

Chapter 13

Physical Properties of Solutions

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Chapter 13 Section 1

Types of Solutions

- Homogeneous mixtures of two or more substances are usually called *solutions*.
They can be liquid, gas, or solid.
- A *solute*: a substance being dissolved.
A *solvent*: a dissolving medium.
- Solutions can be:
 - *Dilute*: a relatively small amount of solute present.
 - *Concentrated*: a relatively large amount of solute present.

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Types of Solutions

- Homogeneous mixtures of two or more substances are usually called **solutions**.

They can be liquid, gas, or solid.

TABLE 13.1 Types of Solutions

Solute	Solvent	State of Resulting Solution	Example
Gas	Gas	Gas*	Air
Gas	Liquid	Liquid	Carbonated water
Gas	Solid	Solid	H ₂ gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Liquid	Solid	Solid	Mercury in silver
Solid	Liquid	Liquid	Saltwater
Solid	Solid	Solid	Brass (Cu/Zn)

*Gaseous solutions can only contain gaseous solutes.

Types of Solutions

- Solutions can be classified based on the amount of solute dissolved relative to the maximum possible amount of solute:
 - Saturated** – maximum amount at a given temperature. (This amount is known as the **solubility** of the solute)
 - Unsaturated** – less than the maximum.
 - Supersaturated** – more than a saturated solution but is an unstable condition and eventually dissolved solute will come out of solution.

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Saturation of Solutions

unsaturated → saturated → supersaturated

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Saturation of Solutions

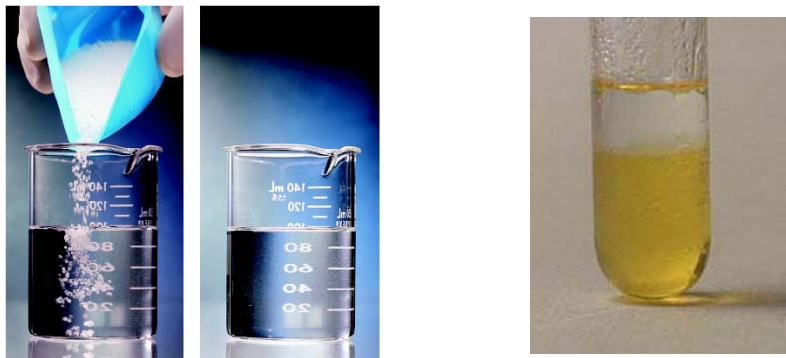
In a supersaturated solution, addition of a tiny seed crystal initiates crystallization of excess solute. Crystallization proceeds rapidly to give a saturated solution and the crystallized solid.

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A Molecular View of the Solution Process

- Why can water dissolve NaCl but can't dissolve oil?



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A Molecular View of the Solution Process

- Why can water dissolve NaCl but can't dissolve oil?
- Intermolecular forces present in the formation of a solution are:
 - Solute-solute interactions.
 - Solvent-solvent interactions.
 - Solute-solvent interactions.
- This process is called *solvation*.

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Energies of Solution Formation

- The formation of a liquid solution is assumed to take place in three distinct steps.

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{\text{soln}} \quad (\text{Enthalpy of solution})$$

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Energies of Solution Formation

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Energies of Solution Formation

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{\text{soln}} \text{ (Enthalpy of solution)}$$

ΔH_1 and ΔH_2 are always **endothermic**

ΔH_3 is always **exothermic**

ΔH_{soln} can be **exothermic** or **endothermic**

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Energies of Solution Formation

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{\text{soln}} \text{ (Enthalpy of solution)}$$

(a) $\Delta H_{\text{soln}} < 0$
Solute would be soluble in solvent as the overall process is exothermic.

(b) $\Delta H_{\text{soln}} > 0$
Solute would be insoluble in solvent as the overall process is endothermic.

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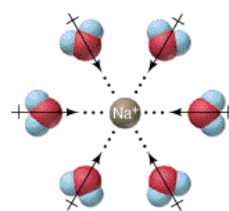
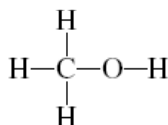
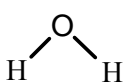
Like Dissolves Like

- **Like dissolves like.**

Polar solvents (water, ethanol, liquid methanol, etc.) can dissolve polar/ionic solutes.

Nonpolar solvents (benzene, hexane, chloroform “CCl₄”) can dissolve nonpolar solutes.

- Water can dissolve NaCl and methanol. but can't dissolve oil.



Hydration

Two liquids that are soluble in each other in all proportions are termed **miscible**.

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Energy and Entropy in Solution Formation

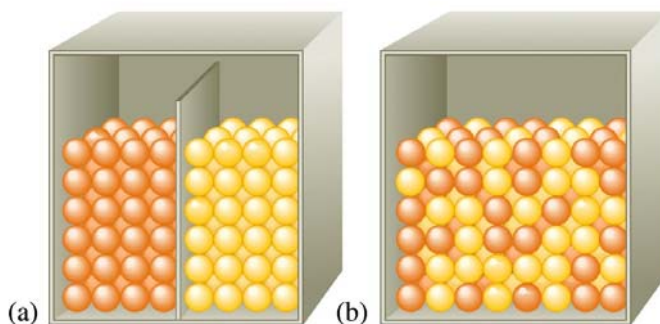
- In many cases, solutions do form although the overall process is endothermic ($\Delta H_{\text{soln}} > 0$).
- **Entropy** is the measure of randomness or disorder in a given process.
- Do you think the entropy for a natural process increases or decreases?
 - A process where some stones you hold in your hand fall down.
 - Water pours from a cup.

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Energy and Entropy in Solution Formation

- Entropy contributes to the solution process.
 - Entropy tends to increase for all natural process.
 - A solution is more disordered than the isolated solute and solvent, even if the solution process is endothermic.



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Energy and Entropy in Solution Formation

- Two opposite factors:
 - The tendency of a system to achieve higher probabilities. (**Entropy**)
 - The large amount of energy needed to carry out the solvation process. ($\Delta H_{\text{soln}} > 0$)
- A process that requires higher energy tends not to occur (**oil in water**). However, for a small amount of required energy, the process tends to happen due to the increase in probability (**salt in water**).

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Vitamin Solubility

- A structure of a molecule affects its solubility in different solvents.

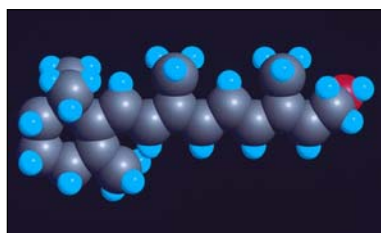
Structure ↔ intermolecular forces ↔ Solubility

- Vitamins:

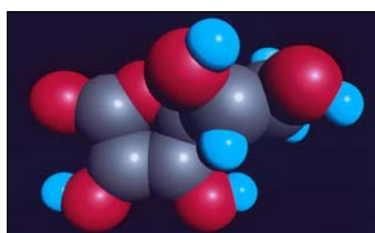
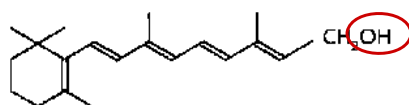
- **Fat-soluble vitamins** (vitamins A, D, E, and K)
- **Water-soluble vitamins** (vitamins B and C)

The different structures of these two types of vitamins explain the solubility differences.

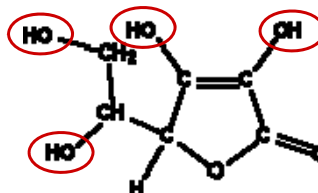
Vitamin Solubility



Vitamin A

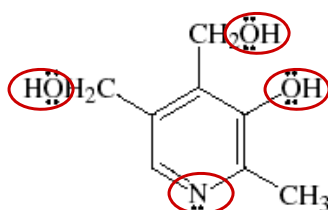


Vitamin C



Vitamin Solubility

- Predict whether the vitamin below is water soluble or fat soluble.



It is water soluble.

Concentration Units

<i>Molarity</i>	# mol of solute per liter of solution	<i>M</i>
<i>Percent by mass</i>	% of mass of solute in the solution	<i>mass%</i>
<i>Mole fraction</i>	ratio of # of moles of one component to the total # of moles.	<i>χ_A</i>
<i>Molality</i>	# mol of solute per kilo-gram of solvent	<i>m</i>

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Calculation on Concentration Units

In an automobile battery there is 3.75 M sulfuric acid solution with a density of 1.230 g/mL. Calculate mass percent and molality of the sulfuric acid solution.



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Chapter 13 Section 3

Calculation on Concentration Units

Calculate the molarity and mole fraction of acetone in a 1.00 M solution of acetone (CH_3COCH_3) in ethanol ($\text{C}_2\text{H}_5\text{OH}$). (Density of acetone = 0.788 g/cm³; density of ethanol = 0.789 g/cm³). Assume that the volumes of acetone and ethanol add.

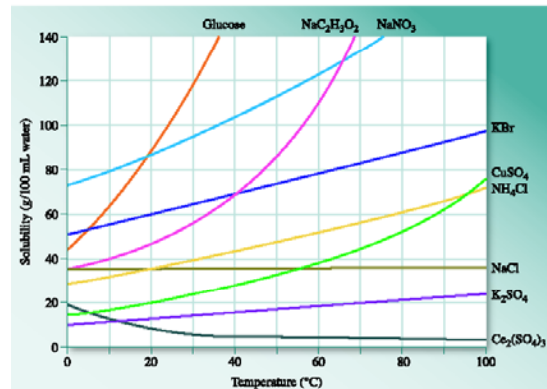
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Factors That Affect Solubility

Temperature effect (in aqueous solutions).

- Solids:** The solubility of most of the solids increases with the increase of temperature. For some solids, such as Na_2SO_4 and $\text{Ce}_2(\text{SO}_4)_3$, the solubility decreases with increasing temperature.



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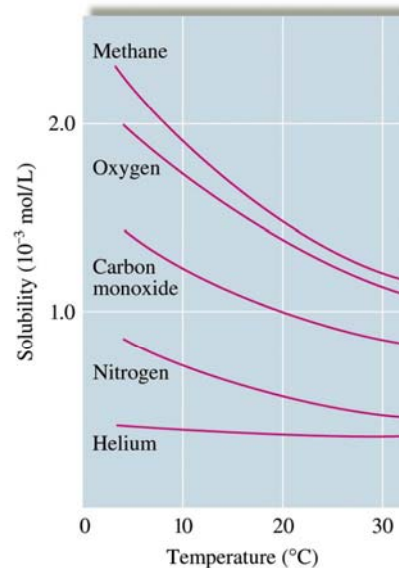
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Factors That Affect Solubility

Temperature effect (in aqueous solutions).

- Gases:** The solubility of gases in water decreases with temperature.

Thermal pollution
Boiler scale




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Chapter 13 Section 4

Factors That Affect Solubility



- Pressure effect.**
 It greatly affects the solubility of gases.
 Pressure *increases* the solubility of gases.
 In Carbonated drinks (Pepsi, Coca Cola, etc.),
 CO_2 is dissolved in the soda (high concentration under high pressure).



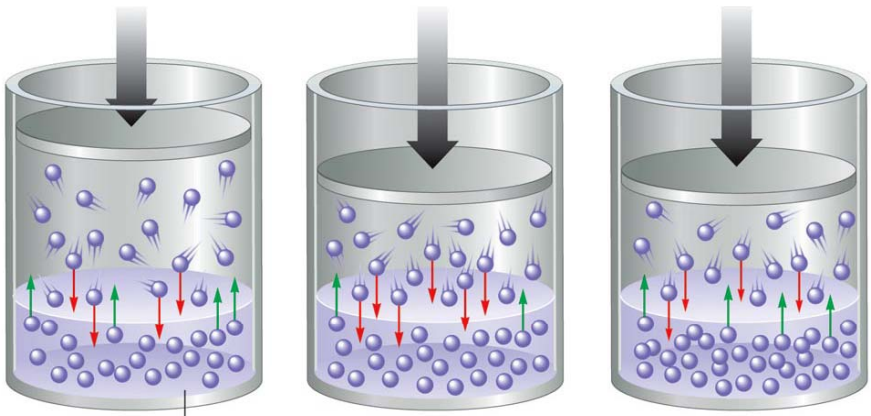
- Henry's Law:**
 The solubility of a gas in a solution is directly proportional to the pressure of the gas above the solution.

$$C = k P$$

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Chapter 13 Section 4

A Molecular View of Henry's Law



(a) Solution

(b)

(c)

Equilibrium Equilibrium being disturbed Equilibrium back with more dissolved gas

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Application of Henry's Law

Mirinda® soft drink is bottled at 25°C with CO₂ gas at a pressure of 5.0 atm over the liquid. If the partial pressure of CO₂(g) in the atmosphere is 4.0×10⁻⁴ atm, calculate the equilibrium concentration for CO₂(g) in the Mirinda® soft drink both before and after the bottle is opened. The Henry's law constant for CO₂ is 3.1×10⁻² mol/L·atm @ 25°C.



Colligative Properties

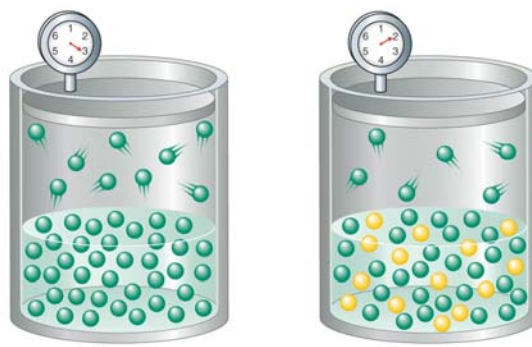
- Colligative properties for solutions depend on the number of the solute particles (solute's concentration), NOT on the nature or identity of the solutes.

- Colligative properties:**

- Vapor-pressure lowering
- Boling-point elevation.
- Freezing-point depression.
- Osmotic pressure.

Vapor-Pressure Lowering

- Adding a *non-volatile solute* to the solvent decreases the rate of solvent molecules trying to escape from the solution. This causes the vapor pressure of the solution to be lowered.



Pure solvent

Solution with a nonvolatile solute

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Raoult's Law

- The *difference* between the vapor pressure of a pure solvent (P°_1) and that of the corresponding solution (P_1) depends on the *concentration* of the non-volatile solute in the solution.



Solution with a nonvolatile solute

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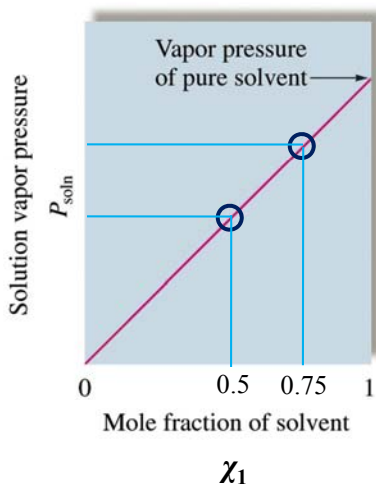
Raoult's Law

$$P_1 = \chi_1 P_1^\circ$$

- A solution of half solute and half solvent.

$$P_{\text{soln}} = (0.5) P_{\text{solvent}}^\circ$$
- A solution with three-fourth of its molecules is solvent.

$$P_{\text{soln}} = (0.75) P_{\text{solvent}}^\circ$$



Raoult's law is a **linear** relationship

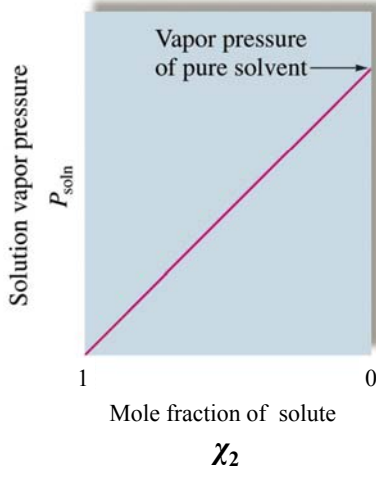
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Raoult's Law

$$P_1 = \chi_1 P_1^\circ$$

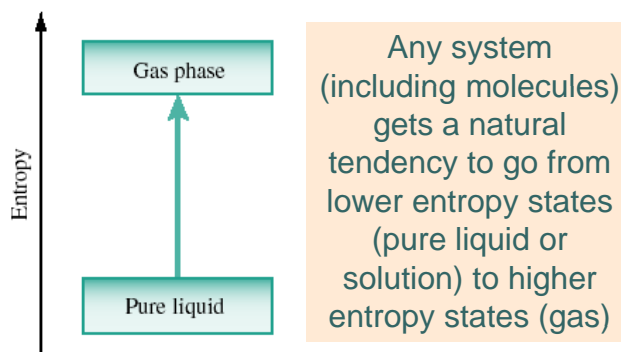
The lowering in the solution vapor pressure is directly proportional to the mole fraction of the non-volatile solute.

$$P_1^\circ - P_1 = \Delta P = \chi_2 P_1^\circ$$


Raoult's law is a **linear** relationship

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Why Does it Happen?



Because there is a smaller difference in entropy between the solution and the gas phase than there was between the pure liquid and the gas phase, there is a decreased tendency for molecules to leave the solution and enter the gas phase. This results in lowering of the vapor pressure of the solution.

Application of Raoult's Law

A solution made by dissolving 158.0g of table sugar ($MM=342.3$ g/mol) in 643.5 cm³ of pure water @ 25°C. The density and vapor pressure of water @ 25°C is 0.9771 g/cm³ and 23.76 torr, respectively. Calculate the vapor pressure of the solution @ 25°C.

Application of Raoult's Law

A solution prepared by dissolving 35.0g Na_2SO_4 (MM=142 g/mol) in 175g of pure water @ 25°C. The vapor pressure of water @ 25°C is 23.76 torr. Calculate the vapor pressure of the solution @ 25°C.

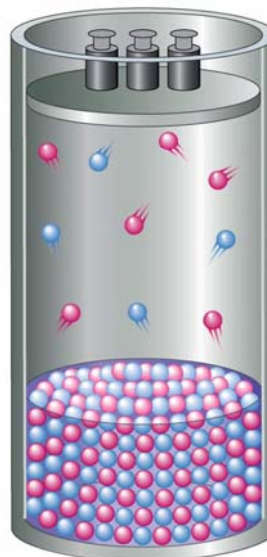
In the case of ionic solutes, the vapor pressure of the solvent is lowered depending on how many ionic species are produced in the solution.

Volatile Solutes

- In the real sense, **both** the solution and solute are volatile to some extent and, thus, both of them are contributing to the vapor pressure above the solution.
- For solutes that are relatively volatile, the partial pressure of the solution is given by:

$$P_{\text{Total}} = P_{\text{solvent}} + P_{\text{solute}} = P_A + P_B$$

$$P_{\text{Total}} = \chi_A P_A^\circ + \chi_B P_B^\circ$$

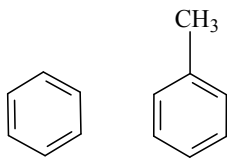


Ideal Solutions

- **Ideal solution** obeys Raoult's law.

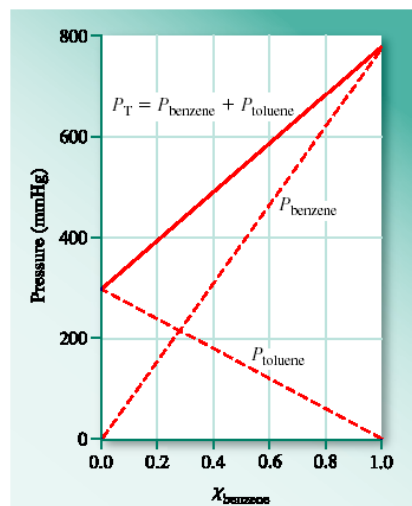
$$P_{\text{Total}} = \chi_A P_A^\circ + \chi_B P_B^\circ$$

- Benzene and toluene are both volatile and have similar chemical structures. They give an example of an ideal solution.



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Ideal Solutions

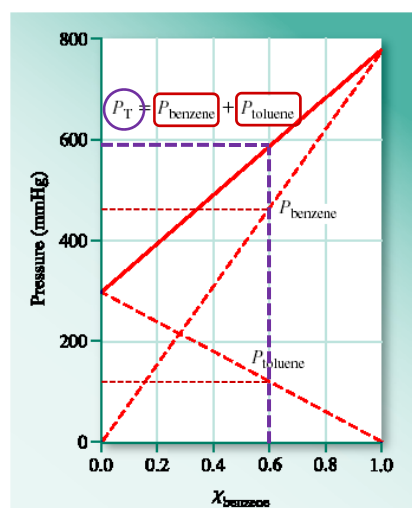
$$P_{\text{Total}} = \chi_A P_A^\circ + \chi_B P_B^\circ$$

- What is P_{Total} of a benzene-toluene solution that is 60% benzene?

$$P_{\text{Total}} = 590 \text{ mmHg}$$

$$P_{\text{benzene}} = 460 \text{ mmHg}$$

$$P_{\text{toluene}} = 130 \text{ mmHg}$$



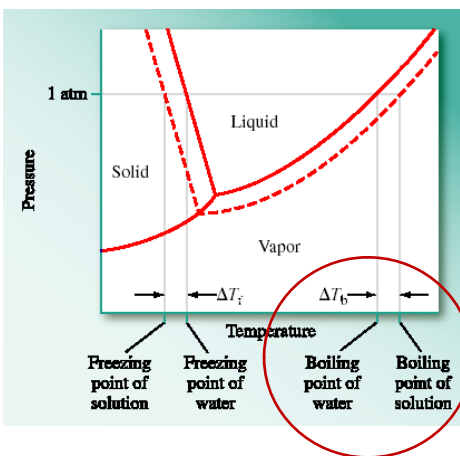
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Boiling-Point Elevation

- Nonvolatile solutes cause the vapor pressure of the solvent to decrease. Thus, a higher temperature is needed to boil the solution as compared to the pure liquid state.

A nonvolatile solute elevates the boiling point of the solvent.



Boiling-Point Elevation

- The boiling point elevation depends on the *concentration* of the solute.

$$\Delta T_b = K_b m_{\text{solute}}$$

$$\Delta T_b = T_{\text{b.p.}}(\text{solution}) - T_{\text{b.p.}}(\text{pure solvent})$$

m : molality of the solute in solution.

K_b : molal boiling-point elevation constant and it is characteristic of each solvent.

Boiling-Point Elevation

$$\Delta T_b = K_b m_{\text{solute}}$$

TABLE 13.2 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Solvents

Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
Water	100.0	0.52	0.0	1.86
Benzene	80.1	2.53	5.5	5.12
Ethanol	78.4	1.22	-117.3	1.99
Acetic acid	117.9	2.93	16.6	3.90
Cyclohexane	80.7	2.79	6.6	20.0

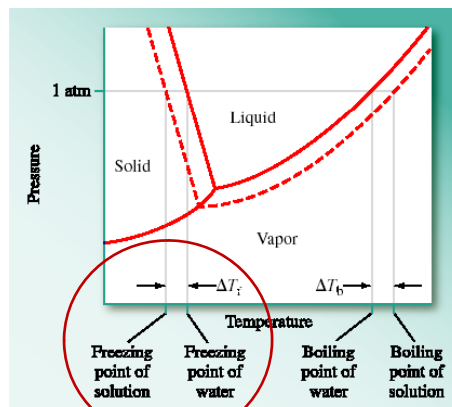
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Freezing-Point Depression

- Adding a nonvolatile solute to a solvent **decreases** the freezing point temperature of the pure solvent.

$$\Delta T_f = K_f m_{\text{solute}}$$



$$\Delta T_f = T_{\text{b.p.}}(\text{solution}) - T_{\text{b.p.}}(\text{pure solvent})$$

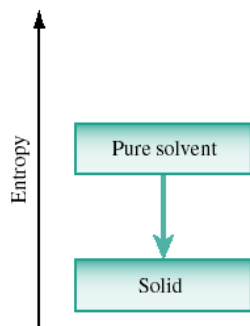
m : molality of the solute in solution.

K_f : molal **freezing**-point depression constant.

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Why Does it Happen?



Any system (including molecules) gets a natural tendency to go from a lower entropy state (solid) to a higher entropy state (pure solvent or solution)

The disorder for the solution is higher than that in pure solvent. So the difference in entropy between the solution and solid is greater than that between the pure solvent and solid. More energy must be removed from the solution than the pure solvent for the sample to freeze. Thus, the solution freezes at a lower temperature than the pure solvent.

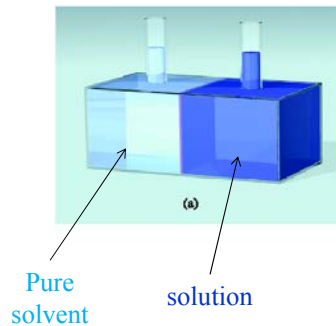
Calculations with Boiling Point Elevation

A solution was prepared by dissolving 18.00g of glucose in 150.0g of water. The resulting solution's b.p was found to be 100.34°C. Calculate the molar mass of glucose.

Osmosis

- A solution and pure solvent are separated by a *semipermeable* membrane, which allows solvent and not solute molecules to pass through.

The flow of the solvent through the membrane is called *osmosis*.



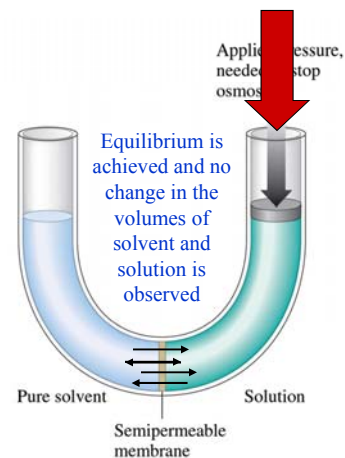
Change in height due to osmosis

Osmotic Pressure

- In the U-tube shown, the normal flow of the solvent molecules through the membrane can be prevented by applying an external pressure to the solution.
- **Osmotic pressure (π)** of a solution is the minimum pressure required to stop osmosis process.

$$\pi = MRT$$

π : Osmotic pressure.
 M : Solution molarity.
 R : Gas constant.
 T : Kelvin temperature.

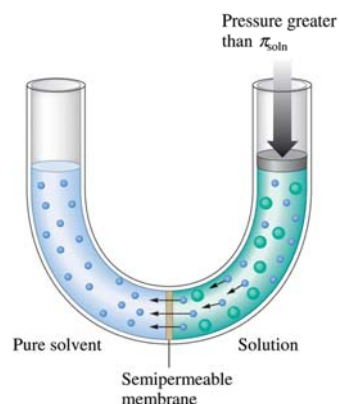


Reverse Osmosis

- **Reverse osmosis** occurs when the external pressure is larger than the osmotic pressure of the solution.

The membrane in this case acts as a “molecular filter” to remove solute particles from the solution.

- One major application is **seawater desalination**.



Colligative Properties of Electrolyte Solutions

- Compare the freezing point depression, $\Delta T = K_f m_{\text{solute}}$, for the following aqueous solutions:

- 0.1 *m* glucose solution:

$$\Delta T = 0.186^\circ\text{C}$$

- 0.1 *m* sodium chloride solution:

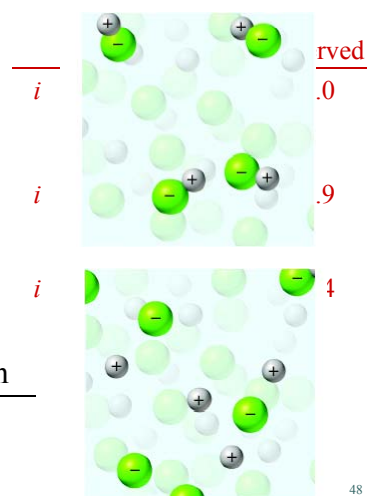
$$\Delta T = 0.37^\circ\text{C}$$

- 0.1 *m* FeCl₃ solution:

$$\Delta T \text{ is expected to be } 0.74^\circ\text{C}$$

- **Van't Hoff factor:**

$$i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolves}}$$



Colligative Properties of Electrolyte Solutions

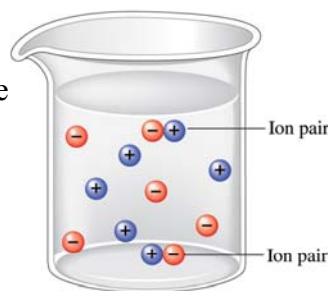
TABLE 13.3 Calculated and Measured van't Hoff Factors of 0.0500 M Electrolyte Solutions at 25°C

Electrolyte	i (Calculated)	i (Measured)
Sucrose*	1	1.0
HCl	2	1.9
NaCl	2	1.9
MgSO ₄	2	1.3
MgCl ₂	3	2.7
FeCl ₃	4	3.4

*Sucrose is a nonelectrolyte. It is listed here for comparison only.

Colligative Properties of Electrolyte Solutions

- Some observed i 's are in general smaller than the expected ones by van't Hoff equation due to the **ion pairing** effect.
- Observed i becomes **less smaller** than the expected i when the solution is diluted.
- The colligative properties of electrolyte solutions can be described using the equations we studied earlier:



$$\Delta T_b = iK_b m$$

$$\Delta T_f = iK_f m$$

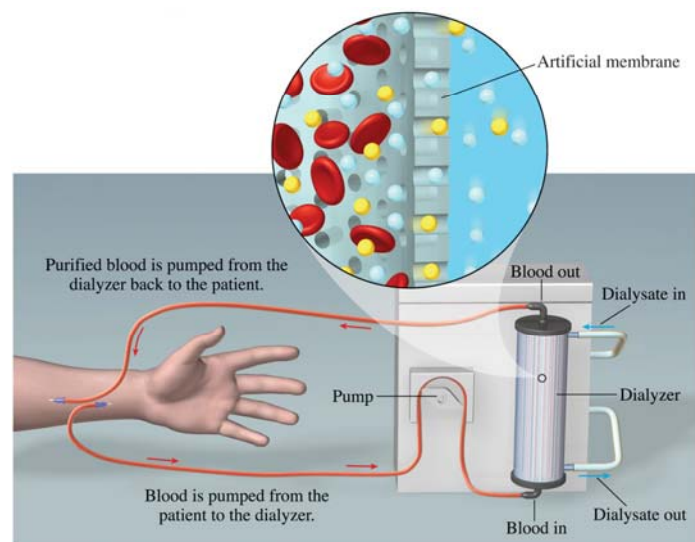
$$\pi = iMRT$$

Applications of Osmotic Pressure

- **Dialysis** is a special type of osmosis. In dialysis, the membrane allows transfer of solvent molecules and **small** solute molecules /ions.
- One important application of dialysis is the artificial kidney machine that is used to purify blood.



Applications of Osmotic Pressure



Calculations Using Colligative Properties

The freezing-point depression of a 0.100 m MgSO_4 solution is 0.225°C . Determine the experimental van't Hoff factor of MgSO_4 at this concentration. The molal freezing-point depression constant for water is $1.86^\circ\text{C}/m$.

$$\Delta T_f = iK_f m$$

$$0.225^\circ\text{C} = i \frac{1.86^\circ\text{C}}{m} \times 0.100 m$$

$$i = 1.21$$

Note, at this concentration the dissociation of MgSO_4 is not complete.

Calculations Using Colligative Properties

1.00×10^{-3} g of a certain protein was dissolved in enough water to make 1.00 mL of solution. The osmotic pressure of this solution was found to be 1.12 torr @ 25°C . Calculate the molar mass of the protein.

Calculations Using Colligative Properties

A solution made by dissolving 25.0 mg of insulin in 5.00 mL of water has an osmotic pressure of 15.5 mmHg at 25°C. Calculate the molar mass of insulin.

$$\pi = 15.5 \text{ mmHg} \times \frac{\text{atm}}{760 \text{ mmHg}} = 2.039 \times 10^{-2} \text{ atm}$$

$$M = \frac{\pi}{RT} = 2.039 \times 10^{-2} \text{ atm} \times \frac{\text{mol} \cdot \text{K}}{0.08206 \text{ L} \cdot \text{atm}} \times \frac{1}{298 \text{ K}}$$

$$M = 8.338 \times 10^{-4} \text{ M} = \frac{8.338 \times 10^{-4} \text{ mol}}{\text{L}}$$

$$\text{mol} = \frac{8.340 \times 10^{-4} \text{ mol}}{\text{L}} \times 5.00 \text{ mL} \times \frac{10^{-3} \text{ L}}{\text{mL}} = 4.169 \times 10^{-6} \text{ mol}$$

$$\text{Molarity} = 25.0 \text{ mg} \times \frac{10^{-3} \text{ g}}{\text{mg}} \times \frac{1}{4.169 \times 10^{-6} \text{ mol}} = \frac{6.00 \times 10^3 \text{ g}}{\text{mol}}$$

Review Questions

21. Which of the following statements is(are) true? Correct the false statements.
- ✗ The vapor pressure of a solution is directly related to the mole fraction of solute.
 - ✓ When a solute is added to water, the water in solution has a lower vapor pressure than that of pure ice at 0°C.
 - ✗ Colligative properties depend only on the identity of the solute and not on the number of solute particles present.
 - ✗ When sugar is added to water, the boiling point of the solution increases above 100°C because sugar has a higher boiling point than water.

Review Questions

Which solvent, water or hexane (C₆H₁₄), would you choose to dissolve each of the following?

- ✓ NaCl ✓ octane (C₈H₁₈)
 ✓ HF ✓ (NH₄)₂SO₄

What factors cause one solute to be more strongly attracted to water than another? For each of the following pairs, which substance would be more soluble in water.

- a. CH₃CH₂OH or CH₃CH₂CH₃
 b. CHCl₃ or CCl₄
 c. CH₃CH₂OH or CH₃(CH₂)₁₄CH₂OH

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Review Questions

The solubility of nitrogen in water is 8.21×10^{-4} mol/L at 0°C when the N₂ pressure above water is 0.790 atm. Calculate the Henry's law constant for N₂ in units of mol/L · atm for Henry's law in the form $C = kP$, where C is the gas concentration in mol/L. Calculate the solubility of N₂ in water when the partial pressure of nitrogen above water is 1.10 atm at 0°C.

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Review Questions

A solution is prepared by mixing 0.0300 mol CH_2Cl_2 and 0.0500 mol CH_2Br_2 at 25°C . Assuming the solution is ideal, calculate the composition of the vapor (in terms of mole fractions) at 25°C . At 25°C , the vapor pressures of pure CH_2Cl_2 and pure CH_2Br_2 are 133 and 11.4 torr, respectively.

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Review Questions

A 0.500-g sample of a compound is dissolved in enough water to form 100.0 mL of solution. This solution has an osmotic pressure of 2.50 atm at 25°C . If each molecule of the solute dissociates into two particles when dissolved in water, what is the molar mass of the solute?

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Review Questions

Calculate the mole fraction and molarity of acetone in a 1.00 *m* solution of acetone (CH_3COCH_3) in ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). Densities of acetone and ethanol are 0.788 and 0.789 g/cm^3 , respectively.

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Review Questions

In each of the following groups of substances, pick the one that has the given property. Justify each answer.

- highest boiling point: CCl_4 , CF_4 , CBr_4
- lowest freezing point: LiF , F_2 , HCl
- smallest vapor pressure at 25°C : CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_3$
- greatest viscosity: H_2S , HF , H_2O_2
- greatest heat of vaporization: H_2CO , CH_3CH_3 , CH_4
- smallest enthalpy of fusion: I_2 , CsBr , CaO

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Review Questions

The structure of manganese fluoride can be described as a simple cubic array of manganese ions with fluoride ions at the center of each edge of the cubic unit cell. What is the charge of the manganese ions in this compound?

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Review Questions

Carbon tetrachloride, CCl_4 , has a vapor pressure of 213 torr at $40.^\circ\text{C}$ and 836 torr at $80.^\circ\text{C}$. What is the normal boiling point of CCl_4 ?

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Review Questions

For the following species:

NO^+ , NO and NO^- ,

Which ones are paramagnetic?

Place them in order of increasing bond length.

Place them in order of increasing bond energy.



Review Questions

Give the expected hyb. For the S atom

SF_2

SF_5^+



Review Questions

The successive ionization energies for an unknown element are:

$$I_1 = 780 \text{ kJ/mol}$$

$$I_2 = 1571 \text{ kJ/mol}$$

$$I_3 = 3220 \text{ kJ/mol}$$

$$I_4 = 4350 \text{ kJ/mol}$$

$$I_5 = 16100 \text{ kJ/mol}$$

$$I_6 = 18700 \text{ kJ/mol}$$

To which family this does this element belong to?

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Review Questions

Carbon-oxygen double bond in a certain molecule absorbs radiation with a frequency of $6.0 \times 10^{13} \text{ s}^{-1}$.

- What is the wavelength of this radiation?
- What is the energy of this radiation per photon/ per 1 mole of photons?

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