Lecturer Ghaidaa S. Hameed

Nonelectrolyte cont...

Elevation of the Boiling Point

- 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.
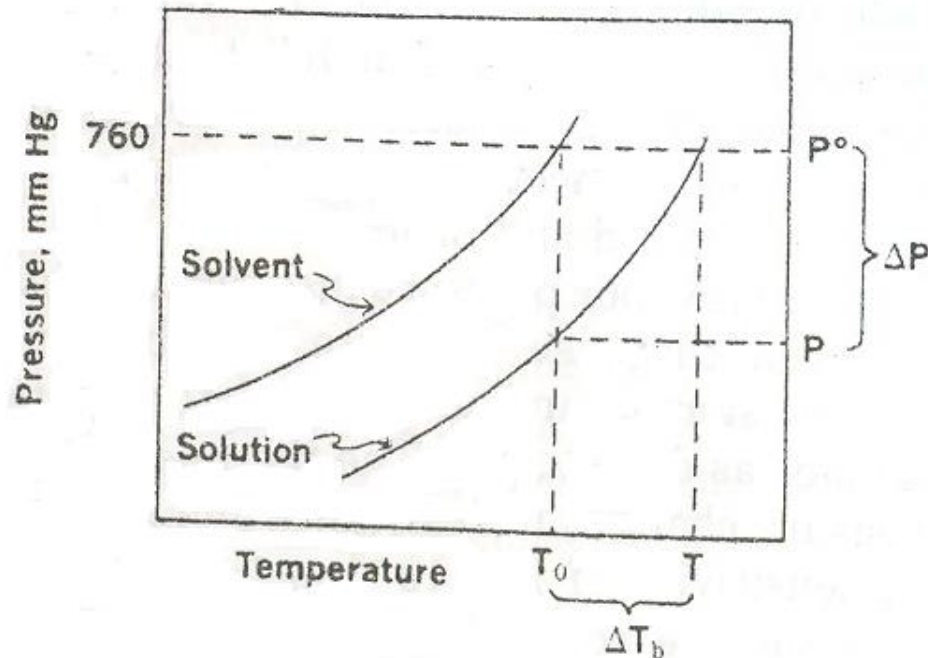

Figure – Boiling point elevation of the solvent due to addition of a solute (not to scale)

The elevation of the boiling point can be written as $T - T_0 = \Delta T_b$

Elevation of the Boiling Point

- An exact equation to calculate ΔT_b (boiling point elevation)

$$\Delta T_b = \frac{RT_b^2}{\Delta H_v} X_2 = kX_2$$

where ΔH_v is the latent heat of vaporization of the solvent, T_b is the boiling point of the solvent, R is the gas constant, X_2 is the mole fraction of the solute

- A less exact equation (more commonly used) is

$$\Delta T_b = \frac{RT_b^2 M_1}{1000 \ \Delta H_v} m = K_b m$$

where M_1 is the molecular weight of the solvent, m is the molal concentration of the solute ($mol.kg^{-1}$), K_b is the molal elevation constant or the ebullioscopic constant ($deg.kg.mol^{-1}$)

Elevation of the Boiling Point

- K_b (ebullioscopic constant) has a characteristic value for each solvent; K_b for water is 0.51 deg.kg/mole.

- K_b may be considered as the boiling point elevation for an ideal 1m 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.

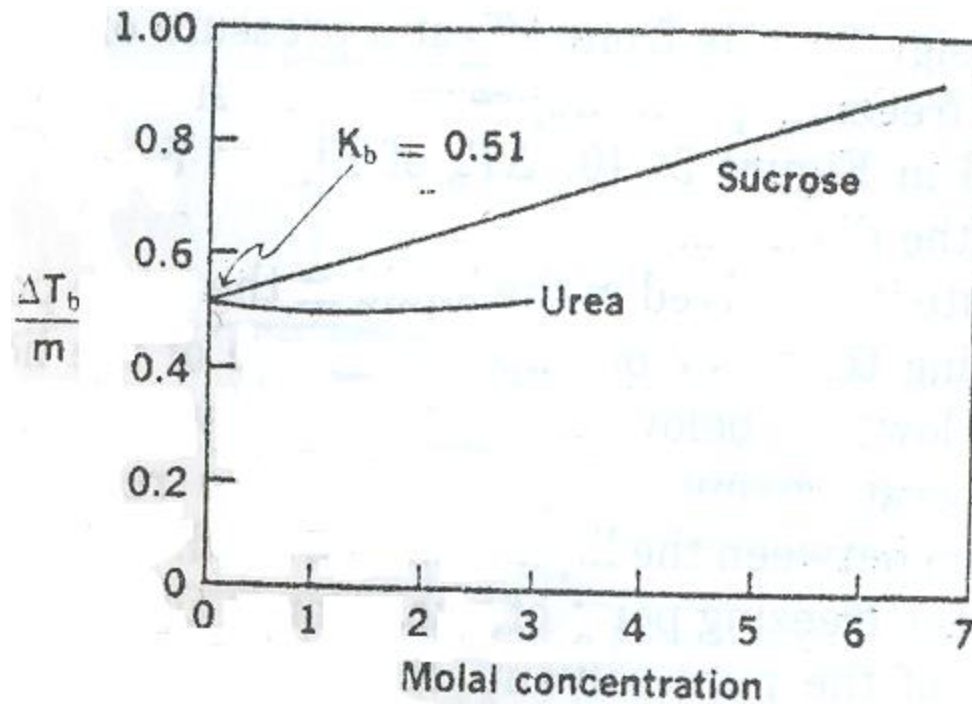# Elevation of the Boiling Point

Figure - the influence of concentration on the ebullioscopic constant.

Depression of 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 1atm. Equilibrium here means that the tendency for the solid to pass into the liquid 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 T_o value for water saturated with air at this pressure is arbitrary assigned a temperature of 0ºC – see figure.

- The triple point of air-free water, at which solid, liquid, and vapor are in equilibrium, lies at a pressure of 4.58 mmHg and a temperature of 0.0098ºC.
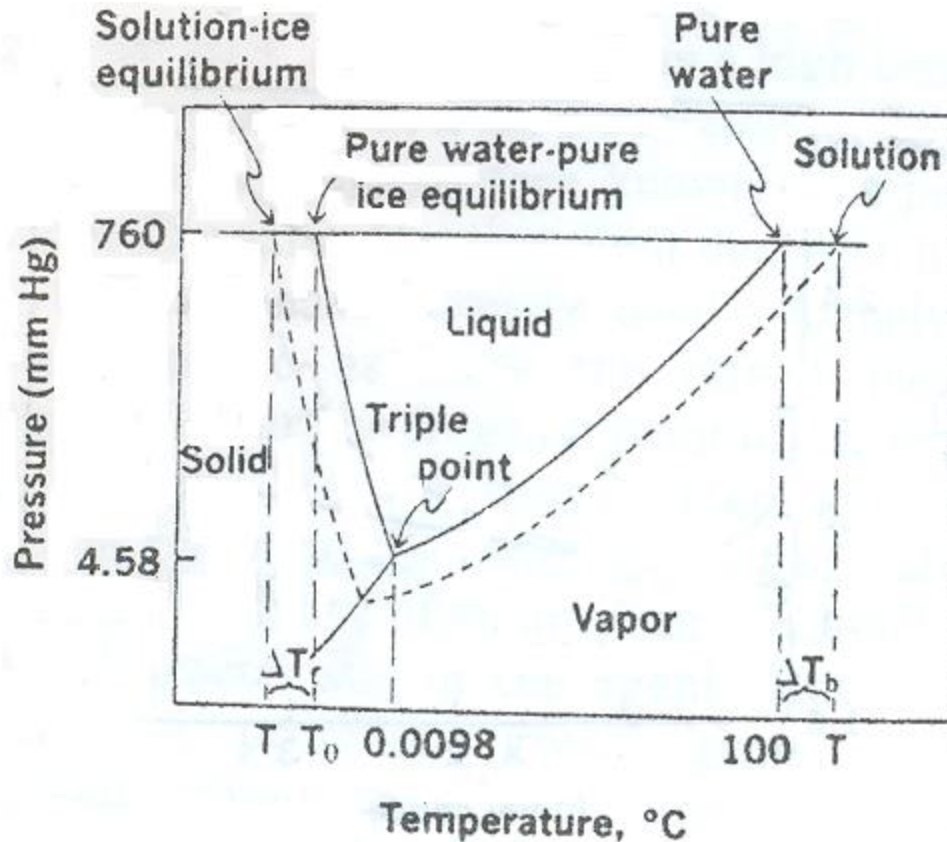
Depression of Freezing Point

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

Depression of Freezing Point

- The more concentrated is the solution, the farther apart are the solvent and the solution curves and the greater is the freezing point depression (ΔT_f).

- ΔT_f is proportional to the molal concentration of the solute and can be determined as follows:

$\Delta T_f = K_f m$ or

$$\Delta T_f = K_f \frac{1000 \ w_2}{w_1 M_2} \quad \text{or} \quad \Delta T_f = \frac{RT_f^{\ 2} M_1}{1000 \ \Delta H_f} m$$

where ΔT_f is the freezing point depression, ΔH_f is molal heat of fusion, T_f is the freezing point of the solvent and K_f is the molal depression constant or the cryoscopic constant, which depends on the physical and chemical properties of the solvent, K_f for water is 1.86 deg.kg/mole.

Depression of Freezing Point

- 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.

- K_f may be determined experimentally by measuring $\Delta T_f/m$ at several molal concentrations and extrapolating to zero concentration – i.e. K_f is the intercept. Electrolytes don't follow this relationship. The equation is

$$\frac{\Delta T_f}{m} = cons \tan t = K_f$$
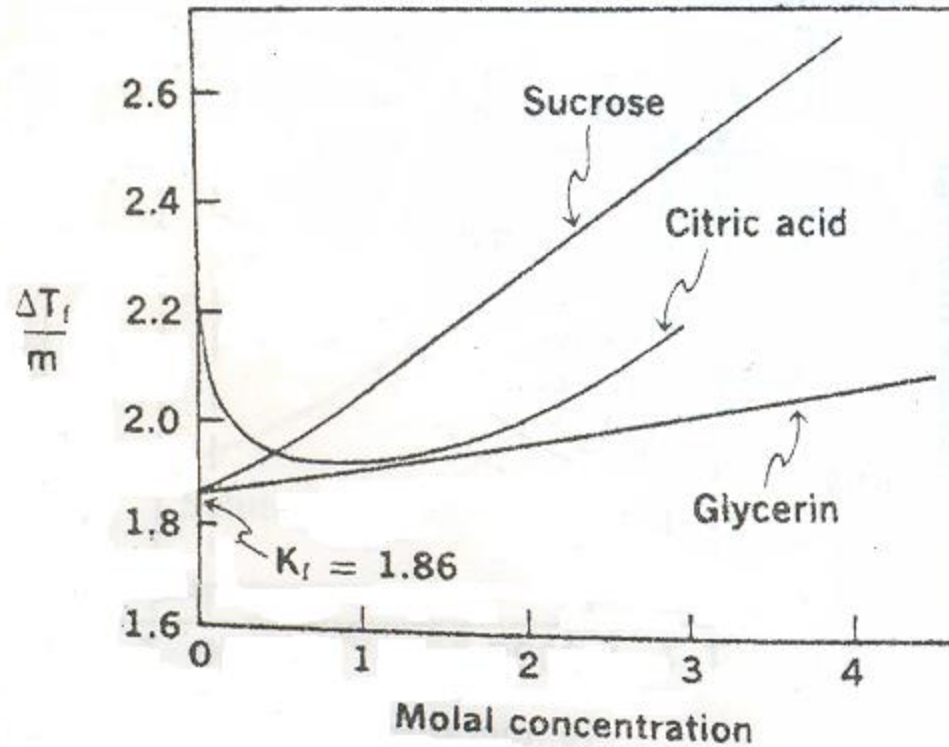
Depression of Freezing Point

Figure – The influence of concentration on the cryoscopic constant for water

Depression of Freezing Point

- Citric acid shows abnormal behavior as seen in the previous figure – This abnormal behavior is to be expected when dealing with electrolytes.

- Freezing point depression can also be calculated from the following equation:

$$\Delta T_f = \frac{RT_f T}{\Delta H_f} X_2$$

where T_f is the freezing point of the solvent, T is the freezing point of the solution, X_2 is the mole fraction of the solute, R is the gas constant and ΔH_f is the heat of fusion of the solvent.