

Solutions 6.6

Colligative Properties of Solutions

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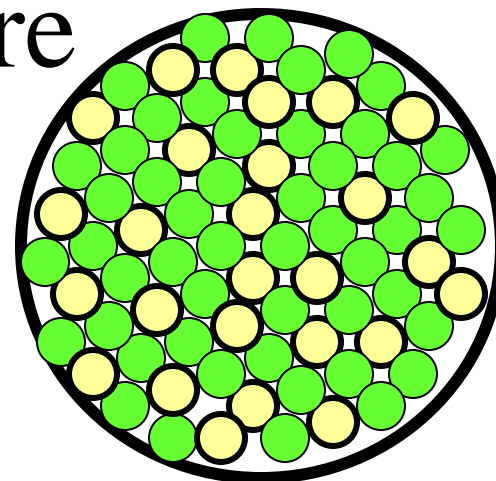
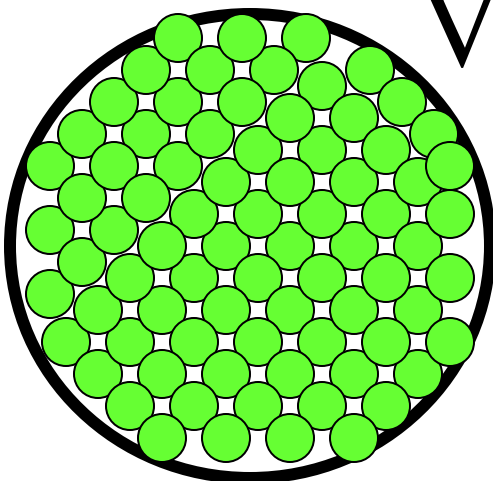
Liquids solutions experience the following four colligative properties:

- Vapor Pressure Reduction,
- Boiling Point Elevation,
- Freezing Point Depression, and
- Osmotic Pressure,

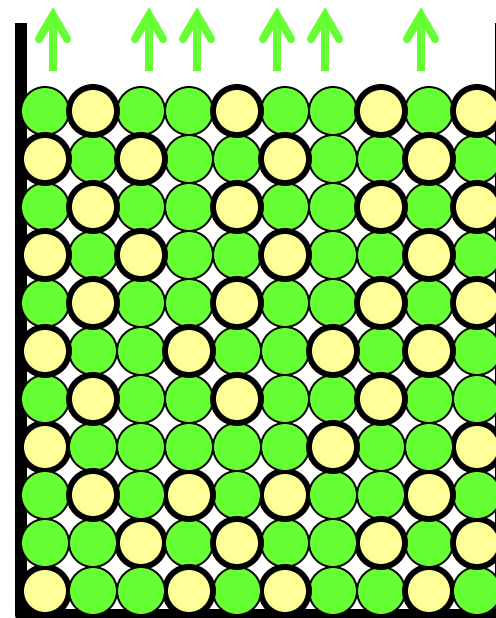
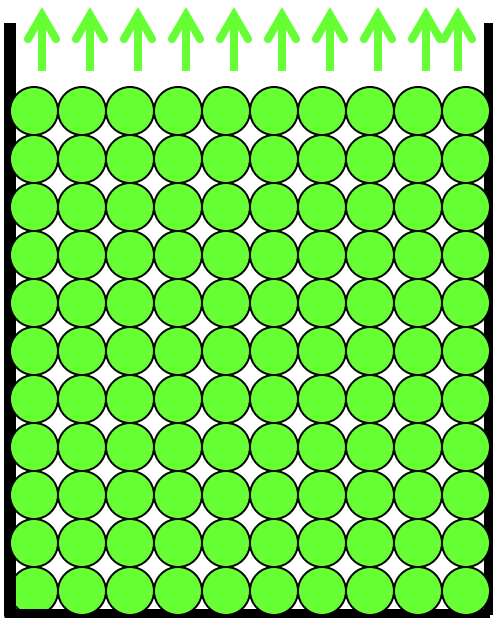
over that of the pure solvent.

Vapor Pressure Reduction

Top View



Side View



Pure Solvent

Solvent and
Non-Volatile Solute

Vapor Pressure Reduction

- When a non-volatile solute dissolves in a solvent it becomes evenly distributed throughout the liquid.
 - This means non-volatile particles are on the liquid's surface.
- Non-volatile particles reduce the surface area from which evaporation is possible.
 - Reduces incidents of evaporation per unit area per unit of time
 - Reduces vapor pressure

Raoult's Law: Non-Volatile Solute

- The partial pressure of a solvent over a solution is equal to the vapor pressure of the pure solvent times the mole fraction of that solvent in the solution.

Vapor pressure of
the pure solvent

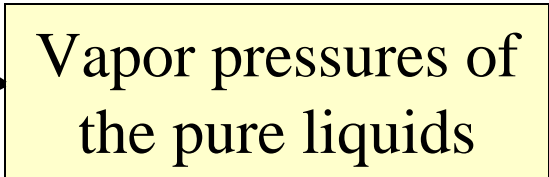
$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}}$$

This means that **vapor pressure reduction** is **determined by the concentration**, and not the type, of non-volatile particles in the solution.

Raoult's Law: Volatile Solute

- If you have a volatile solute, such as an alcohol, there are two vapor pressures which are additive.

$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}}$$

$$P_{\text{solute}} = X_{\text{solute}} \cdot P^{\circ}_{\text{solute}}$$


In the case of a volatile solute, the vapor pressure could go up or down.

Raoult's Law: Volatile Solute

$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}}$$

$$P_{\text{solute}} = X_{\text{solute}} \cdot P^{\circ}_{\text{solute}}$$

Ideal Solutions

$$P_{\text{total}} = P_{\text{solvent}} + P_{\text{solute}}$$

- Solutions act most ideally when the solute and solvent have similar structures.
 - Intermolecular forces between the solute and solvent molecules are similar to those between solvent molecules.

Raoult's Law: Volatile Solute

$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}}$$

$$P_{\text{solute}} = X_{\text{solute}} \cdot P^{\circ}_{\text{solute}}$$

Non-Ideal Solutions

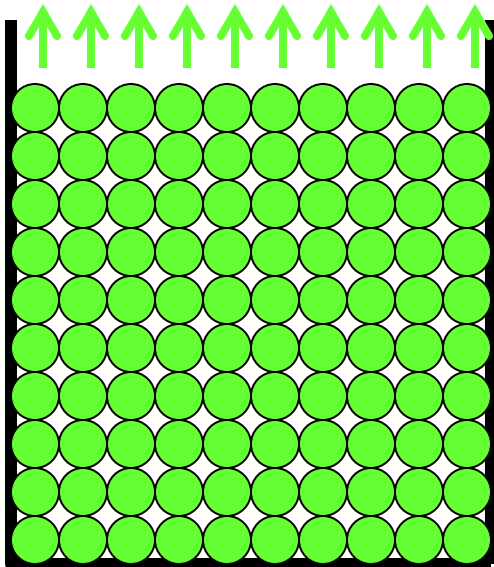
$$P_{\text{total}} < P_{\text{solvent}} + P_{\text{solute}}$$

- Occurs when intermolecular forces between solute and solvent molecules are very strong
 - Intermolecular forces between solute and solvent molecules are stronger than those between solvent molecules.

Boiling Point Elevation

$T = 100^{\circ}\text{C}$

$$P_{\text{vapor}} = P_{\text{H}_2\text{O}} = 1 \text{ atm}$$



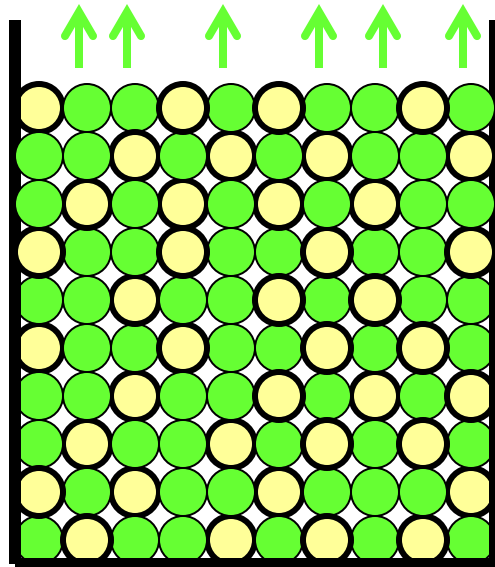
Pure Water

Boiling

$T = 100^{\circ}\text{C}$

$$P_{\text{H}_2\text{O}} < 1 \text{ atm}$$

$$P_{\text{vapor}} = P_{\text{H}_2\text{O}}$$

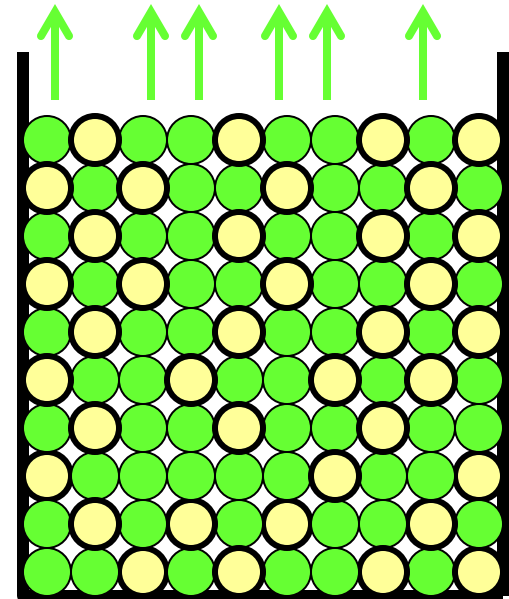


Water and Non-Volatile Solute

Not Boiling

$T > 100^{\circ}\text{C}$

$$P_{\text{vapor}} = P_{\text{H}_2\text{O}} = 1 \text{ atm}$$



Water and Non-Volatile Solute

Boiling

Solutions with Soluble Ionic Compounds

- Soluble ionic compounds completely dissociate in polar solvents.
- Colligative properties depend on the concentration of solute particles in solution.
- Thus, for strong electrolytes you need to know the concentration of ions, not the concentration of formula units, in the solution.

Boiling Point Elevation

$$\Delta T_b = i m K_b$$

ΔT_b = the change in boiling temperature between the solution and the pure solvent.

i = van't Hoff factor (Ideally, the number of ions within one formula unit of a strong electrolyte)

m = molality (moles solute / kg solvent)

K_b = the boiling point constant for the **solvent**.

(K_b for water = 0.512 K•kg/mol)

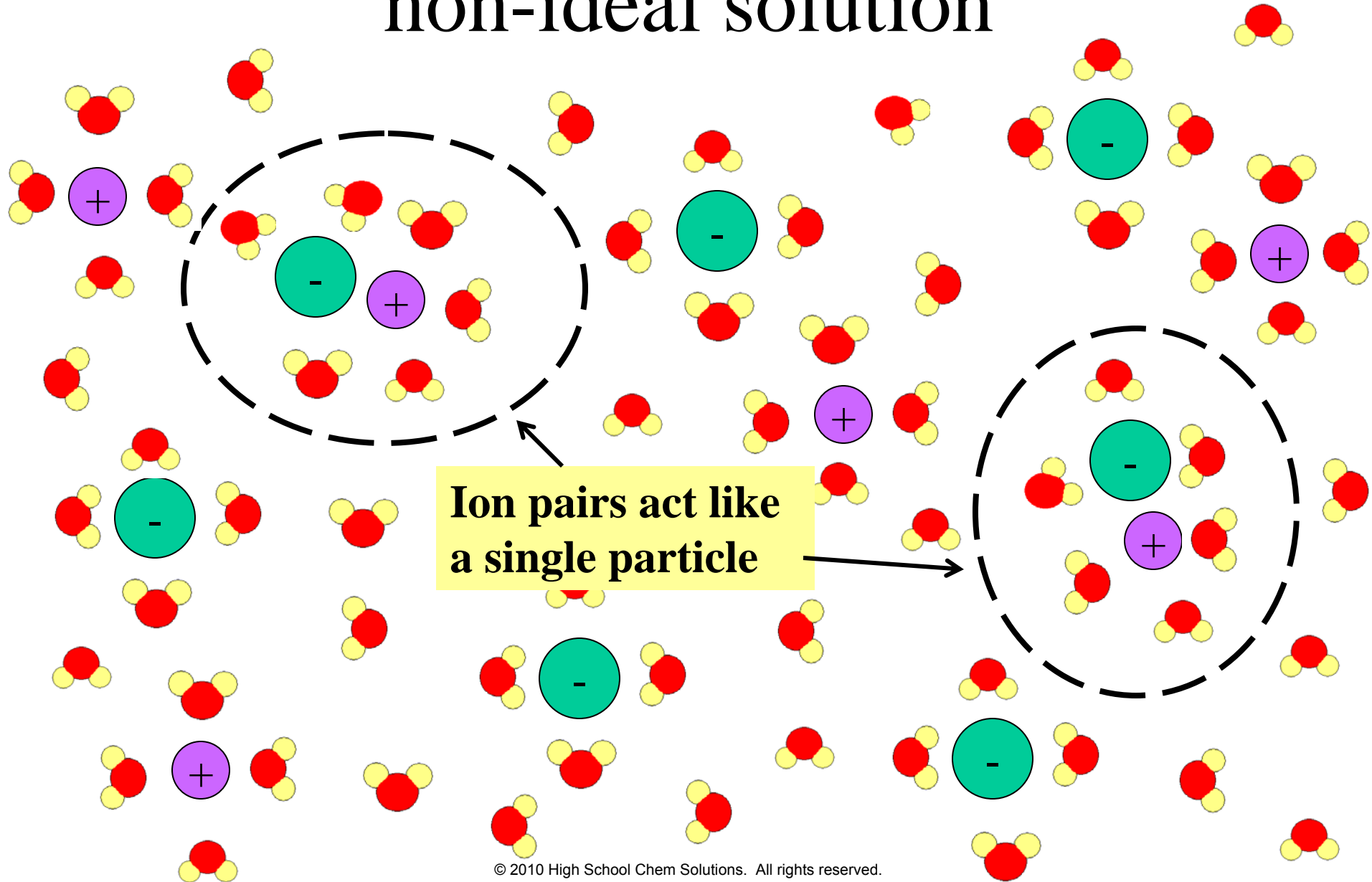
Non-Ideal Solutions and (*i*)

Measured values for (*i*) are usually lower than the ideal values.

This tells us that dissociated ions **are not** completely independent of one another.

- Their lack of independence makes the actual number of moles of solute particles slightly less than expected.

Looking down at the surface of a non-ideal solution



Factors Affecting Non-Ideal Behavior

- The higher the concentration of solute, the less ideal the behavior.
 - Ions are closer together
 - More ion pairs or clustering
- The greater the charge on individual ions, the less ideal the behavior.
 - The greater the charge, the greater the tendency for ion to attract one another.
- Only solutions with solutes that form ions can behave non-ideally

Ex1) Boiling Point Elevation

- a) What is the boiling point elevation when 3.12 g of NaCl is added to 0.65 L of water?
- b) What is the new boiling temperature of the water at sea level in °C?

Step 1. Find molality of solution

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Step 1. Find molality of solution

$$3.12 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 0.0534 \text{ mol NaCl}$$

Ex1) Boiling Point Elevation

- a) What is the boiling point elevation when 3.12 g of NaCl is added to 0.65 L of water?
- b) What is the new boiling temperature of the water at sea level in °C?

Step 1. Find molality of solution

$$3.12 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 0.0534 \text{ mol NaCl}$$

$$0.65 \text{ L water} \times \frac{1 \text{ kg water}}{1 \text{ L water}} = 0.65 \text{ kg water}$$

Ex1) Boiling Point Elevation (cont.)

Step 2. Find the boiling point elevation.

Ex1) Boiling Point Elevation (cont.)

$$\text{molality} = \frac{\text{moles solute}}{\text{kg solvent}} = \frac{0.0534 \text{ mol NaCl}}{0.65 \text{ kg water}}$$

$$\text{molality} = 0.082m$$

Step 2. Find the boiling point elevation.

$$\Delta T_b = i m K_b$$

Ex1) Boiling Point Elevation (cont.)

$$\text{molality} = \frac{\text{moles solute}}{\text{kg solvent}} = \frac{0.0534 \text{ mol NaCl}}{0.65 \text{ kg water}}$$

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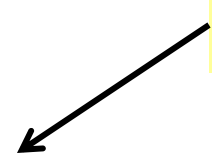
Step 2. Find the boiling point elevation.

$$\Delta T_b = i m K_b$$

$$\Delta T_b = (2)(0.082m)(0.512 \text{ K} \cdot \text{kg} / \text{mol})$$

$$\Delta T_b = 0.084 \text{ K}$$

K_b for water



The new boiling temperature is 100.084°C

Ex2) Boiling Point Elevation

Ex2) How much NaCl (in grams) must be added to 0.65 L of water to raise the boiling temperature to 101.0 °C at 1 atm?

Step 1. Find molality

Ex2) Boiling Point Elevation

Ex2) How much NaCl (in grams) must be added to 0.65 L of water to raise the boiling temperature to 101.0 °C at 1 atm?

Step 1. Find molality

$$\Delta T_b = i m K_b$$
$$m = \frac{\Delta T_b}{i K_b} =$$

Ex2) Boiling Point Elevation

Ex2) How much NaCl (in grams) must be added to 0.65 L of water to raise the boiling temperature to 101.0 °C at 1 atm?

Step 1. Find molality

$$\Delta T_b = i m K_b$$

$$m = \frac{\Delta T_b}{i K_b} = \frac{1.0 \text{ K}}{(2)(0.512 \text{ K} \cdot \text{kg} / \text{mol})}$$

$$m = 0.98m$$

Ex2) Boiling Point Elevation (cont.)

Step 2. Find mass of NaCl

Ex2) Boiling Point Elevation (cont.)

Step 2. Find mass of NaCl

$$m = \frac{n_{\text{NaCl}}}{\text{kg H}_2\text{O}}$$

$$n_{\text{NaCl}} = m(\text{kg H}_2\text{O})$$

$$n_{\text{NaCl}} = (0.98m)(0.65 \text{ kg})$$

$$n_{\text{NaCl}} = 0.64 \text{ mol NaCl}$$

Ex2) Boiling Point Elevation (cont.)

Step 2. Find mass of NaCl

$$m = \frac{n_{\text{NaCl}}}{\text{kg H}_2\text{O}}$$

$$n_{\text{NaCl}} = m(\text{kg H}_2\text{O})$$

$$n_{\text{NaCl}} = (0.98m)(0.65 \text{ kg})$$

$$n_{\text{NaCl}} = 0.64 \text{ mol NaCl}$$

$$0.64 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} = 37 \text{ g NaCl}$$

Freezing Point Depression

Freezing requires the transition from a disordered to a more ordered arrangement of particles. ($-\Delta S$)

Heat must be removed from the system to facilitate this change. ($-\Delta H$)

A solution is more disordered than its pure solvent, so freezing a solution requires an even greater decrease in entropy. (more $-\Delta S$)

Thus, more energy must be removed to freeze a solution. (more $-\Delta H$)

Occurs in all Solutions

- Volatile and Non-Volatile Solutes

Freezing Point Depression

$$\Delta T_f = i m K_f$$

ΔT_f = the change in freezing temperature between the solution and the pure solvent.

i = van't Hoff factor (ideally, the number of ions within one formula unit of a strong electrolyte)

m = molality (moles solute / kg solvent)

K_f = the freezing point constant for the solvent.

(K_f for water = 1.86 K•kg/mol)

Non-Ideal Solutions

- Like all colligative properties, freezing point depression depends on the number of solute particles.
- Ion pairing and clustering slightly reduces the effective concentration of solute particles.
- For ionic compounds, freezing point depressions are, in reality, slightly less than would be expected from ideal calculations.
- Deviations from ideal solutions increase as the charges of ions and concentrations increase.

Ex) Freezing Point Depression

Ex) How much ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) must be added to 6.00 L of water to depress the freezing point to -15.0°C ?

Step 1. Calculate the molality

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$$m = \frac{\Delta T_f}{i K_f} =$$

Ex) Freezing Point Depression

Ex) How much ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) must be added to 6.00 L of water to depress the freezing point to -15.0°C ?

Step 1. Calculate the molality

$$\Delta T_f = i m K_f$$

$$m = \frac{\Delta T_f}{i K_f} = \frac{15.0 \text{ K}}{(1)(1.86 \text{ K} \cdot \text{kg} / \text{mol})}$$

$$m = 8.06m$$

K_f for water

Ex) Freezing Point Depression (cont.)

Step 2. Find mass of $C_2H_6O_2$

Ex) Freezing Point Depression (cont.)

Step 2. Find mass of $\text{C}_2\text{H}_6\text{O}_2$

$$m = \frac{n_{\text{C}_2\text{H}_6\text{O}_2}}{\text{kg H}_2\text{O}}$$

$$n_{\text{C}_2\text{H}_6\text{O}_2} = m(\text{kg H}_2\text{O})$$

$$n_{\text{C}_2\text{H}_6\text{O}_2} = (8.06m)(6.00 \text{ kg})$$

$$n_{\text{C}_2\text{H}_6\text{O}_2} = 48.4 \text{ mol C}_2\text{H}_6\text{O}_2$$

Ex) Freezing Point Depression (cont.)

Step 2. Find mass of $\text{C}_2\text{H}_6\text{O}_2$

$$m = \frac{n_{\text{C}_2\text{H}_6\text{O}_2}}{\text{kg H}_2\text{O}}$$

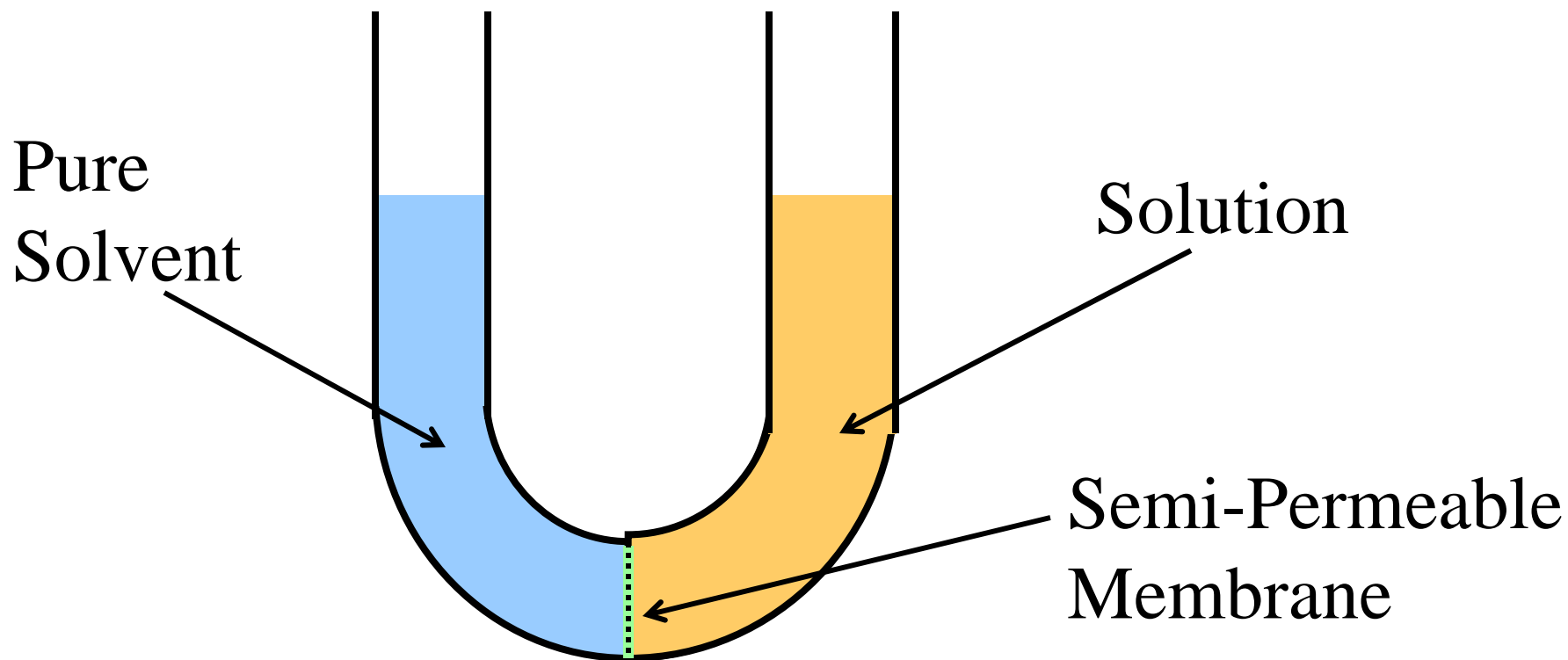
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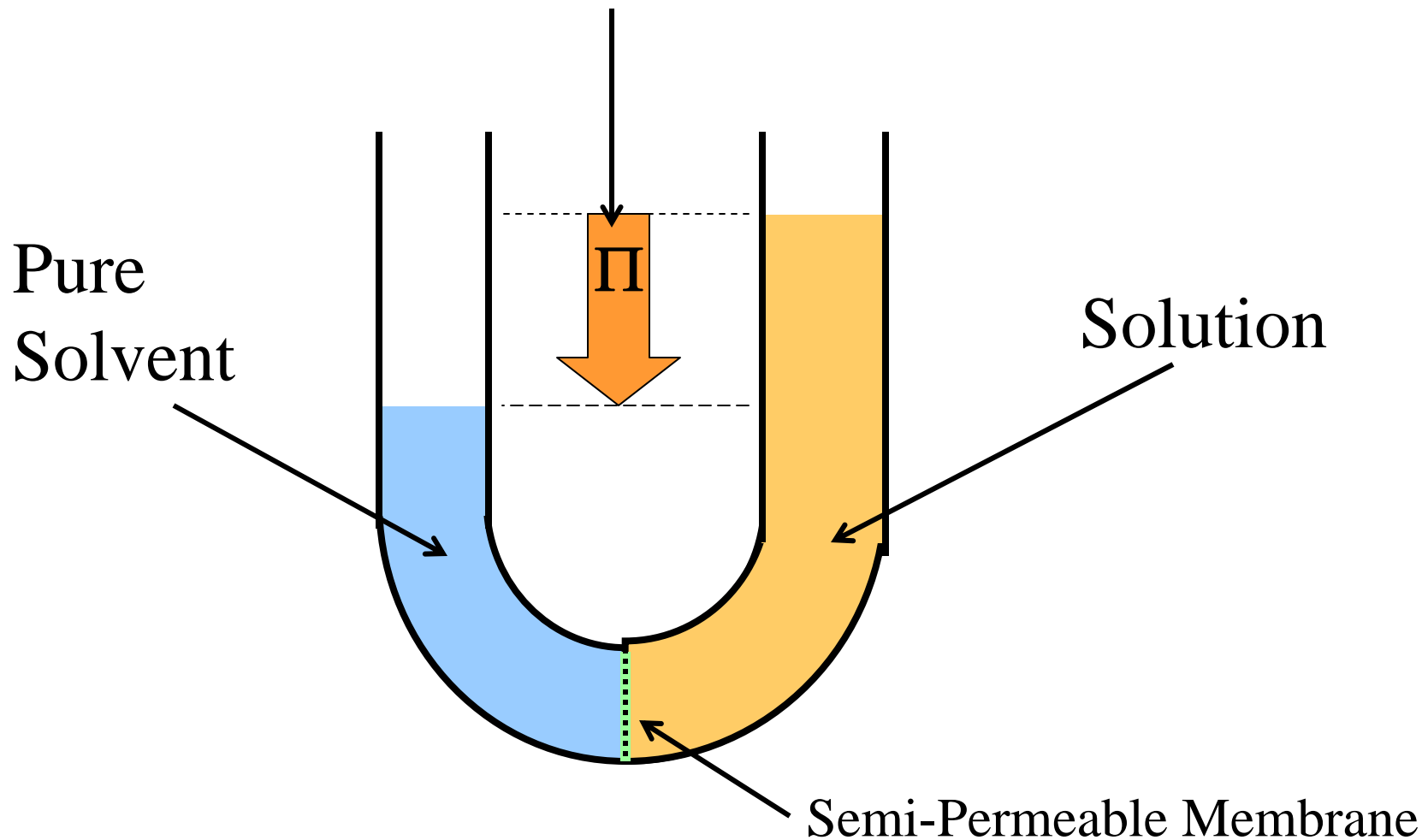
$$48.4 \text{ mol C}_2\text{H}_6\text{O}_2 \times \frac{62.08 \text{ g C}_2\text{H}_6\text{O}_2}{1 \text{ mol C}_2\text{H}_6\text{O}_2} = 3.00 \times 10^3 \text{ g C}_2\text{H}_6\text{O}_2$$

Osmotic Pressure



A filter that only solvent can pass through

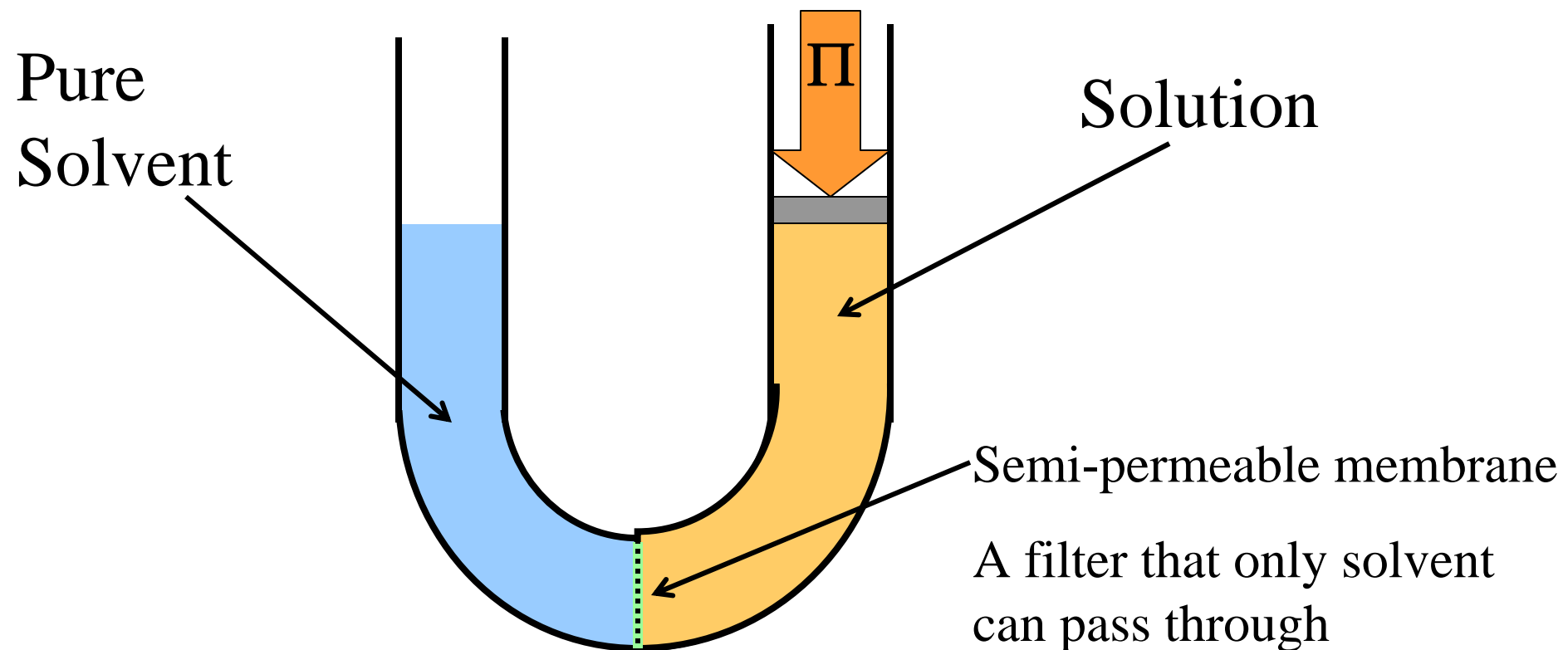
Osmotic Pressure



A filter that only solvent
can pass through

Osmotic Pressure

- The pressure required to prevent osmosis.
- It is a colligative property because it depends on the concentration of solute and not its identity.



Osmotic Pressure

Osmotic Pressure can be used to find molarity.

$$\Pi = i MRT$$

Π = osmotic pressure (atm)

i = van't Hoff factor (# of ions in a formula unit)

M = molarity (mol/L)

R = 0.0821 L•atm/mol•K

T = absolute temperature (K)

Ex) Osmotic Pressure

Ex) 0.15 grams of an unknown non-acidic organic compound is added to 0.85 L of water at 25°C. This creates an osmotic pressure of 0.0127 atm. Find the molar mass of the solute.

Step 1. Find the concentration of the solution

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$$\Pi = i MRT$$

$$M = \frac{\Pi}{i RT} =$$

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Step 1. Find the concentration of the solution

$$\Pi = i MRT$$

$$M = \frac{\Pi}{i RT} = \frac{0.0127 \text{ atm}}{(1)(0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K})(298\text{K})}$$

$$M = 5.19 \times 10^{-4} M$$

Ex) Osmotic Pressure (cont.)

Step 2. Find the number of moles of solute

Step 3. Find the molar mass

Ex) Osmotic Pressure (cont.)

Step 2. Find the number of moles of solute

$$0.85 \text{ L solution} \times \frac{5.19 \times 10^{-4} \text{ mol solute}}{1 \text{ L solution}} = 4.41 \times 10^{-4} \text{ mol solute}$$

Step 3. Find the molar mass

Ex) Osmotic Pressure (cont.)

Step 2. Find the number of moles of solute

$$0.85 \text{ L solution} \times \frac{5.19 \times 10^{-4} \text{ mol solute}}{1 \text{ L solution}} = 4.41 \times 10^{-4} \text{ mol solute}$$

Step 3. Find the molar mass

$$MM = \frac{0.15 \text{ g solute}}{4.41 \times 10^{-4} \text{ mol solute}} = 340 \text{ g/mol}$$