

سبحان الله الحمدلله

لا إله إلا الله الله أكد

# تفريغ فيزيكال

اسم الموضوع: (additional)

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تعریع إمنان لتفاریع زملای ملل و مبه کی

اللهم اغفر لي ولوالدي وللمؤمنين والمؤمنات والمسلمين والمسلمات الاحياء منهم والاموات انك سميع قريب مجيب الدعوات

اللهم إني ظلَمتُ نفسي ظلمًا كثيرًا فاغفِرْ لي مَغفِرَةً من عِندِك

اللهم أعز الإسلام والمسلمين

اللهم انصر اخواننا المسلمين المستضعفين في

اللَّهمَّ اغفِر لي ذنبي كُلَّهُ دِقَّهُ، وجِلَّهُ، وأَوَّلَهُ وآخرَهُ وعلانيتَه

اللهم افتح علي فتوح العارفين بحكمتك وانشر علي رحمتك، وذكرني ما نسيت، واطلق لساني وقوي به عزمي بحولك وقوتك اللهمَّ انفعْني بما علَّمتني وعلِّمْني ما يَنفعُني وزِدْنِي علمًا والحمدُ للهِ على كلِّ حالٍ وأعوذُ باللهِ من عذابِ النار

# **Solutions of nonelectrolytes**

## **Solutions**

- Solution is a mixture of two or more components that form a homogenous molecular dispersion (one phase).
- It consists of one or more solutes dissolved in one or more solvents.
- Solute molecules or ions are "dissolved" and uniformly distributed in the solvent medium.

#### **Solutions**

- A true solution is a single phase system.
- NaCl and water, ethanol and water
  - Form a solution (one phase) ⇒ a solution
- Talc and water
  - Form a suspension (two phase)  $\Rightarrow$  not solution
- Oil and water
  - Form an emulsion (two phase)  $\Rightarrow$  not solution

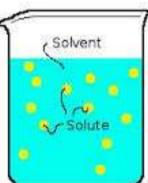
Solutions are composed of:

- **Solute:** is the substance that dissolves which may be solid, liquid, or gas.
- **Solvent:** is the substance that does the dissolving which may be solid, liquid, or gas.

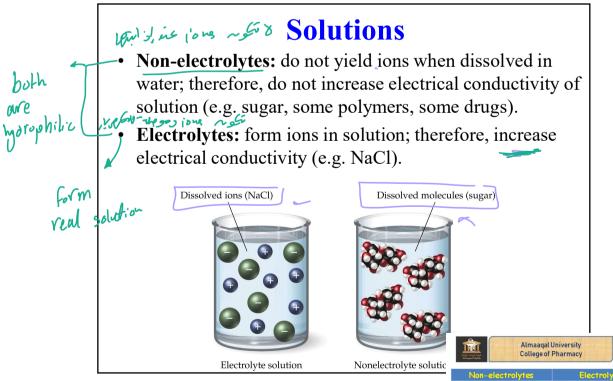
#### **Solutions**

#### Which the solvent and which is the solute?

- Solvent: component in greater extent.
- Solute: component in minor extent.
- **Note:** When a solid is dissolved in liquid, it is the solute irrespective of relative amount.



Types of Solutions			
Solute	Solvent	Solution	Example
Gas	Gas	Gas	Air $(O_2 \text{ in } N_2)$
Gas	Liquid	Liquid	Carbonated beverages (CO <sub>2</sub> in H <sub>2</sub> O) Swimming pool (Cl <sub>2</sub> in H <sub>2</sub> O)
Liquid	Liquid	Liquid	Wine (ethanol in H <sub>2</sub> O)
			Vinegar (acetic acid in H <sub>2</sub> O)
Liquid	Solid	Solid	Dental amalgam for fillings (liquid
			mercury in solid silver)
Solid	Liquid	Liquid	Saline (NaCl in H <sub>2</sub> O)
			Sugar in water
Solid	Solid	Solid	14-karat gold (Ag in Au)
			Steel (carbon in iron)



All solutions are aqueous? F

Electrolytes are 1 ? T

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Non-electrolytes

Form solutions that don't conduct electricity

Dissolve to form molecules in solution

Have some effect on freezing & boiling points of their solutions

Examples: Sugar, alcohols

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College of Pharmacy

Electrolytes

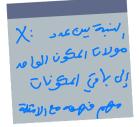
Form solutions that conduct electricity

Dissolve to form ions in solution

Have a greater effect on freezing & boiling points of their solutions

Examples: Acids, Bases, and Salts





#### **Solutions**

#### **Concentration expressions**

- Molarity(M): no. of moles of solute in 1 litre of solution.
- Molality (m): no. of moles of solute in 1 kg of solvent.
- **Normality(N):** no. of equivalents in 1 liter of solution.
- Mole fraction (X): ratio of number of moles of one component to total moles of all constituents (solute and solvent).
- Percent by weight (w/w): no. of grams of solute in 100 g of solution.
- Percent by volume (v/v): no. of milliliters of solute in 100 ml of solution.
- **Percent weight in volume (w/v):** no. of grams of solute in 100 ml of solution.

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#### **Ideal solutions**

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- Solutions in which there is no change in the properties of ... ① the components when they are mixed.
- For a mix of molecules of A and B, the interactions between unlike neighbors (UAB) and like neighbors U<sub>AA</sub> and U<sub>BB</sub> must be of the same average strength, i.e.,

 $2U_{AB} = U_{AA} + U_{BB}$ 

No heat is evolved or absorbed, the final volume is the sum of the volume of the individual components.

هراء منع في أن فحلولنا المعالمة

## هور مثال توضير الحجم قبل وبعد خلط (مزج) المكونات

#### **Ideal solutions**

#### **Ideal solution:**

• E.g.100 ml of ethanol + 100 ml of methanol = 200 ml solution.

No heat is evolved or absorbed.

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Real solution:

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E.g. 100 ml of sulfuric acid + 100 ml of water =

180 ml solution.

Heat is evolved (exothermic).

#### **Ideal solutions**

#### Raoult's Law

- Cohesive interactions in liquid prevent all molecules from escaping as a vapor. Disrupting the cohesion (by increasing T) will increase the tendency of molecules to escape from the liquid as a vapor.
  - When the vapor pressure equals the external pressure, the system is said to be in equilibrium, and the vapor pressure is known as the equilibrium vapor pressure (P)
  - A substance with a high vapor pressure at normal temperatures is often referred to as volatile.

فسي المحلول متطابر بعال كان الرضي البخاري عالى مدرجه الحرارة العادية.

#### **Ideal solutions**

#### Raoult's Law:

• The partial vapor pressure of each component in an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.

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P < P;

#### **Ideal solutions**

#### Raoult's Law

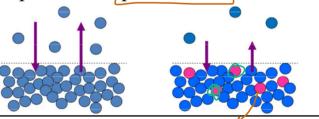
• For a non-volatile solute, the total vapor pressure  $(P_{total})$  is equal to the vapor pressure of the solvent  $(P_{solvent})$  only:  $P_{total} = P_{solvent}$ 

$$P_1 = X P_1^{\circ}$$

X: mole fraction of solvent

Salvet ale ) sou!

P<sub>1</sub>: vapor pressure of pure solvent



حجود هاي علم المختلف ما المحتلف المحت

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ا حا 131كان محلي عيومتركام عا: non *Volat* خان الفخط البفاري تتيا سب طردي سع المذبي

> ومکن مع اکذاب Solute

#### **Ideal solutions**

Raoult's Law

- If components constituting a solution are volatile, each will produce a partial pressure above the solution, which can be calculated from Ideal Solutions Raoult's Law
- The total pressure is the sum of the partial pressures of all nts. لا يجاد التي الول اي نجد فغل على مكون لوهره بعد بن نجم على الم the constituents.

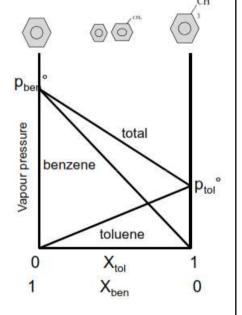
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#### **Ideal solutions**

#### Raoult's Law

- For two constituents, toluene and benzene:

- $P_{total} = P_{tol} + P_{ben}$   $P_{tol}, P_{ben}: partial vapor pressures$ 
  - $P_{to} P_{ben}$ : vapor pressures of pure components.
  - $X_{tol}$ ,  $X_{ben}$ : mole fractions



•  $P_{tol} = P_{tol}^{\circ} X_{tol}$  $P_{ben} = P_{ben}^{\circ} X_{ben}$ 

#### **Ideal solutions**

map)

Aerosols and Raoult's law /

- Raoult's law is important because it allows the calculation of vapour pressure from a knowledge of the composition of the solution.
- The requirement of the Montreal Protocol in 1989 for the replacement of chlorofluorocarbon (CFC) propellants in pressurised metered-dose inhalers with hydrofluoroalkanes (HFAs), because of the ozone-depleting properties of CFCs, led to a substantial review of the formulation of these devices as a consequence of major differences in physical and chemical properties of these propellants.
- The two most widely used HFAs are HFA 227 and HFA 134a.

The vapour pressure of metered dose inhalers determines the aerosol droplet size and consequently has an important influence on the efficiency of deposition in the lungs

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#### **Ideal solutions**

**Example:** 

صهم ننتيج شحالاه والمطلوبة

• Calculate the vapour pressure (in Pa) at 20°C above an aerosol mixture consisting of 30% w/w of HFA 134a (tetrafluoroethane, molecular weight 102) with a vapour pressure of 68.4 psig and 70% w/w of HFA 227 (heptafluoropropane, molecular weight 170) with a vapour pressure of 56.0 psig. Assume ideal behaviour.

Answer

No. of moles of HFA 134a in 100 g mixture = 30/102 = 0.2941 moles

No. of moles of HFA 227 in 100 g mixture = 70/170 = 0.4118 moles

 $x_{134} = 0.2941/0.7059 = 0.4166$ 

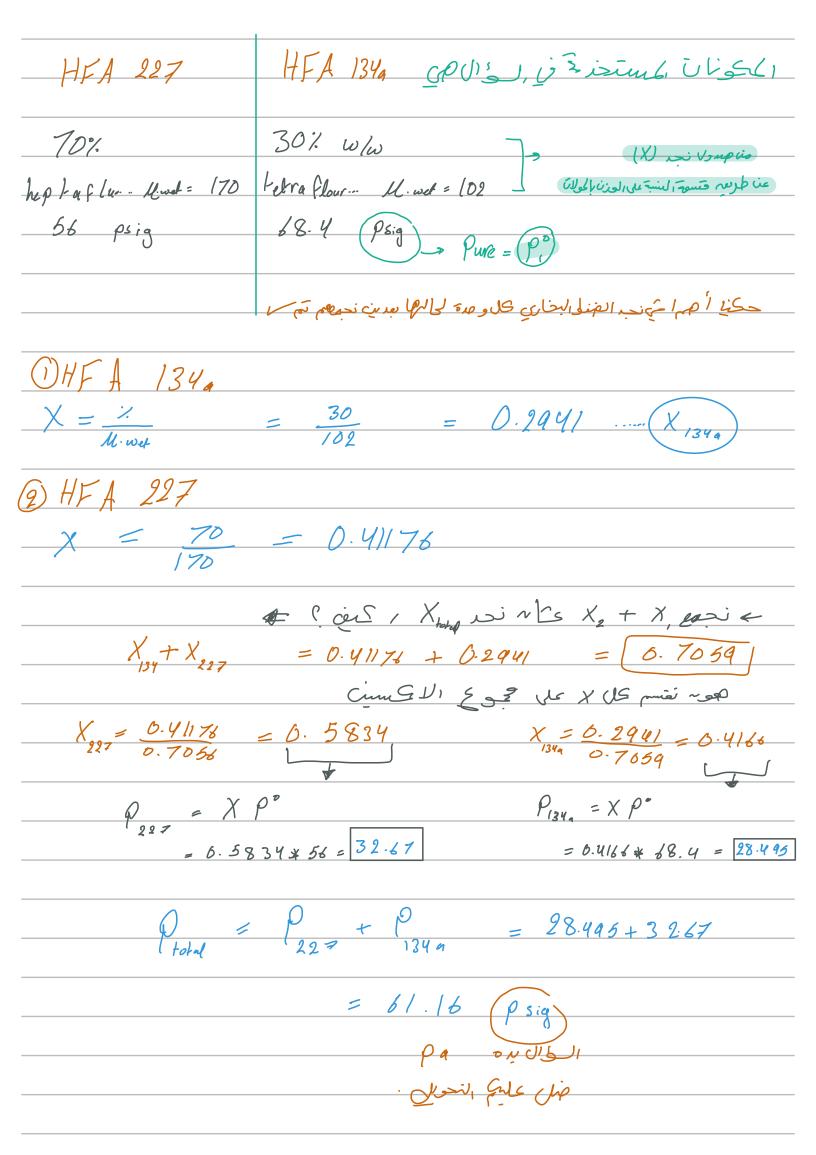
 $x_{227} = 0.4118/0.7059 = 0.5834$ 

 $P = p^{o}_{134} X_{134} + p^{o}_{227} X_{227}$ 

 $P = (68.4 \times 0.4166) + (56.0 \times 0.5834)$ 

 $P = 61.17 \text{ psig} = 5.23 \times 10^5 \text{ Pa}$ 

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#### **Real solutions**

• In real solutions, the attractive forces are not uniform.

The adhesive attraction of A for B might be <u>less or exceed</u> the cohesive attraction between A and A or B and B.

• This can happen even if the liquids are completely miscible.

• The more dissimilar the nature of A and B, the more strongly the solution is expected to deviate from ideality.

• These real solutions may not obey Raoult's law. There can be negative or positive deviations.

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ideal solution

UAB = UAA +UBR

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#### **Real solutions**

Partial pressures of components less than in ideal solution.

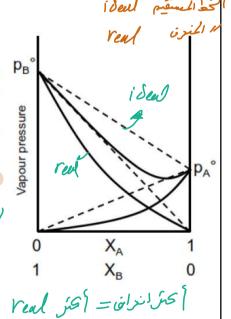
Adhesive attractions (AB) greater than cohesive attractions (AA and BB).

A holds B back and B holds A back.

Total vapor pressure may show a minimum.

E.g. chloroform and acetone form hydrogen bonds

CHCl<sub>3</sub> - - O=C(CH<sub>3</sub>)<sub>2</sub>

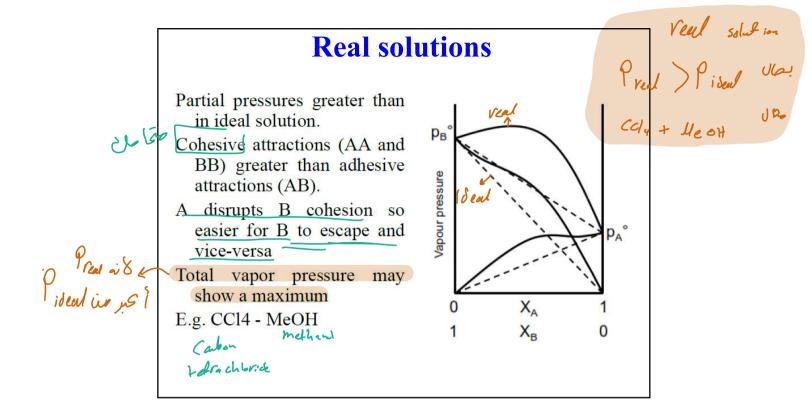


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• Colligative properties are properties of solutions that depend upon the ratio of the number of solute particles to the number of solvent molecules in a solution, and not on the type of chemical species present.

• Colligative properties of solution include:

- 1. Lowering of vapor pressure
- 2. Elevation of boiling point solution > solute / solvent
- 3. Depression of freezing point solution < 50 to / solved
- 4. Osmotic pressure

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Non Volatile

Solutes

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Volatile solvent

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#### **Colligative Properties of Solutions**

#### Lowering of vapor pressure

- When a non-volatile solute is dissolved in a volatile solvent, the vapor above the solution is provided by the solvent only. The solute particles (atoms, molecules or ions) at the surface reduce the escaping tendency of the solvent
- Therefore, the tendency of the solvent molecules to exert vapor pressure is lowered in the presence of the solute.

nonvolatile

### **Colligative Properties of Solutions**

#### Lowering of vapor pressure

- Vapor pressure lowering of a solution depends on the number of solute molecules (mole fraction) present in the solution.
- The higher the solute fraction, the lower the vapor pressure above the solution.
- Vapor pressure lowering is the key to all four of the colligative properties.



- Colligative properties of solution include:
  - 1. Lowering of vapor pressure
  - 2. Elevation of boiling point solution
  - 3. Depression of freezing point
  - 4. Osmotic pressure

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#### Lowering of vapor pressure

• The change of vapour pressure following the addition of a nonvolatile solute to a solvent may be determined by application of Raoult's law.

$$p = p_1 = p_0^1 x_1 = p_1^0 (1 - x_2)$$

$$(p_0^1 - p_1) / p_1^0 = x_2 = n_2 / (n_1 + n_2)$$

 $p_1$ : the vapor pressure of the solvent (with solute),  $p_1^0$ : vapor pressure of the pure solvent x<sub>1</sub>: mole fraction of solvent  $x_2$  = mole fraction of solute,

$$\frac{\Delta \rho}{\rho \sigma} = \frac{h_2}{h_1 + h_2}$$

## **Colligative Properties of Solutions**

Sucrose - Solute m = 171.29 M.m = 342.3

12

#### Lowering of vapor pressure: Example

What is the relative vapor pressure lowering for a solution containing 171.2 g of sucrose (MW = 342.3) in 1000 g of water (MW = 18.02)?

$$\Delta P/P_1^{\circ} = n_2/(n_1 + n_2)$$

n = m/MW

Moles of water =  $n_1 = m_1/MWt_1 = 1000/18.02 = 55.5$ 

Moles of sucrose =  $n_2 = m_2/MWt_2 = 171.2/342.3 = 0.5$ 

 $\Delta P/P_1^{\circ} = n_2/(n_1 + n_2) = 0.5/(55.5 + 0.5) = 0.0089$ 

The vapor pressure of this solution has been lowered 0.89% by sucrose

$$\frac{\Delta P}{P_1^0} = \frac{h_2}{(n_1 * h_2)} = \frac{0.6}{0.5 + 55.5}$$

$$= 0.0089 * 100 = 0.897$$
Significant pilot, USE C(2)

#### **Boiling Point Elevation**

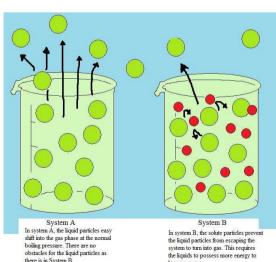
- Normal Boiling Point: is the temperature at which the vapor pressure (P) of the liquid becomes equal to the atmospheric pressure.
- Presence of solute particles lower the vapor pressure of the solution (we need to increase temperature to increase p to make it boil).
- The boiling point of a solution (T) is higher than that of the pure solvent alone (T°)

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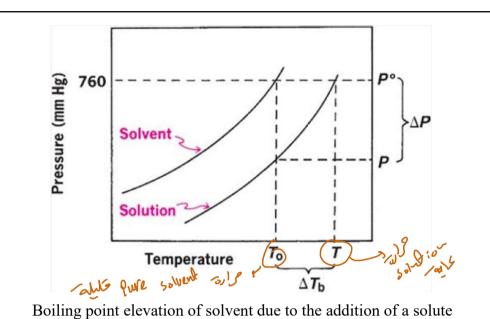
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## **Colligative Properties of Solutions**

**Boiling Point Elevation** 



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## **Colligative Properties of Solutions**

#### **Boiling Point Elevation**

• The boiling point elevation,  $\Delta T_b$  is estimated by this equation.

$$\Delta T_b = K_b m$$

$$T - T_0 = \Delta T_b$$

- $\mathbf{K}_{\mathbf{b}}$ : molal elevation constant (ebullioscopic constant)
- m: molality



$$\Delta T_b = k_6 m$$

**Boiling Point Elevation: Example** 

صفهايه بنوف أي فاؤم تستنم

An aqueous solution of a drug gave a boiling point elevation of 0.103 °C. Approximate Kb (ebullioscopic constant) for the solvent, water is 0.515 deg.kg/mol.

m ?a. What is the molality of the drug?

b. If the M.wt of the drug is 185, what is the concentration in % w/w?

 $\Delta T_b = K_b m$   $m = \Delta T_b / K_b$   $= 0.103 / 0.515 = 0.2 \text{ mol kg}^{-1} = 0.0002 \text{ mol g}^{-1}$   $\% \text{ w/w} = \text{m} \times \text{M.wt}$   $= 0.0002 \times 185$  = 0.037 g/g = 3.7 g/100 g = 3.7 % w/w

1000

## **Colligative Properties of Solutions**

Depression of the Freezing Point

• Solute particles will lower the freezing point of the solution

- The freezing point of pure water is 0°C, but freezing point of aqueous solutions is lower
- Applications:
  - Anti-freeze solution (ethylene glycol)
  - Addition of salt to icy roads to melt the ice
- Solute interferes with ice crystal formation (ordered structure).
- Solute causing disorder (random state) preventing pure solvent to ice at 0°C and staying melted.

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## **Colligative Properties of Solutions**

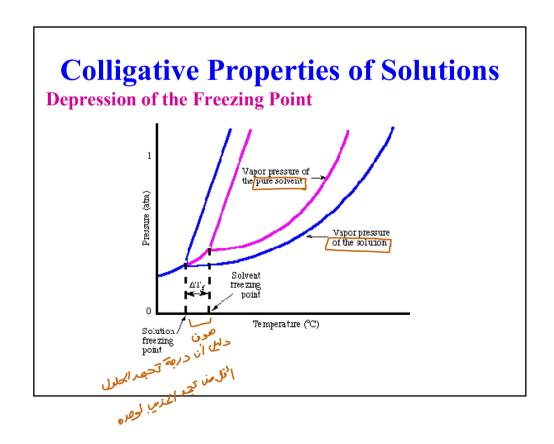
**Depression of the Freezing Point** 

molar Conc of colute

• The lowering of the freezing point of a solution is directly proportional to the molar concentration of the solute (i.e. number of particles in solution, (molecules or ions).

$$\Delta T_f = K_f m$$

- $\Delta T_f$ : Freezing point depression
- K<sub>f</sub>: Cryoscopic constant
- m: molality of solution



**Depression of the Freezing Point: Example** 

What is the freezing point of a solution comprising 3.42 g of sucrose (MW = 342) and 500 g of water? Take kf to be 1.86 (°C kg mol-1)

$$\Delta T_f = K_f m$$

m = molality of sucrose

$$= \frac{\text{no. of mole}}{\text{Wt}_{\text{solvent}}} = \frac{\text{Wt/MW}}{\text{Wt}_{\text{solvent}}} = \frac{3.42/342}{0.5} = 0.02 \text{ mol kg}^{-1}$$

$$\Delta T_f = K_f m = 1.86 \times 0.02 = 0.037 \, ^{\circ}\text{C}$$
 (i.e.  $\Delta T_f$ , freezing point depression)

Hence, the freezing point of this solution is -0.037 °C as (pure water  $T_f = 0$  °C)

This solution will stay melted at temp of 0 °C

0.01 = 0.02 = m

## **Colligative Properties of Solutions**

**Osmotic pressure** 

ضفذ للمنين فقط

- Whenever a solution is separated from a solvent by a membrane that is permeable only to solvent molecules (referred to as a <u>semipermeable membrane</u>), there is a passage of solvent across the membrane into the solution.
- This is the phenomenon of *osmosis*.
- If the solution is totally confined by a semipermeable membrane and immersed in the solvent, then a pressure differential develops across the membrane, which is referred to as the *osmotic pressure*.

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#### **Osmotic pressure**

- Osmotic pressure is determined by the total number of particles in the solution, regardless of chemical nature
- Van't Hoff recognized a proportionality between osmotic pressure concentration and temperature and suggested a relationship that corresponds to an ideal gas:

 $\pi v = n R T$   $\Rightarrow$  Van't Hoff equation:  $\pi = c R T$ 

 $\pi$ : Osmotic pressure in atmospheres

Pressure molarit

c: molarity of solution

R: Gas constsant (0.082 L.atm/mol.deg)

T: Absolute temperature

## **Colligative Properties of Solutions**

#### **Osmotic pressure**

• Morse and others have shown that when the concetration is expressed in molality rather than in molarity, the results compare more nearly with the experimental findings:

Morse equation:  $\pi = m R T$ 

 $\pi$ : Osmotic pressure in atmospheres

m: molality of solution

R: Gas constsant (0.082 L.atm/mol.deg)

T: Absolute temperature

Van't Hoff equation:  $\pi = c R T$ 

Morse equation:  $\pi = m R T$ 

مبالعَوانين هدول الحج الهيج بعض لمفن النبَرُهو .

## **Colligative Properties of Solutions**

#### Osmotic pressure: Example

One gram of sucrose, molecular weight 342, is dissolved in 1000 gmof solution at 25° C. What is the osmotic pressure in the solution?

#### **Answer**

Number of moles of sucrose = Wt/M.wt = 1/342 = 0.0029

Molality = number of moles/kg = 0.0029/1kg =  $2.9x10^{-3}$  m

 $\pi = mRT$ 

T = 273 + 25 = 298 K

 $\pi = 2.9 \times 10^{-3} \times 0.082 \times 298 = 7.08 \times 10^{-2} \text{ atm}$ 

## Molecular weight determination

• The colligative properties can be used to calculate molecular weights of non-electrolytes present as solutes.

Determination of molecular weight by boiling point elevation

$$\Delta T_b = K_b m$$
  $m = \frac{w_2/M_2}{w_1} \times 1000 = \frac{1000w_2}{w_1 M_2}$ 



 $W_2$  = weight of solute,  $W_1$  = weight of solvent,  $M_2$  = molecular weight of solute

## Molecular weight determination

#### **EXAMPLE 5-15**

#### Determination of the Molecular Weight of Sucrose by Boiling Point Elevation

A solution containing 10.0 g of sucrose dissolved in 100 g of water has a boiling point of  $100.149^{\circ}$ C. What is the molecular weight of sucrose? We write

$$M_2 = 0.51 \times \frac{1000 \times 10.0}{100 \times 0.149}$$
  
= 342 g/mole

## Molecular weight determination

Determination of molecular weight by freezing point depression

$$M_2 = K_f \frac{1000 w_2}{\Delta T_f w_1}$$

#### EXAMPLE 5-16

#### Calculating Molecular Weight Using Freezing Point Depression

The freezing point depression of a solution of 2.000 g of 1,3-dinitrobenzene in 100.0 g of benzene was determined by the equilibrium method and was found to be 0.6095°C. Calculate the molecular weight of 1,3-dinitrobenzene. We write

$$M_2 = 5.12 \times \frac{1000 \times 2.000}{0.6095 \times 100.0} = 168.0 \text{ g/mole}$$

## **Solutions of electrolytes**

## **Solutions of electrolytes**

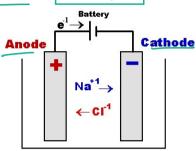
- An electrolyte is a substance that ionizes when dissolved in suitable ionizing solvents such as water.

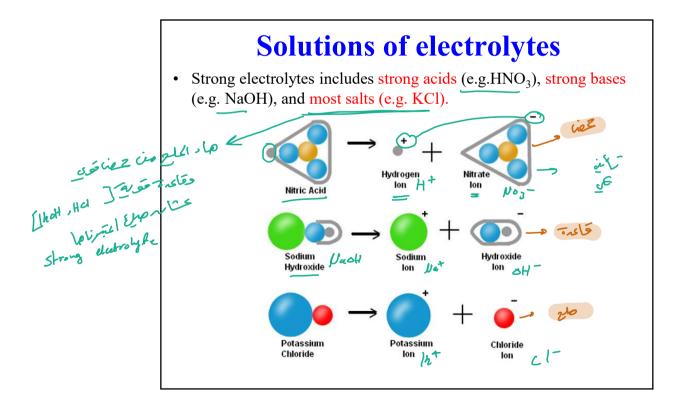
  This includes most soluble salts, acids, and bases.
- Electrolytes in solution have the capacity to conduct electricity through a process known as electrolysis
- Electrolytes can be classified as strong electrolytes and weak electrolytes. electrolytes.
- Strong electrolytes ionize completely (~100%), while weak electrolytes ionize only partially (1–10%).



### **Solutions of electrolytes**

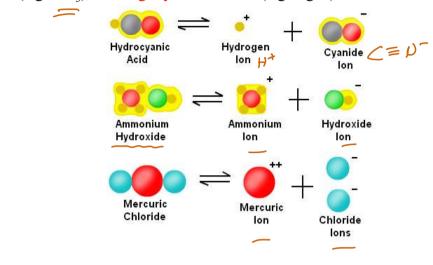
• Electrolytes in solution have the capability to conduct electricity through a process known as electrolysis





### **Solutions of electrolytes**

• Weak electrolytes include weak acids (e.g. CH<sub>3</sub>COOH), weak bases (e.g. NH<sub>3</sub>), and slightly soluble salts (e.g. AgCl).



### **Colligative properties**

• Van't Hoff observed that the osmotic pressure  $(\pi)$  of dilute solutions of nonelectrolytes such as sucrose and urea, can be expressed by the equation:

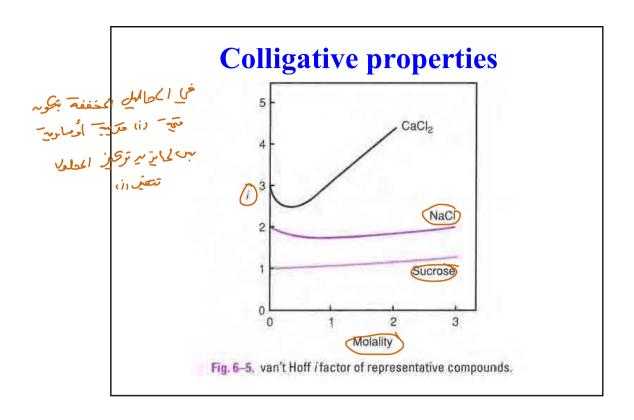
$$\pi = RTc$$

- R: Gas constant, T: absolute temperature, c: concentration in mole/L
- However; he found that solutions of electrolytes gave osmotic pressures approximately two, three, and more times larger than expected from this equation.
- Van't Hoff Introduced a correction factor (i) to account for the irrational behavior of ionic solutions, he wrote:

$$\pi = iRTc$$

• The (i) factor approximately equals the number of ions formed upon dissociation (e.g. 2 for NaCl, 3 for CaCl<sub>2</sub>, and 4 for FeCl<sub>3</sub>).





### **Colligative properties**

**Example:** 

What's the osmotic pressure of a 2.0 m solution of sodium chloride at 20°C? \_\_ /h

Answer: the i factor for a 2 m solution of sodium chloride as observed in the figure is about 1.9

$$\pi = iRTm$$

= 1.9\*0.082\*293\*2= 91.3 atm

• تكله لرح بتفريع عبه إن شاء الله بفير عمله الله وبرعاته والسلام عله عمر معه الله وبرعاته