

Colligative properties depend on the number of solute particles, not on the type. Solvent properties change after adding a solute.

- Vapor pressure decreases
- Boiling point increases
- Melting point decreases
- Osmosis/osmotic pressure can occur

Vapor pressure(P):  $X_{\text{solvent}} \uparrow, P_{\text{solvent}} \uparrow$

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

**Raoult's Law**

$P^{\circ}$  = equilibrium vapor pressure of pure solvent

**Ideal solutions obey Raoult's Law**

$$P_A = X_A \cdot P^{\circ}_A$$

A=solvent, B=solute

$X_A$ , is less than 1, so  $P_A$  is less than  $P^{\circ}_A$ .

Vapor pressure of solvent over a solution is lowered

As  $X_B \uparrow, X_A \downarrow$ , so

as  $X_B \uparrow, P_A \downarrow$

Example: Assume ideal behavior for a solution containing 124.2g of glycol in 500.0g of water. What is the vapor pressure of water over the solution at 25°C?

(VP of pure  $H_2O$  is 23.76 mmHg.  $X_{\text{glycol}} = 2.000 \text{ mol glycol} / (2.000 \text{ mol glycol} + 27.75 \text{ mol } H_2O)$ )

Answer:

$$X_{\text{glycol}} = 0.06722 \text{ and so } X_{\text{water}} = ?$$

$$\text{Because } X_{\text{glycol}} + X_{\text{water}} = 1$$

$$X_{\text{water}} = 1.000 - 0.0672 = 0.9328$$

$$P_{\text{water}} = X_{\text{water}} \cdot P^{\circ}_{\text{water}} = (0.9328)(23.76 \text{ mm Hg})$$

$$P_{\text{water}} = 22.16 \text{ mm Hg}$$

Lowering of vapor pressure above solutions (compared to pure solvents) helps explain increases in boiling points of solutions (compared to pure solvents).

The boiling point of a solution is higher than the pure solvent from which it was made.

**Calculate Boiling Point Elevation,**

$$\Delta T_{\text{BP}} = K_{\text{BP}} \cdot m$$

where  $K_{\text{BP}}$  ( $^{\circ}\text{C}/m$ ) can be found in tables for the solvent

### Example: Boiling Point Increase

Dissolve 124.2 g of glycol (2.000 mol) in 500.0 g of water. What is the BP of the solution?

$K_{BP} = +0.512 \text{ }^\circ\text{C/molal}$  for water

Solution

1. Calculate solution molality = 4.000m

2.  $\Delta T_{BP} = K_{BP} \cdot m$

$$\Delta T_{BP} = +0.512 \text{ }^\circ\text{C/molal} (4.000\text{m})$$

$$\Delta T_{BP} = +2.05 \text{ }^\circ\text{C}$$

$$\text{BP} = 102.05 \text{ }^\circ\text{C}$$

### Calculate Freezing Point Decrease,

$$\Delta T_{FP}$$

Pure water

Ethylene glycol/water solution

The freezing point of a solution is **lower** than that of the pure solvent.

$$\text{FP depression} = \Delta T_{FP} = -K_{FP} \cdot m$$

Note: some books put a negative sign in the  $K_{FP}$  constant. If the  $K_{FP}$  constant is negative, then the equation above does not have a negative sign

### Lowering the Freezing Point

- When a solution freezes, the solid phase is pure water.
- The solution becomes more concentrated.

### Calculate Freezing Point Depression

Example: Calculate the FP of a 4.000m glycol/water solution,  $K_{FP}(\text{H}_2\text{O})=1.86^\circ\text{C/m}$

Answer:

$$\Delta T_{FP} = -K_{FP} \cdot m$$

$$= -(1.86 \text{ }^\circ\text{C/m})(4.000 \text{ m})$$

$\Delta T_{FP} = -7.44 \text{ }^\circ\text{C}$  ( $\Delta T_{BP}$  was  $+2.05 \text{ }^\circ\text{C}$ , so the freezing point was lowered more than the boiling point was raised.)

### Calculate Freezing Point Depression

How much NaCl must be dissolved in 2.00kg of water to lower FP to  $-5.00^\circ\text{C}$ ?

Solution

Calculate the molality needed

$$\Delta T_{FP} = -K_{FP} \cdot m$$

$$-5.00 \text{ }^\circ\text{C} = -(1.86 \text{ }^\circ\text{C/m}) \cdot m$$

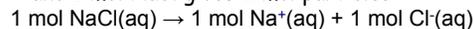
$$m = 2.69 \text{ molal of particles}$$

### Calculate Freezing Point Depression

How much NaCl must be dissolved in 2.00kg of water to lower FP to  $-5.00^\circ\text{C}$ ?

Need 2.69mol of dissolved particles per kg of solvent.

$m$  is the concentration of all dissolved particles and 1 mol NaCl gives 2 mol particles:



$$2.00\text{kg} \cdot (2.69 \text{ mol particles/kg}) \cdot (1 \text{ mol NaCl} / 2 \text{ mol particles}) \cdot (58.4 \text{ g NaCl/mol NaCl})$$

$$= 157\text{g NaCl}$$

## Boiling Point Elevation and Freezing Point Depression

$$\Delta T = K \cdot m \cdot i$$

$i$  = van't Hoff factor = number of particles produced per formula unit.

| Compound                              | Theoretical value of $i$ |
|---------------------------------------|--------------------------|
| Glycol, ethanol, sugar                | 1                        |
| NaCl, KCl, KI                         | 2                        |
| CaCl <sub>2</sub> , MgBr <sub>2</sub> | 3                        |

## Osmosis is diffusion through a semipermeable membrane

- Osmosis can occur when solvent is able to pass through the membrane but the solute cannot.

Semipermeable membrane passes only solvent molecules in order to attempt to get equal solution concentrations on both sides. This builds osmotic pressure.

The driving force is entropy (randomness)

$$\Pi = cRT$$

$c$  is concentration in M (mol/L)

$$R = 0.0821 \text{ (L} \cdot \text{atm)/(mol} \cdot \text{K)}$$

$T$  is temperature (K)

Osmosis can continue until the solutions are isotonic (have the same concentration).

- **Osmotic pressure** can destroy living cells

## Osmosis: calculating a molar mass

Dissolve 70.0 g of hemoglobin (Hb) in enough water to make 2.00 L of solution.  $\Pi$  is 10.2 mmHg at 27 °C. Calculate the molar mass of Hb.

Solution

1. Calculate  $\Pi$  in atmospheres

$$\begin{aligned}\Pi &= 10.2 \text{ mmHg} \cdot (1 \text{ atm} / 760 \text{ mmHg}) \\ &= 0.01342 \text{ atm}\end{aligned}$$

2. Calculate concentration from  $\Pi = cRT$

$$\begin{aligned}c &= 0.01342 \text{ atm} / [(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(300. \text{K})] \\ c &= 5.449 \times 10^{-4} \text{ mol Hb/L}\end{aligned}$$

## Osmosis: calculating a molar mass

Dissolve 70.0 g of hemoglobin in enough water to make 2.00 L of solution.  $\Pi$  measured to be 10.2 mmHg at 27 °C. Calculate the molar mass of hemoglobin.

3. Calculate moles hemoglobin from  $c$   
 $\text{mol Hb} = 2.00 \text{ L} \cdot (5.449 \times 10^{-4} \text{ mol Hb/L}) = 1.09 \times 10^{-3}$
4. Knowing the number moles of Hb that is 70.0g of Hb, calculate the molar mass of Hb  
 $\text{MM} = 70.0 \text{ g Hb} / 1.09 \times 10^{-3} \text{ mol Hb}$   
Molar mass = 64,200 g Hb/mol Hb