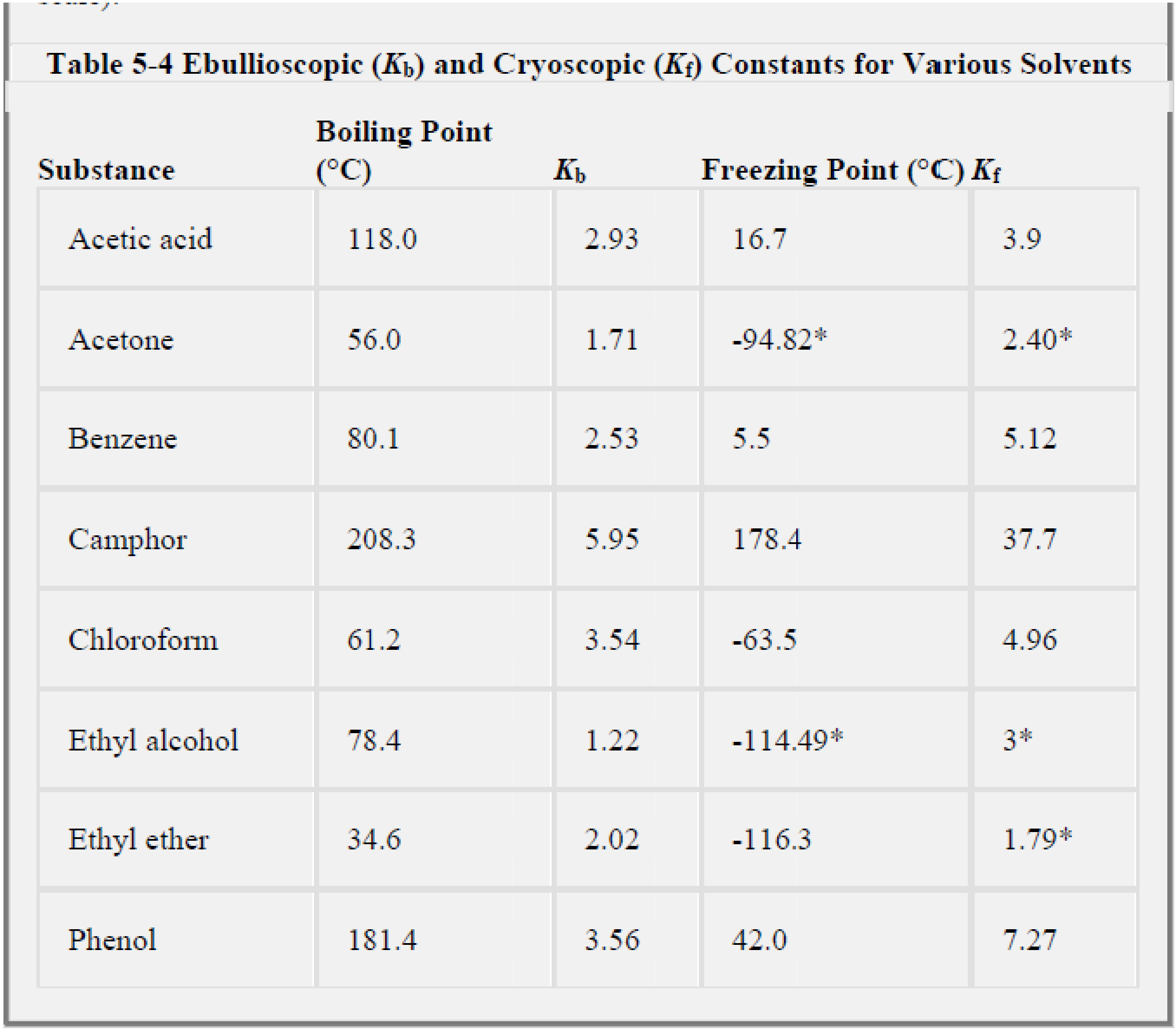
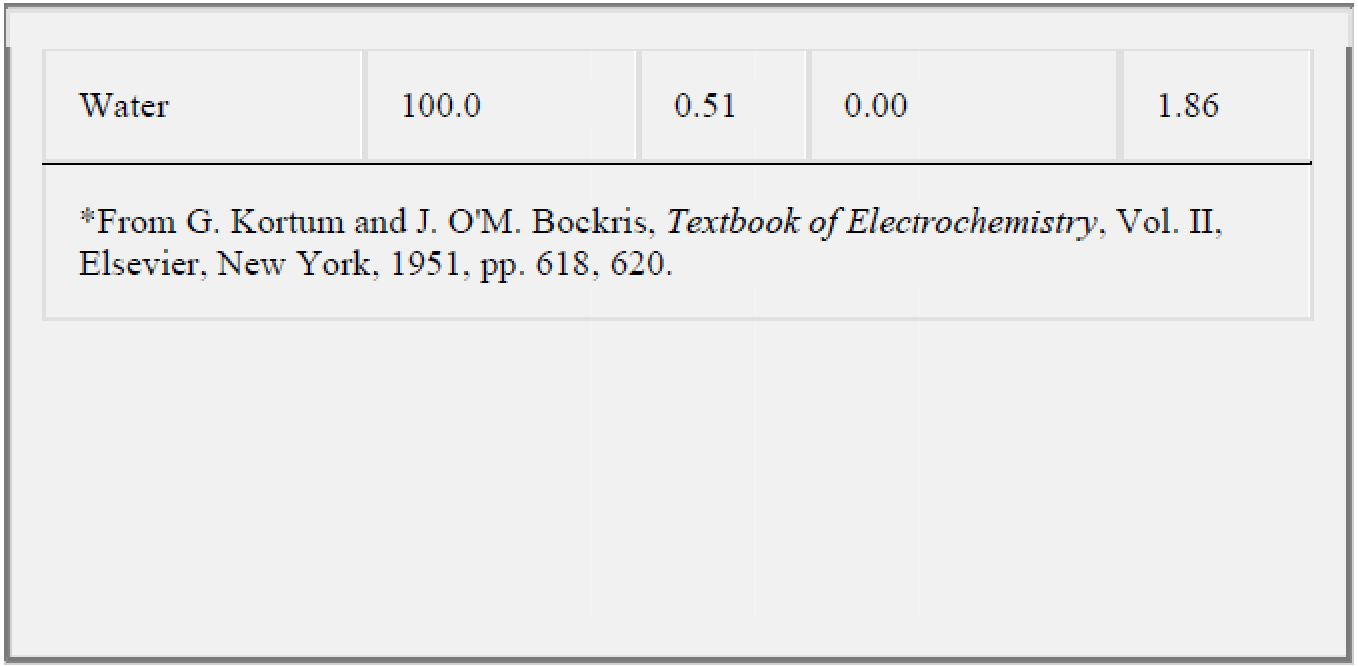


Table 5-4 Ebullioscopic (K_b) and Cryoscopic (K_f) Constants for Various Solvents

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



Water	100.0	0.51	0.00	1.86

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

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

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

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

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

or

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

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

- $K_f = \Delta T_f / m$
- At very dilute concentration $m \rightarrow 0$ and when $\Delta T_f / m$ plotted against **m**, k_f will be equal to the intercept of $\Delta T_f / m$ axis .
- K_f = **1.86** for aqueous solution
- Note: Citric acid is electrolyte solution

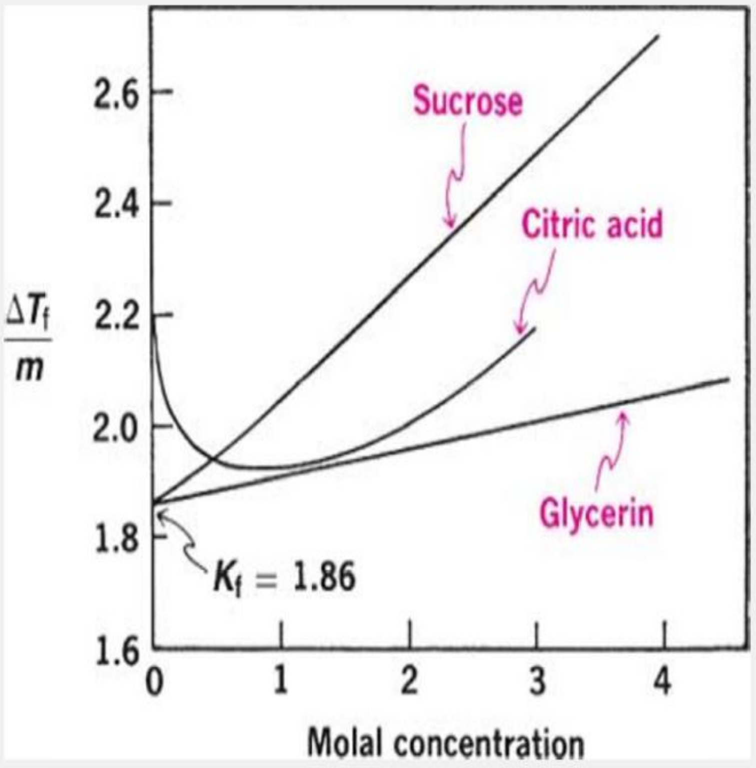


Fig. 5-9. The influence of concentration on the cryoscopic constant fo

are given in Table 5-4.

Example 5-11

Calculation of Freezing Point

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

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

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

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

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

Example 5-12

Freezing Point Depression

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

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

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

Osmotic Pressure

4- Osmotic pressure(π)

Osmosis defined as the passage of the solvent into a solution through a semi permeable membrane

The membrane may act a sieve having a pore size sufficient to allow passage of solvent but not of solute molecules.

The escaping tendency or ΔG of

Pure solvent molecules >

solvent molecules in solution

$\Delta G_{\text{solution}} - \Delta G_{\text{solvent}} < 0$

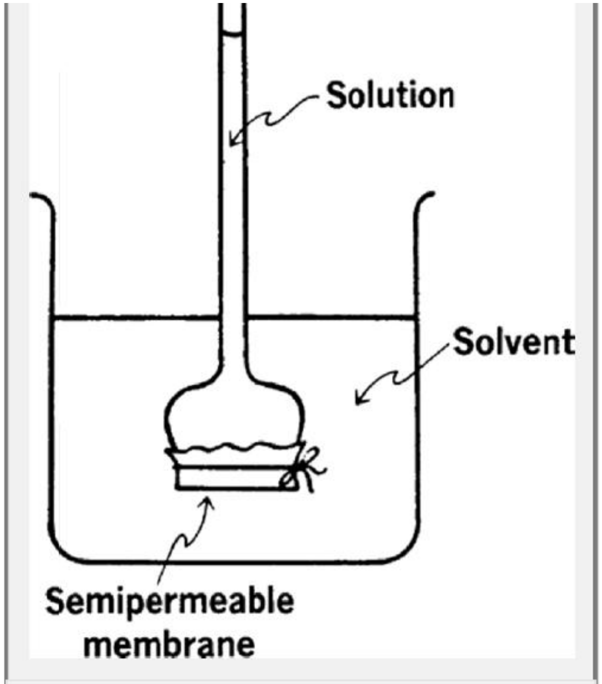


Fig. 5-10. Apparatus for demonstrating osmosis.

Solvent therefore passes spontaneously in to the solution until the chemical potential are identical (at equilibrium) or $\Delta G = o$

The osmotic pressure **π** obtained by movement of solvent molecules into the solution through the membrane, and proportional to concentration of solute present.

$$\pi V = nRT \longrightarrow \pi = nRT/V \longrightarrow \pi = CRT$$

C:- molarity ***(Van't Hoff equation)***

C:- molality ***(morse equation)*** more accurate simplifies into this form from a more exact expression [equation (5-36)] only after introducing a number of assumptions that are not valid for real solutions.

Example 5-13

Calculating the Osmotic Pressure of a Sucrose Solution

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

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

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

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

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

Molecular weight determination

1- from lowering of vapor pressure:

$\Delta P/P^0 = X_2 \approx n_2/n_1 = (w_2/Mw_2)/(w_1/Mw_1) \Longrightarrow$ $\mathbf{Mw_2 = (w_2 Mw_1 P^0)/(w_1 \Delta P)}$

2- from boiling point elevation:

$\Delta T_b = K_b m = K_b\ (w_2/Mw_2)(1000/w_1) \Longrightarrow$ $\mathbf{Mw_2 = K_b\ 1000\ w_2/(\Delta T_b w_1)}$

3- from freezing point elevation:

$\Delta T_f = K_f\ m \Longrightarrow$ $\mathbf{Mw_2 = K_f\ 1000\ w_2/(\Delta T_f\ w_1)}$

4- from Osmotic pressure:

$\pi = CRT = (w_2/Mw_2)RT/(V/1000) \Longrightarrow$ $\mathbf{Mw_2} = [(w_2\ 1000)/V] * RT/\pi$

$\mathbf{Mw_2} = \mathbf{cRT/\pi}$ .... c: g/L

Example 5-15

Determination of the Molecular Weight of Sucrose by Boiling Point Elevation

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

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

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

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

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

Example 5-16

Calculating Molecular Weight Using Freezing Point Depression

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

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

Example 5-17

Determining Molecular Weight by Osmotic Pressure

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

We write

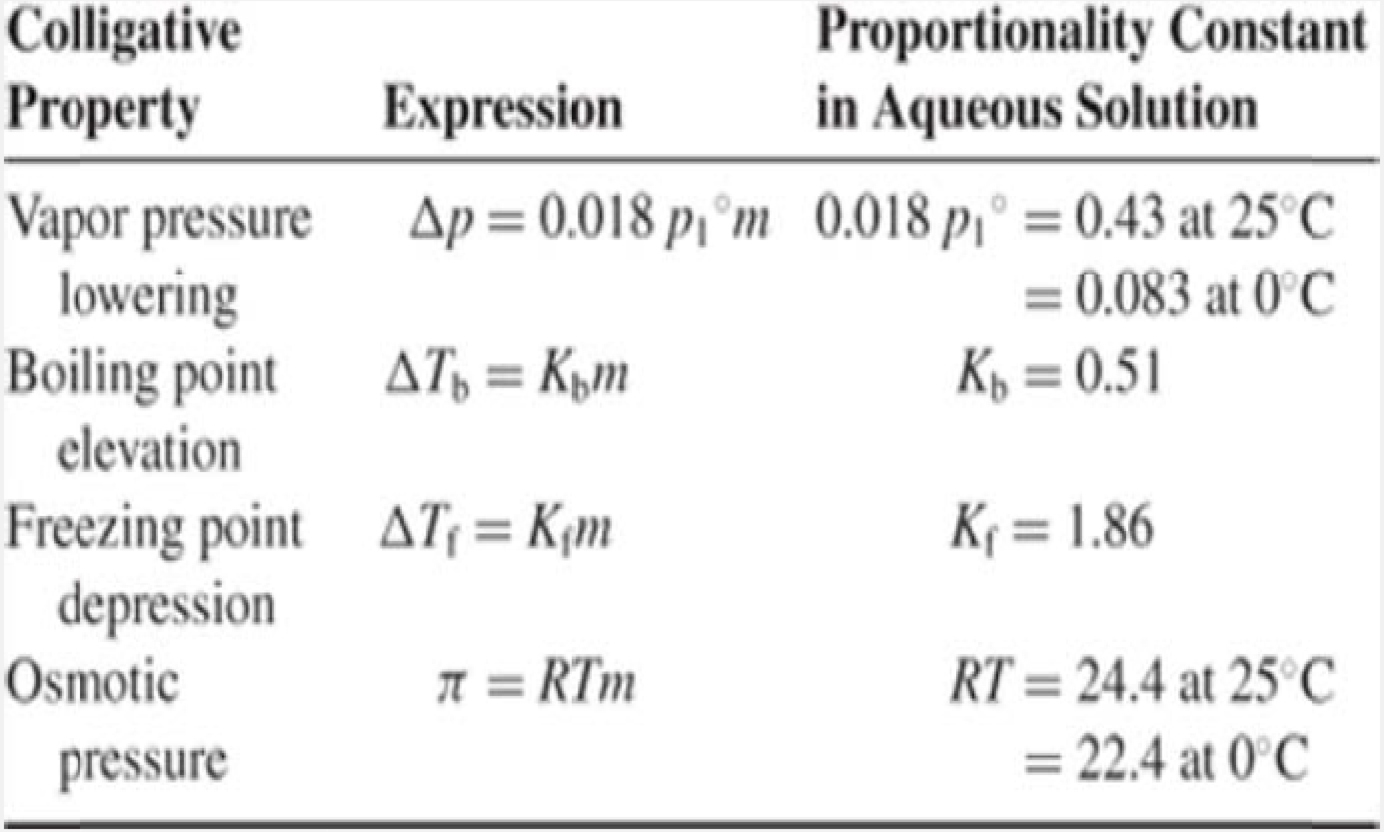
$$\pi = cRT = \frac{c_g RT}{M_2} \qquad (5\text{–}53)$$

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

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

or

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



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

Table 5-5 Approximate Expressions for the Colligative Properties

Relation-ship between colligative properties

$\pi = \mathbf{m}RT$, $\Delta T_f = \mathbf{m}K_f$, $\Delta T_b = \mathbf{m}K_b$, $\Delta p = \mathbf{m}\ 0.018\ P^0$

$\mathbf{m} = \pi/RT = \Delta T_f/K_f = \Delta T_b/K_b = \Delta p/\ 0.018\ P^0$

$\pi = (RT/K_f)\Delta T_f$, $(RT/K_f) = 22.4/1.86 = 12$

So

$\pi = 12\ \Delta T_f$ for aqueous solution

Lewis suggested the equation:

$\pi = 12.06\ \Delta T_f - 0.021\ \Delta T_f^{\ 2}$

and $\pi = (RT/K_b)\ \Delta T_b$, $(RT/K_b) = 22.4/0.51 = 44$

$\pi = 44\ \Delta T_b$ for aqueous solution

Example 5-18

Osmotic Pressure of Human Blood Serum

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

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

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

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

Chapter Summary

This chapter focused on an important pharmaceutical mixture known as a molecular dispersion or true solution. Nine types of solutions, classified according to the states in which