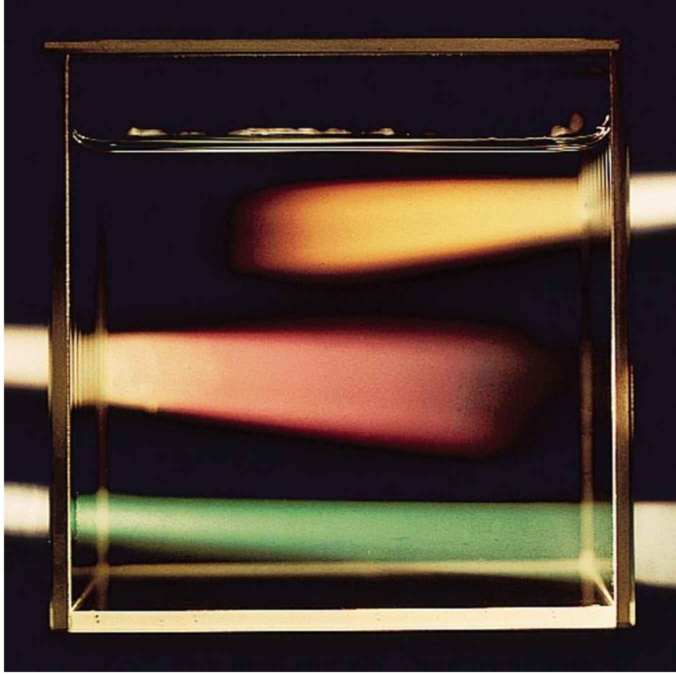


Physical Properties of Solutions

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.

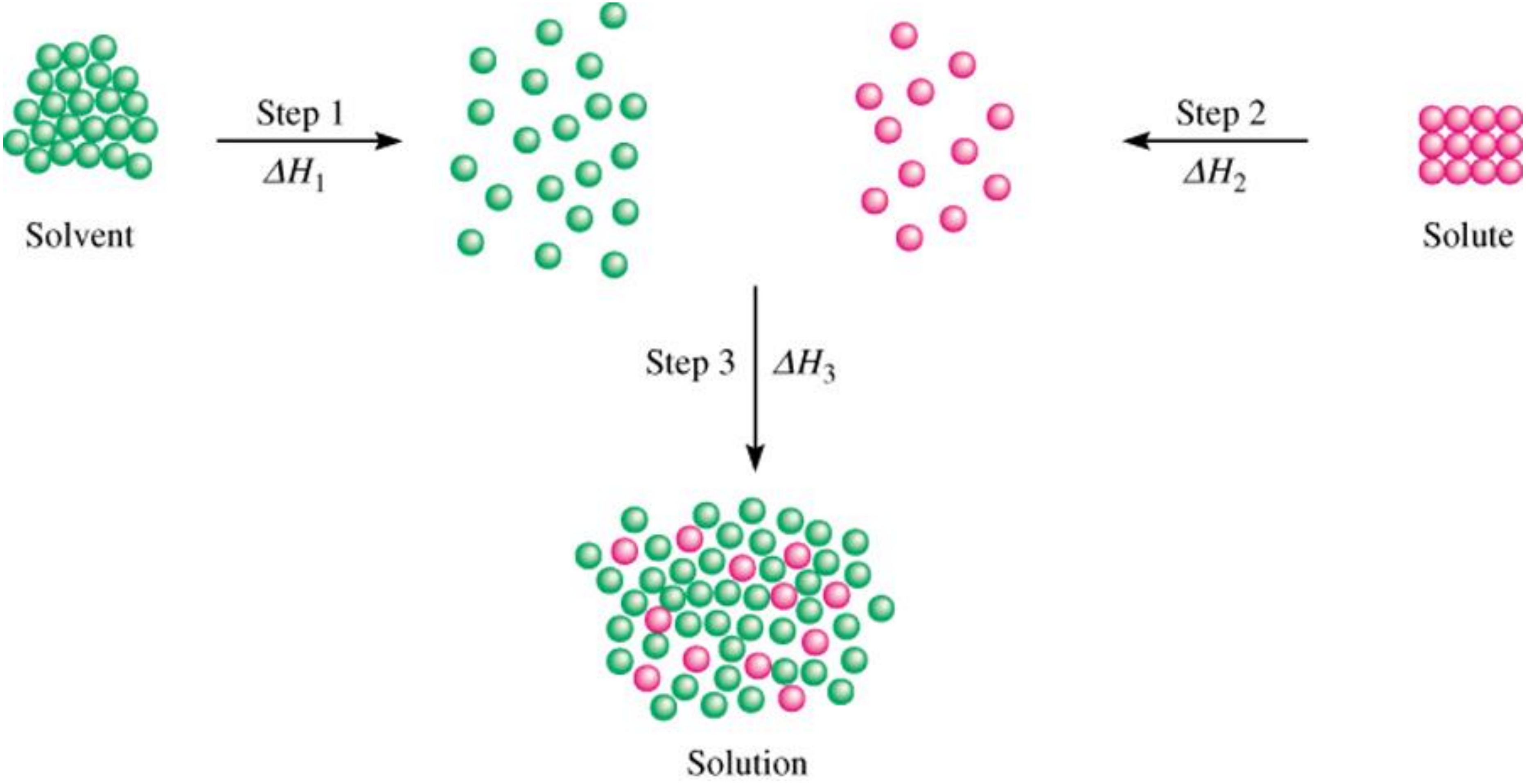
An ***unsaturated solution*** contains less solute than the solvent has the capacity to dissolve at a specific temperature.

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



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

"**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

  CCl_4 in C_6H_6

- polar molecules are soluble in polar solvents

  C_2H_5OH in H_2O

- ionic compounds are more soluble in polar solvents

  NaCl in H_2O or NH_3 (l)

Concentration Units

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

Percent by Mass

$$\% \text{ by mass} = \frac{\text{mass of solute}}{\text{mass of solute + mass of solvent}} \times 100\%$$

$$= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

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 .

Mass % of NaCl = (5/ 100) x100

= 5 %

Ex. 3.1

Gases solution contain 2.0 g of the He and 4g of O_2. What are the mole fractions of He and O_2 in the solution?

Ans. 3.1

$X_{He} = n_{He} / n_{He} + n_{O2}$ $X_{O2} = n_{O2} / n_{He} + n_{O2}$

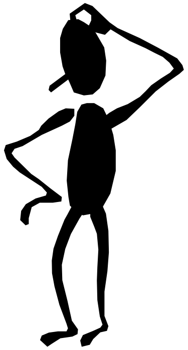
First we find the number of mole of each component present in solution ,n_{He} and n_{O2}

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

n_{O2} = mass of O_2 / Mw ,n_{O2} =4.0g /32.g mol^{-1} = 0.125 mole O_2

X_{He}= 0.5 / 0.5+ 0.125 =0.8 X_{O2} = 0.125 / 0.5+0.125 = 0.2

Note: $X_{He} + X_{O2} = 0.8 + 0.2 = 1$



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

Cu = 63.5 , S = 32 , O = 16

Answer

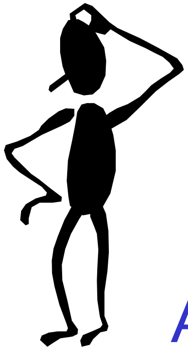
m = n solute / Kg of solvent

n of $CuSO_4$ = mass / MW = 20 g / 159.5 g mol^{-1}

= 0.125 mol

m = n $CuSO_4$ / Mass of H_2O (Kg)

m = 0.125 / 0.1 = 1.25 m



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

Answer : m = n solute / Kg of solvent

1 m = 1 mol / 1 Kg , So mass of water = 1000 g

The MW of H_2O = 18 g / mol

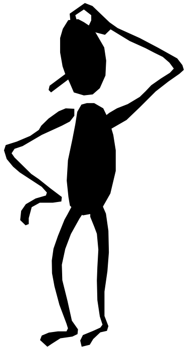
No. of mole of H_2O = 1000 g / 18 g/mol = 55.6 mol H_2O.

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

n_{H2O} = 55.6 mol

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

$X_{H2O} = 55.6 / (1 + 55.6) = 0.982$.



What is the molality of a 5.86 *M* ethanol (C_2H_5OH) solution whose density is 0.927 g/mL?

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

Assume **1 L** of solution: M = number of moles / Volume (L)

5.86 M = number of moles / 1 L

number of moles of ethanol = 5.86 moles

Mass of ethanol = 5.86 x 46 = 270 g ethanol

Mass of solution = 1000 ml x 0.927 g/ml= 927 g

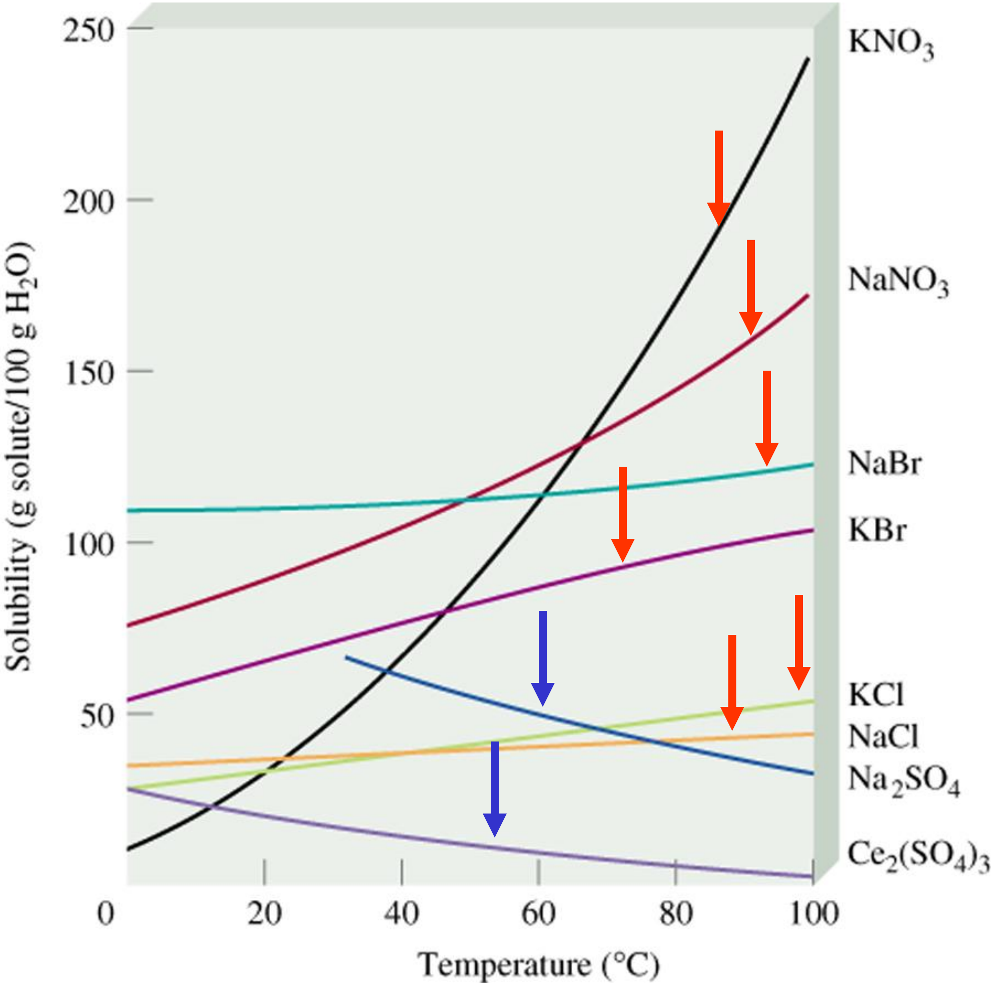
mass of solvent = mass of solution – mass of solute

= 927 g – 270 g = 657 g = 0.657 kg

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles } C_2H_5OH}{0.657 \text{ kg solvent}} = 8.92\ m$$

Temperature and Solubility

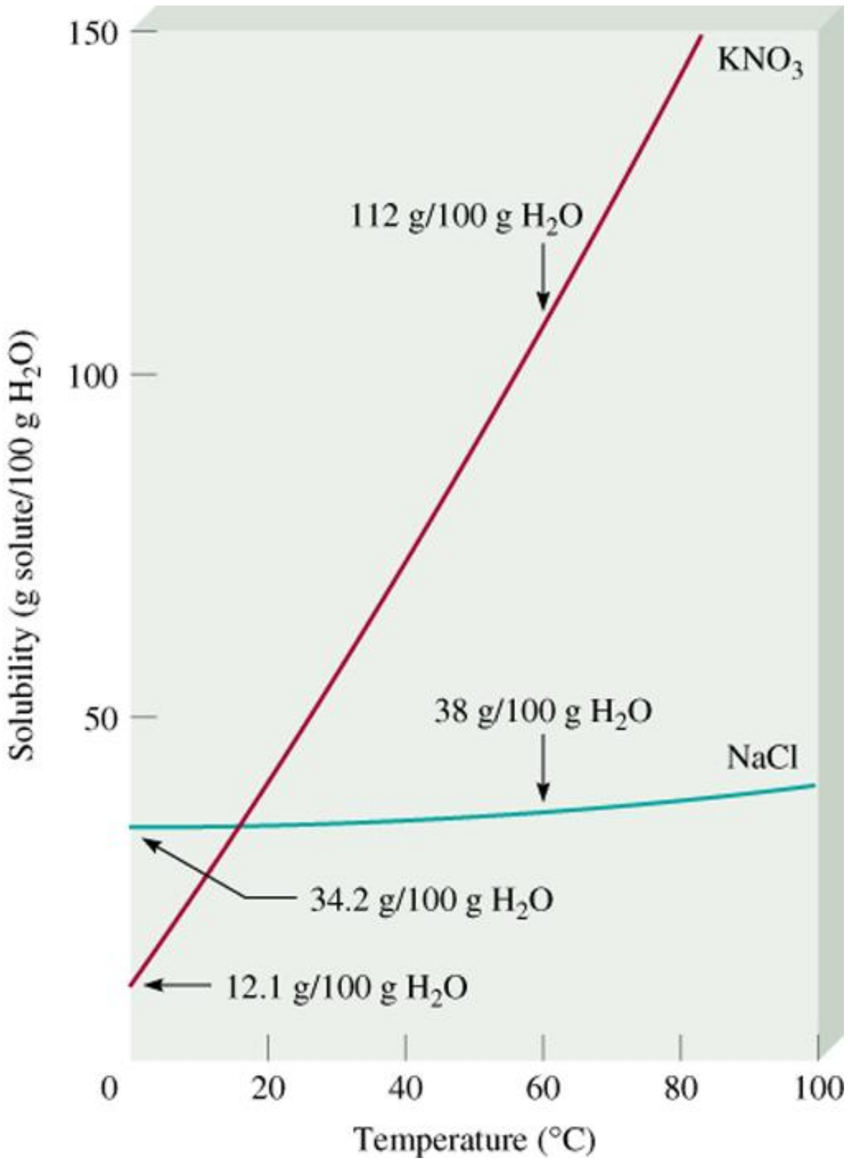
Solid solubility and temperature



solubility increases with increasing temperature

solubility of solids decreases with increasing temperature

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



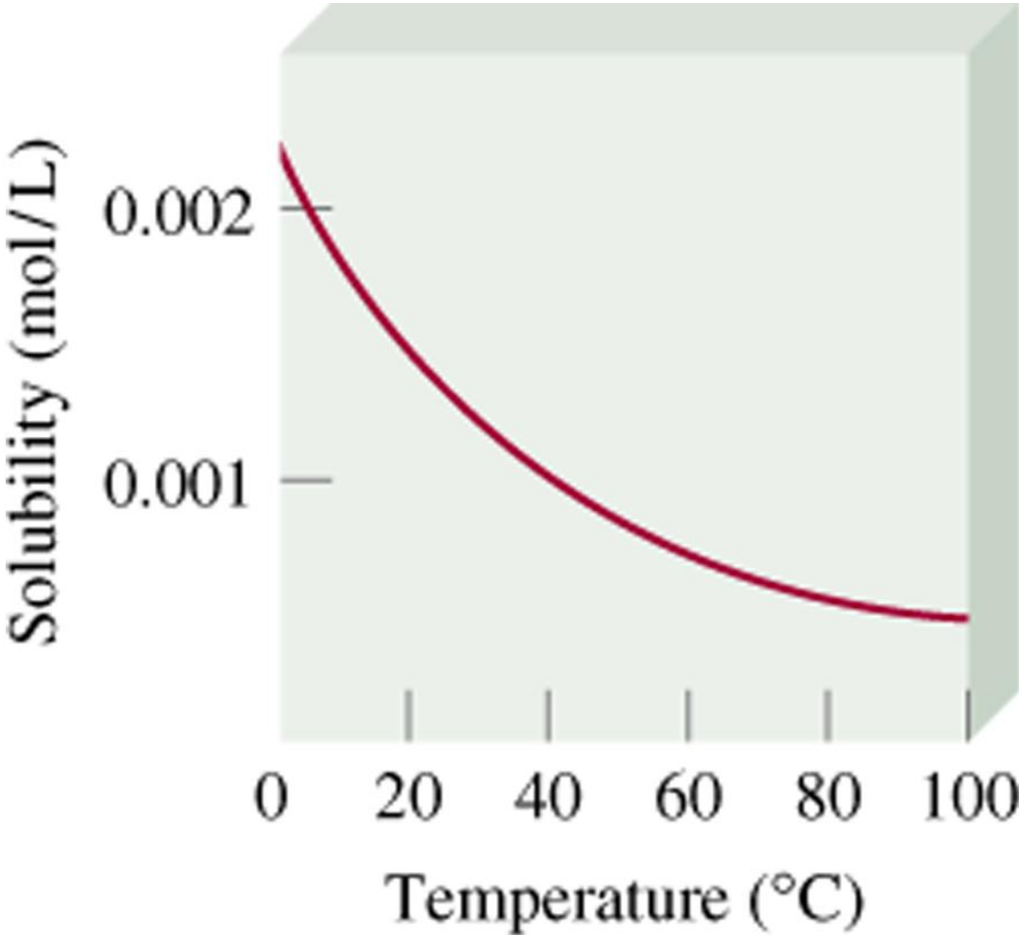
Suppose you have 90 g KNO_3 contaminated with 10 g NaCl.

<u>Fractional crystallization:</u>

1. Dissolve sample in 100 mL of water at 60^0C
2. Cool solution to 0^0C
3. All NaCl will stay in solution (s = 34.2g/100g)
4. 78 g of PURE KNO_3 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

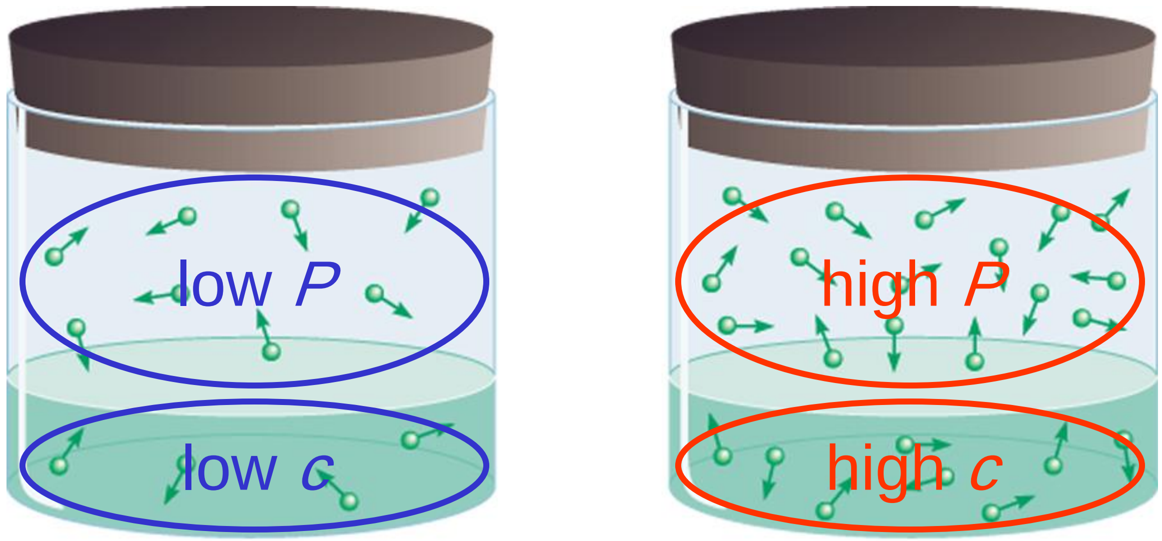
The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (***Henry's law***).

$$c = kP$$

c is the concentration (*M*) of the dissolved gas

P is the pressure of the gas over the solution

k is a constant (mol/L•atm) that depends only on temperature



Example 12.6

The solubility of nitrogen gas at 25 ^{o}C and 1 atm is $6.8x10^{-4}$ 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

$c = k\ p$

$6.8x10^{-4} = k\ x\ (1atm)$

$K = 6.8x10^{-4}$ mol/L.atm

$c = k\ x\ p$

$= 6.8x10^{-4}$ x 0.78 atm = $5.3\ x\ 10^{-4}$ mol/L

mm/Hg / 760 = atm

Chemistry In Action: The Killer Lake

8/21/86
CO_2 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

$$P_1 = X_1 P_1^0$$

Raoult's law

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

X_1 = mole fraction of the solvent

If the solution contains only one solute:

$X_1 = 1 - X_2$ $\quad$ $P_1 = (1 - X_2) P_1^o$ $\quad$ $P_1 = P_1^o - P_1^o X2$

$P_1^o X_2 = P_1^o - P_1 \quad = \Delta P$

X_2 = mole fraction of the solute

ΔP = Lowering of vapor pressure

Rault,s Law:

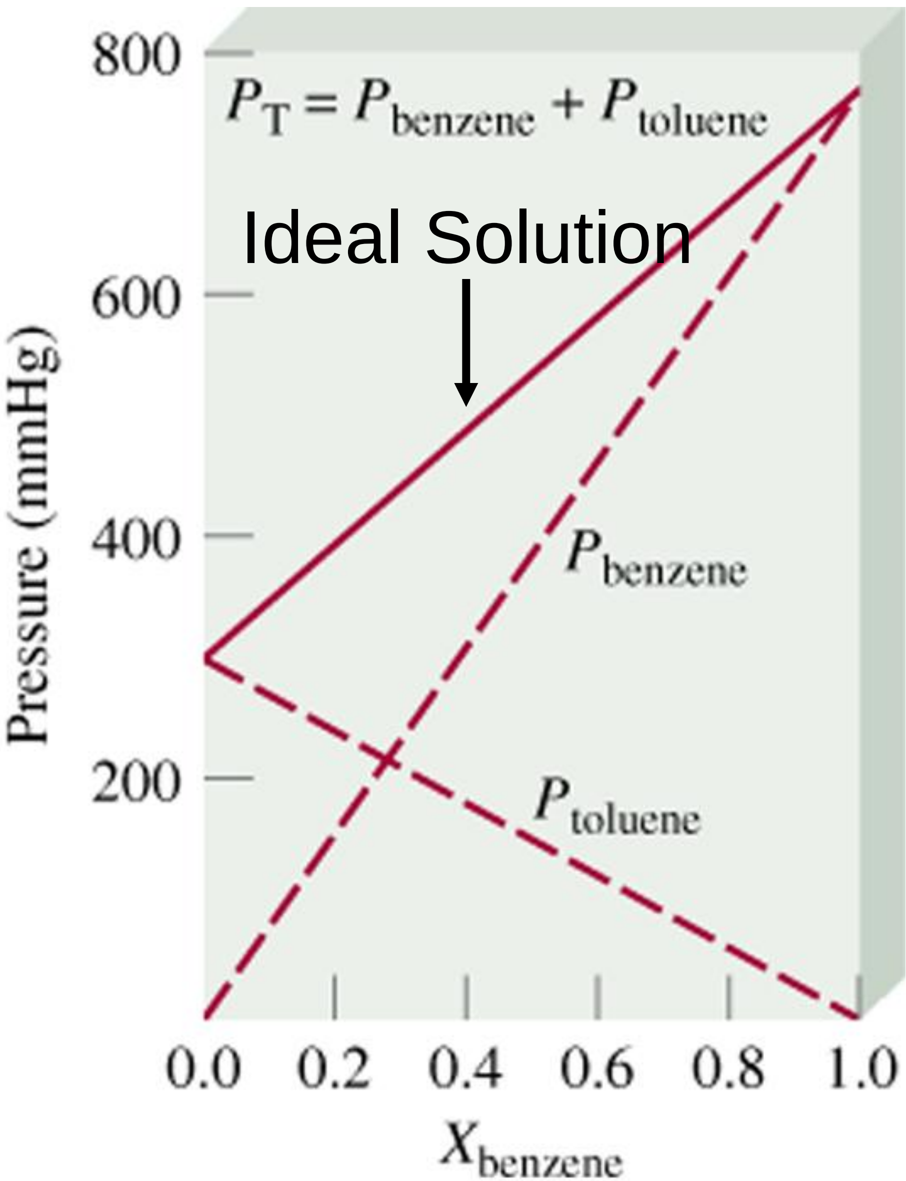
For ideal gases, the vapor pressure of solution (P_T) in two component system A and B is :

$$P_T = P_A + P_B \text{ .... } (1)$$

$$P_A = X_A P^\circ_A \text{ .... } (2)$$

$$P_B = X_B P^\circ_B \text{ .... } (3)$$

$$P_T = X_A P^\circ_A + X_B P^\circ_B \text{ .... } (4)$$



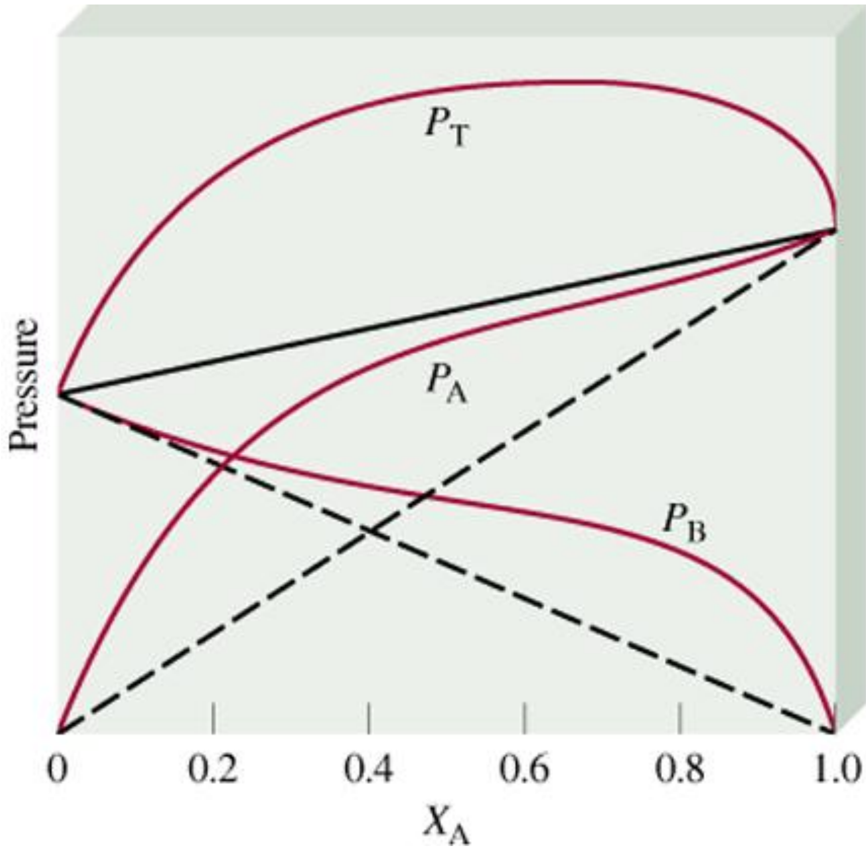
$$P_A = X_A P_A^0$$

$$P_B = X_B P_B^0$$

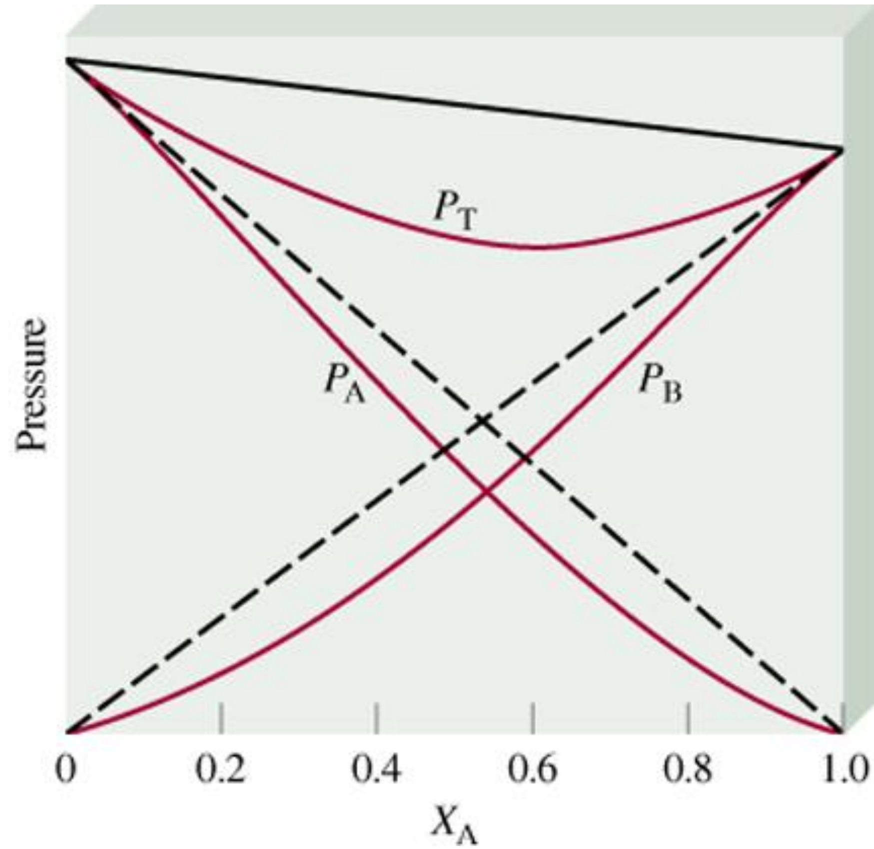
$$P_T = P_A + P_B$$

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

P_T is greater than predicted by Raoults's law	P_T is less than predicted by Raoults's law

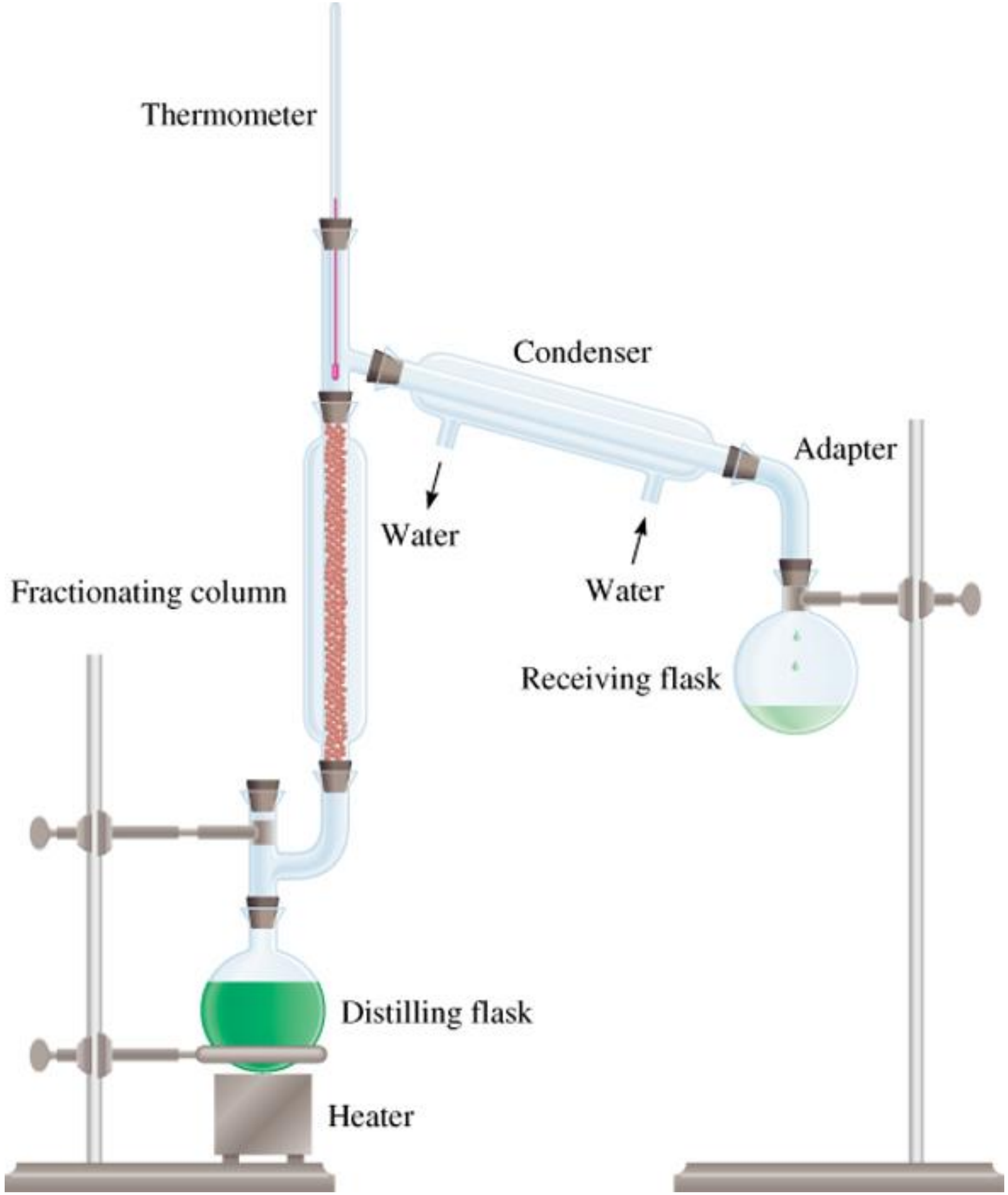


Force A-B < Force A-A & Force B-B



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°C of a solution that contains 3.0 mol of heptane and 5 mol of octane ?

At 40°C $p°_{heptan}$ = 0.121 atm and $p°_{octane}$ = 0.041 atm .

Ans.

$n_h + n_o = 3 + 5 = 8$

$X_h = 3 / 8 = 0.375$

$X_o = 5 / 8 = 0.625$

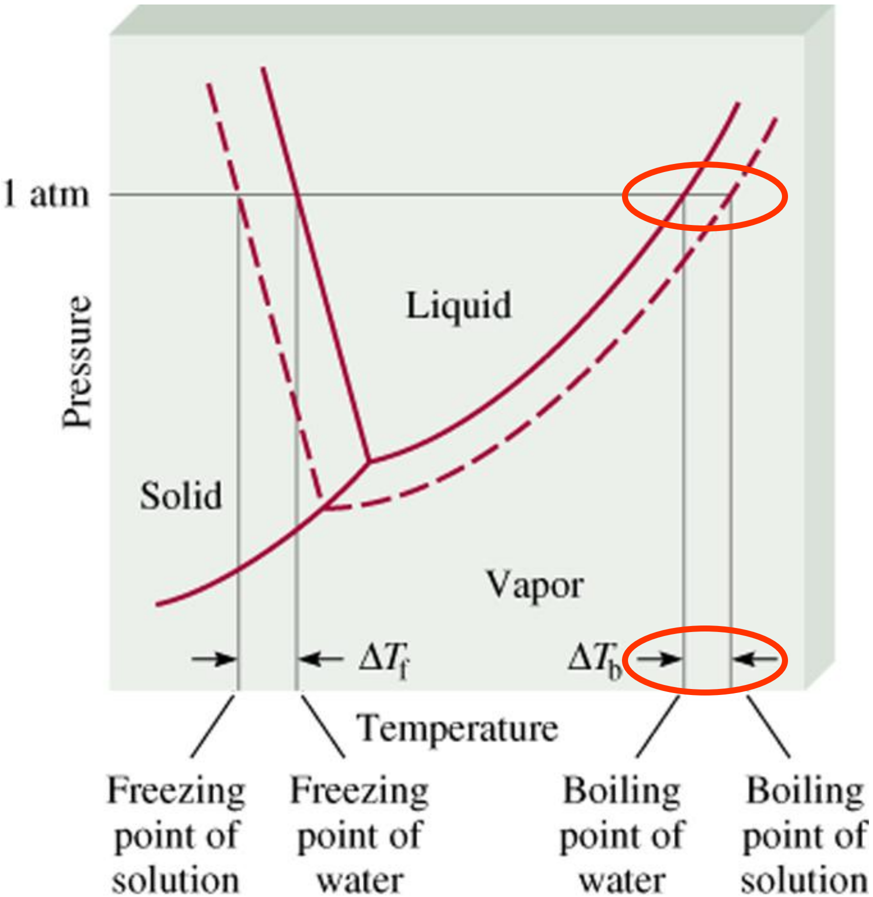
$P_t = X_h\, p°_h + X_o\, P°_o$

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

$= 0.045 + 0.026$

$= 0.071$ 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

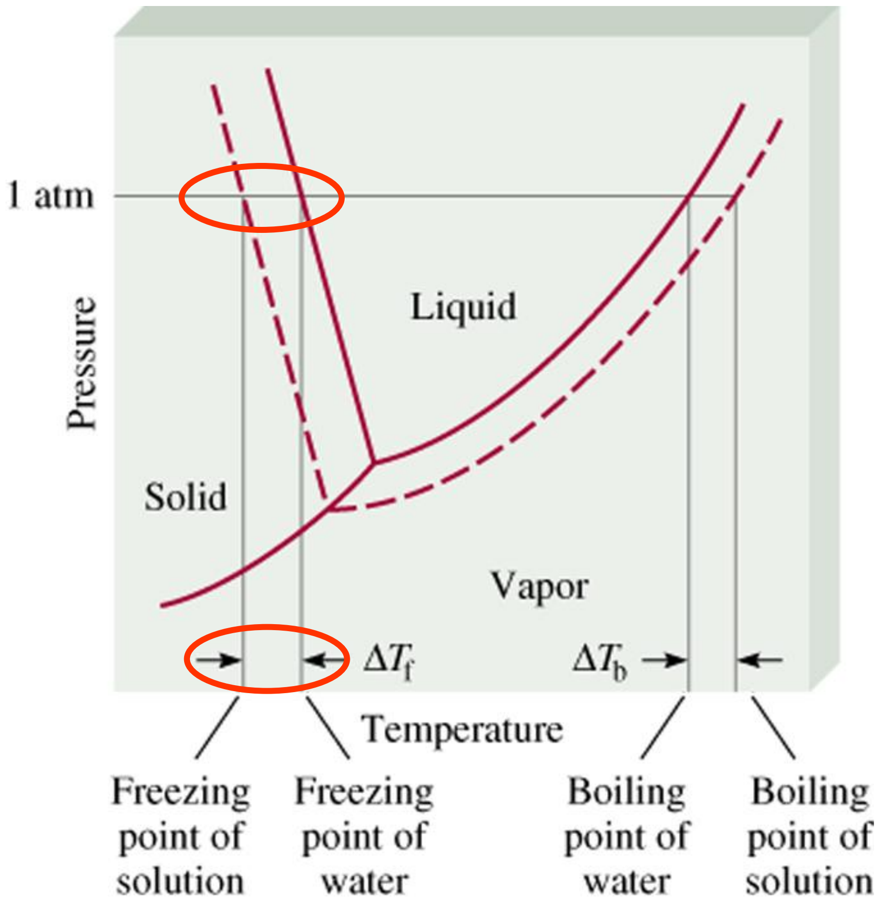
$T_b > T_b^0$ $\Delta T_b > 0$

$$\Delta T_b = K_b\, m$$

m is the molality of the solution

K_b is the molal boiling-point elevation constant (^{0}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

$T_f^0 > T_f \qquad \Delta T_f > 0$

$$\Delta T_f = K_f\, m$$

m is the molality of the solution

K_f is the molal freezing-point depression constant (^{0}C/m)

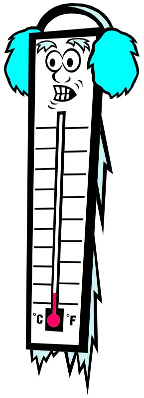
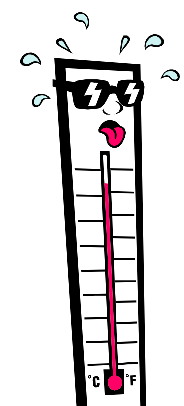


TABLE 12.2

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°C/m and 5.12 °C/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 mol

m = 0.015 mol / 0.075 Kg = 0.208 m

ΔT_b = 2.53 x 0.208 = 0.526°C

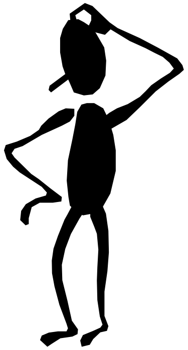
b.p . of solution = b.p of pure solvent + ΔT_b

= 80.1 + 0.526 = 80.626C°

ΔT_f = 5.12 x 0.208 = 1.06C°

f.p. of solution = f.p. of pure solvent - ΔT_f

= 5.5 – 1.06 = 4.4C°



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.

$\Delta T_f = K_f\, m$ $\quad\quad$ K_f water = 1.86 ^{0}C/m

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

$$\Delta T_f = K_f\, m = 1.86\ ^0\text{C}/m \times 2.41\ m = 4.48\ ^0\text{C}$$

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

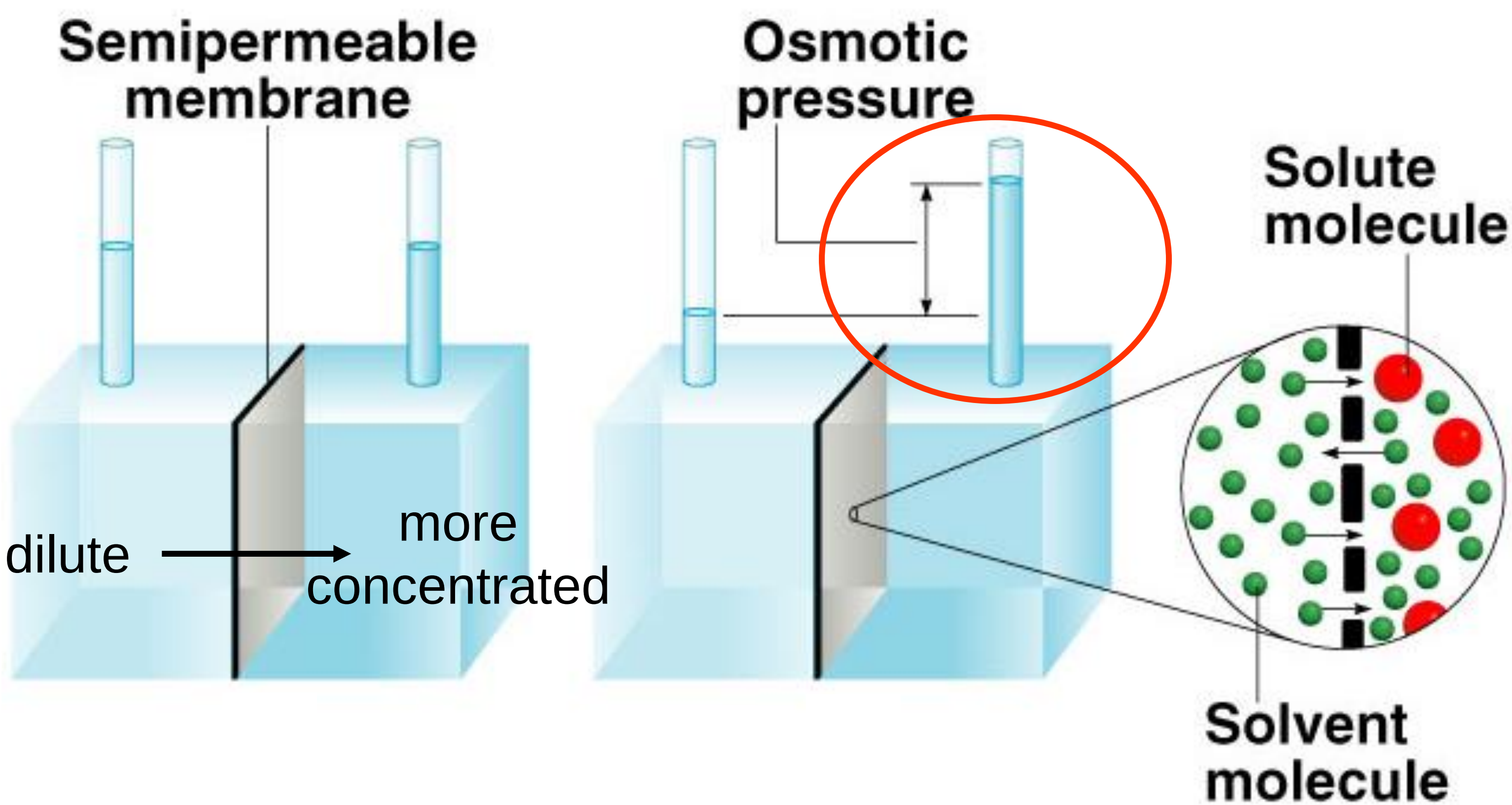
$$T_f = T_f^0 - \Delta T_f = 0.00\ ^0\text{C} - 4.48\ ^0\text{C} = -4.48\ ^0\text{C}$$

Osmotic Pressure (π)

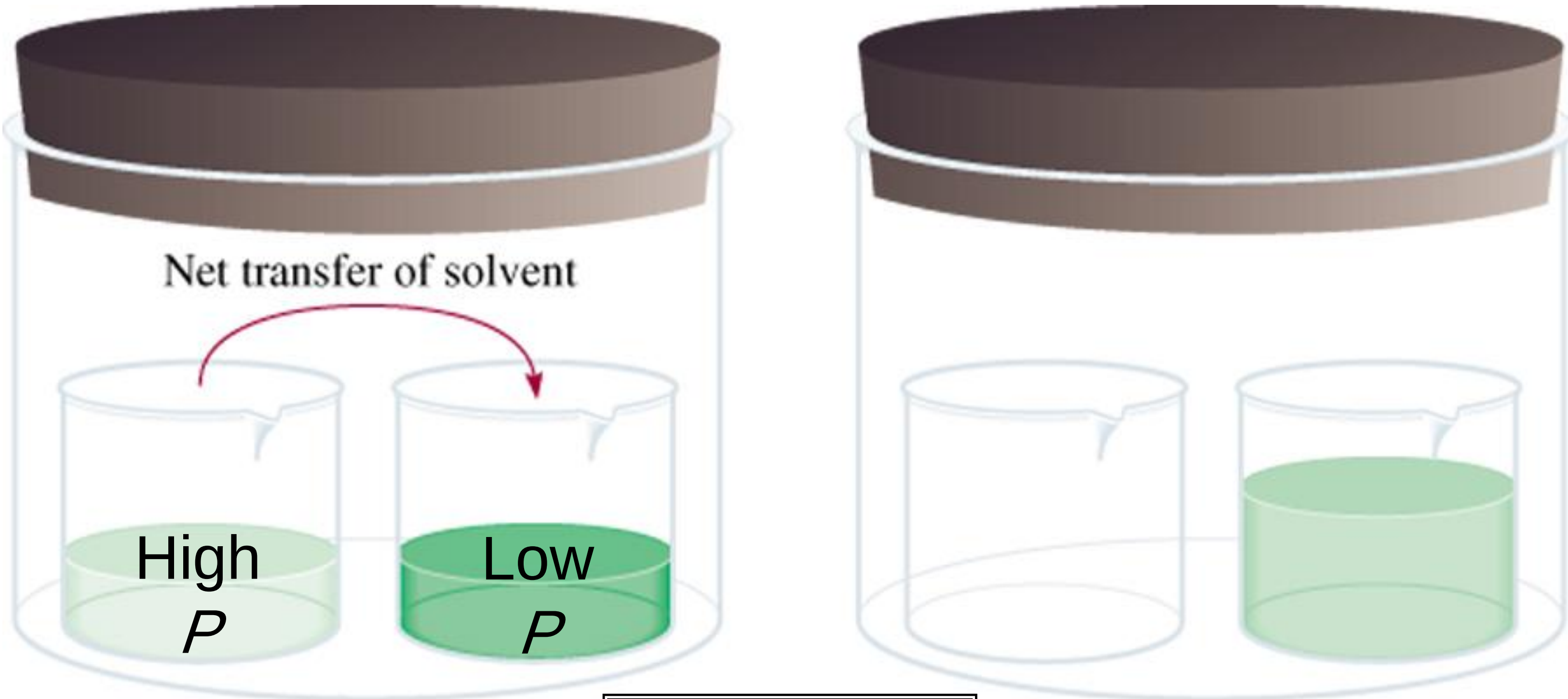
Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

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 ⟶ 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 ⟶ 0.2 *m* ions in solution

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

	i should be
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) $\pi = iMRT$

TABLE 12.3

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

Electrolyte	*i* (Measured)	*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 ºC. Determine the molar mass of the polymer

Solution:

$$\pi = MRT$$

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

$$M = \pi / R\,T = 0.0075 / 0.082\,1 \times 298 = 2.8 \times 10^{-4} \; \textit{molar}$$

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

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

Molar mass = Mass (g) / number of moles of polymer

= 0.833 (g)/ 4.76×10^{-5} mol polymer

= **1.75×10^{4} 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 ^oC below that of the pure benzene. What are the molar mass and molecular formula of this compound?

Solution: molality = ΔT_f / K_f = 1.05 ^oC/ 5.12 $^oC/m$

= 0.205 m

Number of moles of solute = molality x Kg of solvent

= 0.205 m x 0.301 Kg = 0.0617 mol.

Molar mass = Mass (g)/ number of moles

= 7.85 g / 0.0617 mol = 127 g/mol

Molecular formula = C_5H_4 x (molar mass/ mass of empirical formula)

= C_5H_4 x(127 g/mol/ 64 g/mol) = $C_{10}H_8$