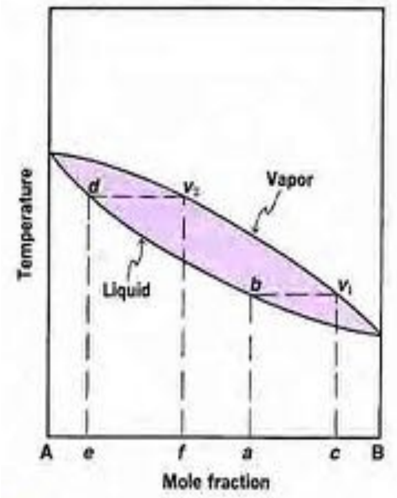
Distillation of Binary system

- Because the vapor of a binary mixture is always richer in the more volatile constituent, the process of distillation can be used to separate the more volatile from the less volatile constituent.
- Ideal mixture



5-4. Boiling point diagram of an ideal binary mix

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Distillation of Binary system

- Azeotropic mixture?

➢Positive deviation: maximum pressure, lowest BP of the azeotropic and pure substance will remain in the flask.

Ex: ethanol and water

➢Negative deviation: minimum pressure, highest BP of the azeotropic (that will remain in the flask) and the pure will distillate of.

Ex: water and acetic acid

➢Immiscible solvents?

Colligative properties

- Why it is called colligative ?
- Conditions:
  - Nonvolatile and nonelectrolyte solutes
  - Volatile solvents
- 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.

Vapor pressure lowering

Molar ratio

$$X_1 + X_2 = 1$$

$$X_1 = 1 - X_2$$

H.W// Mathematically explain why, ΔP is a colligative properties?

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

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

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

$\Delta p = p_1^\circ - p$ is the lowering of the vapor pressure and $\Delta p/p_1^\circ$ is the *relative vapor pressure lo ering*.

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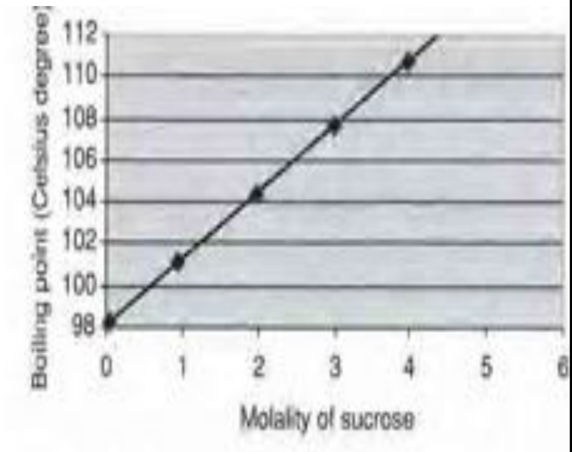
Elevation of boiling point

- The normal boiling point is the temperature at which the vapor pressure of the liquid becomes equal to an external pressure.
- A solution will boil at a higher temperature than will the pure solvent.
- the more of the solute that is dissolved, the greater is the effect.



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$$\frac{\Delta T_b}{\Delta p} = k'$$

$$\Delta T_b = k' \Delta p$$

relative vapor pressure lowering is equal to the mole fraction

By Raoult's law → $\Delta T_b = k X_2$

Bp dep. only on mole fraction of solute

In dilute solu. X_2 is approximately = $m/(1000/M_1)$

$$\Delta T_b = \frac{k M_1}{1000} m \rightarrow \Delta T_b = K_b m$$

Kb (bp elevation constant) is specific for each solvent
Ebullioscopic constant

Depression of freezing point

- The normal T_f of a pure compound is the temperature at which the solid and the liquid phases are in equilibrium under a pressure of 1 atm.
- At these conditions both the liquid and the solid have the same escaping tendency.
- Triple point: is the point at which solid , liquid and vapor are in equilibrium.

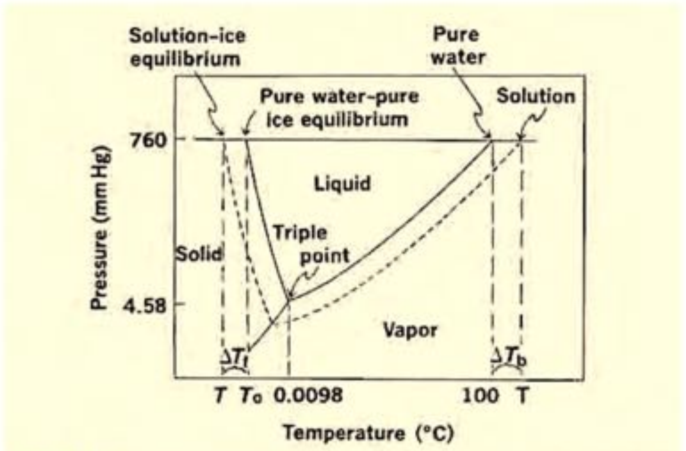

Fig. 5–8. Depression of the freezing point of the solvent, water, by a solute (not to scale).

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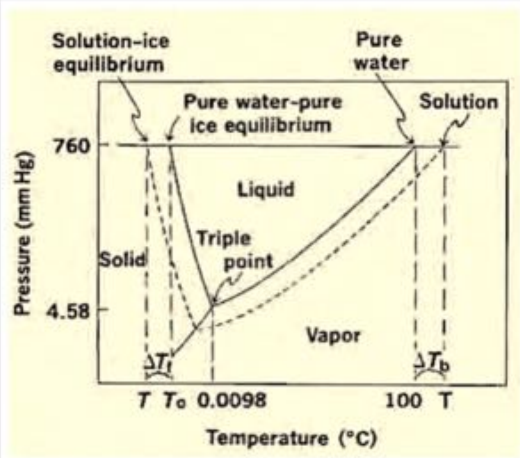
Depression of freezing point

- If a solute is dissolved in the liquid at the triple point, the escaping tendency of the liquid solvent is lowered below that of the pure solid solvent.
- The temperature must drop to reestablish equilibrium between the liquid and the solid.
- The freezing point of a solution is always lower than that of the pure solvent.



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$$\Delta T_f = K_f m$$

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

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.

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Osmotic pressure

- **Diffusion:**
- **Osmosis:**

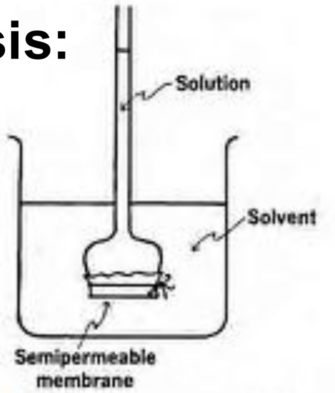
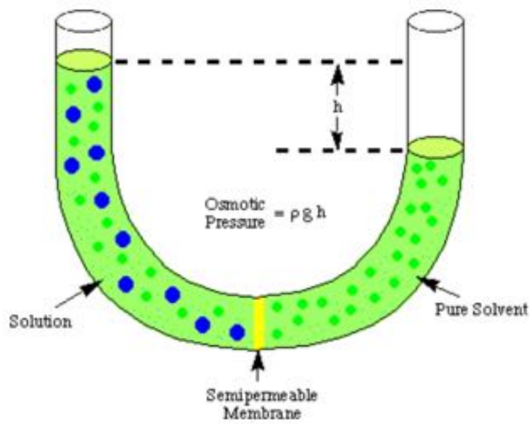


Fig. 5-10. Apparatus for demonstrating osmosis.



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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

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

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

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

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

(*a*)

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

Thermodynamic equation

$$\boxed{\pi = \frac{RT}{V_1} \ln \frac{p^\circ}{p}}$$

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MOLECULAR WEIGHT DETERMINATION

- The four colligative properties can be used to calculate the molecular weights of nonelectrolytes present as solutes.

Using vapor pressure lowering

$$\frac{\Delta p}{p_1^\circ} = \frac{w_2/M_2}{w_1/M_1} \longrightarrow M_2 = \frac{w_2 M_1 p_1^\circ}{w_1 \Delta p}$$

Using boining point elevation

$$\Delta T_b = K_b m$$

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

$$\Delta T_b = K_b \frac{1000 w_2}{w_1 M_2} \longrightarrow M_2 = K_b \frac{1000 w_2}{w_1 \Delta T_b}$$

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Thanks for your attention

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