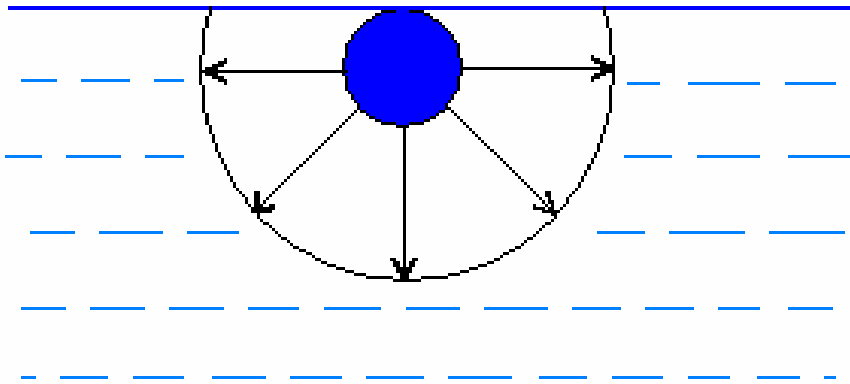


The vapor pressure of solutions

Vapor pressure is the pressure exerted by a vapor in equilibrium with its condensed phase (solid or liquid).



The transition of a liquid substance in gaseous state (evaporation) takes place even before reaching boiling point.

At the liquid – air interface the molecules of the substance are stopped from leaving the liquid due to the intermolecular forces which are orientated towards the mass of the liquid.

But, if the kinetic energy of the molecule becomes very large, this molecule can “escape” from the solution and passes in the gaseous state.

This phenomenon is reversible, and at the interface there is a **dynamic equilibrium**, when the number of molecules that passes from liquid to air is equal to the number of molecules that passes from air to liquid. This means that at equilibrium, the gaseous state is saturated with the molecules of the liquid substance.

The vapor pressure is an indication of a liquid's evaporation rate. A substance with a high vapor pressure at normal temperatures is often referred to as **volatile**.

Substance	Vapor Pressure (SI units)	Vapor Pressure (Bar);	Vapor Pressure (mmHg);	Temperature
Tungsten	100 Pa	0.001	0.75	3203 °C
Ethylene glycol	500 Pa	0.005	3.75	20 °C
Xenon difluoride	600 Pa	0.006	4.50	25 °C
Water (H₂O)	2.3 kPa	0.023	17.5	20 °C
Propanol	2.4 kPa	0.024	18.0	20 °C
Ethanol	5.83 kPa	0.0583	43.7	20 °C
Methyl isobutyl ketone	2.66 kPa	0.0266	19.95	25 °C
Freon 113	37.9 kPa	0.379	284	20 °C
Acetaldehyde	98.7 kPa	0.987	740	20 °C
Butane	220 kPa	2.2	1650	20 °C
Formaldehyde	435.7 kPa	4.357	3268	20 °C
Propane	1.013 MPa	10.133	7600	25.6 °C
Carbonyl sulfide	1.255 MPa	12.55	9412	25 °C
Carbon dioxide	5.7 MPa	57	42753	20 °C

The temperature at which the vapor pressure of a liquid becomes equal to atmospheric pressure (or in case of closed spaces – the pressure above the liquid) is the **boiling temperature**.

Vapor pressure of mixtures

If a non-volatile substance is dissolved in a solvent, the vapor pressure of the solution is smaller than the one of the pure solvent, at the same temperature. The relative drop of vapor pressure is given by:

$$\frac{p_0 - p}{p_0}$$

p_0 = the vapor pressure of the pure solvent

p = the vapor pressure of the solvent above the solution.

Raoult's law (1877): the relative drop of the vapor pressure of a diluted solution is equal to the molar fraction of the solute in solution:

$$\frac{p_o - p}{p_o} = \frac{n_1}{n_1 + n_2}$$

Considering x_1 as the molar fraction of the solute and x_2 the molar fraction of the solvent, the relation can be written:

$$1 - \frac{p}{p_o} = x_1 \quad \text{from which results:} \quad \frac{p}{p_o} = 1 - x_1$$

Considering the fact that $x_1 + x_2 = 1$, we obtain:

$$p = x_2 \cdot p_o$$

The vapor pressure of a solvent in a solution is directly proportional to its molar fraction .

The solutions that respect the Raoult's law are called **ideal solutions**. Diluted solutions are approaching the state of ideal solution.

If a gaseous substance is dissolved in a liquid solvent, the molecules of gas are dispersed in the mass of the solvent. They can reach the liquid – gas interface, and if their kinetic energy is sufficiently high, they pass in the gaseous state.

Equilibrium is reached at a certain concentration of the gas in solution, when the number of the gas molecules that pass from the solution in gaseous state is equal to the number of gas molecules that pass the opposite way. At equilibrium, the solution is saturated in gas.

The variation of the solubility of a gas with the pressure is expressed by Henry's law: *the molar fraction of a gas dissolved in a solvent is proportional to the pressure of the gas in equilibrium with the solution:*

$$x = k \cdot p$$

Increasing the boiling point of the solutions

According to Raoult's law, by dissolving a non-volatile substance in a solvent, the vapor pressure of the solvent above the solution is smaller than the one above the pure solvent.

Thus, the boiling temperature of the solution will be higher than the one of the solvent.

The increase of the boiling point of the solution compared to the solvent is proportional to the decrease of the vapor pressure of the solution compared to the solvent:

$$\Delta T = k \cdot \Delta p$$

The increase of the boiling point is: $\Delta T = T_f - T_f^0$

T_f - the boiling temperature of the solution;

T_f^0 - the boiling temperature of the solvent

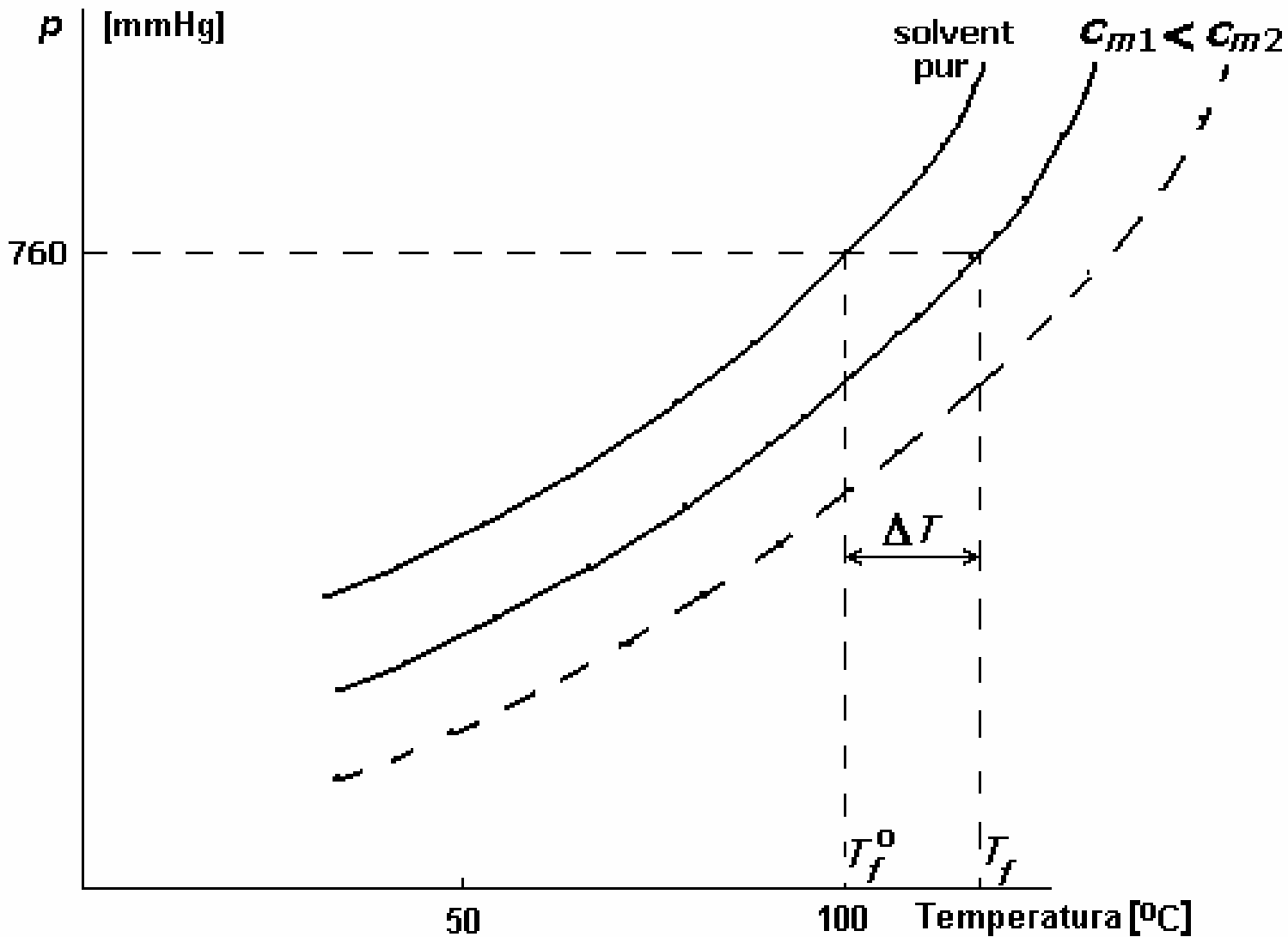
The decrease of the vapor pressure is: $\Delta p = p^0 - p$

p^0 is the vapor pressure of the solvent;

p – is the vapor pressure of the solution.

The variation of the boiling point of the solution depends also on the concentration of the dissolved substance.

Vapor pressure and temperature for different concentrations of the solute expressed in molality



The increase of the boiling point can be expressed by
the relation:

$$\Delta T = K_{eb} \cdot c_m$$

where K_{eb} is the ebullioscopic constant,

c_m – the molal concentration of the solute.

The ebullioscopic constant, K_{eb} represents the increase of the boiling point when one mole of substance is dissolved in 1 kg of solvent.

For diluted solutions, the ebullioscopic constant does not depend on the nature of the dissolved substance, as it is a characteristic of the solvent. This means that solving the same quantity of substance in a solvent, the increase of the boiling point of the solution will be the same.

Ebullioscopic constant for different solvents.

Solvent	H₂O	chloroform	ethanol	benzene	diethyl ether
K_{eb}	0.52	3.88	1.15	2.57	2.11

Replacing the molarity with its expression, it results:

$$\Delta T = K_{eb} \cdot \frac{m_d}{m_{solv} \cdot M}$$

where: m_d is the mass of solute (kg);

m_{solv} – the mass of solvent (kg);

M – the molar mass ($\text{kg} \cdot \text{mol}^{-1}$).

This relation is used for determining the molecular mass of the substances.

The research method, based on the experimental determination of the increase of the solutions boiling point, is called *ebullioscopy*.

Decreasing the freezing point of solutions

Another consequence of Raoult's law is the drop of the freezing point of solutions. The decrease of the freezing point is proportional with the molal concentration of the dissolved substance:

$$\Delta T = T_s - T_s^0 = K_{cr} \cdot C_m$$

where: T_s is the freezing temperature of the solution;
 T_s^0 – the freezing temperature of the solvent;
 K_{cr} – the cryoscopic constant.

The cryoscopic constant represents the drop of the freezing point produced by dissolving one mole of substance in 1 kg of solvent.

Solvent	H ₂ O	Camphor	Naphthalene	Benzene	Cyclohexane
K _{cr}	1.8	40.0	7.0	5.12	20.2

The research method based on the experimental determination of the decrease of the freezing point of solutions is called cryoscopy. The relation used in cryoscopy for determining the molecular masses of substances is:

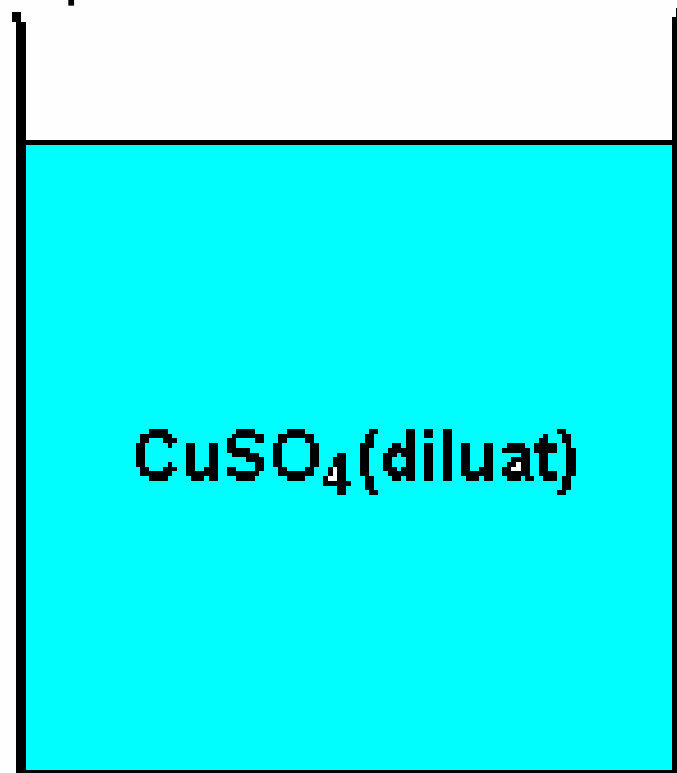
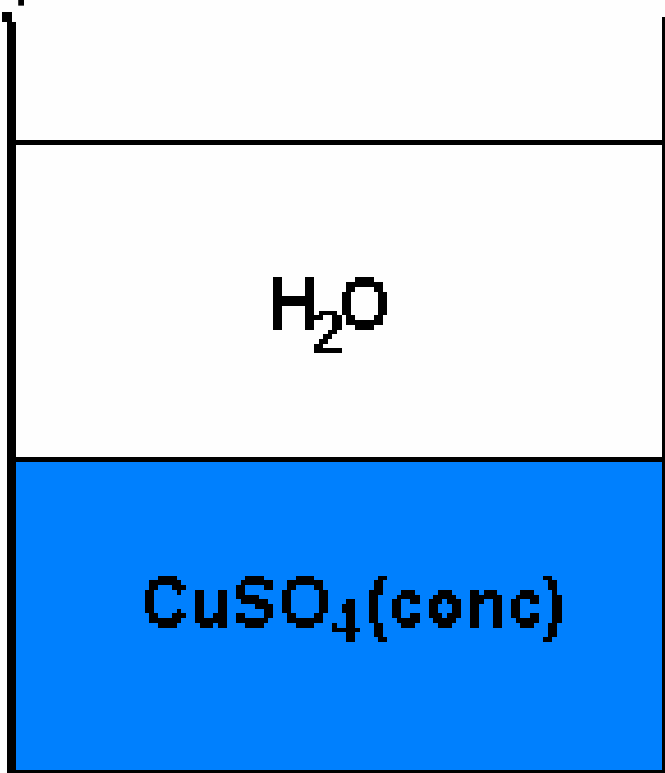
$$\Delta T = K_{cr} \cdot \frac{m_d}{m_{solv} \cdot M}$$

Osmosis and osmotic pressure

If we carefully pour water on a copper sulfate solution (blue), we will see at the beginning a clear separation between the blue-coloured copper sulfate solution and the colorless water. Because of the Brownian movement the Cu^{2+} and SO_4^{2-} ions are dislocated from the solution in the water layer and the water in the copper sulfate solution, so that, after a while, a homogenization of the copper sulfate concentration is produced.

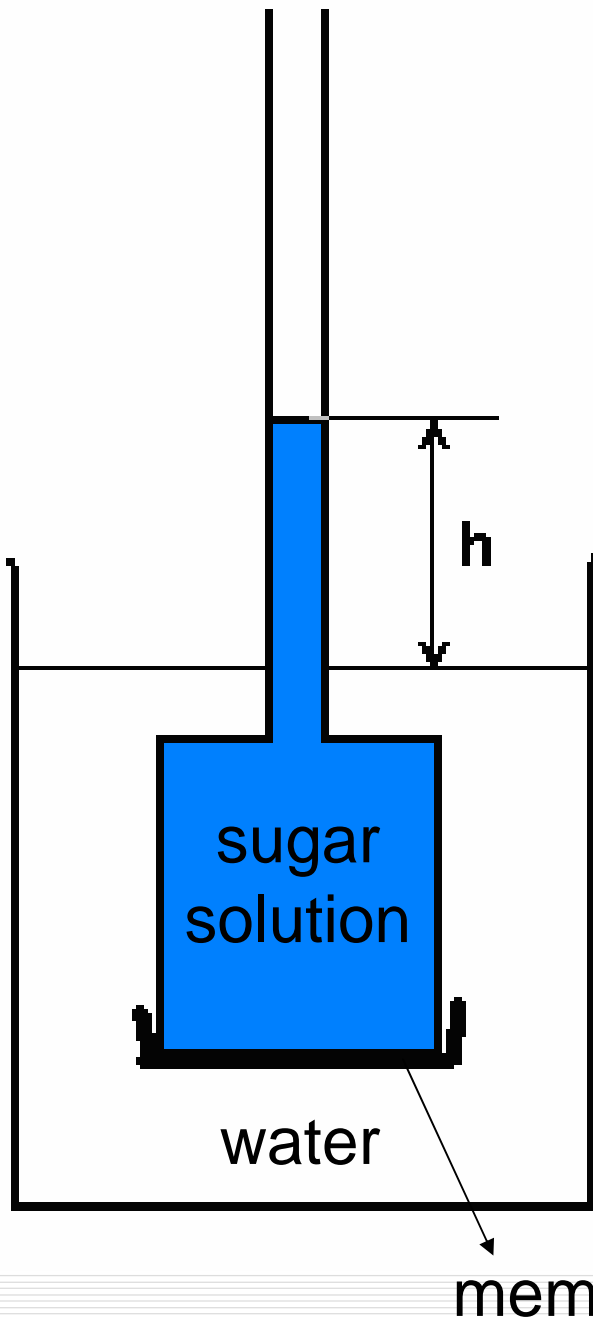
The effective movement of the chemical species, ionic or molecular, under the influence of the difference of concentration is called **diffusion**. At

equal concentrations the diffusion stops.



The diffusion of some chemical species can be prevented using membranes. There are semi-permeable membranes that allow certain molecules or ions to pass through, but prevent the passage of other molecules.

The osmosis can be evidenced by the following experience:



At the beginning, the liquid from the funnel is at the same level with the liquid in the vessel. In time, the liquid ascends in the gradual tube to a certain level. This happens because water diffuses through the membrane in the sugar solution. The membrane is permeable only for the small water molecules but not for the large sugar molecules.

The movement of the solvent through a semi-permeable membrane from the diluted solution into the concentrated solution is called **osmosis**.

The increase of the level stops when the hydrostatic pressure h is sufficiently high to prevent the passage of water. The pressure necessary to stop the diffusion of water is the **osmotic pressure**. It can be measured by the height of the liquid column.

The general osmotic pressure expression was formulated by van't Hoff:

$$\pi = cRT$$

where: π is the osmotic pressure ($\text{N}\cdot\text{m}^{-2}$);
 c – concentration ($\text{mole}\cdot\text{m}^{-3}$);
 R – universal constant of gases;
 T – thermodynamic temperature (K).

The van't Hoff's equation is similar to the general equation of ideal gases.