

Solutions and Colligative Properties

There are several solution properties that depend on the relative numbers of solute and solvent particles. Several of these are:

- 1) depression of vapour pressure
- 2) depression of freezing point
- 3) elevation of boiling point
- 4) osmotic pressure

They are known as colligative properties since they depend on the number of particles present and not their identity. The depression of the vapour pressure of a solution is a function of the mole fraction of solvent as indicated by Raoult's Law.

$$P_{\text{soln}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

The boiling and freezing point changes arise naturally out of this vapour pressure depression. This is illustrated on the following phase diagram, where it can be seen that the intersection of the 1 atm isobar line will occur at higher temperatures for boiling and lower temperatures for freezing. The extent of these changes (ΔT) will depend on;

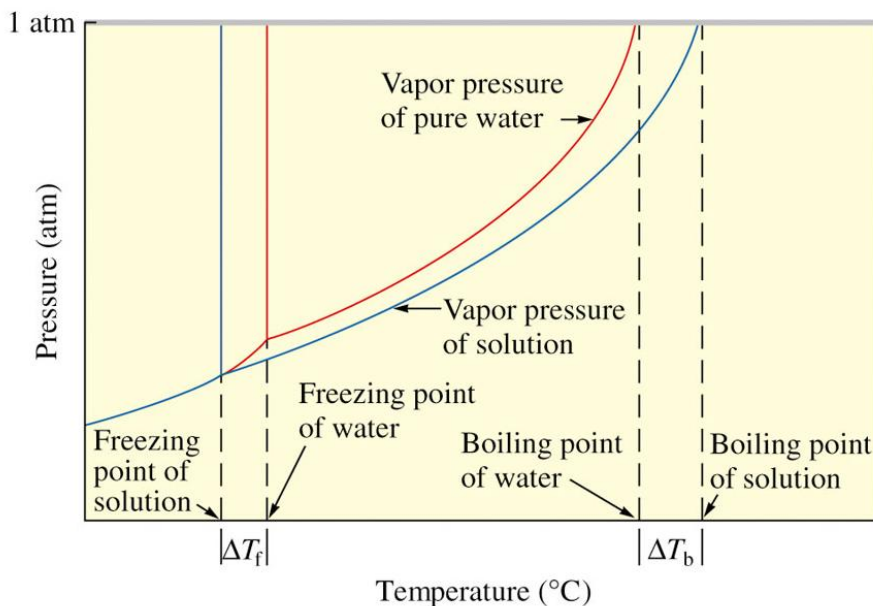
- 1) number of solute particles
- 2) number of solvent particles
- 3) nature of the solvent

The first two are contained in the *molal* concentration (m_{solute}) whereas the last is reflected by the constant K_b and K_f in the equations below.

$$\Delta T_b = K_b m_{\text{solute}}$$

$$\Delta T_f = K_f m_{\text{solute}}$$

$$\Pi = M R T$$



Examples Exercises

1. The boiling point of pure tetralin is 207.3 °C. When 8.0 g of hexane (**C₆H₁₄**) are dissolved in 225 g of tetralin, the solution boils at 210.1 °C. What is the value of K_b for tetralin?

$$\text{Ans: } K_b = 6.8 \text{ } ^\circ\text{C kg mol}^{-1}$$

2. What is the molecular weight of an unknown substance if a solution which contains 10.0 g unknown in 150. g carbon disulfide boils at 48.3 °C? (note: normal Bp of **CS₂** = 46.3°C and $K_b = 2.3 \text{ } ^\circ\text{C kg mol}^{-1}$)

$$\text{Ans: } MW = 77 \text{ g mol}^{-1}$$

3. What is the boiling point of a solution which contains 1.5 g **CHCl₃** in 10.0 g carbon tetrachloride?

$$\text{Ans: } Bp = 83.1 \text{ } ^\circ\text{C}$$

4. How many grams of octane (**C₈H₁₈**) must you add to 500 mL of carbon tetrachloride (density = 1.59 g/mL) to increase the boiling point to 82.8 °C?

$$\text{Ans: } mass = 105 \text{ g}$$

5. A 10 wt% alloy of **Cu** in **Ag** melts at 876 °C. Pure **Ag** melts at 961 °C. What is the molal freezing point depression constant for **Ag**?

$$\text{Ans: } K_f = 49 \text{ } ^\circ\text{C kg mol}^{-1}$$

TABLE 17.5 Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C kg/mol)	Freezing Point (°C)	K_f (°C kg/mol)
Water (H ₂ O)	100.0	0.51	0.	1.86
Carbon tetrachloride (CCl ₄)	76.5	5.03	-22.99	30.
Chloroform (CHCl ₃)	61.2	3.63	-63.5	4.70
Benzene (C ₆ H ₆)	80.1	2.53	5.5	5.12
Carbon disulfide (CS ₂)	46.2	2.34	-111.5	3.83
Ethyl ether (C ₄ H ₁₀ O)	34.5	2.02	-116.2	1.79
Camphor (C ₁₀ H ₁₆ O)	208.0	5.95	179.8	40.

Colligative Properties of Electrolytes (Ionic Solns)

Dissociation of ionic solutes results in the production of more solute particles.

For example, the complete dissociation of **LiCl** will lead to twice as many moles of solute as would be expected based on the number of moles of **LiCl** alone. Likewise, the complete dissociation of 0.40 mol of **Ca(NO₃)₂** will lead to 1.20 mols of ions.

Since colligative properties (such as vapour pressure depression, boiling point elevation, freezing point depression and osmotic pressure) depend on the number of particles of solute, dissociation into ions will result in an enhanced colligative effect.

For instance, calculate the boiling point elevation for a 0.40 *m* aqueous solution of **Ca(NO₃)₂** assuming complete dissociation.

$$\begin{aligned}\Delta T &= K_b m_s && \text{(where } K_b \text{ for H}_2\text{O is } 0.51 \text{ K } m^{-1}\text{)} \\ &= 3 (0.40 m) (0.51 \text{ K } m^{-1})\end{aligned}$$

$$\therefore \text{Bp} = 100.61 \text{ at } 1 \text{ atm}$$

However, colligative effects in ionic solutions are almost always smaller than those predicted on the basis of complete dissociation due to the fact the ions in solution do not behave completely independently of one another, especially at higher concentrations.

Consider the following information for the freezing point depressions of aqueous solutions of **MgSO₄**.

molal conc of MgSO ₄	ΔT_{cal} (based on complete dissociation)	ΔT_{cal} (based on no dissociation)	$\Delta T_{\text{observed}}$	<i>i</i> (expt van't Hoff factor)
1.0 <i>m</i>	3.72	1.86	2.03	1.09
0.01 <i>m</i>	0.0372	0.0186	0.0285	1.53
0.0001 <i>m</i>	0.000372	0.000186	0.00036	1.93

Where *i* = observed colligative effect/calculated effect based on no dissociation

Note: *i* → 2 in the above table as the solution becomes more dilute and contains two ions (**Mg²⁺** and **SO₄²⁻**) for each **MgSO₄**.

E.g., A beaker contains 150.0 g of **H₂O** and 18.0 g of **BaCl₂**. Calculate *i* if the freezing point is observed to be -2.68 °C.

Some species do not completely dissociate in solution (such as weak acids or slightly soluble salts). In these cases, the colligative effect can be measured to determine the extent of dissociation.

E.g., The freezing point depression of 0.50 *m* solution of the weak acid **HF** is 1.00 °C. Calculate the percentage of **HF** molecules in the solution that are dissociated into ions.