

Physical Properties of Solutions

Chapter 12

A **solution** is a homogenous mixture of 2 or more substances



The **solute** is(are) the substance(s) present in the smaller amount(s)

The **solvent** is the substance present in the larger amount

TABLE 12.1

Types of Solutions

Component 1	Component 2	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO ₂ in water)
Gas	Solid	Solid	H ₂ gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

A **saturated solution** contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

An **unsaturated solution** contains less solute than the solvent has the capacity to dissolve at a specific temperature.

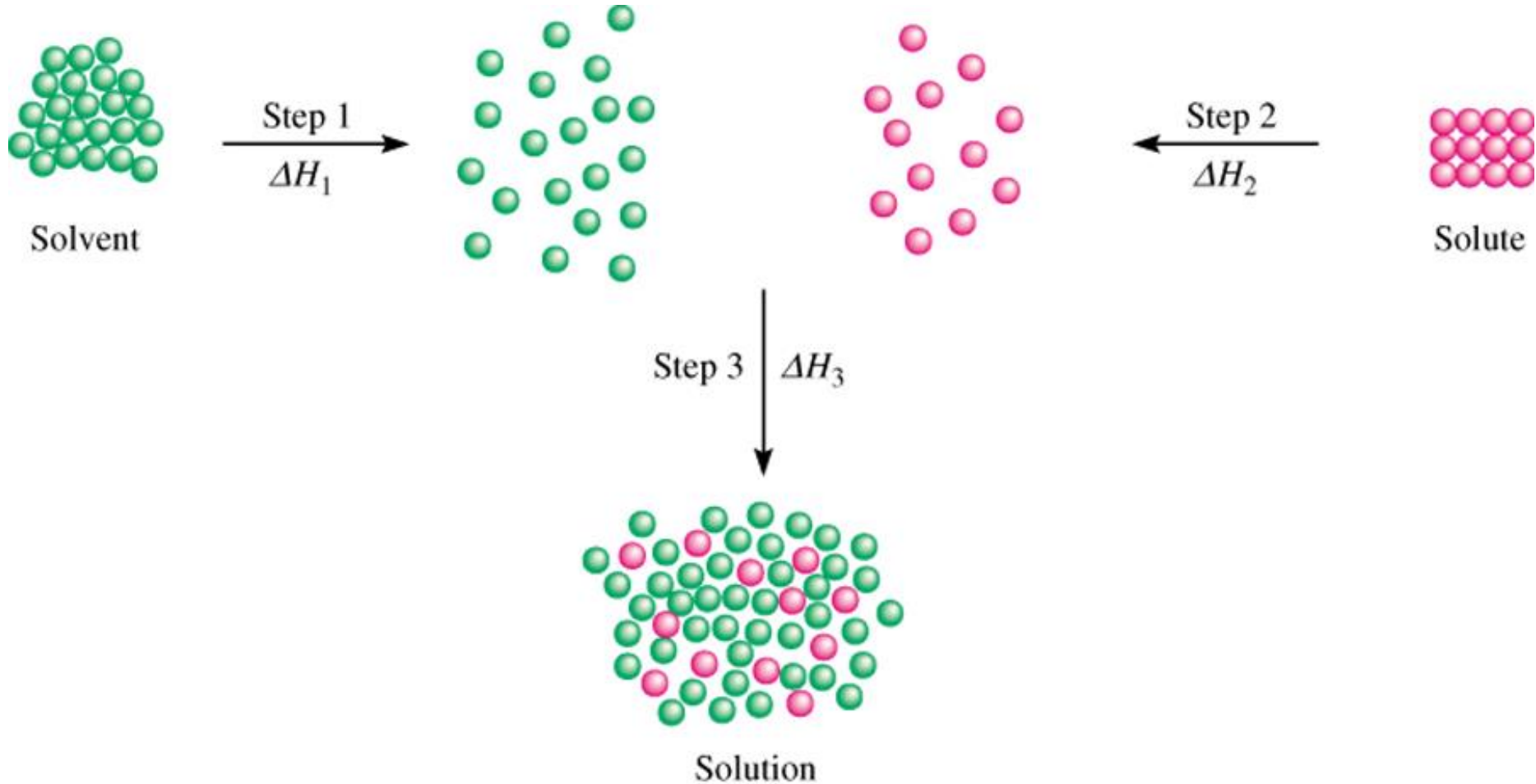
A **supersaturated solution** contains more solute than is present in a saturated solution at a specific temperature.

Sodium acetate crystals rapidly form when a seed crystal is added to a supersaturated solution of sodium acetate.



Three types of interactions in the solution process:

- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction



$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$



“like dissolves like”

Two substances with similar *intermolecular* forces are likely to be soluble in each other.

- non-polar molecules are soluble in non-polar solvents



- polar molecules are soluble in polar solvents



- ionic compounds are more soluble in polar solvents



Concentration Units

The ***concentration*** of a solution is the amount of solute present in a given quantity of solvent or solution.

Percent by Mass

$$\begin{aligned}\% \text{ by mass} &= \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\% \\ &= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%\end{aligned}$$

Mole Fraction (X)

$$X_A = \frac{\text{moles of A}}{\text{sum of moles of all components}}$$

Concentration Units Continued

Molarity (M)

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Molality (m)

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$



EX.

100g of an aqueous solution containing 5g of NaCl ;
what is the mass percentage of NaCl in the solution ?

Ans .

$$\text{Mass \% of NaCl} = (5 / 100) \times 100$$

$$= 5 \%$$

Ex. 3.1

Gases solution contain 2.0 g of the He and 4g of O₂. What are the mole fractions of He and O₂ in the solution?

Ans. 3.1

$$X_{\text{He}} = n_{\text{He}} / n_{\text{He}} + n_{\text{O}_2} \quad X_{\text{O}_2} = n_{\text{O}_2} / n_{\text{He}} + n_{\text{O}_2}$$

First we find the number of mole of each component present in solution , n_{He}
and n_{O_2}

$$n_{\text{He}} = \text{mass He} / \text{Mw} , n_{\text{He}} = 2.0\text{g} / 4.0\text{g mol}^{-1} = 0.5 \text{ mole He}$$

$$n_{\text{O}_2} = \text{mass of O}_2 / \text{Mw} , n_{\text{O}_2} = 4.0\text{g} / 32.\text{g mol}^{-1} = 0.125 \text{ mole O}_2$$

$$X_{\text{He}} = 0.5 / 0.5 + 0.125 \quad X_{\text{O}_2} = 0.125 / 0.5 + 0.125 = 0.2$$
$$= 0.8$$

Note:

$$X_{\text{He}} + X_{\text{O}_2} = 0.8 + 0.2 = 1$$



What is the molality of CuSO_4 solution when 20 g of CuSO_4 dissolved in 100 g of water ?

$\text{Cu} = 63.5$, $\text{S} = 32$, $\text{O} = 16$

Answer

$m = n \text{ solute} / \text{Kg of solvent}$

$n \text{ of } \text{CuSO}_4 = \text{mass} / \text{MW} = 20 \text{ g} / 159.5 \text{ g mol}^{-1}$

$= 0.125 \text{ mol}$

$m = n \text{ CuSO}_4 / \text{Mass of H}_2\text{O (Kg)}$

$m = 0.125 / 0.1 = 1.25 \text{ m}$



What are the mole fractions of solute and solvent in 1.00 m aqueous solution ?

Answer : $m = n \text{ solute} / \text{Kg of solvent}$

$1 \text{ m} = 1 \text{ mol} / 1 \text{ Kg}$, So mass of water = 1000 g

The MW of $\text{H}_2\text{O} = 18 \text{ g} / \text{mol}$

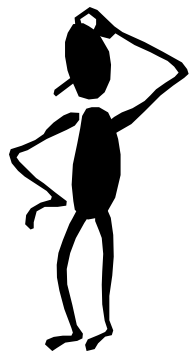
No. of mole of $\text{H}_2\text{O} = 1000 \text{ g} / 18 \text{ g/mol} = 55.6 \text{ mol H}_2\text{O}$.

n_{solute} (no. of mole of solute) = 1 mol

$n_{\text{H}_2\text{O}} = 55.6 \text{ mol}$

$X_{\text{solute}} = 1 / (1+55.6) = 0.018$

$X_{\text{H}_2\text{O}} = 55.6 / (1 + 55.6) = 0.982 .$



What is the molality of a 5.86 M ethanol (C₂H₅OH) solution whose density is 0.927 g/mL?

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \quad M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Assume **1 L** of solution: $M = \text{number of moles} / \text{Volume (L)}$

$$5.86 \text{ M} = \text{number of moles} / 1 \text{ L}$$

number of moles of ethanol = 5.86 moles

$$\text{Mass of ethanol} = 5.86 \times 46 = 270 \text{ g ethanol}$$

$$\text{Mass of solution} = 1000 \text{ ml} \times 0.927 \text{ g/ml} = 927 \text{ g}$$

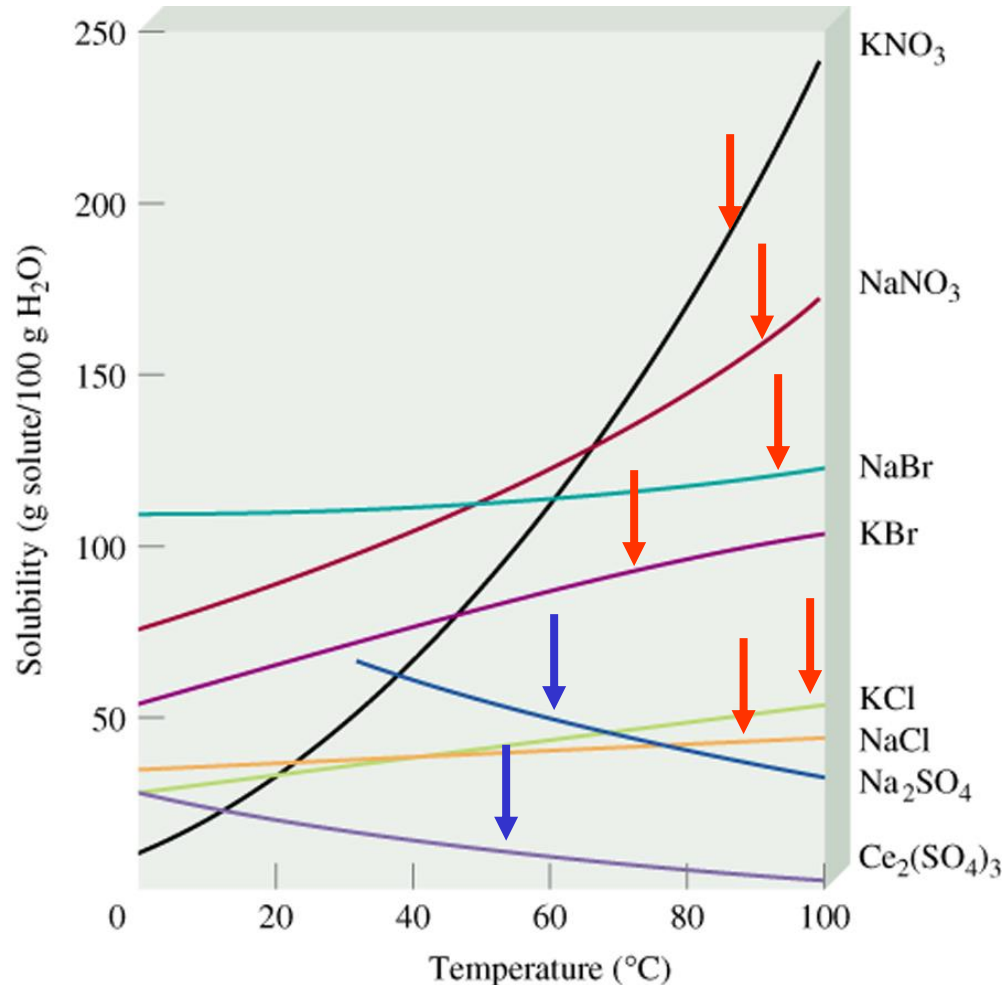
mass of solvent = mass of solution – mass of solute

$$= 927 \text{ g} - 270 \text{ g} = 657 \text{ g} = 0.657 \text{ kg}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles C}_2\text{H}_5\text{OH}}{0.657 \text{ kg solvent}} = 8.92 \text{ m}$$

Temperature and Solubility

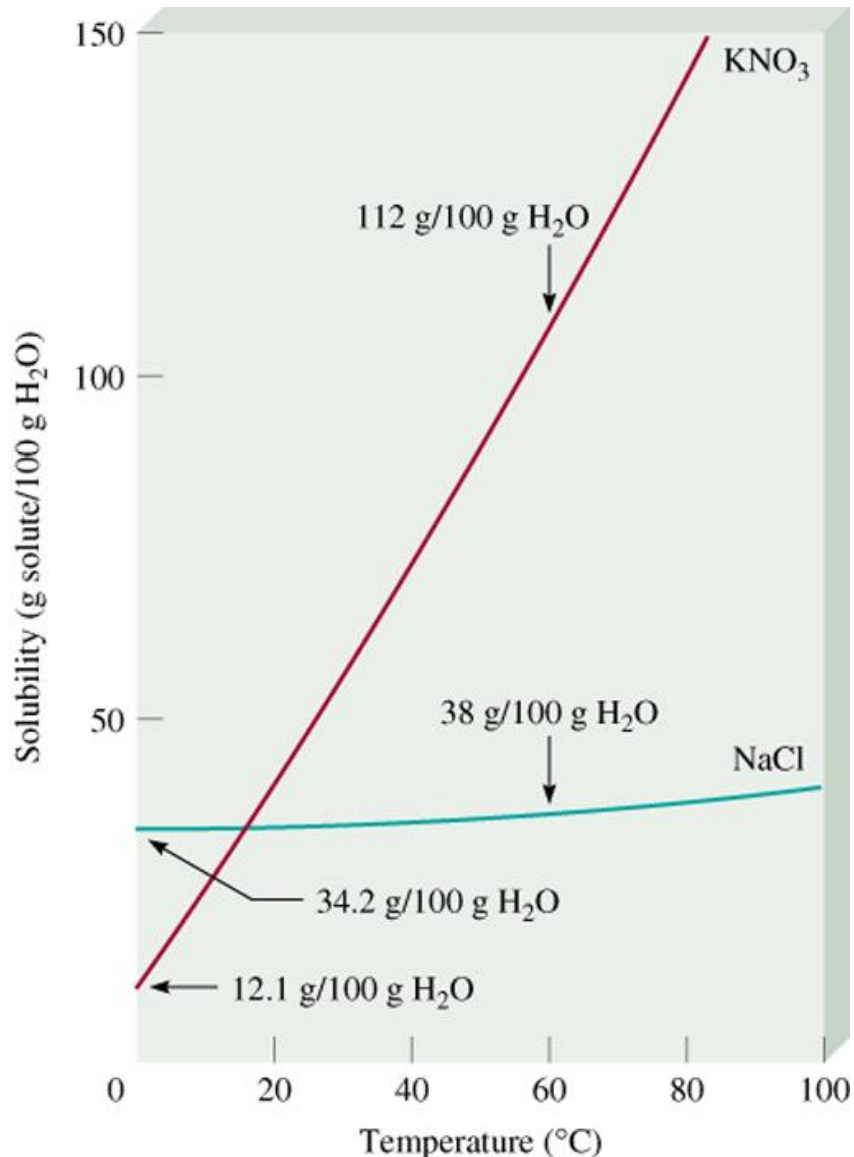
Solid solubility and temperature



solubility of solids decreases with increasing temperature

solubility increases with increasing temperature

Fractional crystallization is the separation of a mixture of substances into pure components on the basis of their differing solubilities.



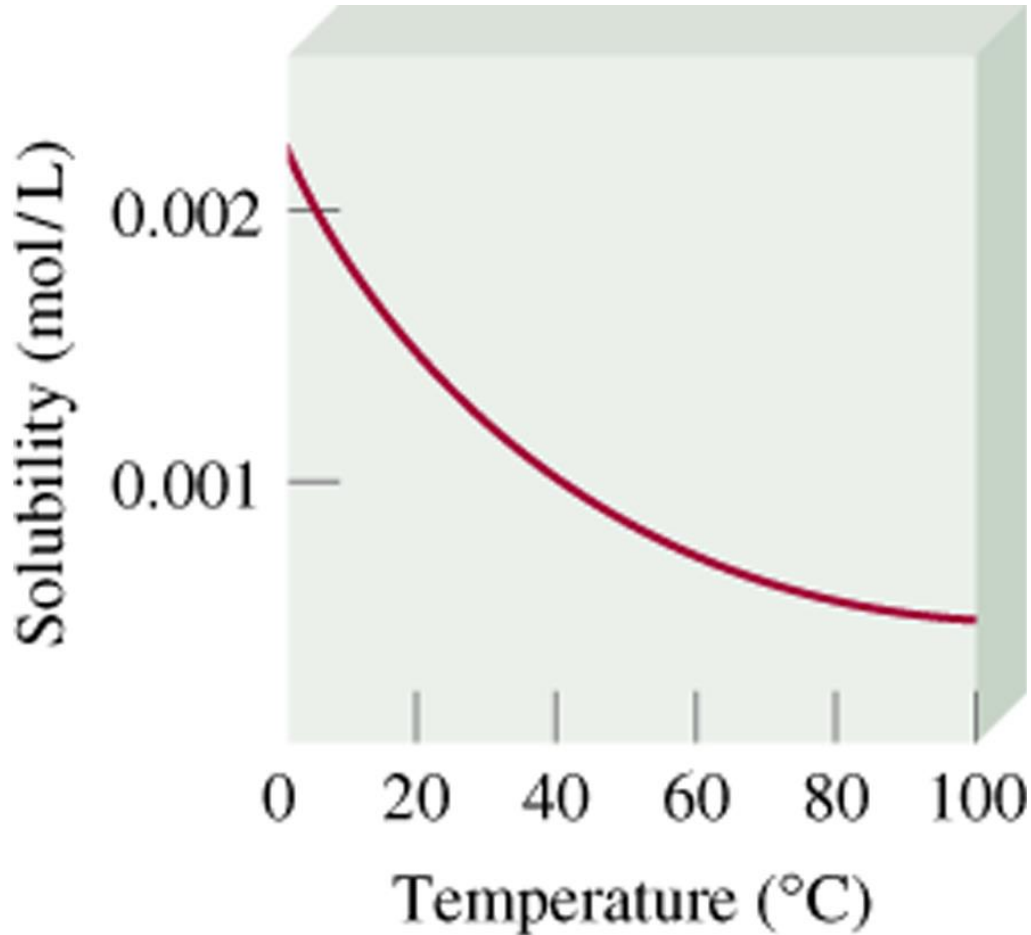
Suppose you have 90 g KNO₃ contaminated with 10 g NaCl.

Fractional crystallization:

1. Dissolve sample in 100 mL of water at 60°C
2. Cool solution to 0°C
3. All NaCl will stay in solution (s = 34.2g/100g)
4. 78 g of PURE KNO₃ will precipitate (s = 12 g/100g).
90 g – 12 g = 78 g

Temperature and Solubility

Gas solubility and temperature



solubility usually
decreases with
increasing temperature

Pressure and Solubility of Gases

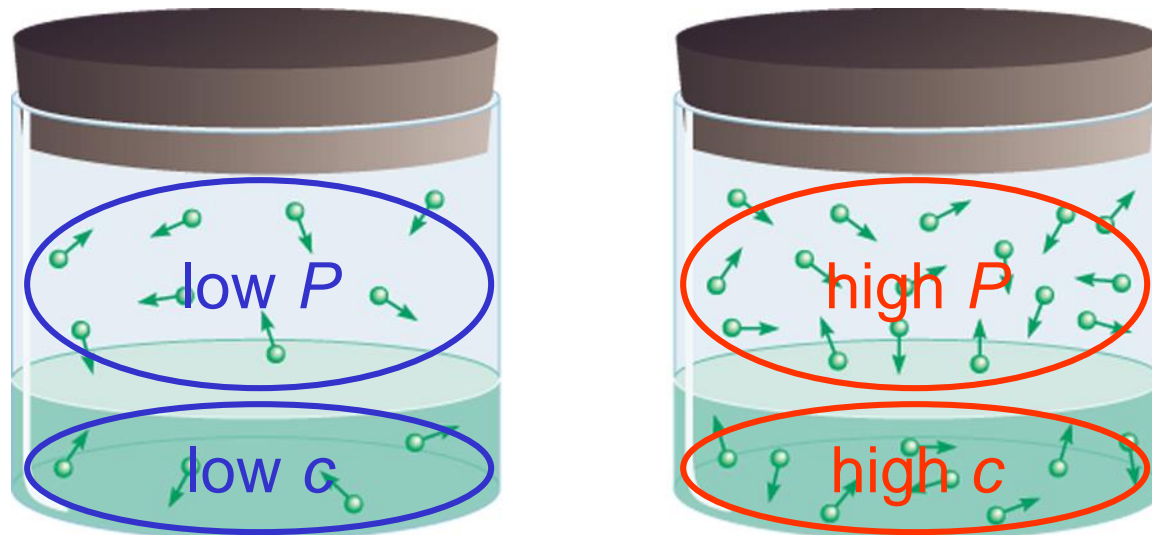
The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (**Henry's law**).

$$c = kP$$

c is the concentration (M) of the dissolved gas

P is the pressure of the gas over the solution

k is a constant ($\text{mol/L}\cdot\text{atm}$) that depends only on temperature



Example 12.6

The solubility of nitrogen gas at 25 °C and 1 atm is 6.8×10^{-4} mol/L. What is the concentration(M) of nitrogen dissolved in water Under atmospheric conditions? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

Solution 12.6

$$c = k p$$

$$6.8 \times 10^{-4} = k \times (1 \text{ atm})$$

$$K = 6.8 \times 10^{-4} \text{ mol/L.atm}$$

$$c = k \times p$$

$$= 6.8 \times 10^{-4} \times 0.78 \text{ atm} = 5.3 \times 10^{-4} \text{ mol/L}$$

Chemistry In Action: The Killer Lake

8/21/86

**CO₂ Cloud Released
1700 Casualties**

Trigger?

- **earthquake**
- **landslide**
- **strong Winds**



Lake Nyos, West Africa

Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number of solute particles** in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering

$$P_1 = X_1 P_1^0$$

P_1^0 = vapor pressure of **pure** solvent

Raoult's law

X_1 = mole fraction of the solvent

If the solution contains only one solute:

$$X_1 = 1 - X_2$$

$$P_1 = (1 - X_2) P_1^0$$

$$P_1 = P_1^0 - P_1^0 X_2$$

$$P_1^0 X_2 = P_1^0 - P_1 = \Delta P$$

X_2 = mole fraction of the solute

ΔP = Lowering of vapor pressure

Rault,s Law:

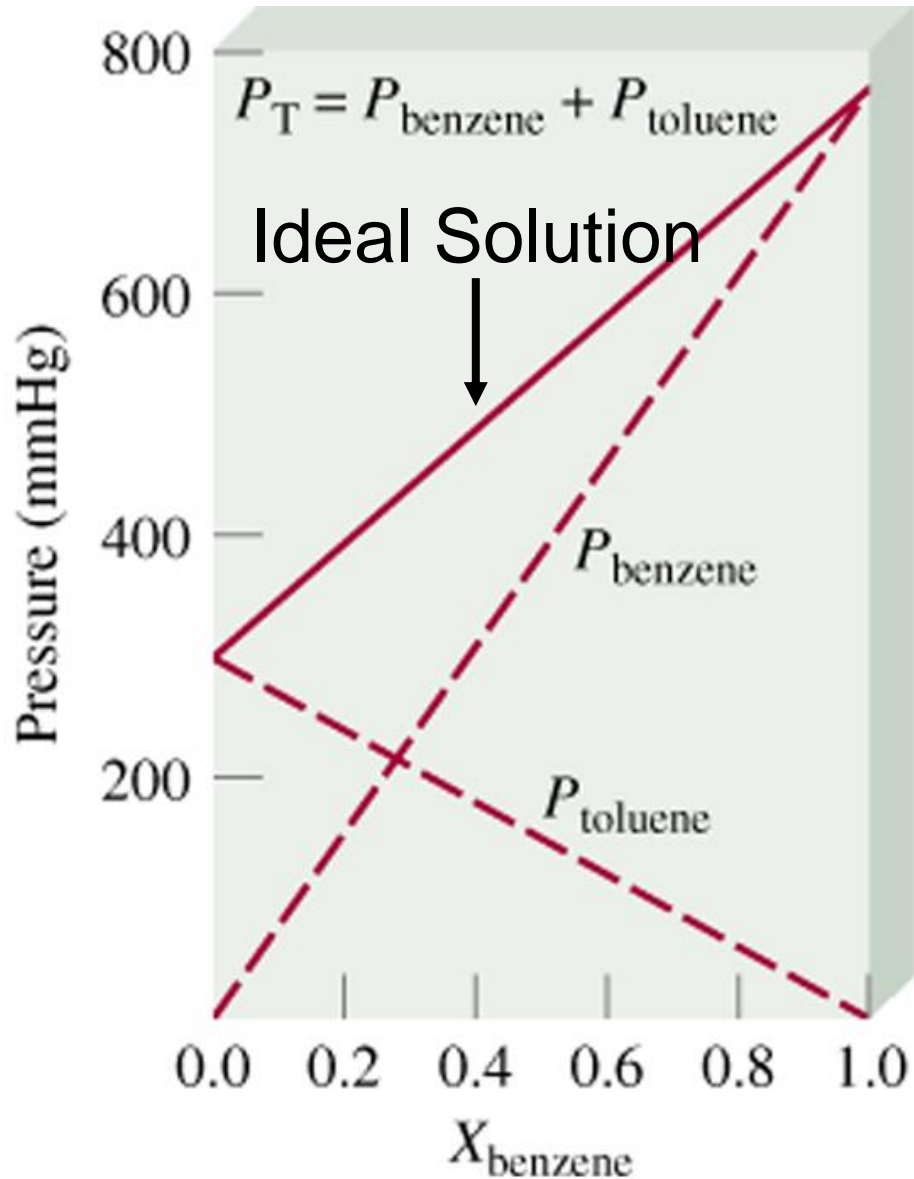
For ideal gases, the vapor pressure of solution (P_T) in two component system A and B is :

$$P_T = P_A + P_B \dots\dots\dots (1)$$

$$P_A = X_A P_A^\circ \dots\dots\dots (2)$$

$$P_B = X_B P_B^\circ \dots\dots\dots (3)$$

$$P_T = X_A P_A^\circ + X_B P_B^\circ \dots\dots\dots (4)$$



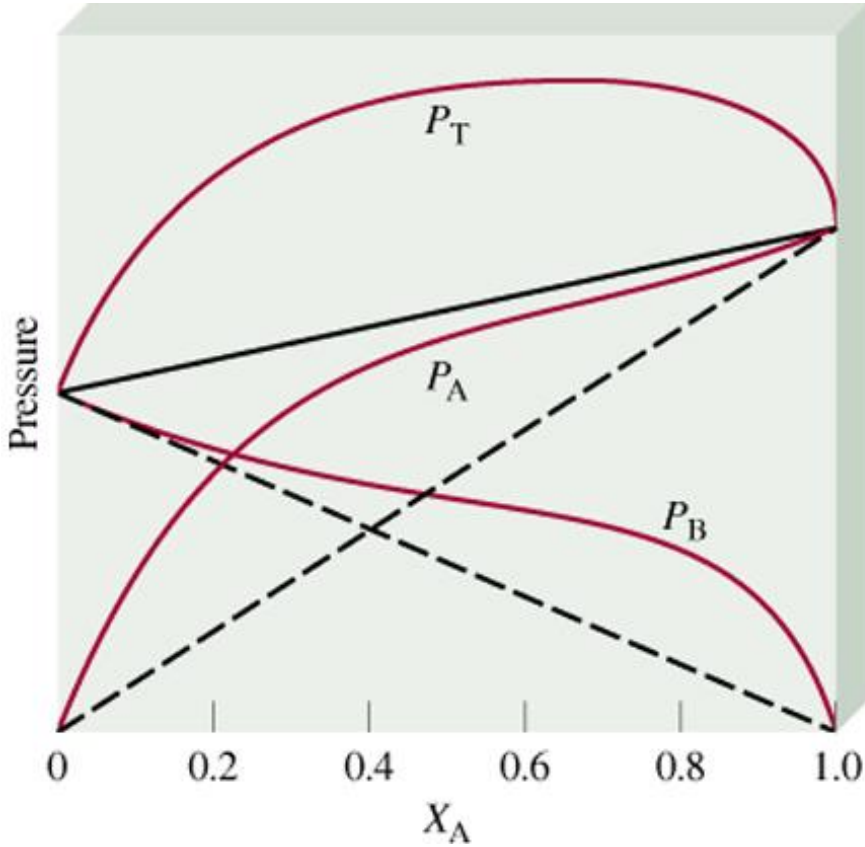
$$P_A = X_A P_A^0$$

$$P_B = X_B P_B^0$$

$$P_T = P_A + P_B$$

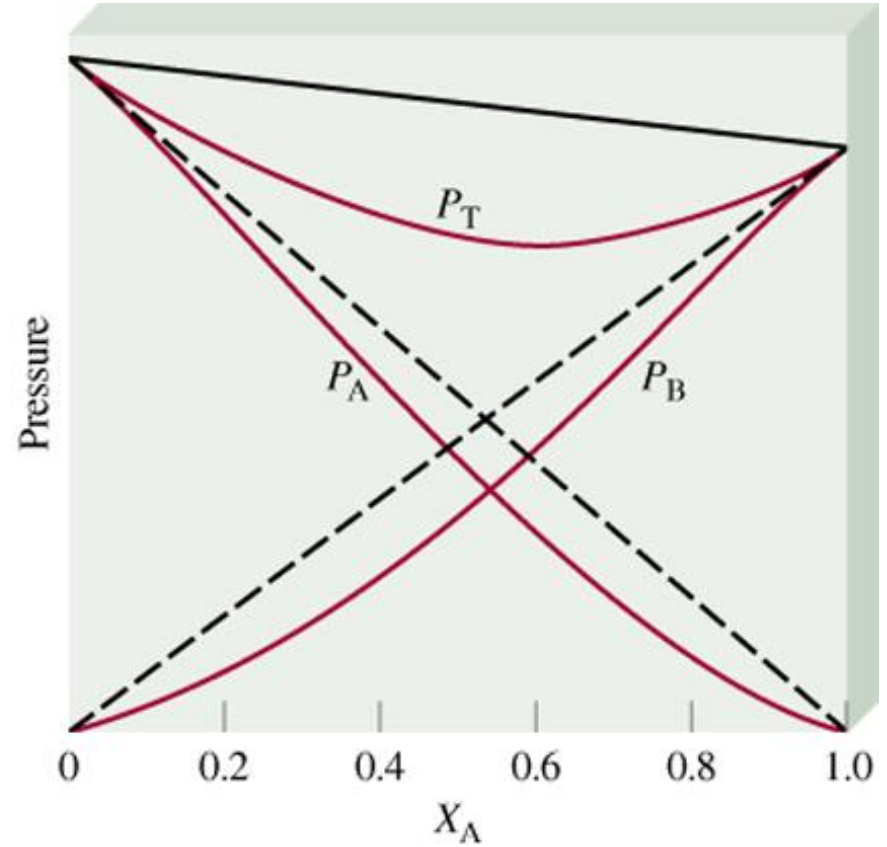
$$P_T = X_A P_A^0 + X_B P_B^0$$

P_T is greater than predicted by Raoult's law



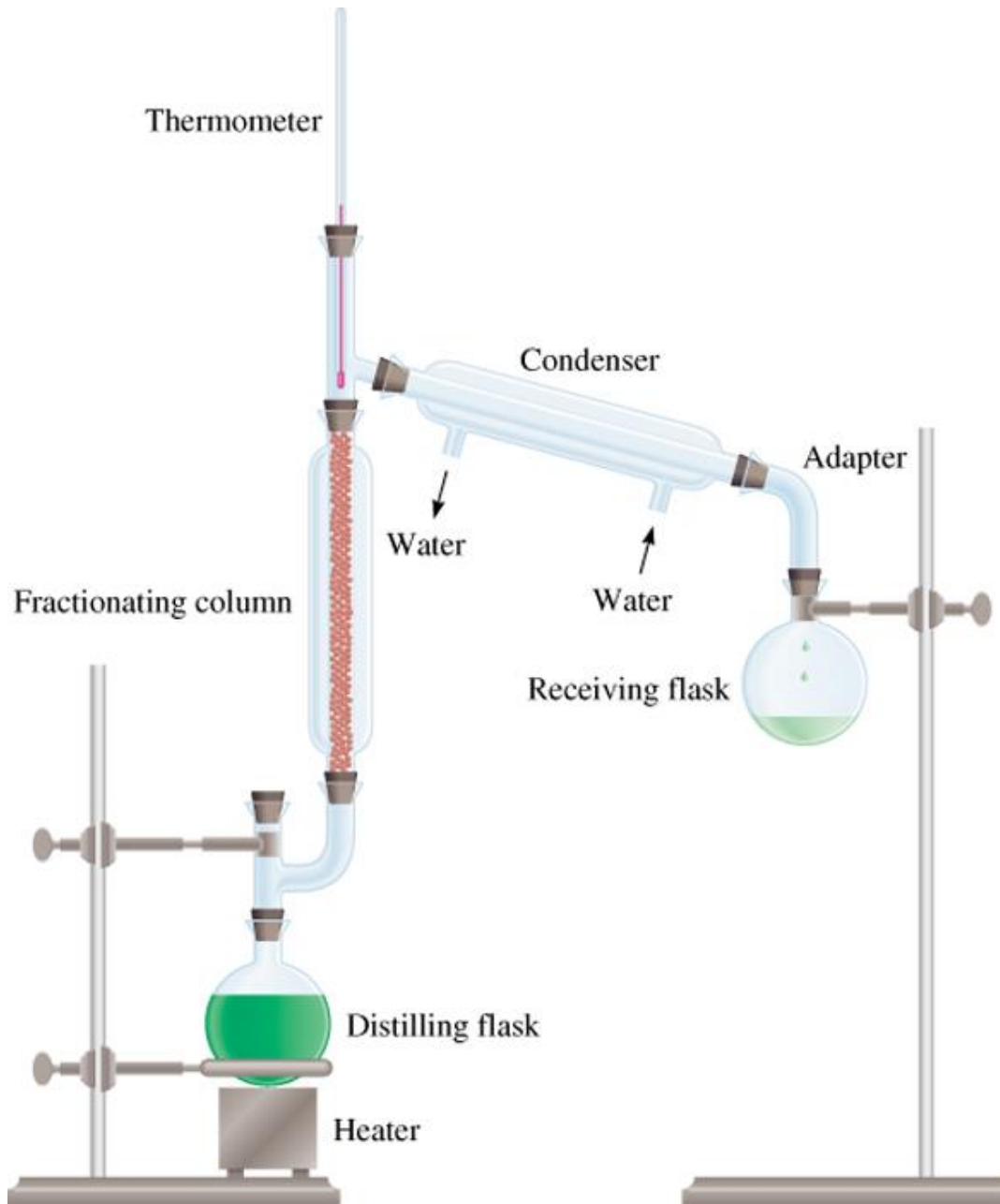
Force A-B < Force A-A & Force B-B

P_T is less than predicted by Raoult's law



Force A-B > Force A-A & Force B-B

Fractional Distillation Apparatus



EX. 1

Heptane (C_7H_{16}) and octane (C_8H_{18}) form ideal solution. **What is the vapor pressure** at $40^\circ C$ of a **solution that contains** 3.0 mol of heptane and 5 mol of octane ?

At $40^\circ C$ $p^\circ_{\text{heptan}} = 0.121 \text{ atm}$ and $p^\circ_{\text{octane}} = 0.041 \text{ atm}$.

Ans.

$$n_h + n_o = 3 + 5 = 8$$

$$X_h = 3 / 8 = 0.375$$

$$X_o = 5 / 8 = 0.625$$

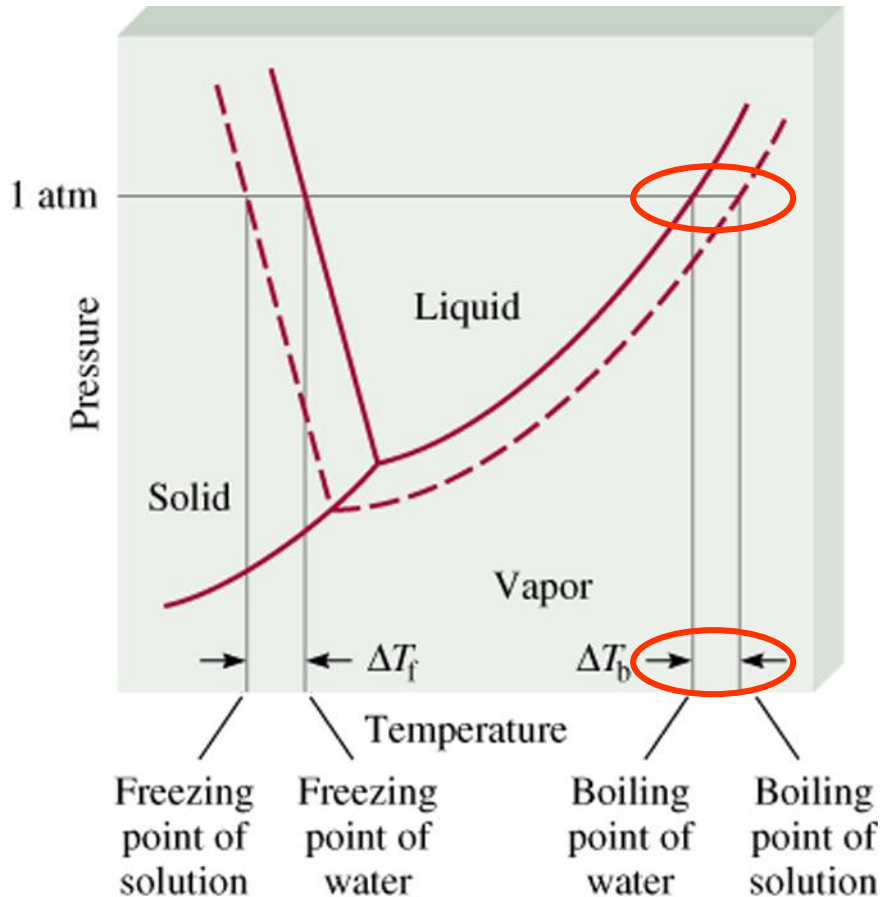
$$P_t = X_h p^\circ_h + X_o P^\circ_o$$

$$= 0.375 \times 0.121 + 0.625 \times 0.041$$

$$= 0.045 + 0.026$$

$$= 0.071 \text{ atm}$$

Boiling-Point Elevation



$$\Delta T_b = T_b - T_b^0$$

T_b^0 is the boiling point of the pure solvent

T_b is the boiling point of the solution

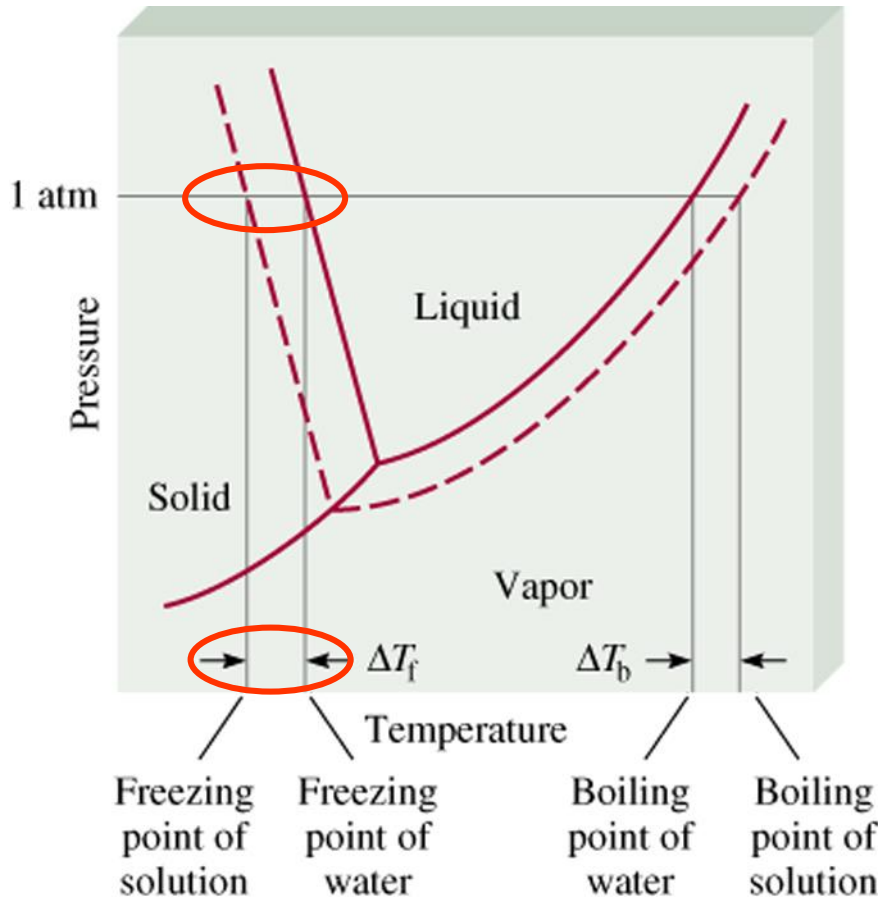
$$T_b > T_b^0 \quad \Delta T_b > 0$$

$$\Delta T_b = K_b m$$

m is the molality of the solution

K_b is the molal boiling-point elevation constant ($^{\circ}\text{C}/m$)

Freezing-Point Depression



$$\Delta T_f = T_f^0 - T_f$$

T_f^0 is the freezing point of the pure solvent

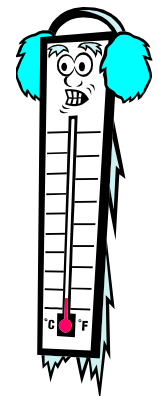
T_f is the freezing point of the solution

$$T_f^0 > T_f \quad \Delta T_f > 0$$

$$\Delta T_f = K_f m$$

m is the molality of the solution

K_f is the molal freezing-point depression constant ($^{\circ}\text{C}/m$)



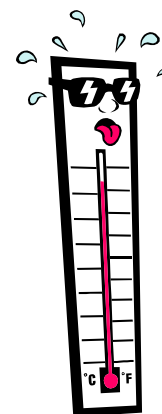
12.2

TABLE

Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

Solvent	Normal Freezing Point (°C)*	K_f (°C/m)	Normal Boiling Point (°C)*	K_b (°C/m)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	-117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

* Measured at 1 atm.



Ex . What are the boiling point and freezing point of a solution prepared by dissolving 2.4 g of biphenyl ($C_{12}H_{10}$) in 75 g of benzene ? If k_b and k_f for benzene are $2.53^\circ\text{C}/\text{m}$ and $5.12^\circ\text{C}/\text{m}$, respectively. The b.p and f.p of benzene are 80.1 and 5.5°C , respectively.

Ans

$$n = 2.4 / 154 = 0.015 \text{ mol}$$

$$m = 0.015 \text{ mol} / 0.075 \text{ Kg} = 0.208 \text{ m}$$

$$\Delta T_b = 2.53 \times 0.208 = 0.526^\circ\text{C}$$

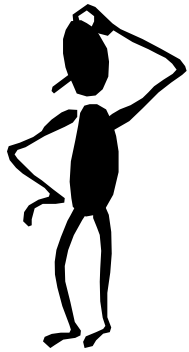
$$\text{b.p . of solution} = \text{b.p of pure solvent} + \Delta T_b$$

$$= 80.1 + 0.526 = 80.626^\circ\text{C}$$

$$\Delta T_f = 5.12 \times 0.208 = 1.06^\circ\text{C}$$

$$\text{f.p. of solution} = \text{f.p. of pure solvent} - \Delta T_f$$

$$= 5.5 - 1.06 = 4.4^\circ\text{C}$$



What is the freezing point of a solution containing 478 g of ethylene glycol (antifreeze) in 3202 g of water? The molar mass of ethylene glycol is 62.01 g.

$$\Delta T_f = K_f m \quad K_f \text{ water} = 1.86 \text{ } ^\circ\text{C}/m$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{478 \text{ g} \times \frac{1 \text{ mol}}{62.01 \text{ g}}}{3.202 \text{ kg solvent}} = 2.41 m$$

$$\Delta T_f = K_f m = 1.86 \text{ } ^\circ\text{C}/m \times 2.41 m = 4.48 \text{ } ^\circ\text{C}$$

$$\Delta T_f = T_f^0 - T_f$$

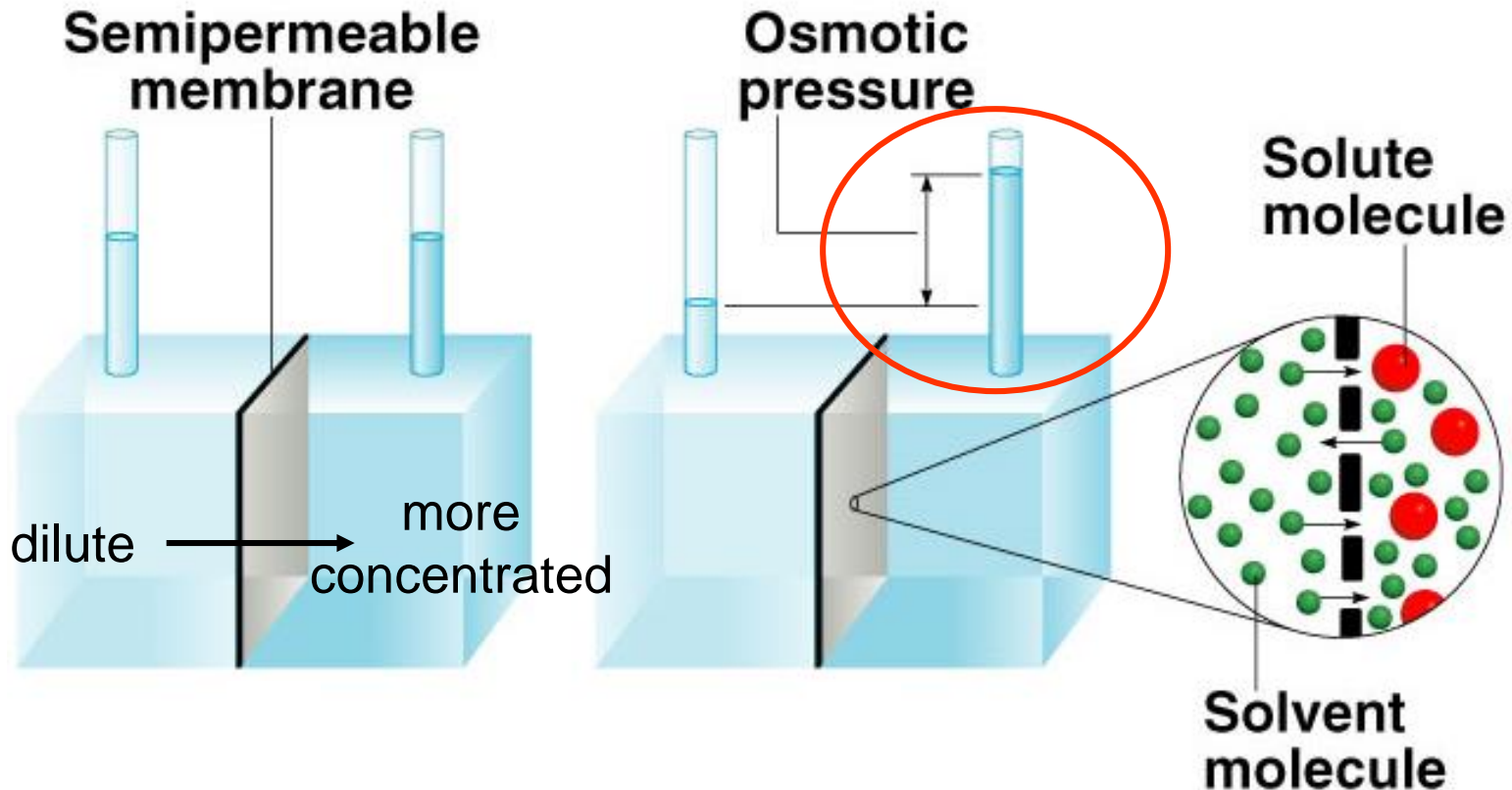
$$T_f = T_f^0 - \Delta T_f = 0.00 \text{ } ^\circ\text{C} - 4.48 \text{ } ^\circ\text{C} = -4.48 \text{ } ^\circ\text{C}$$

Osmotic Pressure (π)

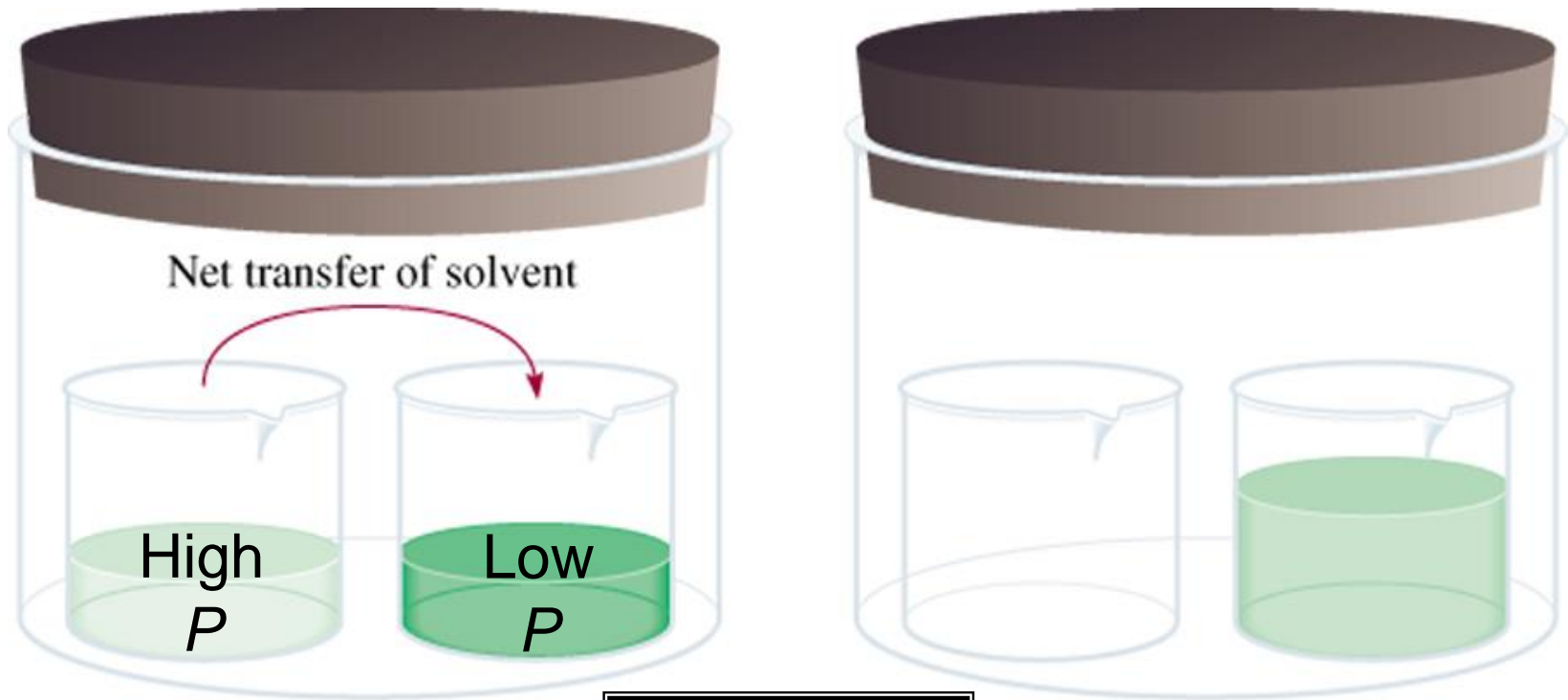
Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

A **semipermeable membrane** allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (π) is the pressure required to stop osmosis.



Osmotic Pressure (π)



$$\pi = MRT$$

M is the molarity of the solution

R is the gas constant

T is the temperature (in K)

Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering $P_1 = X_1 P_1^0$

$$\Delta P = X_2 P_1^0$$

Boiling-Point Elevation

$$\Delta T_b = K_b m$$

Freezing-Point Depression

$$\Delta T_f = K_f m$$

Osmotic Pressure (π)

$$\pi = MRT$$

Colligative Properties of Electrolyte Solutions

0.1 *m* NaCl solution \longrightarrow 0.1 *m* Na⁺ ions & 0.1 *m* Cl⁻ ions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

0.1 *m* NaCl solution \longrightarrow 0.2 *m* ions in solution

van't Hoff factor (i) = $\frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$

	<u><i>i</i> should be</u>
nonelectrolytes	1
NaCl	2
CaCl ₂	3

Colligative Properties of Electrolyte Solutions

Boiling-Point Elevation

$$\Delta T_b = i K_b m$$

Freezing-Point Depression

$$\Delta T_f = i K_f m$$

Osmotic Pressure (π)

$$\pi = iMRT$$

12.3

The van't Hoff Factor of 0.0500 *M* Electrolyte Solutions at 25°C

TABLE

Electrolyte	<i>i</i> (Measured)	<i>i</i> (Calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
MgSO ₄	1.3	2.0
MgCl ₂	2.7	3.0
FeCl ₃	3.4	4.0

Example : A solution containing 0.833 g of a polymer of unknown structure in 170 ml of an organic solvent was found to have an osmotic pressure of 5.2 mmHg at 25 °C. Determine the molar mass of the polymer

Solution:

$$\pi = MRT$$

$$\pi = 5.2 / 760 = 0.0075 \text{ atm}$$

$$M = \pi / R T = 0.0075 / 0.0821 \times 298 = 2.8 \times 10^{-4} \text{ molar}$$

Multiplying the molarity by the volume of solution (in L) gives moles of solute (polymer)

$$? \text{ mol of polymer} = (2.80 \times 10^{-4} \text{ mol/L})(0.170 \text{ L}) = 4.76 \times 10^{-5} \text{ mol polymer}$$

$$\text{Molar mass} = \text{Mass (g)} / \text{number of moles of polymer}$$

$$= 0.833 \text{ (g)} / 4.76 \times 10^{-5} \text{ mol polymer}$$

$$= \mathbf{1.75 \times 10^4 \text{ g/mol}}$$

Example: A 7.85 g sample of a compound with the empirical Formula C_5H_4 is dissolved in 301 g of benzene. The freezing Point of the solution is $1.05\text{ }^\circ\text{C}$ below that of the pure benzene. What are the molar mass and molecular formula of this compound?

$$\begin{aligned}\text{Solution: molality} &= \Delta T_f / K_f = 1.05\text{ }^\circ\text{C} / 5.12\text{ }^\circ\text{C}/\text{m} \\ &= 0.205\text{ m}\end{aligned}$$

$$\begin{aligned}\text{Number of moles of solute} &= \text{molality} \times \text{Kg of solvent} \\ &= 0.205\text{ m} \times 0.301\text{ Kg} = 0.0617\text{ mol.}\end{aligned}$$

$$\begin{aligned}\text{Molar mass} &= \text{Mass (g)} / \text{number of moles} \\ &= 7.85\text{ g} / 0.0617\text{ mol} = 127\text{ g/mol}\end{aligned}$$

$$\begin{aligned}\text{Molecular formula} &= C_5H_4 \times (\text{molar mass} / \text{mass of empirical formula}) \\ &= C_5H_4 \times (127\text{ g/mol} / 64\text{ g/mol}) = C_{10}H_8\end{aligned}$$