Solutions and Their Properties

LECTURE 1

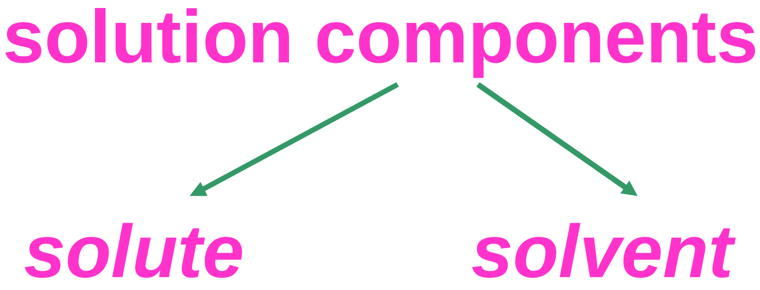
1. The Solution Formation Process. Properties of water
2. Thermodynamics of the Process of Solution Formation
3. The Ideal and Non-ideal Solutions
4. Colligative Properties of Solutions

1.The Solution Formation Process

- ***Solution*** is a homogeneous system consisting of two or more components
  - All biological fluids (blood, plasma, lymph) are solutions

Composition of an solution

- Any solution consists of a dissolved substance called ***the solute*** and the medium in which the solute is uniformly distributed as molecules or ions, called ***the solvent***



solution components

solute ***solvent***

- Solution1: **3% C_2H_5OH + 97% H_2O**
- Solution2: **97% C_2H_5OH + 3% H_2O**

- **Solvents** can be polar (H_2O, concentrated H_2SO_4 ,alcohols) and non-polar (benzene, acetone,CCl_4)
- **Solutes** can be polar (salts) and non-polar (iodine I_2)

Polar solvent + polar solute

Non-polar solvent + non-polar solute

Hydration

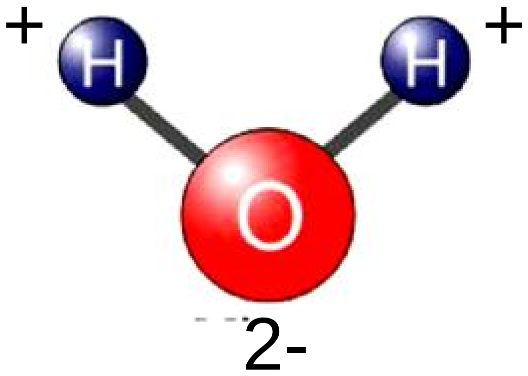
- When solutes are dissolved, they become ***solvated*** if solvent molecules are bonded firmly to solute molecules or ions
- If water is the solvent, this is called more specifically ***hydration***

SOLUTION

solute **+** ***solvent*** **=** ***solvated particles***

Solvent H_2O

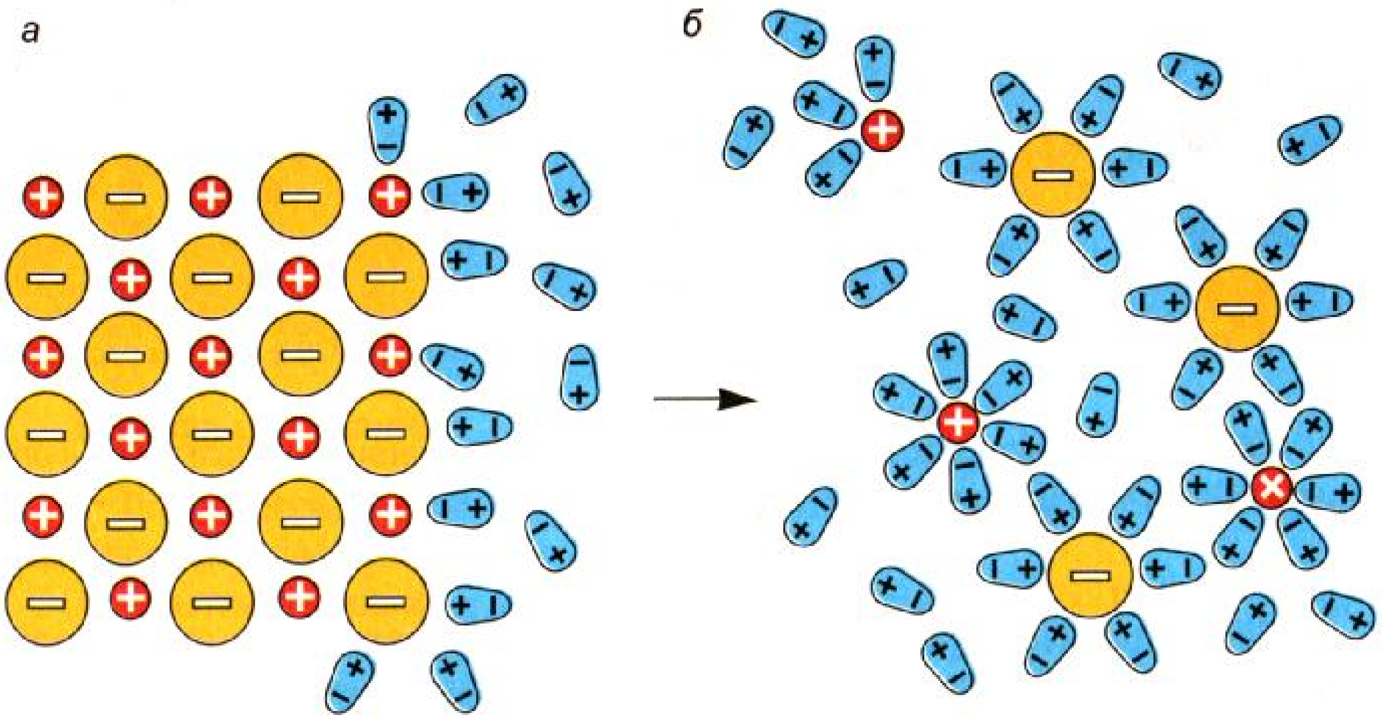
- Water has one of the highest polarities of all liquids



dipole

- This property makes water an excellent solvent for ionic compounds

The dissolution process of ionic compounds



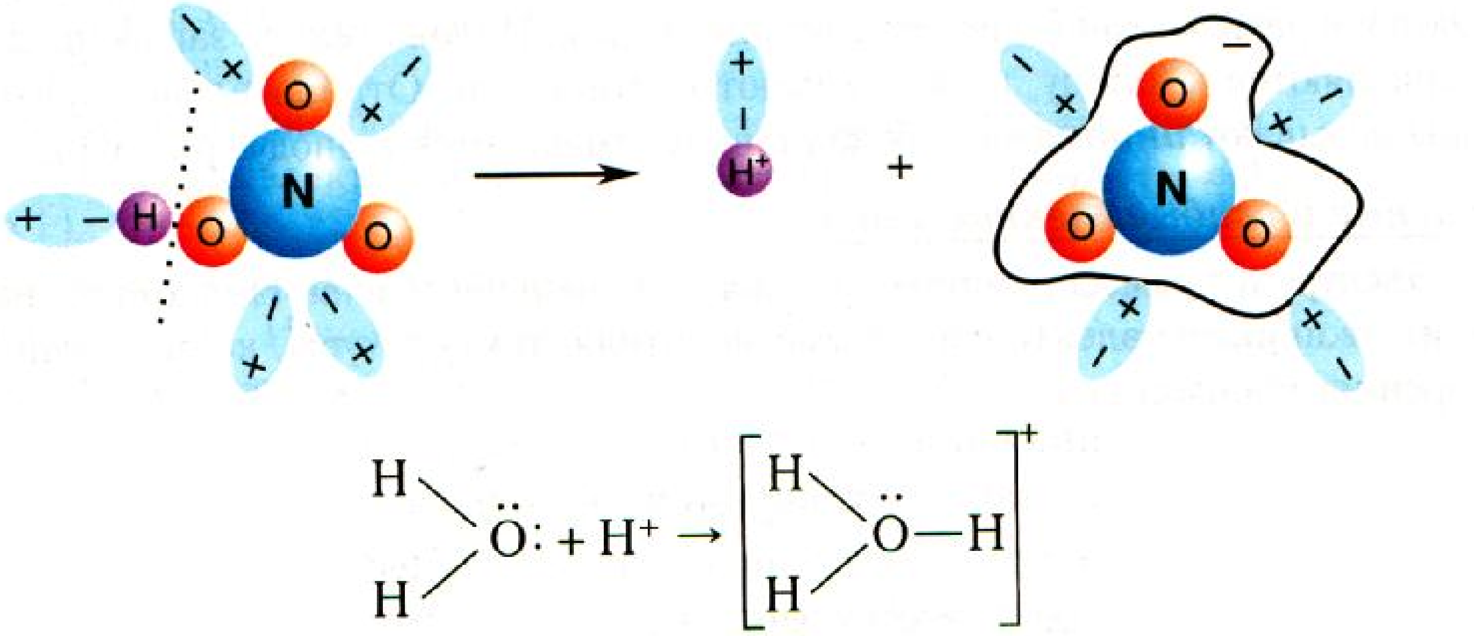
$$NaCl_{(solid)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

Ion-dipole forces

- Salt (NaCl) dissolves in water because strong ion-dipole forces lead to strong ion hydration and help to break down the cation-anion attraction in the crystal lattice

Hydrogen bonding

$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$



The solution process of HNO_3

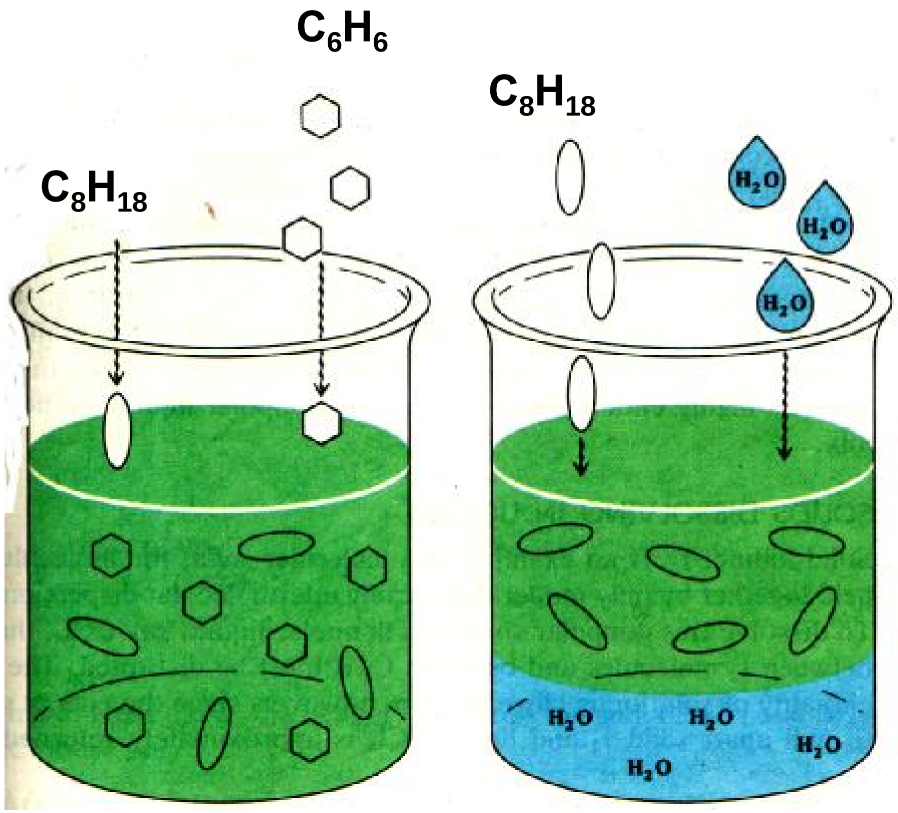
Hydrogen bonding

- A sugar ($C_{12}H_{22}O_{11}$) is soluble in water
- Hydrogen bonding between sugar and water is strong enough that energy is supplied to disrupt the sugar/ sugar and water/ water interactions
- Sugar is not soluble in nonpolar liquids

Immiscible liquids

- If two liquids mix to a considerable degree to form a solution they are said to be mixable

- In contrast, immiscible liquids will not mix to form a solution; they will exist in contact with each other as separate layers



- The nonpolar liquids octane (C_8H_{18}) and benzene (C_6H_6) are miscible; they mix in all proportions to form a homogeneous solution

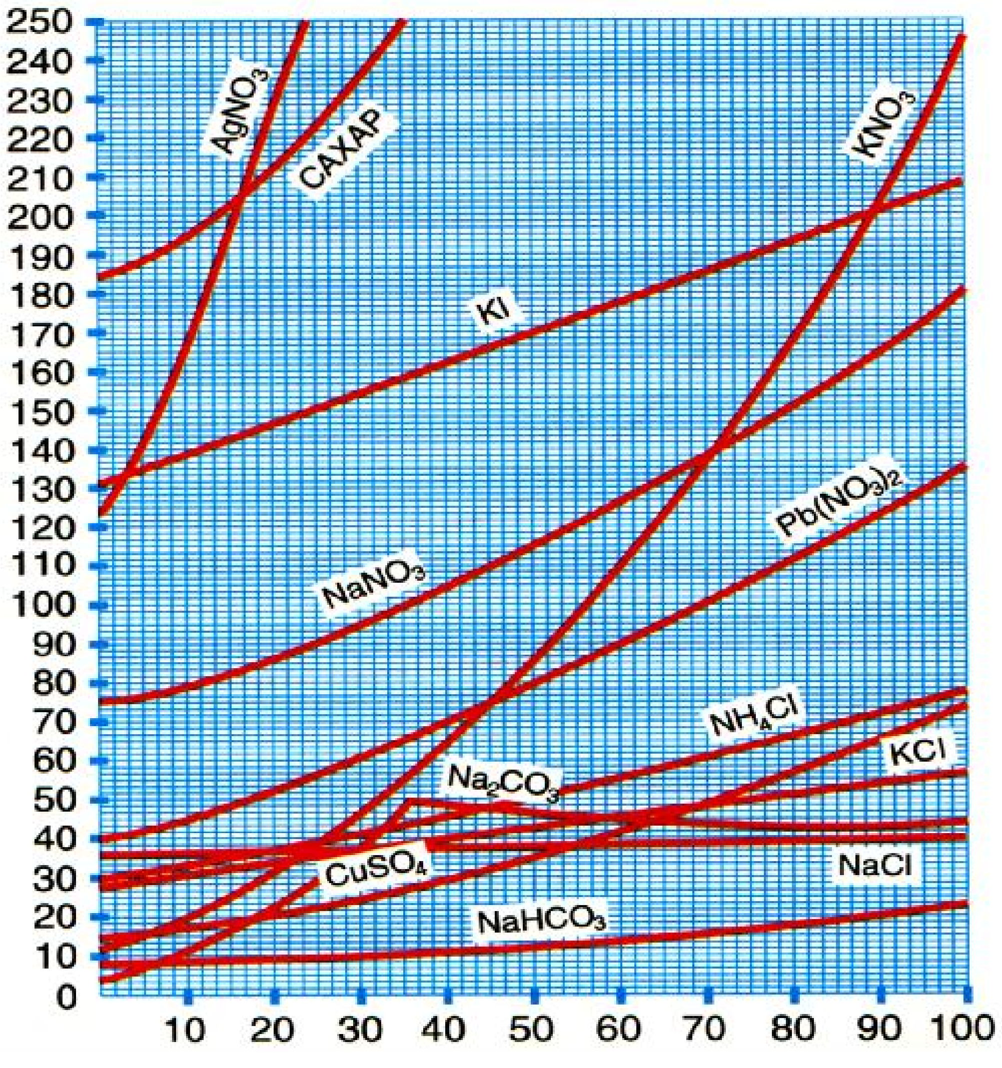
- On the other hand, polar water and nonpolar octane are immiscible

Solubility

- ***Solubility*** is the maximum amount of material that will dissolve in a given amount of solvent at a given temperature to produce a stable solution

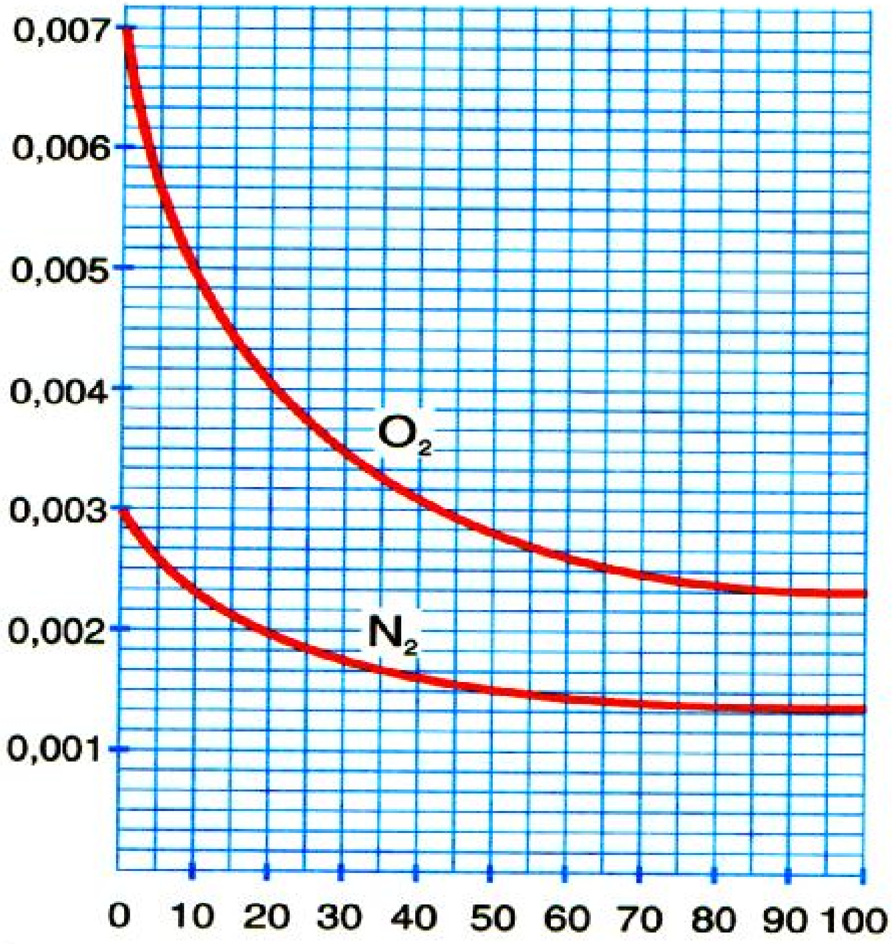
- According to the solubility amount the solutes are divided into ***soluble, unsoluble and low-soluble***

Solubiliti, g in 100g H_2O



t, C^0

Solubiliti, g in 100g H_2O



t, C^0

Properties of water

- Water is the most important solvent in nature and the most abundant substance in the world
- The unique physicochemical properties of water are responsible for its numerous biological functions in a human body

- Due to its very high **heat capacity** water regulates temperature of a cell from the heat generated by metabolic processes
- Due to its high **molar heat of vaporization** water protects a human body from overheating

- The human body is made mainly of water (**2/3** of the body mass)
  - **m (H_2O)~ 60 %** of total body mass
    - **70 кg - 45 L** of water

H_2O in our organism

H_2O

70%
intocellular fluid

30%
extracellular fluid

particles	intocellular fluid In mmol/L	extracellular fluid In mmol/L
Na^+	10	**140**
K^+	**140**	4
Ca^{2+}	0,1	2,5
Mg^{2+}	30	1,5
$C1^-$	4	**100**
HCO_3^-	10	27
PO_4^{3-}	60	2
glucose	0,1	5,5
protein	0.016 g /*L*	*0.002* g /*L*

Extracellular fluid

(30%)

Extra-vessel

(7%)

blood plasma

protein

0.016 g /L

Tissue extra-cellular

(23 %)

protein

0.002 g /L

Different organs and tissues contain variable amount of water

- Brain contains 75% of water and even moderate dehydration or lack of water can cause headaches;
- heart and muscles - 75% of water;
- bones - 22% of water;
- lungs and liver - 86% of water;
- kidneys and blood - 83% of water.

- The loss of 2/3 volume of extracellular fluid may cause death
- The excess of water is also dangerous; it may result in cell swelling and edema

2.*Thermodynamics of the Process of Solution Formation*

- When a solute is dissolved in a solvent, we mean that ***the attractive forces between solute and solvent particles are great*** enough to overcome the attractive forces within the pure solute and solvent

Heat of the dissolution process

- ***Heat of a dissolution process***

$$\Delta H_{\text{dissolution}}$$

is defined as a heat amount absorbed or released when one mole of a solute is dissolved in the endless amount of a solvent under standard conditions

- A dissolving is ***a physicochemical process*** composed of three main steps

Dissolving steps

- 1) A destruction of a solute’s crystal lattice which proceeds with heat absorption

$$\Delta H_{\text{phase transformation}} > 0$$

- 2) A formation of solvates or hydrates complexes which runs with heat releasing

$$\Delta H_{\text{hydration}} < 0$$

- 3) A diffusion of solute particles throughout a solution

$$\Delta H_{\text{diffusion}} \approx 0$$

- Thus, there are two variants:

1) if $\Delta H_{\text{phase transformation}} > \Delta H_{\text{hydration}}$, then $\Delta H_{\text{dissolution}} > 0$ and the process *is endothermic*
2) if $\Delta H_{\text{phase transformation}} < \Delta H_{\text{hydration}}$, then $\Delta H_{\text{dissolution}} < 0$ and the process *is exothermic*

- For NaCl the heat or enthalpy of solution ($\Delta H_{solution}$) can be estimated from the lattice energy of NaCl (ΔH_1) and the heat of ion hydration to form aqueous hydrated ions (ΔH_2)

- According to Hess's law, the heat of solution is the sum of ΔH_1 and ΔH_2

- For NaCl there are:

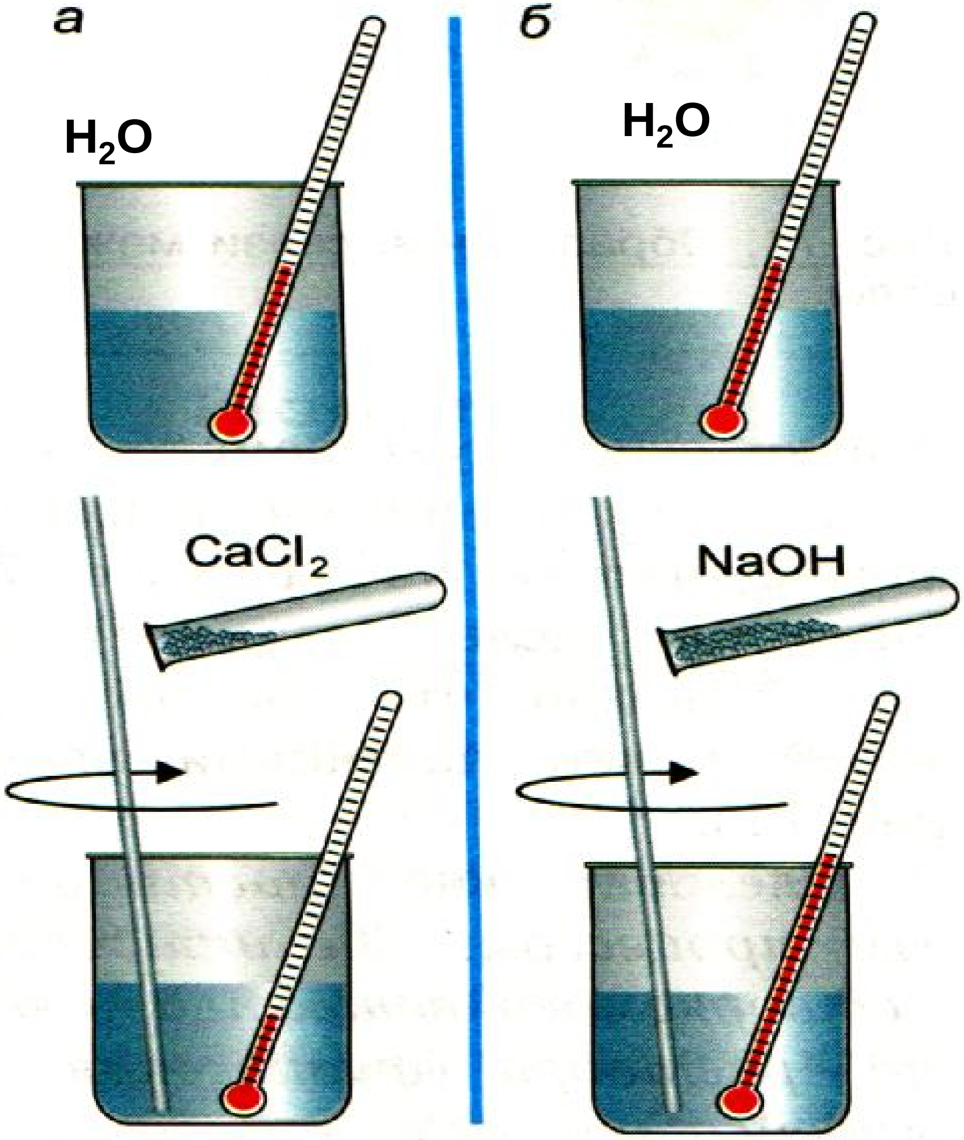
ΔH solution = 774kJ/mole + (-760 kJ/mole) = +14 kJ/mole

the dissolution process is only slightly endothermic

- For NaCl the energy required to break down the lattice (lattice energy) is smaller the energy given off in case the ions are hydrated (enthalpy of hydration)

Dissolving of solids

- Dissolving of most solids is endothermic **($\Delta H_{dissolution} > 0$)** since the amount of heat absorbed in the first step exceeds the amount of heat released in the second step of a process


а
H_2O
$CaCl_2$
б
H_2O
NaOH

- If the NaOH is dissolved

  $DH_{\text{phase transformation}} << DH_{\text{hydration}}$

- NaOH is transformed from the solid state to the liquid one
- $\Delta H_{\text{phase transformation}}$ is greater than zero,

  $DH_{\text{phase transformation}} > 0$ (the heat is absorbed)
- The ions in solution form hydrates and this process is always exothermic, i.e. **$DH_{\text{hydration}} < 0$**

  $DH_{\text{ dissolution}}$ NaOH **< 0,** exothermic

Dissolving of gases

- Dissolving of most gases is exothermic

$$\Delta H_{dissolution} < 0$$

since gases do not form crystals under normal conditions

Free energy Δ G

- The dissolution is a spontaneous process and free energy change ΔG is less than zero

$$\Delta G < 0$$

- The quantity and the sign of ΔG is determined by entropy and enthalpy factors

$$\Delta G = \Delta H - T\Delta S$$

$\Delta S_{\text{dissolution}}$

- The process of dissolution (endothermic or exothermic) depends on the entropy factor

$$\Delta S_{\text{dissolution}} = \Delta S_{\text{phase transformation}} + \Delta S_{\text{hydration}}$$

- Because $\Delta S_{\text{phase transformation}} > 0$

  solid substance transforms into liquid,

  $\Delta S_{\text{hydration}} < 0$

  the disorder is diminished in system

  $\Delta S_{\text{phase transformation}} >> \Delta S_{\text{hydration}}$

- ΔS of dissolution is always greater than zero

  ΔS dissolution > 0

3.The Ideal and Non-ideal Solutions

- In thermodynamics all solutions are divided in two groups: ideal and non-ideal (or real) solutions
- There is no interaction between molecules of a solute and molecules of a solvent in an ideal solution

Mixing of two substances results in an ideal solution only when:

- 1) ΔH mixing is zero, i.e. no heat is absorbed or released during dissolution:

  $$\Delta H = 0$$

- 2) ΔV mixing is zero, i.e. the total volume of the solution is equal to the sum of the volumes of the pure components mixed to form a solution:

  $$\Delta V = 0$$

Ideal solution

- Liquid heptane and hexane form an ideal solution because

the interaction between a hexane molecule and another hexane molecule

is the same as the interaction between a heptane molecule and another heptane molecule

or between a hexane molecule and a heptane molecule

- There are no such solutions in nature
- Non-ideal solutions are formed with a change in volume and enthalpy
- The ideal solutions are close to dilute solutions

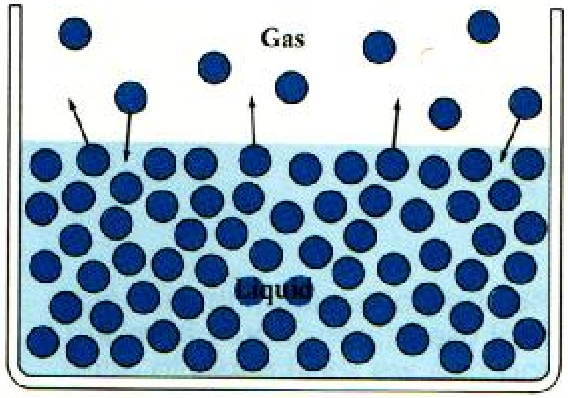
4. Colligative Properties of Solutions

- All solutions have definite physical properties which depend on the nature of a solute, solvent and concentration: density, viscosity, conductivity

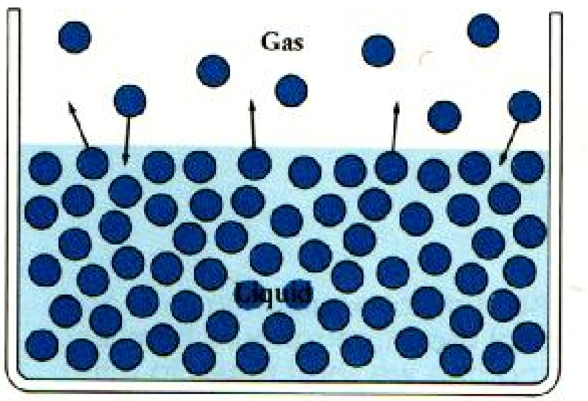
- But solutions have a number of properties quantitative expression of which depends only on ***the number of solute particles in a solution*** and not on the nature of the solute

- They are:
  1. Depression of the vapour pressure of a solvent over a solution;
  2. Elevation of the boiling point of a solution;
  3. Depression of the freezing point of a solution;
  4. Osmos and the osmotic pressure of the solution

1. Depression of the vapour pressure of a solvent over a solution



- In a liquid, its molecules are constantly moving in a random manner
- They collide with each other and walls of the container
- This results in change in their kinetic energies
- Some molecules acquire low energies and others have high energies
- Those having high kinetic energies have a tendency to escape from the liquid surface in the form of vapour



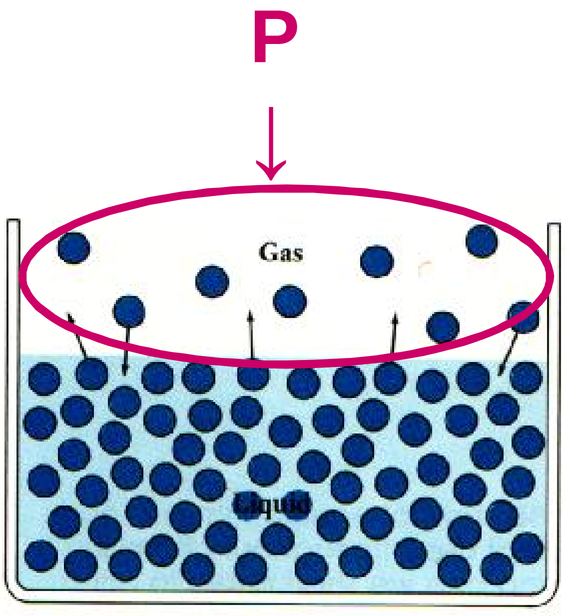
- The process of a passage of some molecules from a liquid phase in the vapour – ***the process of an evaporation***

- The molecules in the vapour state over the liquid surface are also in constant and random motion
- Some of these molecules dissipate their energies in collisions and fall into the liquid - ***the process of a condensation***

- At equilibrium, these two processes just balance each other: the rate of the evaporation process is equal to the rate of the condensation process

- Therefore, ***a dynamic equilibrium*** exists between the molecules in the vapour and those in the liquid

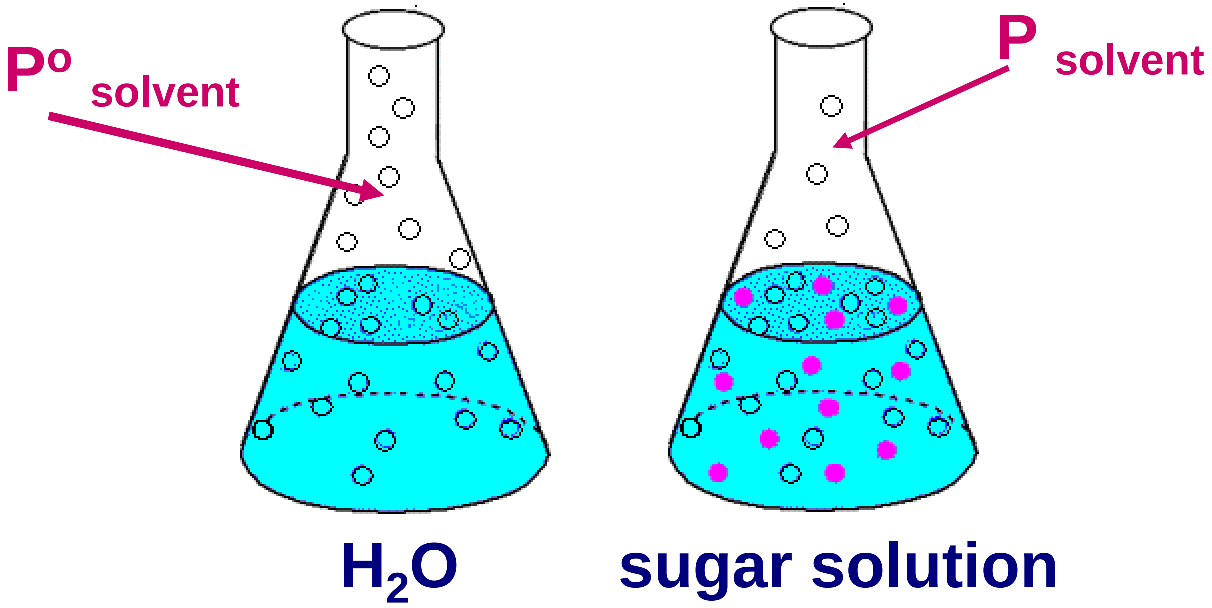
- ***The vapour pressure of a liquid*** is the pressure exerted by its vapour over the liquid surface



The first Raoult's law

- The vapour pressure of the solvent ***over the solution*** **($P_{solvent}$)** containing the nonvolatile solute is always smaller than that ***over the pure solvent*** **($P^o_{solvent}$)**

$$P^o_{solvent} > P_{solvent}$$



$$P^{o}_{solvent} > P_{solvent}$$

- At the surface of a solution there are molecules of water as well as sugar molecules
- The vapor pressure over the solution is different from that over pure water

- The vapor pressure of the solvent over the solution, P_{solvent}, will be proportional to the relative number of solvent molecules in a solution, that is, to their mole fraction, c_{solvent}

$$P_{\text{solvent}} = P^{o}_{\text{solvent}} \cdot c_{\text{solvent}}$$

- The vapor pressure lowering, $\Delta P_{solvent}$, is given by:

$$\Delta P_{solvent} = P^{\circ}_{solvent} - P_{solvent}$$

- Substituting $P^{o}_{solvent} \cdot \chi_{solvent}$ for $P_{solvent}$, we obtain

$$\Delta P_{solvent} = P^{\circ}_{solvent} - (P^{o}_{solvent} \cdot \chi_{solvent})$$

or $$\Delta P_{solvent} = P^{\circ}_{solvent} \cdot (1 - \chi_{solvent})$$

- The sum of the mole fractions of the solvent and the solute must be equal to 1: $\chi_{solvent} + \chi_{solute} = 1$

- Therefore, $1 - \chi_{solvent} = \chi_{solute}$

- The equation for $\Delta P_{solvent}$ can be rewritten as

$$\Delta P_{solvent} = P^{\circ}_{solvent} \cdot \chi_{solute}$$

- **Problem**. At 315К the pressure of saturated vapor above water is 8,2 kPa. How will the vapor pressure lower at the given temperature if we dissolve 36 g of glucose $C_6H_{12}O_6$ in 540 g of water?

- *We have:*

T = 315K

$P°_{solvent}$ = 8,2 kPa

m(H_2O) = 540 g

m($C_6H_{12}O_6$) = 36 g

- The lowering of the pressure of saturated vapour of the solvent above the solution is calculated using the formula: $\Delta P_{solvent} = P°_{solvent} - P_{solvent}$

where:

$P°_{solvent}$ – the pressure of saturated vapour above the solvent

$P_{solvent}$ – the pressure of saturated vapour above the solution

- The lowering of the pressure of saturated vapour of the solvent above the solution is equal to the pressure of saturated vapour above the solvent multiplied by the mole fraction of the solute:

$$\Delta P_{solvent} = P^{\circ}_{solvent} \cdot \chi_{solute}$$

$$\chi_{sub} = \frac{n_{sub}}{n_{sub} + n_{solv}}$$

$$n_{solv} = \frac{m(H_2O)}{M(H_2O)} = \frac{540}{18} = 30 \text{ mole}$$

$$n_{sub.} = \frac{m(C_6H_{12}O_6)}{M(C_6H_{12}O_6)} = \frac{0,2}{30,2} = \frac{36}{180} = 0,2 \text{ mole}$$

$$\chi_{sub} = \frac{n_{sub}}{(n_{sub} + n_{solv})} = 0,006623$$

- $\Delta P = P°_{solvent} \cdot c_{solute}$

$= 0{,}0066232 \times 8{,}2 = 0{,}054$ кPa

***Answer:** 0,054 kPa or 54 Pa*

THE SECOND RAOULT'S LAW

- The ebullioscopic Raoult's law:

  the boiling-point of the solution containing the nonvolatile solute is always higher than that of the pure solvent

- ***The boiling-point of a liquid*** is a temperature under which its vapor pressure equals the external atmospheric pressure

$$\Delta T_b = E\ C_m$$

where $\Delta\ T_b$ is boiling-point elevation

$\Delta\ T_b = T_2 - T_1$, where T_1 and T_2 are boiling-points of a solvent and a solution respectively,

C_m – molality, mol/kg,

E– molar boiling-point elevation constant

(0.52 for water)

- **Problem**. How many grams of glucose should be dissolved in 270 g of water for increasing the boiling temperature by one degree?

- *We have:*

$m(H_2O) = 270\ g = 0,27\ kg$

$\Delta T_{boiling} = 1^o$

$E(H_2O)=0,52(kg \cdot degree/mol)$

$M(C_6H_{12}O_6)=180\ g/mol$

- $\Delta T_{boiling} = E\,(H_2O) \cdot C_m$

where:

$E\,(H_2O)$ – ebullioscopic constant of water,

$\Delta T_{boiling}$ – the rise in the boiling temperature of the solution compared to a pure solvent

C_m – molality (mol/kg)

$$C_m = n\ (C_6H_{12}O_6)\ /\ m\ (H_2O)$$

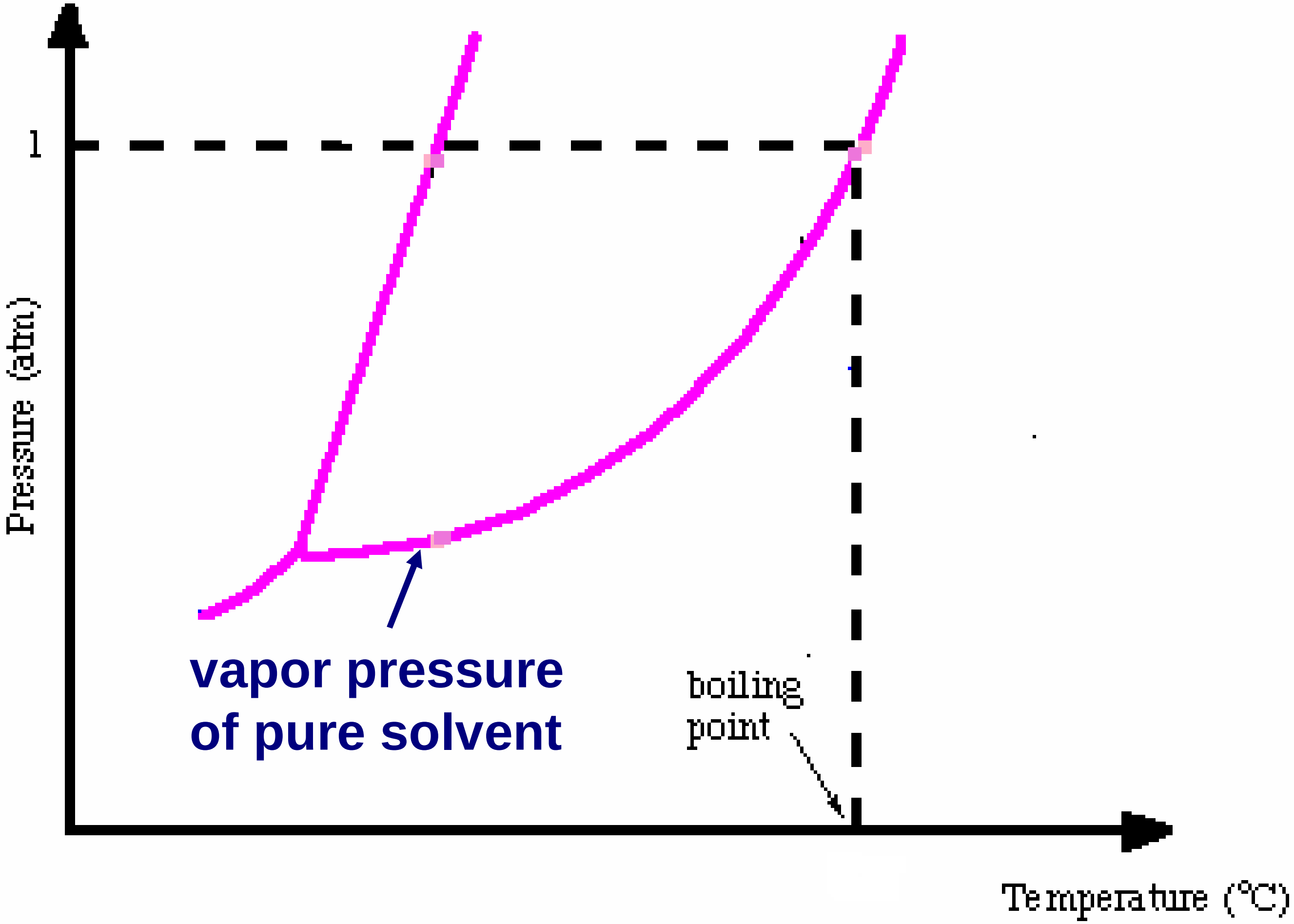
$$n\ (C_6H_{12}O_6) = m\ (C_6H_{12}O_6)\ /\ M\ (C_6H_{12}O_6)$$

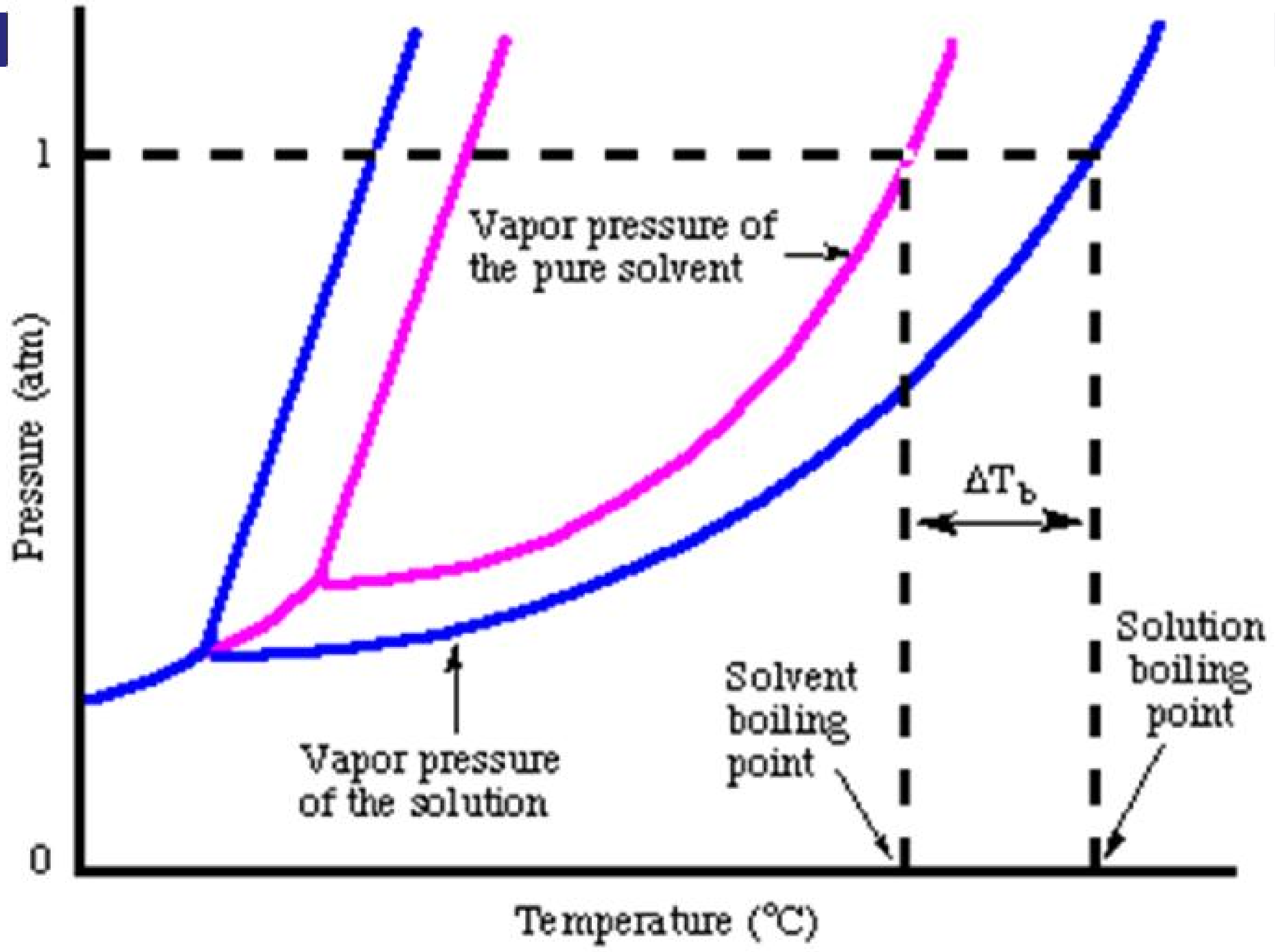
$$m(C_6H_{12}O_6) = \frac{\Delta T_b \cdot m(H_2O) \cdot M(C_6H_{12}O_6)}{E(H_2O)}$$

$$m(C_6H_{12}O_6) = \frac{1 \times 0{,}27 \times 180}{0{,}52} = 93{,}54\ \mathrm{g}$$

- The boiling point of elevation phenomena can be understood by studying ***phase diagrams*** of pure solvent and a solution

Phase diagrams of pure solvent





- At 1 atm the boiling point of a solution lie at the intersection point of the blue curve and the horizontal line at 1 atm
- We can use this graph to determine ΔT_b

- *The cryoscopic Raoult’s law*:

the freezing-point of the solution containing the nonvolatile solute is always lower than that of the pure solvent

- ***The freezing-point of a liquid*** is a temperature under which its vapor pressure equals the vapor pressure of solid solvents

$$\Delta T_f = К\ C_m$$

- where ΔT_f is freezing point depression,

  $\Delta T_f = T_1 - T_2,$

  T_1 and T_2 are freezing-points of a solvent and a solution respectively,

  K – the molar freezing-point depression constant (1.86 for water)

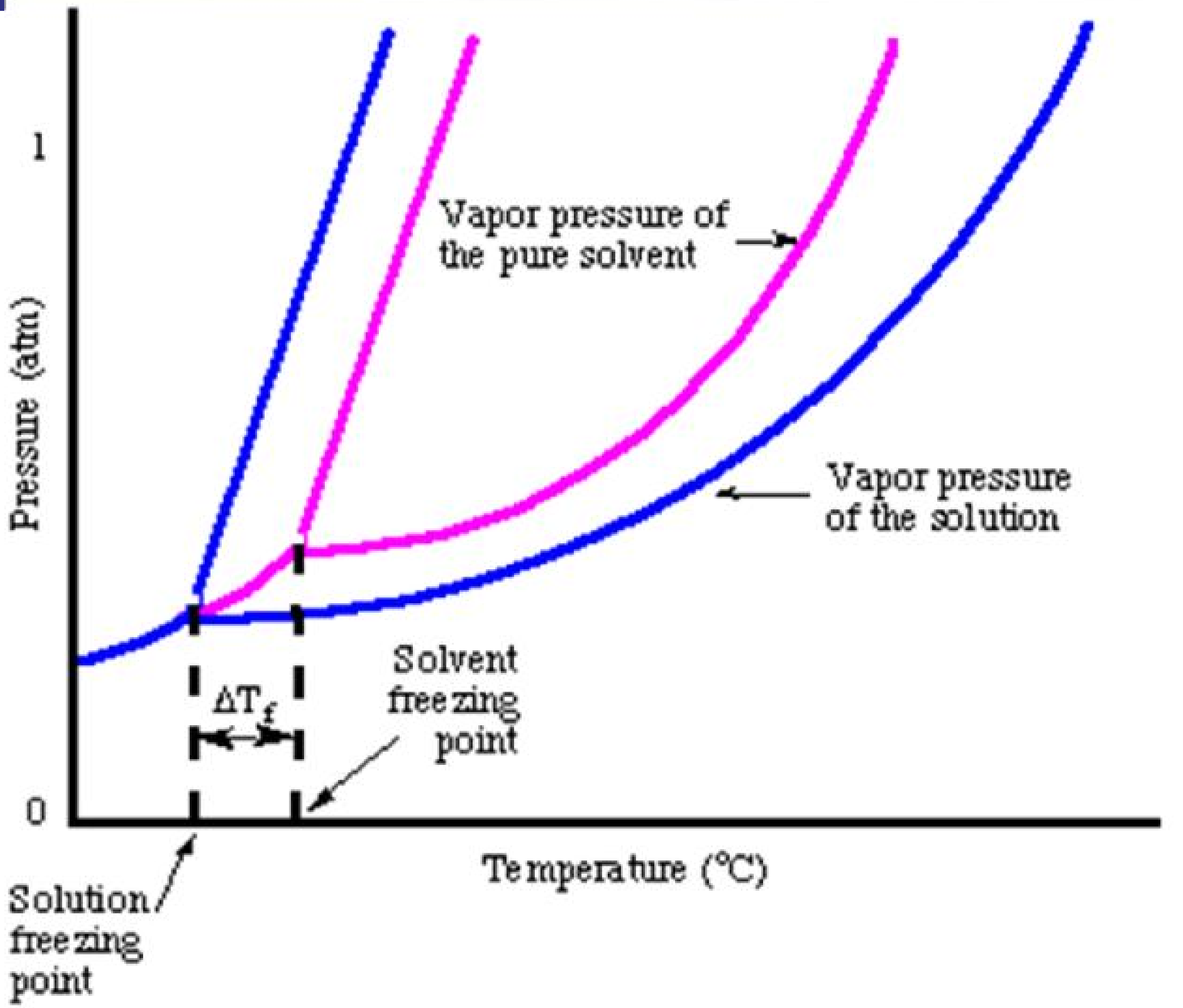
- How many grams of glucose should be dissolved in 270 g of water for decreasing of the freezing temperature by one degree?

- $\Delta T_{freez} = C_m \cdot K(H_2O)$
- $C_m = n\,(C_6H_{12}O_6)\;/\;m\,(H_2O)$
- $n\,(C_6H_{12}O_6) = m\,(C_6H_{12}O_6)\;/\;M\,(C_6H_{12}O_6)$

Hence:

$$\Delta t_{freez.} = \frac{K(H_2O) \cdot m(C_6H_{12}O_6)}{m(H_2O) \cdot M(C_6H_{12}O_6)}$$

$$\mathbf{m(C_6H_{12}O_6) =} \frac{\Delta t_{freez} \cdot m(H_2O) \cdot M(C_6H_{12}O_6)}{K(H_2O)} = \frac{1 \cdot 0{,}27 \cdot 180}{1{,}86} = \mathbf{26{,}15\ g.}$$



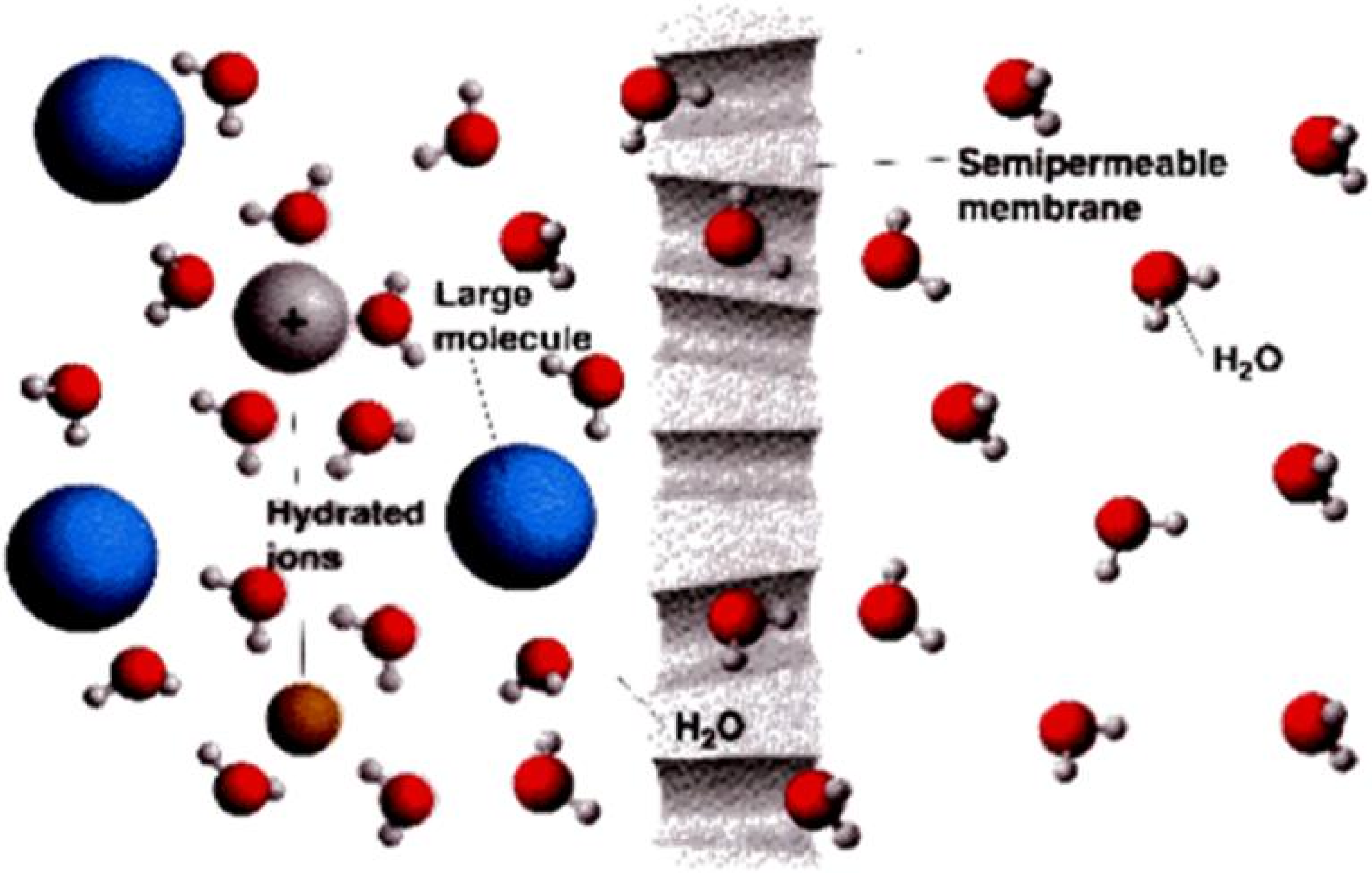
We can use this graph to determine ΔT_f

Osmosis. Osmotic pressure

- ***Osmosis*** is a reversible process of water diffusion through a semipermeable membrane from pure water to a solution, or from a dilute solution into a more concentrated one

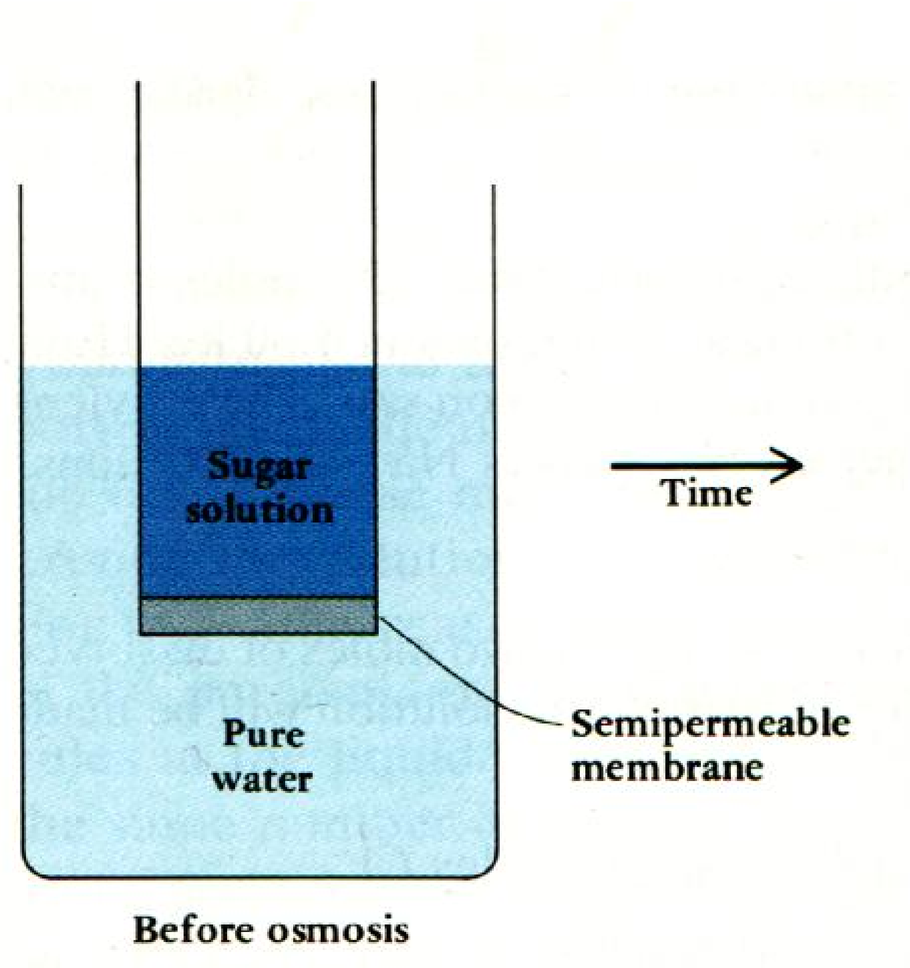
- ***A semipermeable membrane*** – is a thin sheet of material (such as animal or vegetable tissue or cellophane) through which only certain types of molecules may pass

A semipermeable membrane

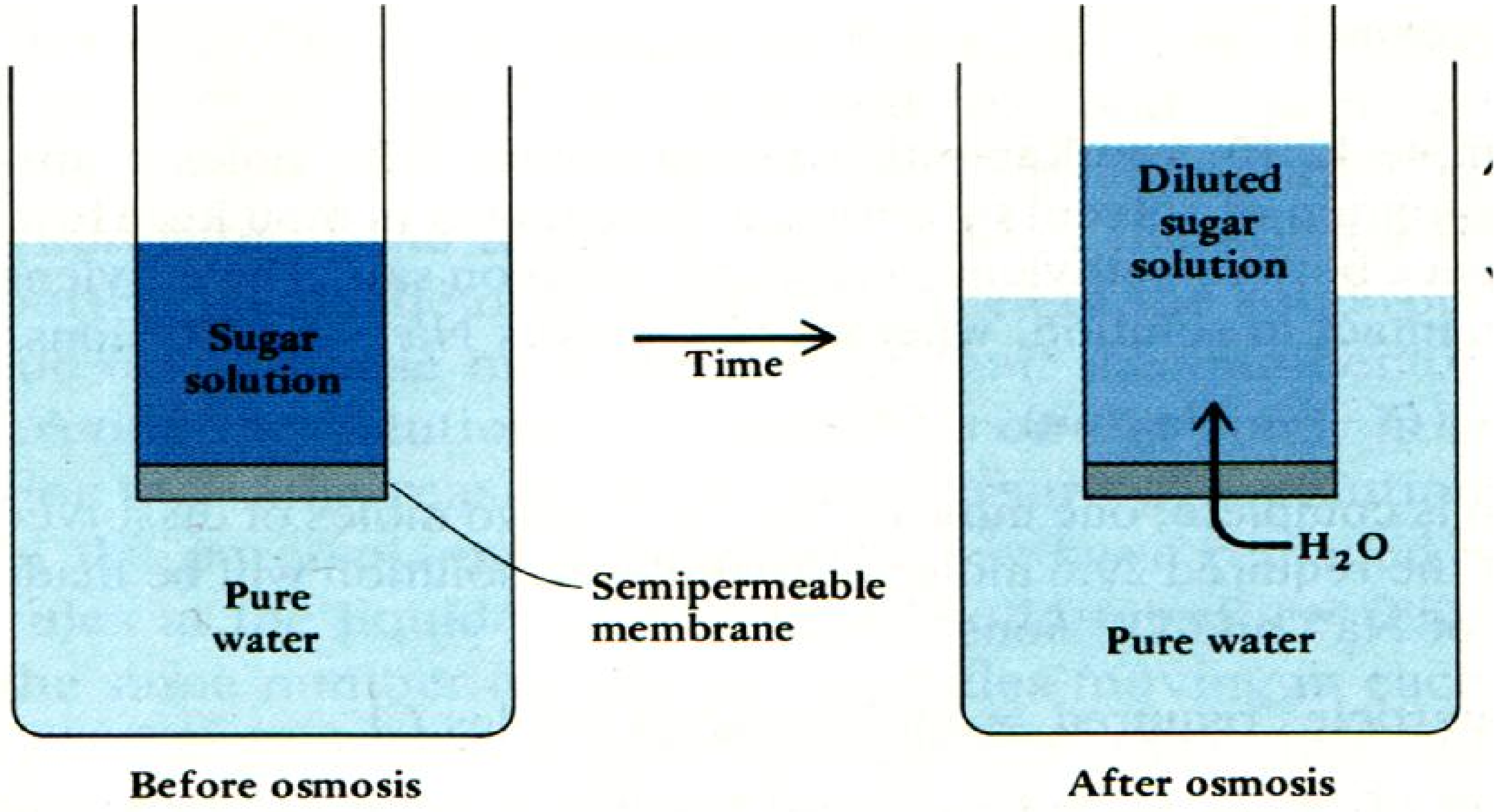


Water molecules can pass, but larger molecules cannot

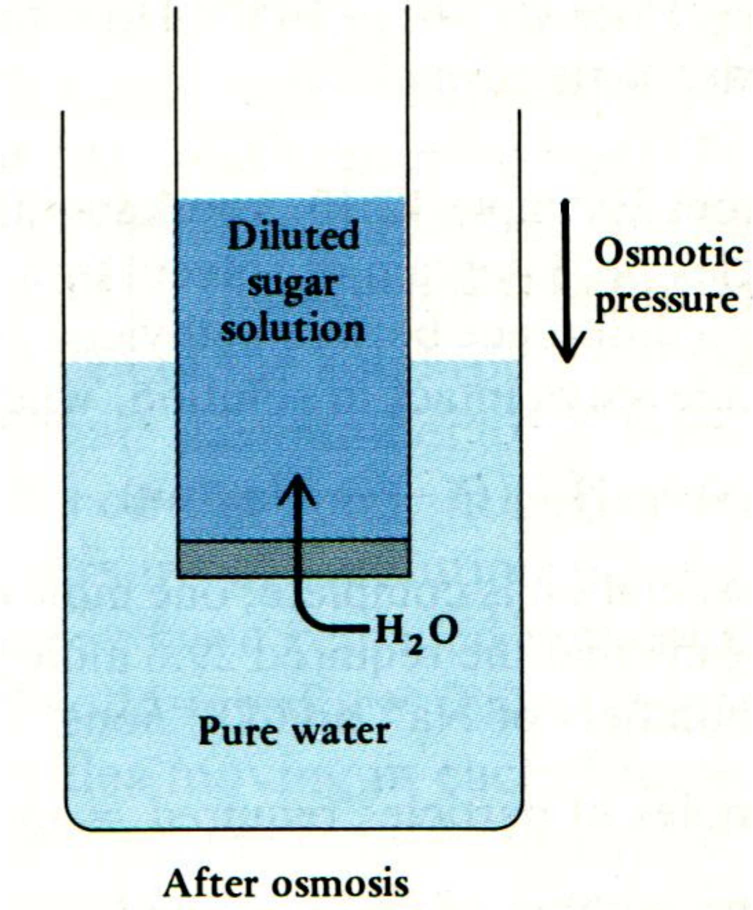
The process of osmosis



- At the beginning of the experiment, a tube of aqueous sugar solution is placed in a beaker of pure water
- The solution and pure water are separated by a membrane permeable only to water molecules and not sugar molecules



- With time, water flows from a region of low solute concentration (pure water) to one of higher solute concentration (the sugar solution)



- Flow will continue until ***the pressure*** of water flowing into the solution is countered by ***the pressure of the column of solution*** in the tube above the water level in the beaker

- The pressure exerted by mass of solution will counterbalance the pressure of the water moving through the membrane from the pure-water side

- ***Osmosis*** is driven by a difference in a solute concentration to the both sides of the membrane

- Solvent molecules moved through the semipermeable membrane from a region of the lower solute concentration to a region of higher solute concentration in the experiment

- ***Osmotic pressure*** is the pressure that should be applied to the solvent to prevent osmosis **(Posm , kPa)**

- Osmotic pressure may be calculated by *the Van't Hoff's equations*:

$$P_{osm} = RTC$$

- where **R** is the gas constant (8.314 J/mol K), **T** is the absolute temperature, **C** is molarity of the solution

- ***Osmosis*** is an important phenomenon, since it is one the factors controlling the flow of material in and out of living cells

- ***Osmosis*** plays a key role in such biological processes as absorption of nutrients, elimination of metabolism waste products, transportation of water

- Normal osmotic pressure of blood plasma is 740-780 kPa

- Osmotic homeostasis is maintained by work of kidneys, lungs and skin

- Mainly electrolytes are responsible for high osmotic pressure of blood plasma and other biological fluids

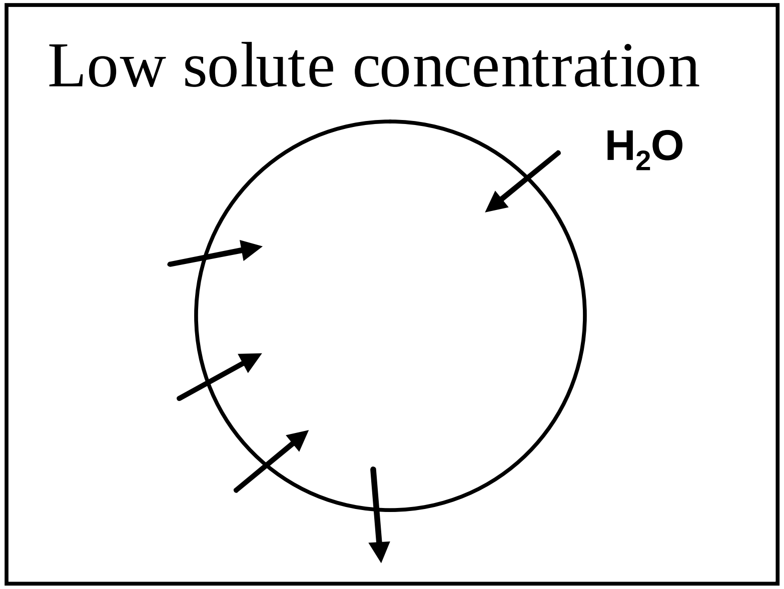
- Molecules of proteins, which are unable to pass through cell membranes, also contribute osmotic pressure of blood plasma, but their ***oncotic pressure*** is rather low (3-4 kPa)

- Solutions which are used in medicine for intravenous injections are isotonic to blood plasma or have the same osmotic pressure as blood
- They are:

(a) 0.85% - 0.9% by mass **NaCl** solution,0.15mol/L

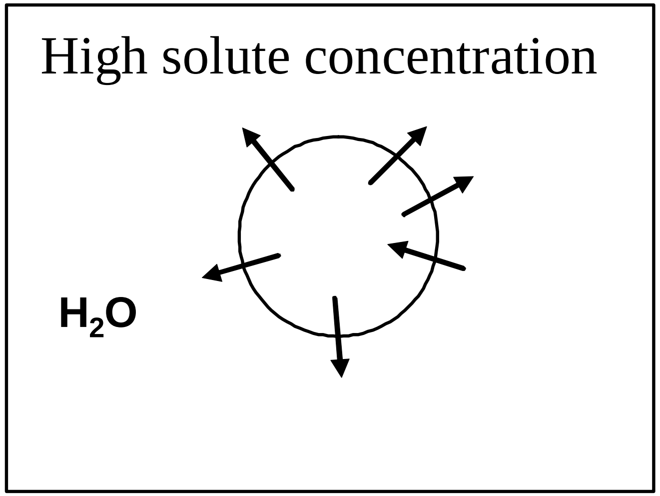
(b) 4.5% - 5% by mass glucose $\mathbf{C_6H_{12}O_6}$ solution,0.3mol/L

- When a red blood cell is placed in **a hypotonic solution (P_{osm} < 760 kPa)** water tends to move into the cell



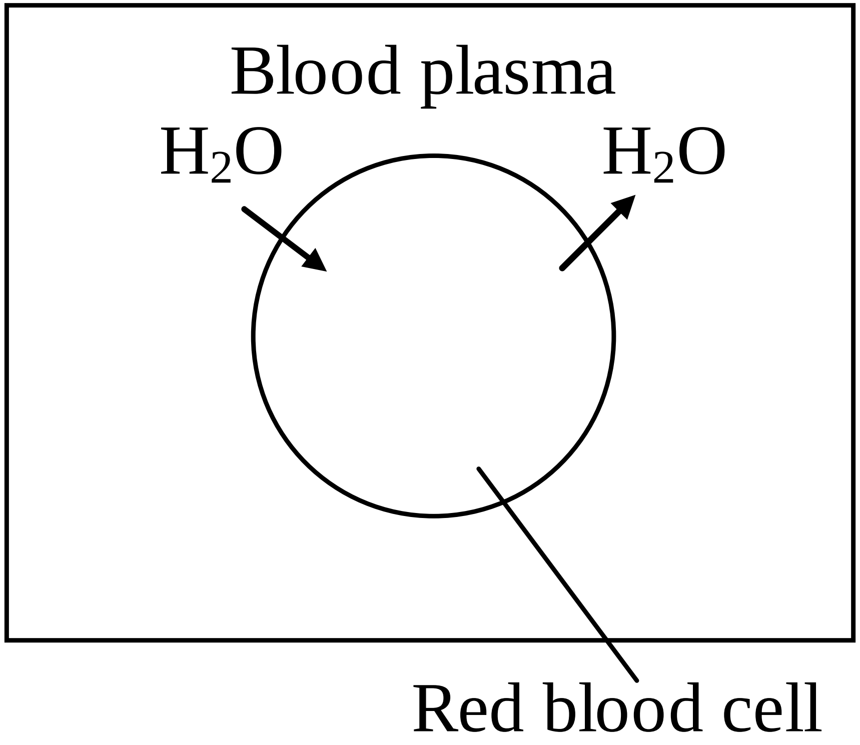
- The cell swells and eventually bursts, releasing hemoglobin and other protein molecules
- This phenomenon is known as ***hemolysis*** or destruction of blood

- When a red blood cell is placed into ***a hypertonic solution*** (P_{osm}>800 kPa) the intracellular water tends to be removed out of a cell by osmosis to a more concentrated, surrounding solution



This process, known as ***plasmolysis***, causes the cell to shrink and eventually cease functioning

- The cell remains unchanged in ***isotonic solution*** $P_{osm} = P_{osm}$ of blood plasma



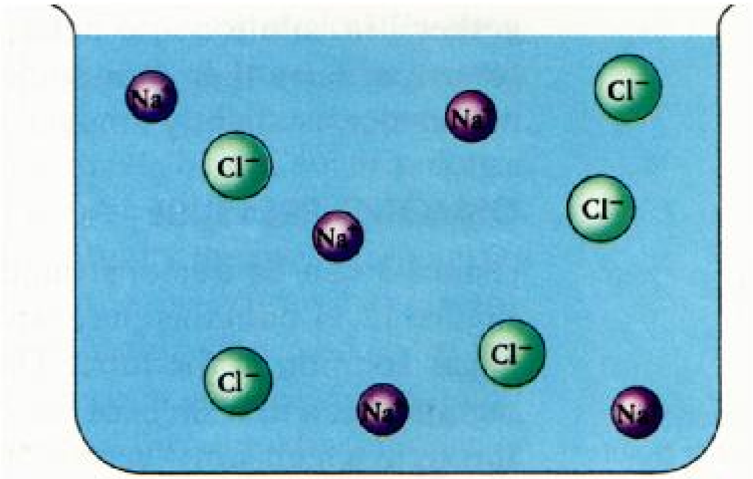
- ***Osmolarity*** and ***osmolality*** are concentration units, which characterize the content of solutes not being able to diffuse through semipermeable membranes
- Sodium cations and coupled anions make the main impact into the maintenance of osmolality of blood serum

The impact of blood serum components on its osmolality

Components	%	mmol/кg
Na^+ + anions	92	270
$К^+$ + anions	2	7
Ca^{2+} + anions	1	3
Mg^{2+} + anions	0,3	1
urea	1,7	5
glucose	1,7	5
proteins	0,3	1
total	100%	292

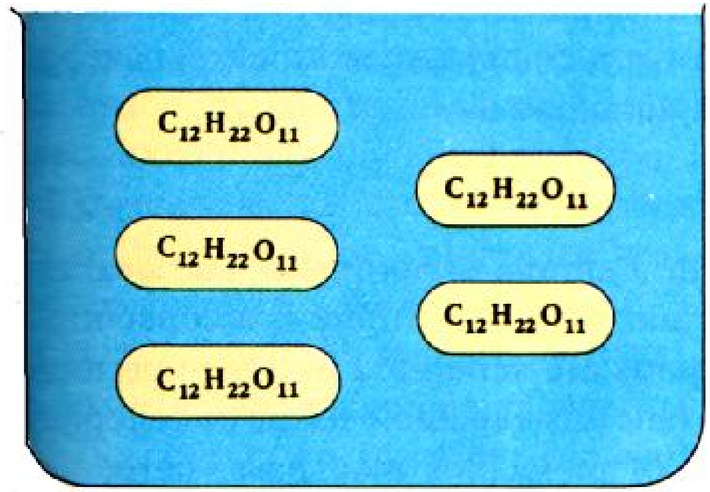
Dissociation of ionic solutes and colligative properties

- ***Colligative properties*** depend only on the number of solute particles in a solution and not on the nature of the solute



NaCl solution

$NaCl \rightarrow Na^+ + Cl^-$



Sugar solution

sugar
nondissociating
compound

1 moles of NaCl produce twice as many particles in solution as 1 moles of sugar

Equal molar quantities of sugar and NaCl affect the freezing point (and boiling point) of a solution differently

Dissolving **1 mole** of NaCl should have the same effect as dissolving **2 moles** of sugar, ***nonionic, nondissociating*** compound

Electrolytes solutions

$$ØP_{osm} = i \times C_{м} \times R \times T$$

$$ØP_{solvent} = i \times P_{0} \times N_{0}$$

$$Ø_{D}T_{b} = i \times E \times C_{m}$$

$$Ø_{D}T_{f} = i \times K \times C_{m}$$

***The Van’t-Hoff’s factor** -i*

$$\frac{i-1}{n-1}$$

- ***The Van’t-Hoff’s factor (i)*** characterizes ionization of electrolytes
- its relationship with the degree of ionization is given below

$$\alpha = \frac{i-1}{n-1}$$

- where n – the number of ions contained in a molecule

- **Which of the following aqueous solutions are isotonic with respect to the blood serum (the solutions are compared at 37^{0}C):**

a) 0,15M KCl solution;

b) 5% $C_6H_{12}O_6$ solution;

c) 0,85% NaCl solution;

d) 0,15M $CaCl_2$ solution?

Osmolarity - 0.3 mol/L

KCl solution – 0.3 mol/L of particles

$C_6H_{12}O_6$ 5% and 0,85% NaCl solutions - isotonic

CaCl2 solution – 0.45 mol/L of particles