

Solutions and Their Behavior

These Notes are to SUPPLEMENT the Text, They do NOT Replace reading the Text Book Material. Additional material that is in the Text Book will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

Entropy (S) – A Spontaneous process where energy goes from being more concentrated to being more dispersed, the system is more stable!

Enthalpy (H) – The sum of the internal energy of the system and the product of its pressure and volume

Solution is a homogeneous mixture of 2 or more substances

Solvent – present in the largest amount

Solute – present in the smaller amount

Rule of thumb, “**like dissolves like**” by analyzing the solution process in terms of forces overcome in the solute and solvent and forces formed between solute and solvent particles.

Colligative Properties are properties of solutions that depend only on the number of solute particles per solvent molecule and not the identity of the solute

Concentration – number of ions of solute per molecule of solvent

Molality – m

$m = \text{Moles of Solute} / \text{Kg of Solvent}$

Mole Fraction – X

$X = n_A / n_A + n_B + n_C + \dots$

Weight Percent = $\text{Wt } \%$

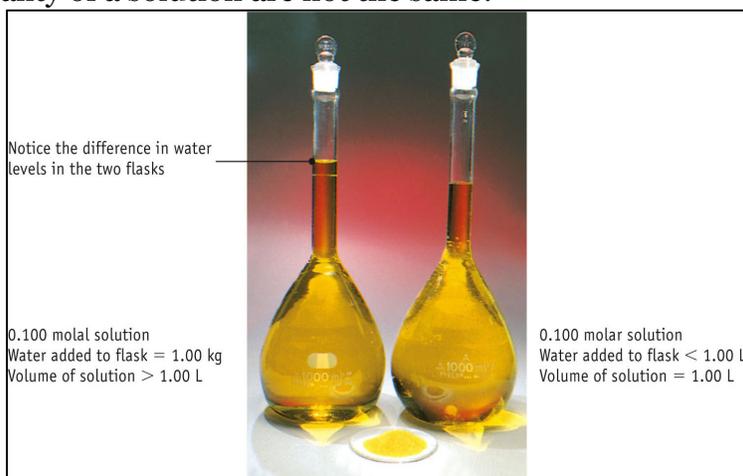
$\text{Wt } \% = 100\% * \text{Mass}_A / \text{Mass}_B + \text{Mass}_C + \text{Mass}_D + \dots$

Wt % used in consumer products: Vinegar = 5% acetic acid, Bleach 6.00% NaOCl

Flask on Right: 0.100 mol K_2CrO_4 and water to make 1.000 L = 0.100 Molar = M

Flask on Left: 0.100 mol of K_2CrO_4 and 1.00 Kg of HOH = 0.100 Molal = m

Molarity and Molality of a solution are not the same!



EXAMPLE 14.1 Calc All. 1.2 kg ethylene glycol, CH₂OHCH₂OH antifreeze in 4.0 kg water

You need to show the calculation of the Mw of ethylene glycol to the correct SD with units!

Mw Ethylene Glycol

2 C 2 * 12/01 24.02
 2 O 2 * 16.00 32.00
 6 H 6 * 1.008 6.048

62.068 Correct for Sig Fig
 62.07 g/Mole

Mw Water H₂O

2 H 2 * 1.008 2.016
 1 O 1 * 16.00 16.00

18.016 Correct for Sig Fig
 18.02 g/Mole

Ethylene Glycol 1.2 kg / 62.07 g/mole = 19.333 mol = **19. Mol** (Note SD!)

Waer 4.0 kg / 18.02 g/mol = 221.97 mol = 220 mol = **2.2 x 10² mol** (Note SD!)

Molality = m = 19 mol ethylene glycol / 4.0 kg water = 4.8 m

Mole Fraction = X = 19 mol ethylene glycol / 19 mol + 220 mol = 0.080 MF

Wt% = (1.2 kg / 1.2 kg + 4.0 kg) * 100% = 23%

14.2 The Solution Process

Saturated Solution a solution in which the maximum amount of solute has been dissolved. There usually are sold particles of the solute visible.

Is a **Dynamic Equilibrium** $CuCl_{2(s)} \leftrightarrow Cu^{2+(aq)} + 2 Cl^{-}(aq)$
 Concentration of solute is in equilibrium with undissolved solute in a Sat Soln.

Super Saturated Solution: a solution that temporarily contains more solute than the saturated amount. There are no sold particles of the solute visible.

And example is to add lots sugar to water, heat the solution to dissolve all of the sugar. Let it cool without being disturbed. Hang a cotton string into the solution, sugar crystals (old fashion sugar candy) will grow on the string.

Liquid dissolving in Liquids – like dissolves like

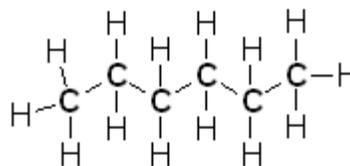
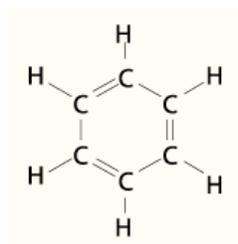
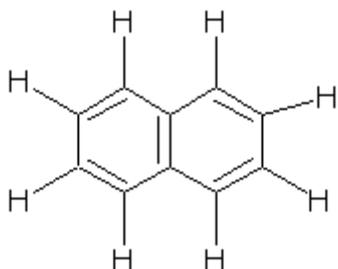
Solvation: the process by which a solute dissolves in a solvent

Miscible two or more liquids mix, to an appreciable amount, to form a solution
 Ethanol / water – polar, hydrogen bonds – **Show 3D image**
 Octane / CCl₄ – both are non-polar so they mix – **Show 3D image**

Immiscible two or more liquids do not mix to form a solution
 Octane or CCl₄ / water, oil and water – non-Polar and Polar do not mix

Solids dissolving in water

Naphthalene (Non Polar) dissolves in benzene (Non Polar) or hexane (Non-Polar)



I₂ (Non Polar) does not dissolve much in water (Polar), but dissolves in CCl₄ (Non-Polar)

Entropy (S) – A Spontaneous process where energy goes from being more concentrated to being more dispersed

Enthalpy (H) – The sum of the internal energy of the system and the product of its pressure and volume (How much heat is given off as the compound dissolves – can be measured via calorimeter)

S / H are complex! “Predicting the solubility of ionic compounds in water is complicated”!

Entropy is the driving force for the solution process. When a solute dissolves in a solvent, the “energy of the system is more dispersed than in the two, separate” states.

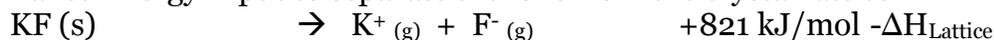
Hydration – an ion is surrounded by water molecules

TO BE SOLUBLE An ionic compound will have an Enthalpy of Solution that is exothermic (ΔH is negative) or only slightly endothermic.

Dissolving ionic KF in water. K^+ and F^- are held together in the solid crystal state by attractive forces of their opposite charges.

To dissolve KF:

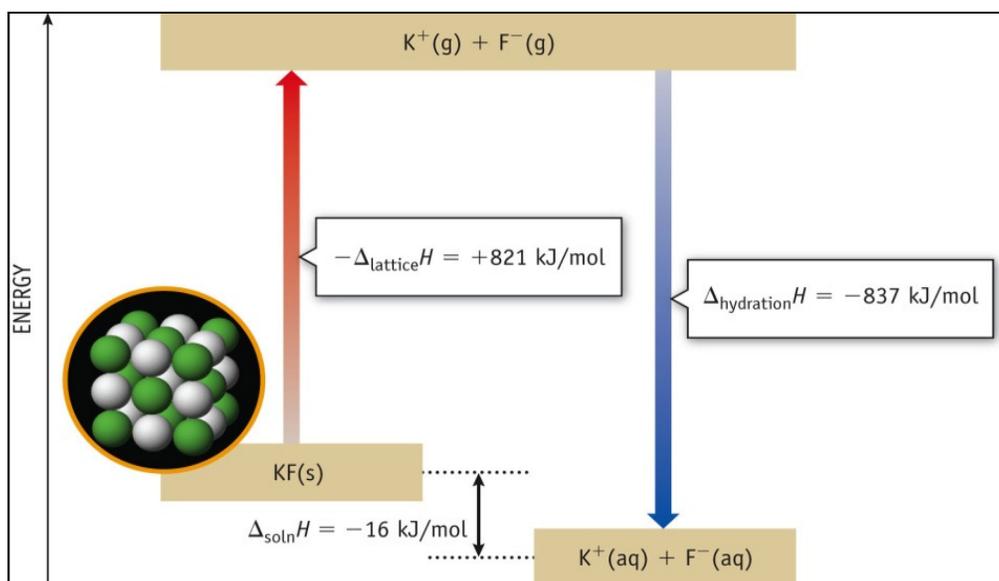
Takes Energy Input to separate the ions from the crystal lattice



Energy is released as the ions are surrounded by water molecules, called Hydration



Overall Enthalpy of Solution ($\Delta H_{\text{Solution}}$) = -16 kJ/mol [Exothermic] and is measured using a calorimeter.



NaOH dissolving in water is strongly exothermic – gets real hot (Drano in your sink)

NH_4NO_3 , a common cold pack, dissolving in water is endothermic; it gets cold as it dissolves

14.3 Factors Affecting Solubility: Pressure and Temperature

Gases dissolving in liquids – Henry’s Law

The solubility of a gas is defined as the concentration of the dissolved gas in equilibrium with the substance in the gaseous state. Soft drinks have CO₂, Diver getting Bent

Gas Solubility $S_g = \text{Henry's Law Constant } k_H * \text{Partial Pressure of the gas } P_g$

$$S_g = k_H * P_g$$

EXAMPLE 14.3 p627 What is the conc of O₂ in water at 25°C at 1.0 bar, give in g O₂ / kg solvent

$$k_H \text{ O}_2 = 1.3 \times 10^{-3} \text{ mol/kg bar}$$

Air is 21% O₂, so the Partial Pressure of O₂ = 0.21 * 1.0 Bar = 0.21 Bar

$$S_g = k_H * P_g = 1.3 \times 10^{-3} \text{ mol/kg bar} * 0.21 \text{ Bar} = 0.27 \times 10^{-3} = 2.7 \times 10^{-4} \text{ mol/kg}$$

$$\text{g O}_2 / \text{kg solvent} = 2.7 \times 10^{-4} \text{ mol/kg} * 32.00 \text{ g/mol O}_2 = 8.64 \times 10^{-3} = 8.6 \times 10^{-3} \text{ g/kg O}_2$$

Temp effect on Solubility: Le Chatelier’s Principle

Gases that dissolve do so in an exothermic process

Gas + liquid solvent $\leftarrow \rightarrow$ saturated solution + heat

The solubility of all gases in water decrease with increase temperature.

“The solubility of solids in water is also affected by temperature ... no general pattern of behavior is observed”

Exploding Lakes – Lake Nyos contains dissolved CO₂. At depth its at high pressure and cold.

Mentos and Coke – Mentos has many nucleation sites to help form CO₂ bubbles

14.4 Colligative Properties: properties depend on relative numbers of solute and solvent particles.

Changes in vapor pressure: Raoult’s Law

VP over a the solvent over the solution is lower than over pure solvent

VP is proportional to the relative number of solvent molecules in solution

$$\text{Pressure of Solvent } P_x = X_{\text{solvent}} * P^{\circ}_{\text{Solvent}}$$

EXAMPLE 14.4 P630 dissolve 651 g ethylene glycol, CH₂OHCH₂OH antifreeze in 1.50 kg water. What is VP of the water over the solution. VP of water at 90°C = 525.8 mm Hg.

$$1.50 \text{ kg Water} * 1000. \text{ g/kg} * 1 \text{ mol} / 18.02 \text{ g} = 83.2 \text{ mol}$$

$$651 \text{ g EtGlycol} * 1 \text{ mol} / 62.07 \text{ g} = 10.5 \text{ mol}$$

$$X_{\text{water}} = 83.2 \text{ mol water} / (83.2 \text{ mol water} + 10.5 \text{ mol glycol}) = 0.888 \text{ MF}$$

$$P_{\text{water}} = X_{\text{water}} P_{\text{water}} = 0.888 \text{ MF} * 525.8 \text{ mm Hg} = 407 \text{ mm Hg}$$

Problem:

Pure iodine (105 g) is dissolved in 325 g of CCl₄ at 65 °C. Given that the vapor pressure of CCl₄ at this temperature is 531 mm Hg, what is the vapor pressure of the CCl₄–I₂ solution at 65 °C? (Assume that I₂ does not contribute to the vapor pressure.). Answer is 444 mm Hg – PROVE IT!

Boiling Point Elevation

Adding a solute lowers the vapour pressure, takes longer to get to 1 atm

Elevation of BP = $\Delta T_{bp} = \text{molal BP elevation constant } K_{bp} * m_{\text{solute}}$

$$\Delta T_{bp} = K_{bp} * m_{\text{solute}}$$

What is the new vapour pressure of benzene with Z dissolved in it. Solute Z is 0.200 moles in 100. g of benzene (C₆H₆ mw 78.11 g/mole). P_{benzene} is 400 mm Hg.

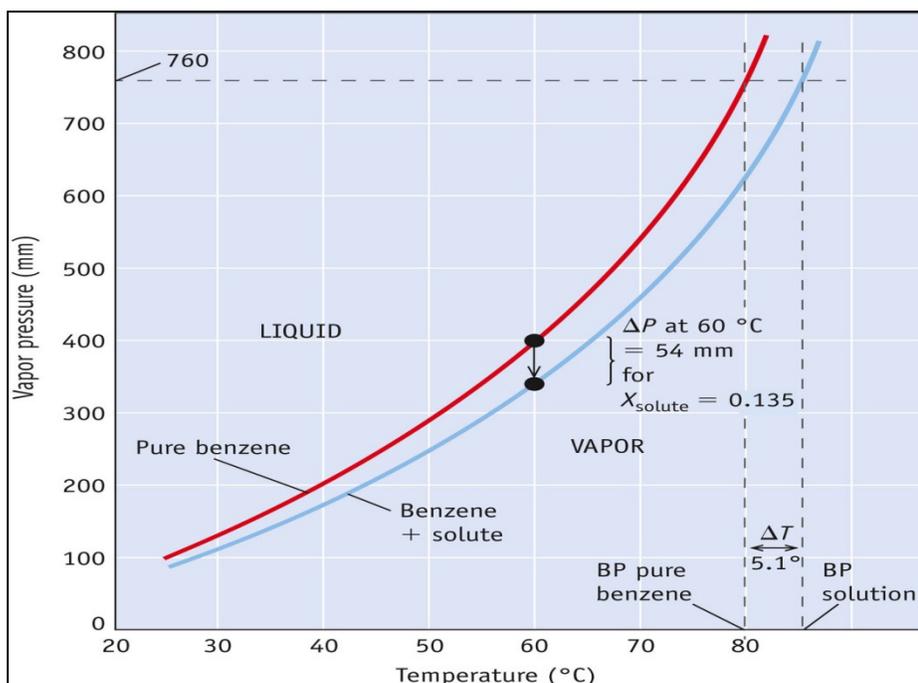
Moles of Z per kg benzene = 0.200 moles / 100. g = X / 1 kg

Moles of Benzene = 100. g * 1 mol / 78.11 g = 1.28 mol benzene

$X_{\text{benzene}} = 1.28 \text{ mol} / (0.200 \text{ mol} + 1.28 \text{ mol}) = 0.865$

Vapour Pressure of benzene = $P_{\text{benzene}} = X_{\text{benzene}} * P^{\circ}_{\text{benzene}} = 0.865 * 400 \text{ mm Hg} = 346 \text{ mm Hg}$

To get Benzene to boil, you need to raise its vapour pressure to atmospheric or 760 mm Hg
So, adding a solute lowers the vapour pressure thus **raises the boiling point!**



$$\Delta T_{bp} = K_{bp} * m_{\text{solute}} = +2.53 \text{ }^\circ\text{C/m} * (0.200 \text{ mol Solute} / 100 \text{ g benzene} * 1 \text{ kg} / 1000 \text{ g}) = + 5.06 \text{ }^\circ\text{C}$$

Example 14.5 p 632 0.144 g Eugenol C₁₀H₁₂O₂ in 10.0 g benzene, what is its BP?

10 C	10 * 12.01	120.10
12 H	12 * 1.008	12.096
2 O	2 * 16.00	<u>32.00</u>

$$164.196 = 164.20 \text{ g/mole}$$

Moles Eugenol = 0.144 g * (1 mol / 164.20 g) = 8.769 x 10⁻⁴ = 8.77 x 10⁻⁴ moles

Molal Eug = 8.77 x 10⁻⁴ mol Eug / 0.0100 kg benzene = 8.77 x 10⁻² m

$\Delta T_{bp} = K_{bp} * m_{\text{solute}} = 8.77 \times 10^{-2} \text{ m} * 2.53 \text{ }^\circ\text{C/m} = 0.222 \text{ }^\circ\text{C}$ not very much increase

TRY AN EXAMPLE OF ADDING 10.0 g salt (NaCl) to 1.00 L water. $K_{bp} = +0.5121$ for water

Freezing Point Depression = $\Delta T_{fp} = K_{fp} * m_{solute}$

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

EXAMPLE 14.6 Freezing Point Depression ? mass of ethylene glycol in 5.50 kg water is needed to lower fp from 0°C to -10.0°C.

From $\Delta T_{fp} = K_{fp} * m_{solute} = K_{fp} * \text{Moles}_{\text{ethylene glycol}} / \text{Kg}_{\text{water}}$

Derive This: $\text{Moles}_{\text{ethylene glycol}} = \Delta T_{fp} * \text{Kg}_{\text{solvent}} / K_{fp}$

$K_{fp} = -1.86 \text{ }^\circ\text{C}/\text{m} = -1.86 \text{ }^\circ\text{C Kg}_{\text{solvent}} / \text{Moles}$

$\text{Moles} = -10.0 \text{ }^\circ\text{C} * 5.50 \text{ kg}_{\text{water}} / -1.86 \text{ }^\circ\text{C Kg}_{\text{solvent}} / \text{Moles}$

$\text{Moles} = 29.569 = 29.6 \text{ moles}$

Grams = $\text{Moles} * M_w = 29.6 \text{ moles} * 62.07 \text{ g/mole} = 1837.2 = 1840 = \mathbf{1.84 * 10^3 \text{ g}}$

Summary

$\Delta T_{bp} = K_{bp} * m_{solute}$ For boiling point elevation $K_{bp} > 0$ is positive

$\Delta T_{fp} = K_{fp} * m_{solute}$ For freezing point depression $K_{fp} < 0$ is negative

BP and FP effects involve IONS. When solutions contain ions (KCl in water gives K^+ and Cl^-), the total concentration of solute particles is used. This is the **Van't Hoff Factor (i)**

$\Delta T_{bp} = K * m_{solute} * I$ I is the number of ions

<u>Compound</u>	<u>In Solution</u>	<u>Type</u>	<u>i</u>
CH ₃ OH	CH ₃ OH	molecular	1
NaCl	Na ⁺ Cl ⁻	strong electrolyte	2
Ba(NO ₃) ₂	Ba ²⁺ 2 NO ₃ ⁻	strong electrolyte	3
HNO ₂	H ⁺ NO ₂ ⁻	weak electrolyte	1 - 2

Problem:

If 52.5 g of LiF is dissolved in 306 g of water, what is the expected freezing point of the solution? (Assume the van't Hoff factor, i, for LiF is 2.)

1 Li 1 * 6.941 6.941

1 F 1 * 19.00 19.00

25.941 = 25.94 g/mole

Molality = m = moles/kg solvent = (52.5 g / 25.94 g/mole) / 0.306 kg = 6.6140 = 6.61 moles

$\Delta T_{fp} = K_{fp} * m_{solute} * 2 = -1.86 \text{ }^\circ\text{C}/\text{m} * 6.61 \text{ moles} * 2 = -24.589 = \mathbf{-24.6 \text{ }^\circ\text{C}}$

Molar Mass by Boiling Point Elevation

Problem:

Benzyl acetate is one of the active components of oil of jasmine. If 0.125 g of the compound is added to 25.0 g of chloroform (CHCl₃), the boiling point of the solution is 61.82 °C. What is the molar mass of benzyl acetate? **Note:** K_{bp} for CHCl₃ is + 3.63 °C/m Bp CHCl₃ = 61.70 °C

1. Solution: The molality of the solution can be found from the BP elevation.
2. Knowing molality and mass of solvent, one can find the moles of solute.
3. Knowing mass and moles of solute, the molar mass of the compound can be determined.

Answer is 150 g/mol PROVE IT.

$\Delta T_{bp} = K_{bp} * m_{solute}$ therefore

$$m_{solute} = \Delta T_{bp} / K_{bp} = (61.82 \text{ }^\circ\text{C} - 61.70 \text{ }^\circ\text{C}) / + 3.63 \text{ }^\circ\text{C}/m = 0.12 \text{ }^\circ\text{C} / +3.63 \text{ }^\circ\text{C}/m = 0.033 m$$

$$m_{solute} = \text{moles}_{solute} / \text{kg}_{solvent} = \text{g}_{solute} / (\text{Mw}_{solute} * \text{kg}_{solvent})$$

Derive

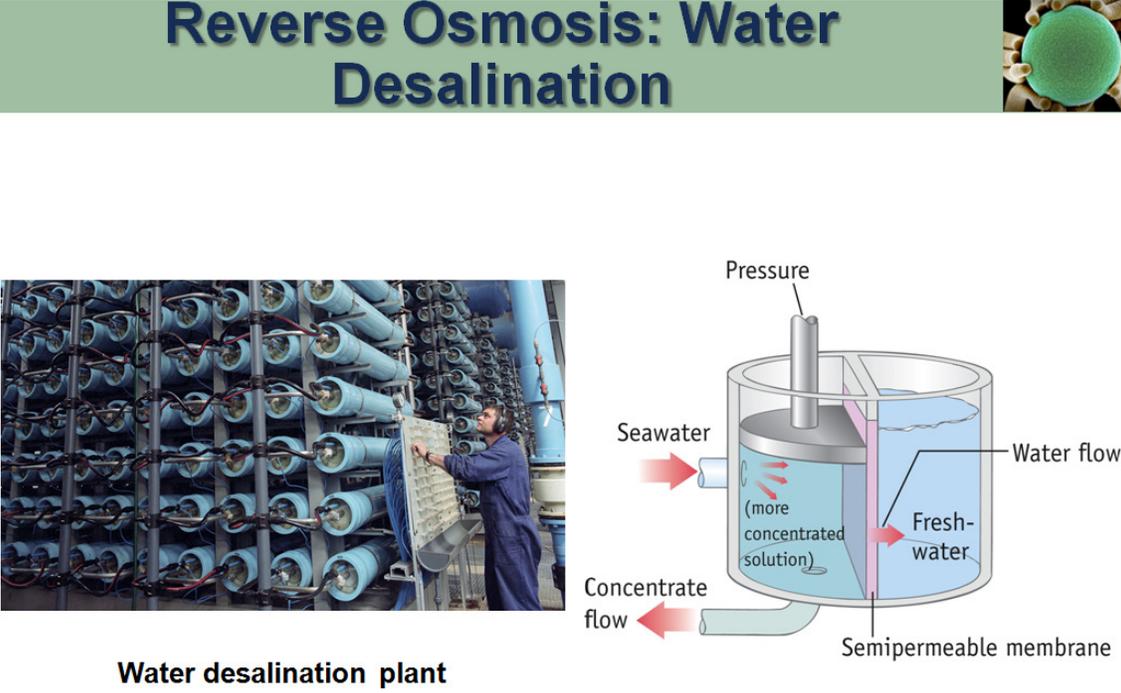
$$\text{Mw}_{solute} = \text{g}_{solute} / (m_{solute} * \text{kg}_{solvent}) = 0.125 \text{ g} / (0.033m * 0.025 \text{ kg}) = 151.5 = \mathbf{150 \text{ g/mole}}$$

Osmotic Pressure is the movement of solvent molecules through a semi permeable membrane from a region of lower solute concentration to a region of higher solute conc.

The point where they have equal osmotic pressure, they are **Isotonic**.

Examples: Bag with 5% sugar in pure water (see below)
Reverse Osmosis for water purification

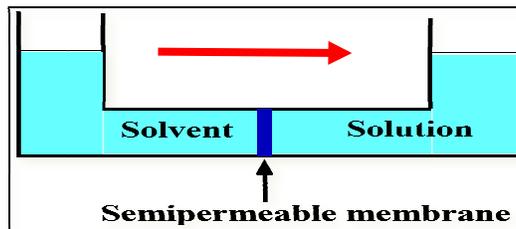
Reverse Osmosis: Water Desalination

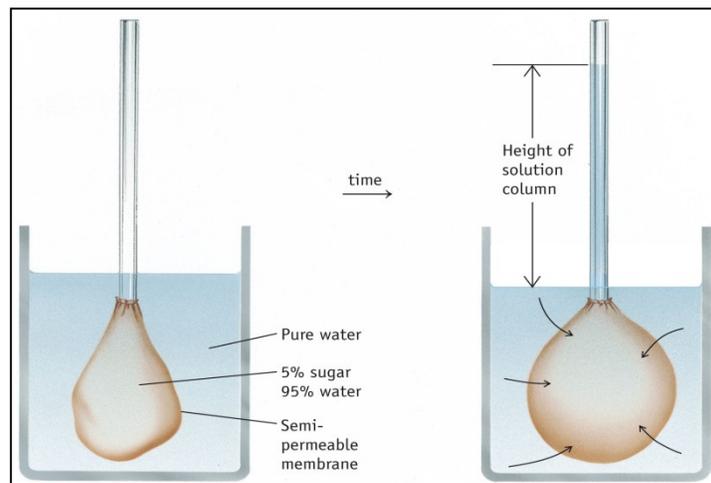


Water desalination plant

$$\text{Osmotic Pressure II} = c (\text{molar conc in moles per l}) * R * T$$

$$R = 0.082057 \text{ L atm /mol K}$$





A dilute solution of $1.00 \times 10^{-3} \text{ M}$ at 298 K has Π of 18.5 mm Hg PROVE IT!

$$\Pi = c * R * T = 1.00 \times 10^{-3} \text{ M} * 0.082057 \text{ L atm / mol K} * 298 = 0.0244 \text{ atm}$$

$$0.0244 \text{ atm} * 760 \text{ mm Hg/atm} = 18.6 \text{ mm Hg}$$

EXAMPLE 14.7 Π of solution of polymer. 18.44 g polyvinyl alcohol mass 28,000 in water to give 150 ml. What is Π

$$\text{Answer} = \Pi = 8.2 \text{ mm Hg} = 110 \text{ mm water} = 4.33 \text{ "}$$

EXAMPLE 14.9 Osmotic Pressure and Molar Mass

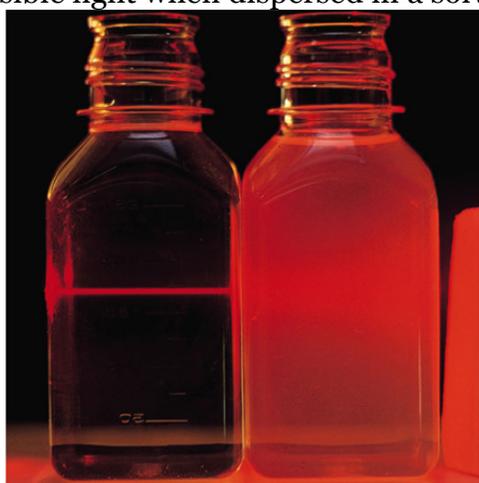
You need to be able to do this problem and understand what it's all about!

14.5 Colloids

A colloid is a state of matter intermediate between a solution and a suspension, the solute particles are large enough to scatter light but too small to settle out.

Colloids usually have high molar masses and the particles are large (1000 nm in dia).

Tyndall Effect scatters visible light when dispersed in a solvent



Sol is a colloidal dispersion of a solid in a fluid

Gel is a colloidal dispersion that has a structure that prevents it from being mobile – JELL-O

