

Topic 5F - Colligative Properties

Vapor Pressure Lowering

Raoult's Law (ideal solutions):

$$P_{\text{v.p. (solution)}} = X_{\text{solvent}} \cdot P_{\text{v.p. (solvent)}}$$

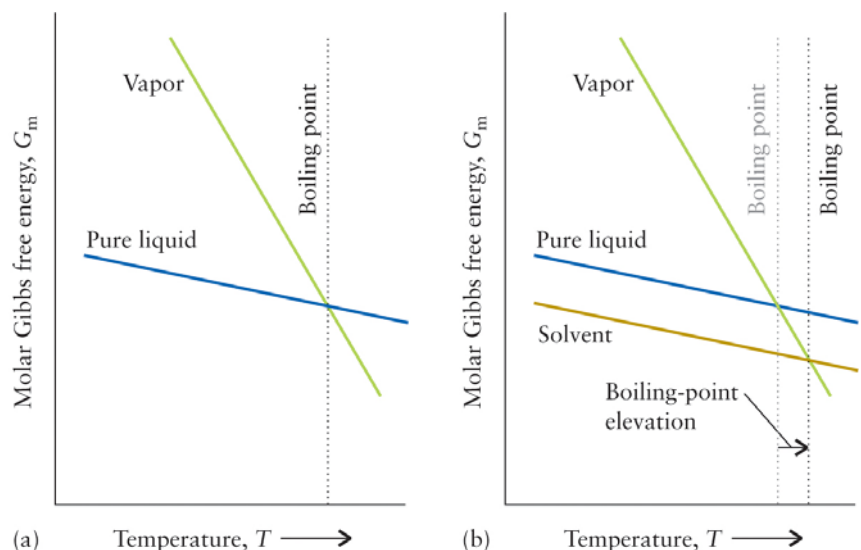
For a pure solvent at equilibrium with its vapor,

$$G_{\text{m (vapor)}} = G_{\text{m (liquid, pure)}}$$

For an ideal solution, $\Delta H_{\text{solution}} = 0$, since solute-solvent interactions are same as solvent-solvent and solute-solute interactions. Thus, since $\Delta S_{\text{liquid}} > 0$ and $\Delta H_{\text{solution}} = 0$, Then $\Delta G_{\text{m (liq., soln.)}} < 0$.

Since $G_{\text{m (vapor)}}^{\circ} = G_{\text{m (liq., pure)}}^{\circ}$ and since $G_{\text{m (liq., soln.)}}^{\circ} < G_{\text{m (liq., pure)}}^{\circ}$, then $G_{\text{m (vapor)}}^{\circ}$ must also be lower than that for the pure liquid solvent. Thus, since $G_{\text{m (vapor)}} = G_{\text{m}}^{\circ} + RT \ln P_{\text{v.p.}}$, then $P_{\text{v.p. (soln.)}} < P_{\text{v.p. (liq., pure)}}$.

FIGURE 10.30 (a) The molar Gibbs free energy of a liquid and its vapor both decrease with increasing temperature, but that of the vapor decreases more sharply. The vapor is the stable phase at temperatures higher than the point of intersection of the two lines (the boiling point). (b) When a nonvolatile solute is present, the molar Gibbs free energy of the solvent is lowered (an entropy effect), but that of the vapor is left unchanged. The point of intersection of the lines moves to a slightly higher temperature.



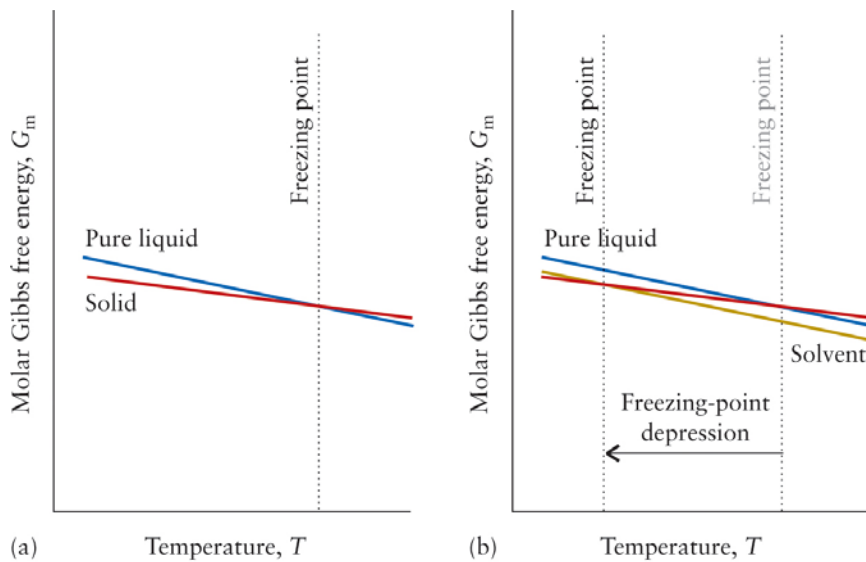
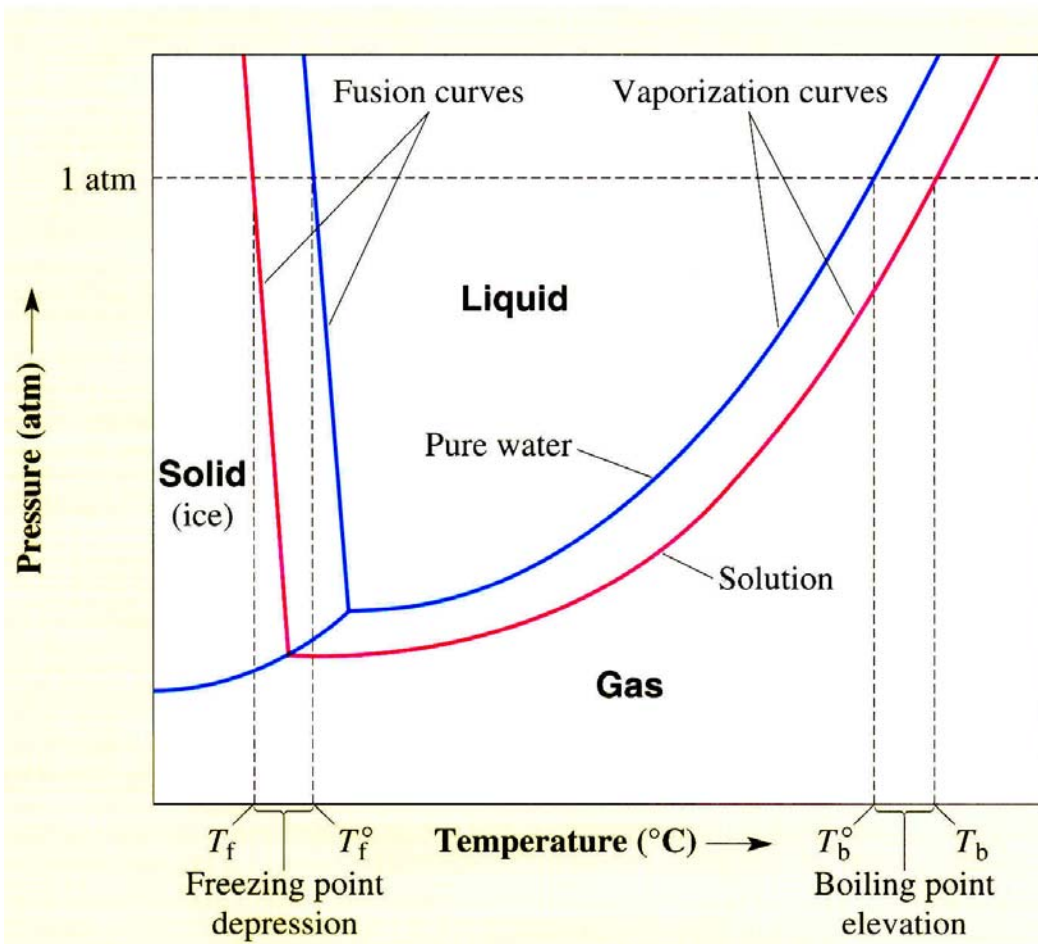


FIGURE 10.31 (a) The molar Gibbs free energy of a solid and its liquid phase both decrease with increasing temperature, but that of the liquid decreases slightly more steeply. The liquid is the stable phase at temperatures higher than the point of intersection of the two lines. (b) When a solute is present, the molar Gibbs free energy of the solvent is lowered (an entropy effect), but that of the solid is left unchanged. The point of intersection of the lines moves to a lower temperature.

Phase Diagram for an Aqueous Solution



Boiling Point Elevation

Since $G_m^{\circ}(\text{liq., soln.}) < G_m^{\circ}(\text{liq., pure})$, resulting in
 $P_{\text{v.p. (soln.)}} < P_{\text{v.p. (liq., pure)}}$, then $T_{\text{b.p. (soln.)}} > T_{\text{b.p. (liq., pure)}}$:

$$T_{\text{b.p. elevation}} = k_B m$$

Freezing Point Depression

Since $G_m(\text{liq., soln.}) < G_m(\text{liq., pure})$, then a lower
 temperature is required in order that $G_m(\text{liq., soln.}) =$
 $G_m(\text{sol., soln.})$ and consequently $T_{\text{f.p. (soln.)}} < T_{\text{f.p. (liq., pure)}}$:

$$T_{\text{f.p. depression}} = k_F m$$

Effect of Solute Ionization

If the solute ionizes in solution, then the total
 number of solute particles will be an integer
 multiple of the molality (at low concentrations):

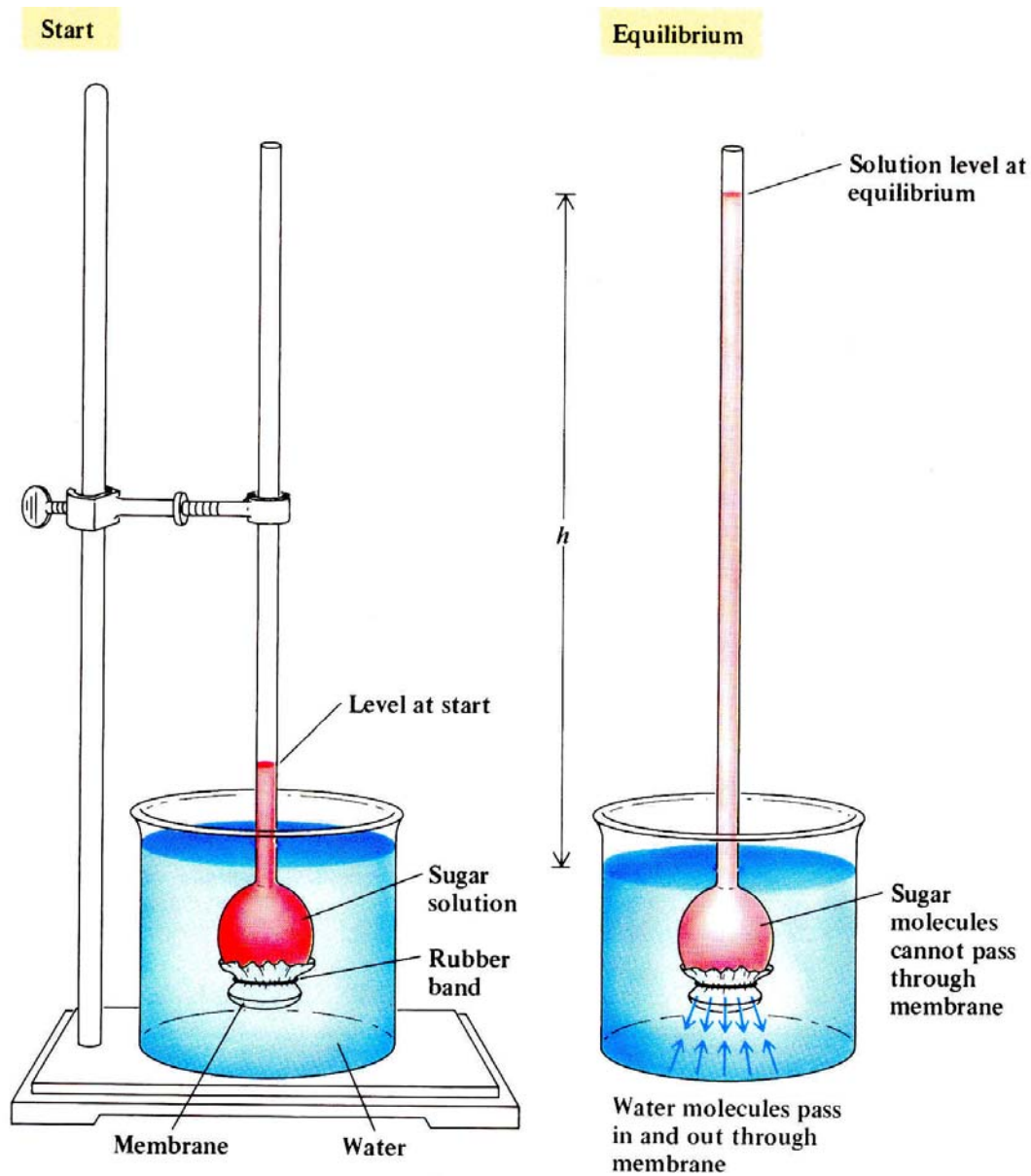
$$T_{\text{b.p. elevation}} = i \times k_B m$$

$$T_{\text{f.p. depression}} = i \times k_F m$$

TABLE 14.2**Freezing point depression and boiling point elevation constants**

Solvent	T_f (°C)	K_f (°C kg/mol) ^a	T_b (°C)	K_b (°C kg/mol) ^a
Water (H ₂ O)	0.0	1.86	100.0	0.512
Carbon tetrachloride (CCl ₄)	−22.9	32.	76.7	5.03
Chloroform (CHCl ₃)	−63.5	4.7	61.7	3.63
Carbon disulfide (CS ₂)	−111.5	3.83	46.2	2.34
Acetic acid (CH ₃ COOH)	16.6	3.9	117.9	3.07
Ethanol (C ₂ H ₅ OH)	−114.2	1.9	78.3	1.22
Benzene (C ₆ H ₆)	5.5	4.9	80.1	2.53
Phenol (C ₆ H ₅ OH)	43.	7.4	181.7	3.56
Camphor (C ₁₀ H ₁₆ O)	178.4	39.7	208.0	5.95

^aMore fully, °C kg solvent/mol solute.



Osmotic Pressure

Since $G_m(\text{liq., soln.}) < G_m(\text{liq., pure})$, then a solution that is separated from its pure solvent by a semi-permeable membrane (*i.e.*, one that allows solvent molecules to pass through, but not solute particles) can lower its G_m if solvent molecules pass through the membrane into the solution. The minimum pressure that is needed to prevent this transport of solvent molecules is the **Osmotic Pressure (Π)**:

$$\Pi = iRTc$$

where c is in **molarity** units, not molality units.

In reverse osmosis, a pressure greater than Π is applied, in order to force the solvent to pass through the membrane in the opposite direction, thus increasing the concentration of the solution and generating additional pure solvent.

FIGURE 10.34 On the left of the semipermeable membrane is the pure solvent with its characteristic molar enthalpy, entropy, and Gibbs free energy. On the right is the solution. The molar Gibbs free energy of the solvent is lower in the solution (an entropy effect), and so there is a spontaneous tendency for the solvent to flow into the solution.

