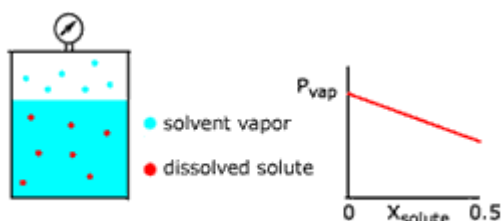


Vapor Pressure Lowering

key concepts:

- A **colligative property** is one that depends on the concentration of the solute but not on the nature of the solute.
- **Raoult's law** states that the **vapor pressure** of the solvent decreases linearly as the mole fraction of the solute increases.



Raoult's law states that as solute is added to a solution the vapor pressure of the solvent decreases.

In an **ideal solution**, solute molecules are completely free to move around and disperse, which increases the entropy of the system. If molecules of the solvent move into the gas phase, the volume of the solvent is reduced, and therefore the entropy of the solution decreases. This decrease in entropy stabilizes the liquid phase. Vapor pressure decreases as a result.

$$P_{\text{solv}} = P_{\text{solv}}^{\circ}(1 - X_{\text{solute}}) \text{ or } P_{\text{solv}} = P_{\text{solv}}^{\circ}(X_{\text{solv}})$$

$$6.04 \text{ g naphthalene} \cdot \frac{\text{mole}}{128.17 \text{ g naphthalene}} = 0.0499 \text{ moles}$$

$$78.0 \text{ g benzene} \cdot \frac{\text{mole}}{78 \text{ g benzene}} = 1.00 \text{ moles}$$

$$X_{\text{benzene}} = \frac{n_{\text{benzene}}}{n_{\text{benzene}} + n_{\text{naphthalene}}}$$

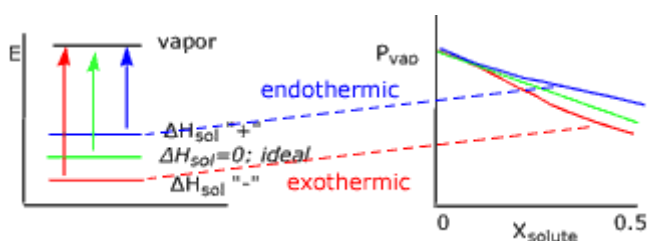
$$X_{\text{benzene}} = \frac{1.00 \text{ mol}}{(1.00 + 0.0499) \text{ mol}} = 0.9525$$

$$P_1 = X_1 \cdot P_1^{\circ} = 0.9525 \cdot 0.1252 = 0.119 \text{ atm}$$

Using Raoult's law, a change in the vapor pressure of 78.0 g of benzene after 6.40 g of naphthalene is dissolved can be calculated from the mole fraction of the solvent and its original vapor pressure (0.1252 atm).

First, the moles of benzene and moles of naphthalene must be calculated in order to obtain the mole fraction of benzene.

The mole fraction of the solvent and its original vapor pressure are then plugged into Raoult's law to give the new vapor pressure.



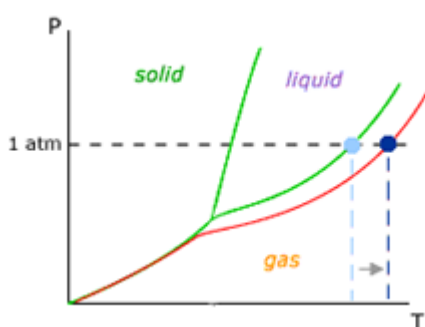
When there are significant attractions between solute and solvent, ΔH is negative (exothermic), and the liquid phase is further stabilized. This means more energy is required to go from liquid to vapor. The vapor pressure will be lower than that expected for an ideal solution.

If the addition of solute causes more bonds between solvent molecules to be disrupted, then ΔH will be positive (endothermic). The formation of solution costs energy, and therefore less energy is required to convert solvent molecules from liquid to vapor. The vapor pressure will be higher than that expected for an ideal solution.

Boiling Point Elevation and Freezing Point Depression

key concepts:

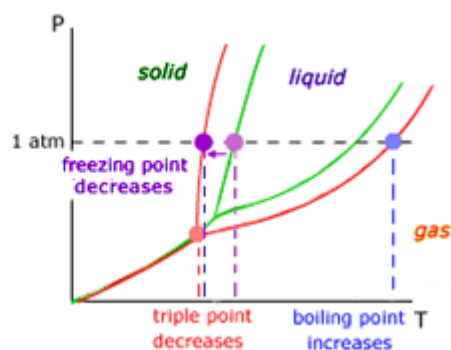
- As **solute** is added to a **solvent**, the **vapor pressure** of the solvent decreases, increasing the **boiling point** of the **solution**.
- As more solute is added and the vapor pressure drops, the **triple point** of the solution decreases causing a depression in the **freezing point**.
- Mathematical relationships relating the **concentration** of solute to the change in freezing or boiling point are $\Delta T_f = -K_f m$ and $\Delta T_b = K_b m$.



As solute is added to a solvent, the vapor pressure of the solvent decreases, increasing the boiling point of the solution. The **normal boiling point** is the temperature at which the liquid-vapor boundary crosses one atmosphere. According to **Raoult's law**, when solute is added, the vapor pressure is lowered, raising the boiling point.

This effect of solute on the boiling point of a solvent is known as **boiling point elevation**. Boiling point is a **colligative property**, depending on the amount of solute, not its identity.

Phase boundary of:
— pure solvent
— ideal solution



When the vapor pressure drops, the temperature at which the triple point occurs also drops, causing the solid-liquid boundary to shift to the left. This shift of the solid-liquid boundary results in a decreased freezing point.

This effect of solute on the freezing point of a solvent is known as **freezing point depression**. Like boiling point elevation, it is also a colligative property.

boiling point elevation

$$\Delta T_b = K_b m$$

change in boiling point

boiling point elevation constant

molal concentration
molar, not molar!
 $m = \frac{\text{moles solute}}{\text{kg solvent}}$

freezing point depression

$$\Delta T_f = -K_f m$$

change in freezing point

freezing point depression constant

molal concentration

notice "-" sign for depression

The mathematical expressions for the relationship between solute concentration and change in freezing and boiling point are shown to the left.

The term ΔT_b represents the change in the boiling point between the pure solvent and the solution.

K_b (or K_f) represents a boiling (or freezing) point constant, which is specific to the solvent. The larger the constant, the more pronounced the effect on the boiling or freezing point.

Concentration is in **molality** (m) (moles solute per kilogram solvent).

Boiling Point Elevation Problem

key concepts:

- **Combustion analysis** can be used to identify the ratios of elements in an unknown sample.
- **Boiling point** elevation can provide information useful in identifying an unknown substance.

Determining an unknown substance

strategy:

1. combustion analysis \Rightarrow empirical formula

2. find molecular weight:

Find molar ratio:

Divide the mass of each element by its atomic weight.

$$\frac{93.7 \text{ g C}}{12.0107 \frac{\text{g}}{\text{mol}}} = 7.81 \text{ mol C} \quad \frac{6.3 \text{ mol H}}{1.00794 \frac{\text{g}}{\text{mol}}} = 6.3 \text{ mol H}$$

Ratio C:H

7.81:6.3 or 5:4

The substance could be C_5H_4 , C_{10}H_8 , $\text{C}_{15}\text{H}_{12}$. . .

Combustion analysis can be used to identify the ratios of elements in an unknown sample.

In the example, the ratios by weight of the amounts of carbon and hydrogen in the unknown are divided by their **atomic weight** to obtain the **molar mass** ratios. The molar mass ratio is simplified to whole numbers giving the **empirical formula** for the compound.

strategy:

2. find molecular weight:

$$\Delta T_b = K_b m$$

$$m = \frac{\text{moles solute}}{\text{kg solvent}}$$

$$\Delta T = 1.42^\circ\text{C} = 1.42 \text{ K} = \frac{3.63 \text{ kg} \cdot \text{K}}{\text{mol}^{-1}} \cdot m$$

$$0.391 = m$$

$$0.391 \frac{\text{mol solute}}{\text{kg solvent}} \cdot 0.100 \text{ kg solvent} = 0.0391 \text{ moles of solute}$$

$$3. \left(\frac{\text{grams solute}}{\text{moles of solute}} \right) = \text{molecular weight}$$

$$4. \left(\frac{\text{molecular weight}}{\text{empirical weight}} \right) = \text{molecular ratio} \rightarrow \text{molecular formula}$$

$$\frac{5.00 \text{ g}}{0.0391 \text{ mol solute}} = 128 \frac{\text{g}}{\text{mol}}$$

what we know:

sample 5.00 g

normal boiling point 61.2°C

100 g of chloroform =

0.100 kg of chloroform

$$\Delta T_b = 1.42^\circ\text{C} = 1.42 \text{ K}$$

$$K_b = 3.63 \frac{\text{kg} \cdot \text{K}}{\text{mol}}$$

empirical weight of C_5H_4

$$= 64 \frac{\text{g}}{\text{mol}}$$

$$\frac{128 \frac{\text{g}}{\text{mol}}}{64 \frac{\text{g}}{\text{mol}}} = 2$$

$$2 \cdot (\text{C}_5\text{H}_4) = \text{C}_{10}\text{H}_8$$

C_{10}H_8 is naphthalene or MOTHBALLS!

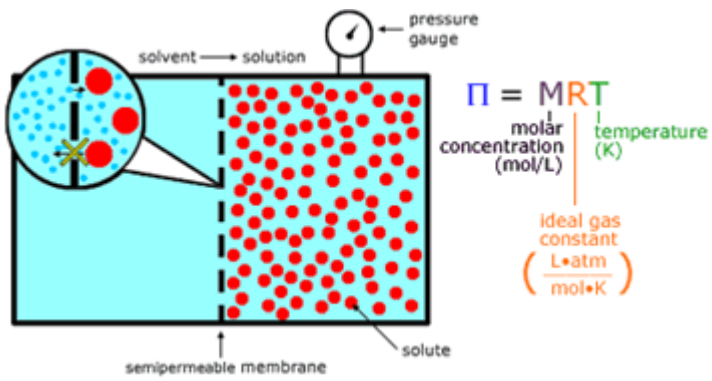
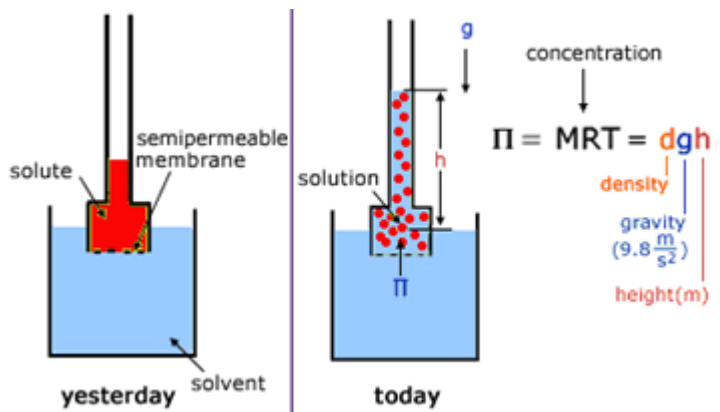
Boiling point elevation can provide information useful in identifying an unknown substance. Boiling point elevation can be used to calculate the **molecular weight** of the unknown. Combining the molecular weight with the empirical formula gives the **molecular formula** for the unknown.

In the example, the relationship between **concentration** and boiling point elevation is used to calculate the number of moles of **solute**. The number of moles of solute is used with the known weight of solute (5.00 g) to calculate the molecular weight of the solute. The molecular weight is found to be twice the molecular weight of the empirical formula, leading to the conclusion that the unknown compound is naphthalene (C_{10}H_8)

Osmosis

key concepts:

- **Osmotic pressure** is related to **concentration** by $\Pi = M \cdot R \cdot T$.
- The osmotic pressure at the membrane is equal to **density** times **gravity** times height ($d \cdot g \cdot h$), thus $\Pi = M \cdot R \cdot T = d \cdot g \cdot h$.
- Osmotic pressure is the most sensitive **colligative property**.
- The osmotic pressure generated by the sugar **solution** in a maple tree is able to raise sap to a height of about 25 meters.

 <p>Osmotic pressure is related to concentration by $\Pi = M \cdot R \cdot T$.</p> <p>A semi permeable membrane allows passage of some molecules but not others. In this case the solvent is able to cross the membrane, but the solute is not. In the illustration, the solvent will try to move across the semipermeable membrane until the concentration of solute is equal on both sides. The osmotic pressure (Π) can be measured if the solution is held in a rigid container as in the illustration.</p> <p>The osmotic pressure is related to the product of the concentration of the solution (M), the temperature of the solution in kelvins (T) and the gas constant (R).</p>	<p>Osmotic pressure is related to concentration by $\Pi = M \cdot R \cdot T$.</p> <p>A semi permeable membrane allows passage of some molecules but not others. In this case the solvent is able to cross the membrane, but the solute is not. In the illustration, the solvent will try to move across the semipermeable membrane until the concentration of solute is equal on both sides. The osmotic pressure (Π) can be measured if the solution is held in a rigid container as in the illustration.</p> <p>The osmotic pressure is related to the product of the concentration of the solution (M), the temperature of the solution in kelvins (T) and the gas constant (R).</p>
 <p>A more convenient way to measure osmotic pressure in the lab is by measuring the height of a column of solution as illustrated.</p> <p>The osmotic pressure at the membrane is equal to $d \cdot g \cdot h$ (density times gravity times height), thus $\Pi = MRT = dgh$.</p>	<p>A more convenient way to measure osmotic pressure in the lab is by measuring the height of a column of solution as illustrated.</p> <p>The osmotic pressure at the membrane is equal to $d \cdot g \cdot h$ (density times gravity times height), thus $\Pi = MRT = dgh$.</p>

Osmosis

If 2.0 g of a protein with a molecular mass of 23,000 g/mol is dissolved in 100 mL of water:

change in vapor pressure: 4.8×10^{-7} atm

change in boiling point: 0.00044 K

change in freezing point: 0.0016 K

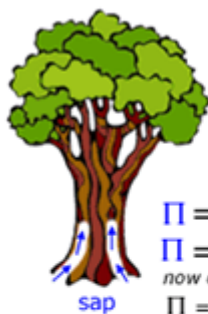
What about osmotic pressure? $\Pi = MRT = dgh$

$$h = 220 \text{ mm}$$

The height is easily measured!

Osmotic pressure is the most sensitive colligative property.

The example illustrates the ease of measuring osmotic pressure (as the height of the solution) compared to the measures for the other colligative properties of the solution.



sap

A maple tree has an average sucrose concentration of 3% that indicates a 0.10 M solution of nutrients in the tree. The rising of the sap is due primarily to osmosis. At a temperature of 20°C, how far up the tree will the sap rise?

$$\Pi = MRT$$

$$\Pi = 2.40 \text{ atm}$$

now convert

$$\Pi = 2.40 \text{ atm} \cdot (1.01 \times 10^5 \frac{\text{Pa}}{\text{atm}})$$

$$\Pi = 2.43 \times 10^5 \text{ Pa} \quad 1 \text{ Pa} = 1 \frac{\text{kg}}{\text{m} \cdot \text{s}^2}$$

$$2.43 \times 10^5 \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = dgh$$

$$2.43 \times 10^5 \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = \frac{100 \text{ g}}{\text{cm}^3} \cdot \frac{1 \text{ kg}}{1,000 \text{ g}} \cdot \frac{1 \times 10^6 \text{ cm}^3}{\text{m}^3} \cdot \frac{9.8 \text{ m}}{\text{s}^2} \cdot h$$

$$h = \frac{2.43 \times 10^5 \cdot 1000 \text{ m}}{1.0 \times 10^6 \cdot 9.8} = 24.8 \text{ m}$$

Assume: sap solution has a density of $1.00 \frac{\text{g}}{\text{mL}} = 1.00 \frac{\text{g}}{\text{cm}^3}$

An application of the osmotic pressure relations allows the determination of the height to which a maple tree is able to raise sap.

The concentration of the sap solution is used to calculate the osmotic pressure (Π). Using the osmotic pressure and the density of the sap (converting atmospheres to **pascals**) allows the calculation of the height of the column of sap.

The osmotic pressure generated by the sugar solution in a maple tree is able to raise sap to a height of about 25 meters.

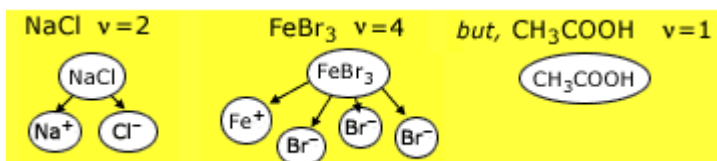
Colligative Properties of Ionic Solutions

key concepts:

- The **van't Hoff factor** is a correction factor used in relationships involving **colligative properties** of a solution to account for the dissociation of solute particles.

$$\Delta T_b = v K_b m \quad \Delta T_f = -v K_f m$$

van't Hoff factor
(also expressed as *i*)



If a solute added to a solution dissociates, the number of particles in solution is greater than the original number of particles of solute.

For example, when sodium chloride (NaCl) dissociates in solution, two particles are present (a sodium ion and a chloride ion) for each particle of NaCl.

The van't Hoff factor (*v* or *i*) is a correction factor used in relationships involving colligative properties of a solution to account for the dissociation of solute particles. For example, the van't Hoff factor for NaCl is 2, while the van't Hoff factor for iron(III) bromide (FeBr₃) is 4.



given:
solute = 0.494 g
solvent = 100.0 g
= 0.1 kg
 $\Delta T_f = -0.11$ K

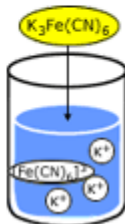
$$\Delta T_f = -v K_f m \quad v = \frac{-\Delta T_f}{K_f m}$$

$$\text{moles of solute} = 0.494 \text{ g} \cdot \frac{1 \text{ mol}}{329 \text{ g}} = 0.0015 \text{ mol}$$

$$\frac{0.0015 \text{ mol}}{0.1 \text{ kg}} = 0.015 \text{ m}$$

$$v = \frac{-(-0.11) \text{ K}}{(1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1})(0.015 \text{ m})}$$

$$v = 3.9 \approx 4$$



Problem: When 0.494 g of K₃Fe(CN)₆ is dissolved in 100.0 g of water, the freezing point is lowered by 0.11°C. How many ions are formed from the dissociation of K₃Fe(CN)₆?

First, the number of moles of K₃Fe(CN)₆ must be calculated from the number of grams and the molar mass of K₃Fe(CN)₆. This value is then used to calculate the molality of the K₃Fe(CN)₆ solution (0.015 m).

Plugging the known values into the freezing point depression equation yields a van't Hoff factor of about 4. This value indicates that K₃Fe(CN)₆ dissociates into four particles in solution: three potassium ions, and one hexacyanoiron(III) ion (Fe(CN)₆³⁻).