Colligative properties of solutions

Glucose and gycerol in the blood of the frog prevent it from freezing.

Alcune immagine sono state prese e modificate da “Chimica” di Kotz, Treichel & Weaver, Edises 2007, III edizione

Colligative properties

Some properties of solutions, such as density and pH, depend not only on the concentration of solute particle but, also on the nature of the solution components.

solution 0.1 M NaOH: pH =13
solution 0.1 M HCl: pH = 1

The colligative properties are physical properties of solutions that depend only on the number of discrete particles (molecules, ions, macromolecules) in the solution and not the nature of the particles themselves.

at 25 °C:
solution 0.1 M NaOH: p = 4.9 atm
solution 0.1 M HCl: p = 4.9 atm
solution 0.067 M Na_2SO_4: p = 4.9 atm

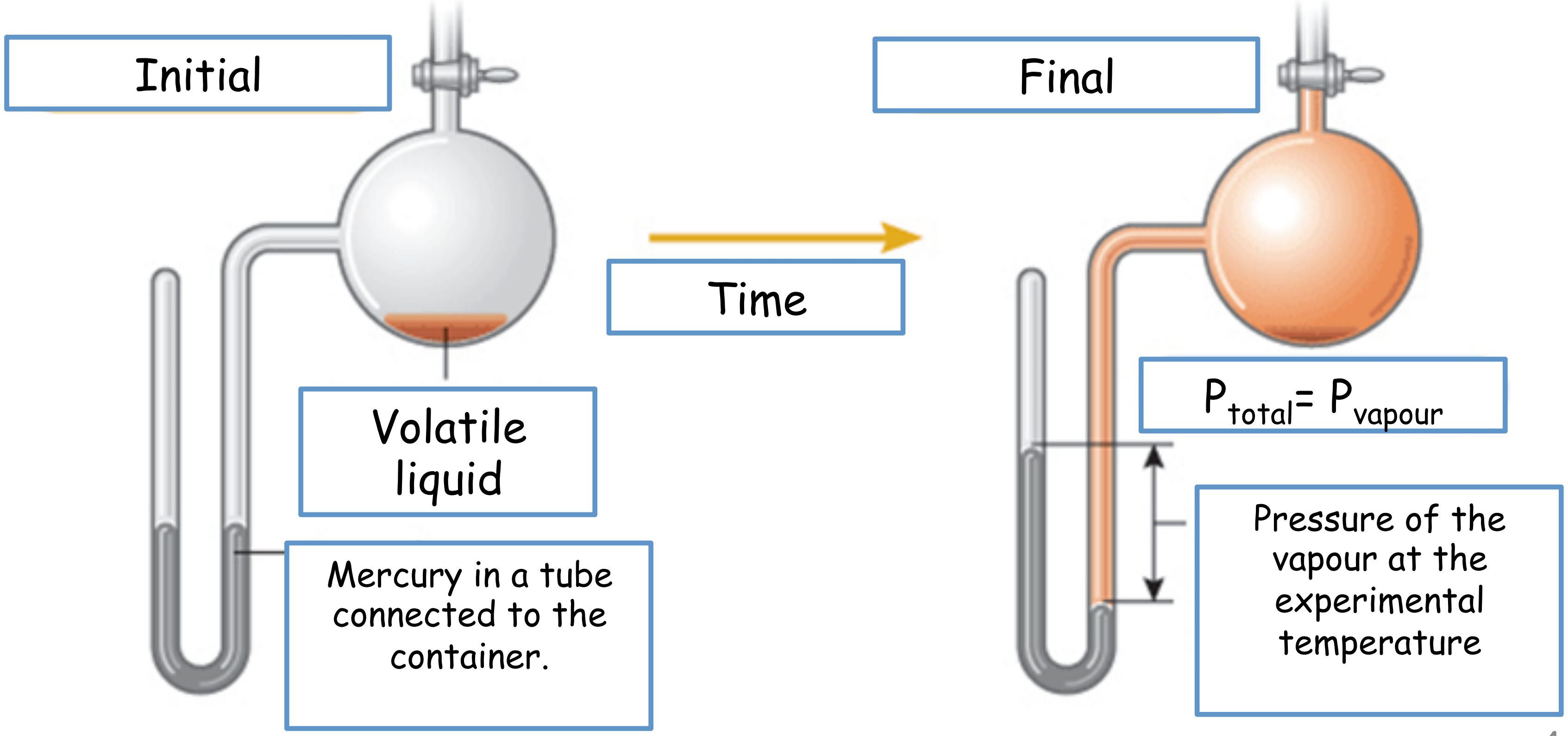
When you add a non-volatile solute to a solvent, the physical properties of the solution are different from those of the pure solvent.

Colligative properties

- vapour pressure variation ($P_{solvent} = -i\ x_{solvent}\ P^{o}_{solvent}$)
- boiling point elevation ($DT_{eb} = i\ K_{eb}\ m$)
- freezing point depression ($DT_{cr} = i\ K_{cr}\ m$)
- osmotic pressure ($p = i\ cRT$)

Vapour tension – Raoult’s law

If volatile liquid is placed in a closed container, it evaporates until the evaporation rate equals the rate of condensation. In this final state the system is in dynamic equilibrium. At equilibrium it is possible to measure the vapor pressure.



Initial

Volatile liquid

Mercury in a tube connected to the container.

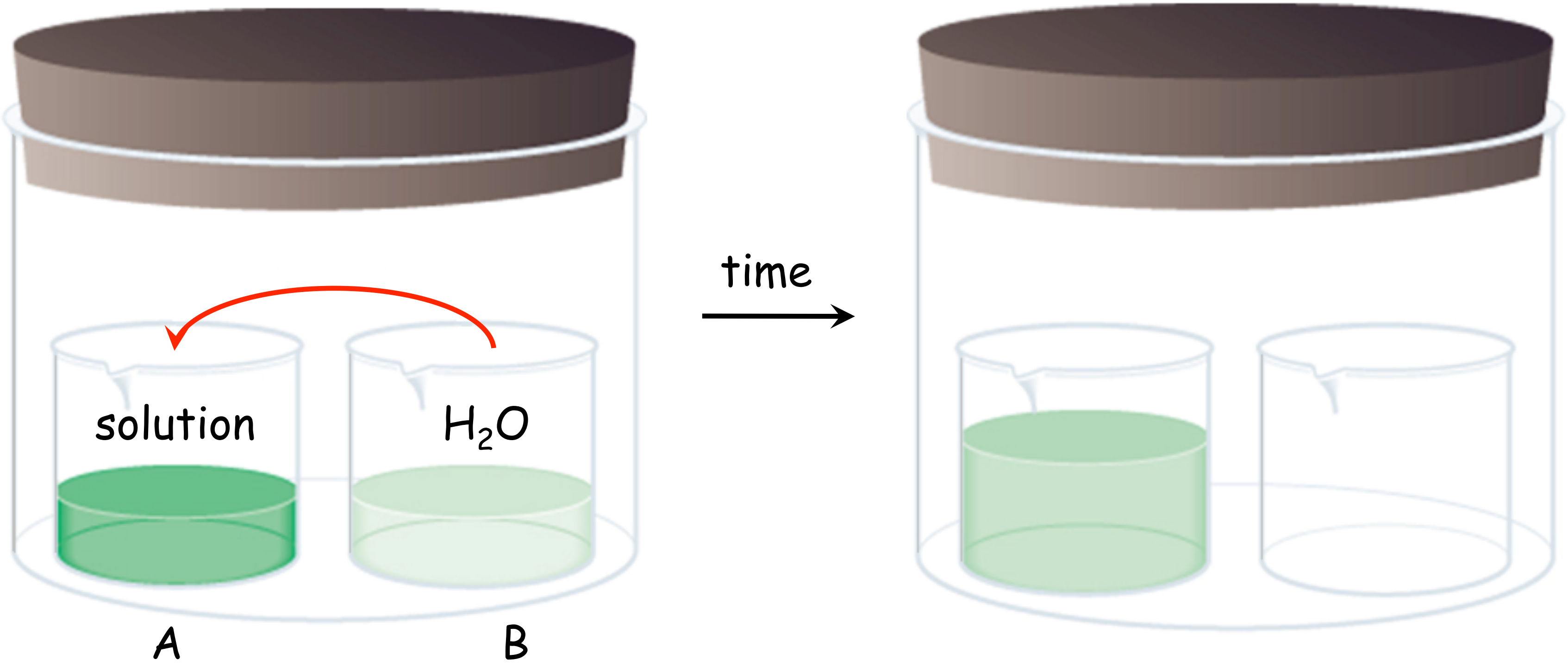
Time

Final

$P_{total} = P_{vapour}$

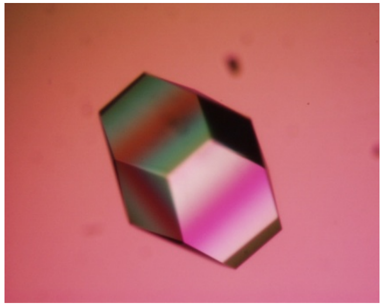
Pressure of the vapour at the experimental temperature

Vapour diffusion



When a solute is dissolved in water, the vapor pressure above the solution is less than that over pure water. At equilibrium water vapour from container B condenses into container A.

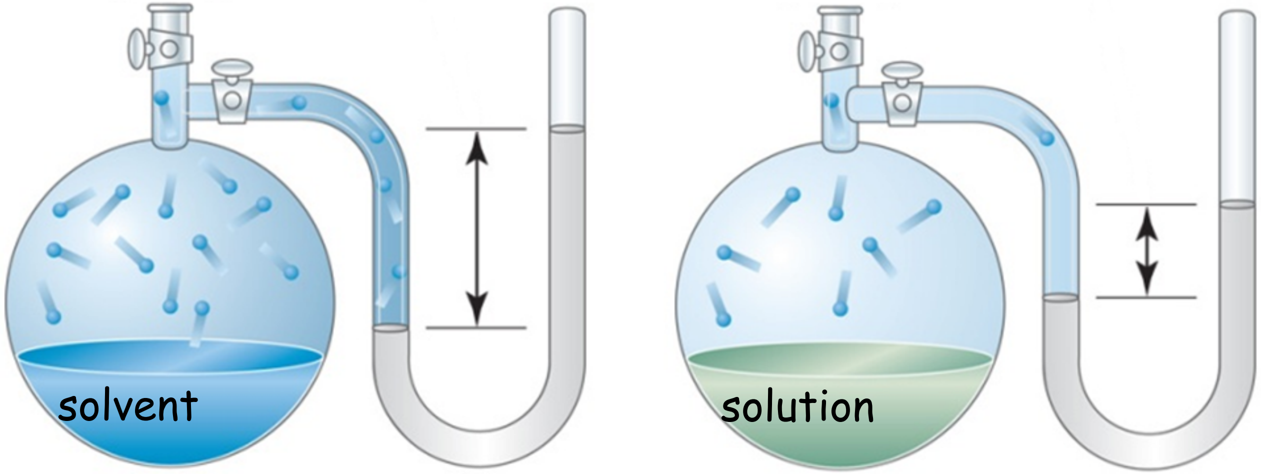
Vapour diffusion used in the preparation of protein crystals
(image: a crystal of lysozyme)



Raoult's law

Consider the solution of a non-volatile, non-electrolytic solute in a volatile solvent.

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



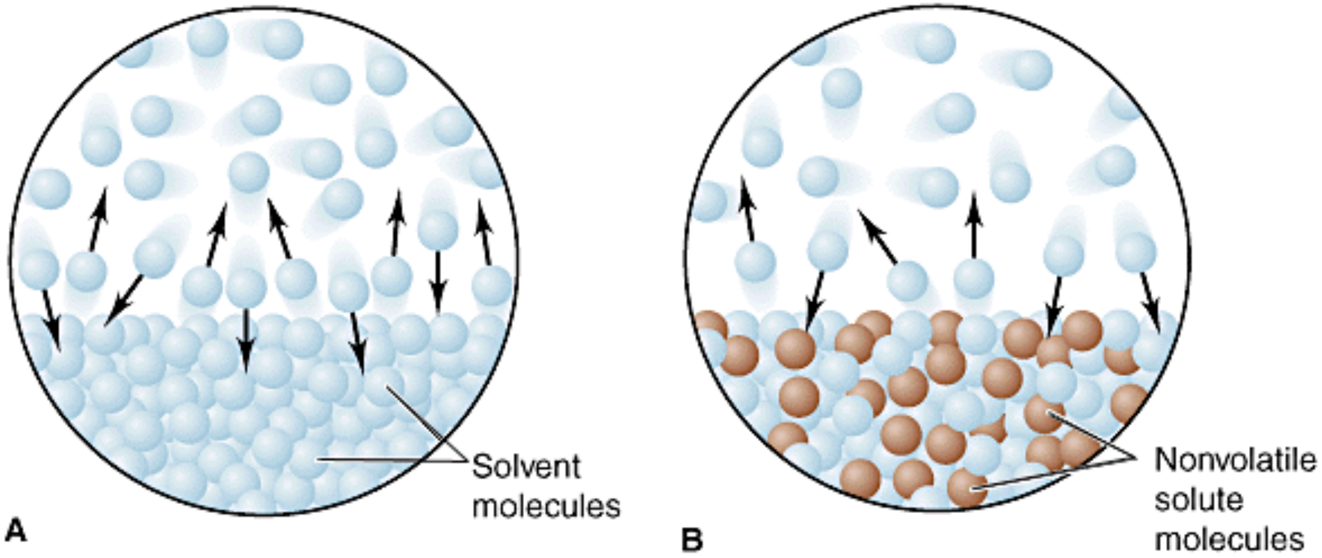
François-Marie Raoult
(1830-1901)

Raoult' law:

$$P_{solvent} = x_{solvent} P^{o}_{solvent}$$

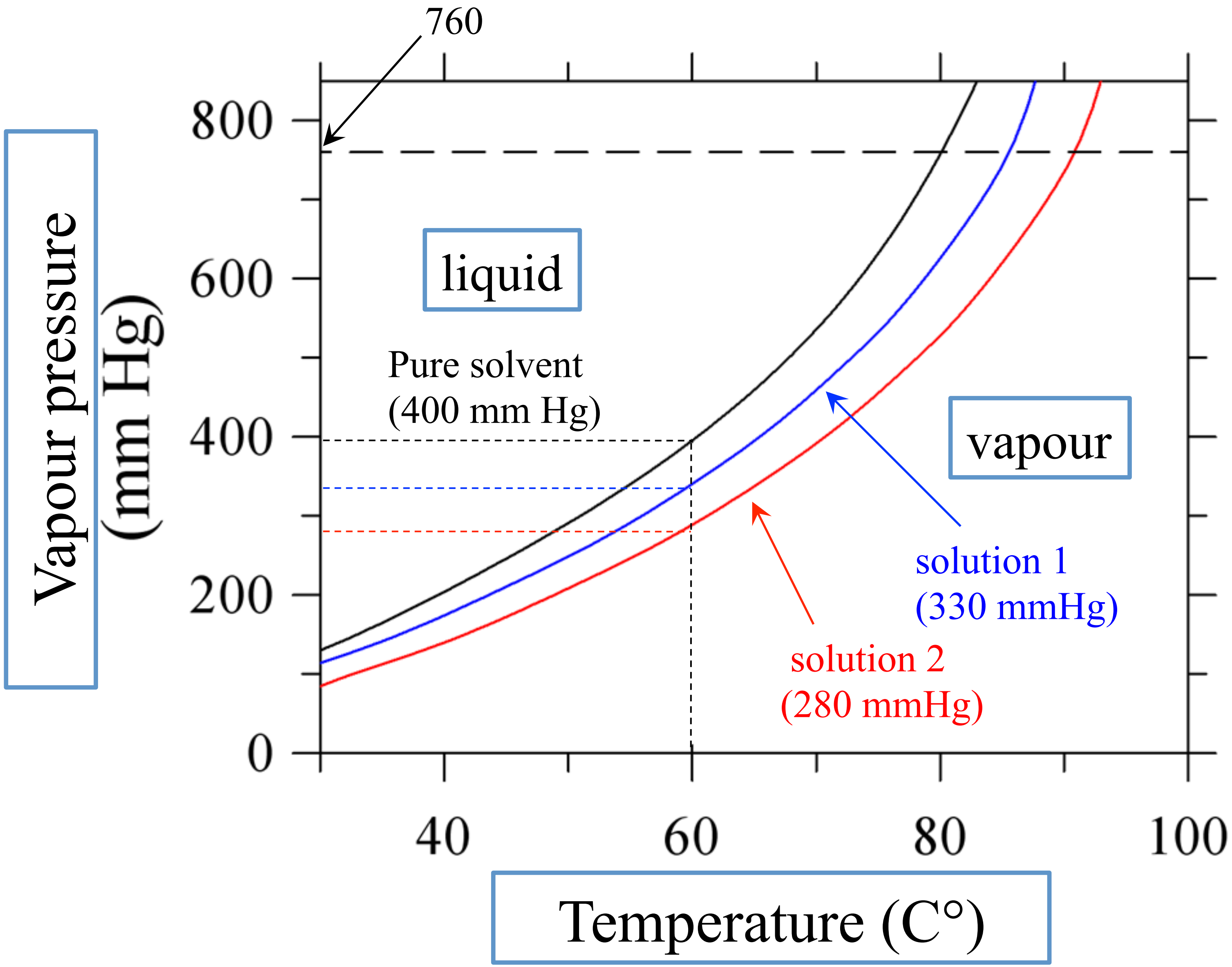
where $$x_{solvent} = \frac{n_{solvent}}{n_{solute} + n_{solvent}}$$

The vapour pressure over the solution multiplied by the molar fraction of the solvent $x_{solvent}$. Since $x_{solvent} < 1$, we will observe a decrease of the vapour pressure, with respect to the pure solvent



The non volatile solute interacts with the solvent,
at the interface fewer molecules evaporate.

Diagramma di stato di una soluzione di benzene (C_6H_6) con un soluto non volatile



A modified for of the Raoult's law can be used to calulate the of the vapour pressure of the solbent in the solution, $Dp_{solvent}$ as a function of the molar fraction of the solute:

$$DP_{solvent} = P_{solvent} - P^{o}_{solvent} \quad (< 0)$$

In base alla legge di Raoult: $P_{solvente} = x_{solvente} \, P^{o}_{solvente}$

che sostituita nella precedente:

$$DP_{solvent} = x_{solvent} \, P^{o}_{solvent} - P^{o}_{solvent} = -(1 - x_{solvent}) \, P^{o}_{solvent}$$

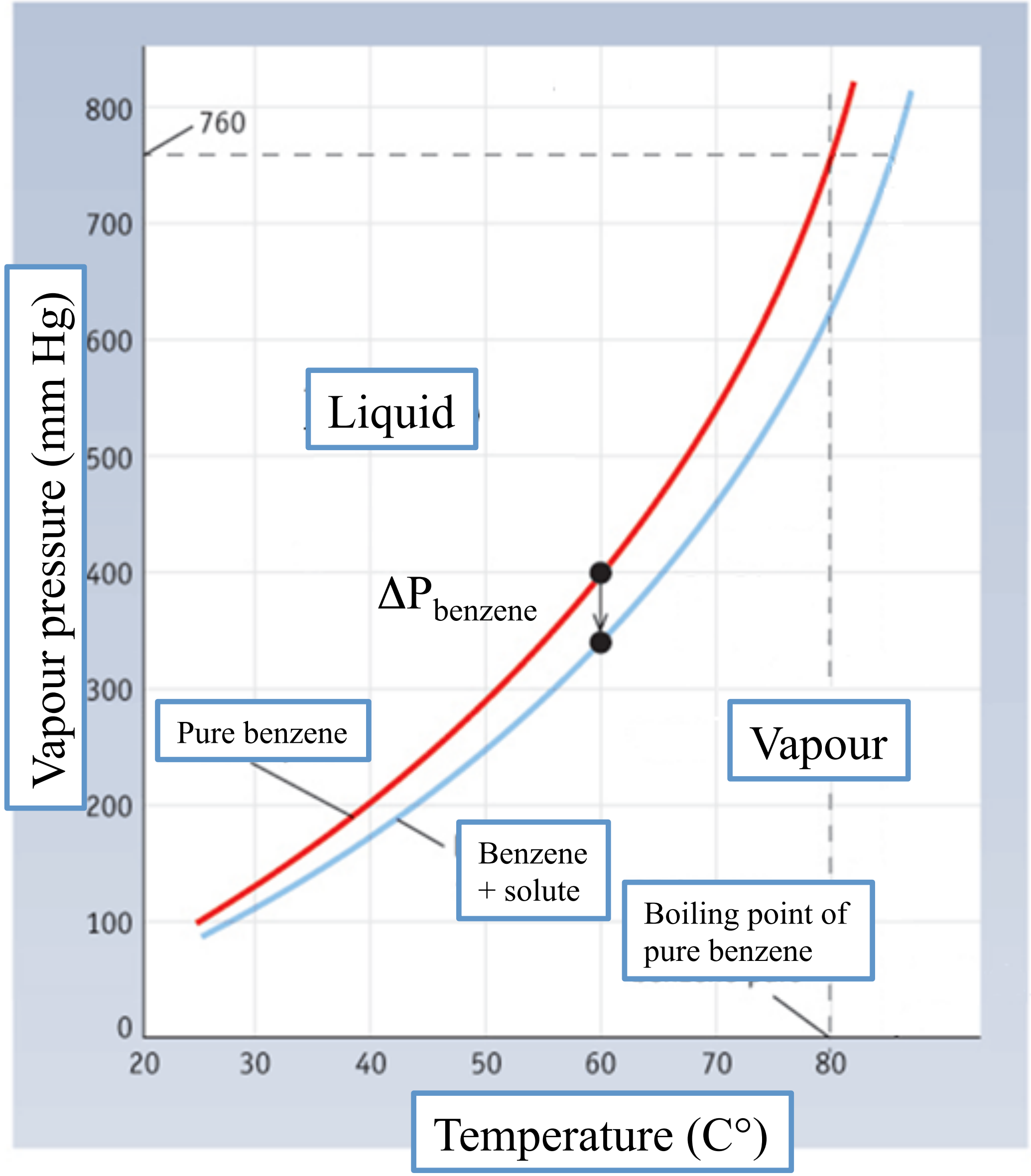
$$DP_{solvent} = -x_{solute} \, P^{o}_{solvent}$$

Therefore the decrease of the vapor pressure of the solvent in the solution is proportional to the molar fraction of the solute.

N.b.: $x_{solvent} + x_{solut} = 1$

Example. If 45% of the molecules in a solution are solute molecules ($x_{solute} = 0.45$), then the decrease of the vapor pressure of the solvent is equal to 45% of the vapor pressure of pure solvent.

State diagram of pure benzene (solvent) and of its solutions



The red curve represents the dependence of the vapor pressure of benzene (M = 78 g / mol) on temperature.

The blue curve represents the vapor pressure of a solution obtained by dissolving 0.20 moles of a solute in 0.1 kg of benzene (c=2 m).

At 60 °C $P^{\circ}_{benzene}$ = 400 mm Hg. In this solution the molar fraction of the solute is:

$x_{solute} = n_{solute} / (n_{solute} + n_{benzene}) = 0.135$

$\Delta P_{benzene} = - 0.135 \cdot 400 = -54$ mm Hg

The vapour pressure of benzene decreases of 45 mm Hg.Hg.

As the ideal gas law, Raoult's law describes an idealized model of solution: the ideal solution.

In an ideal solution intermolecular interactions all have the same strength:

- solute-solute
- solvent-solvent
- solute-solvente

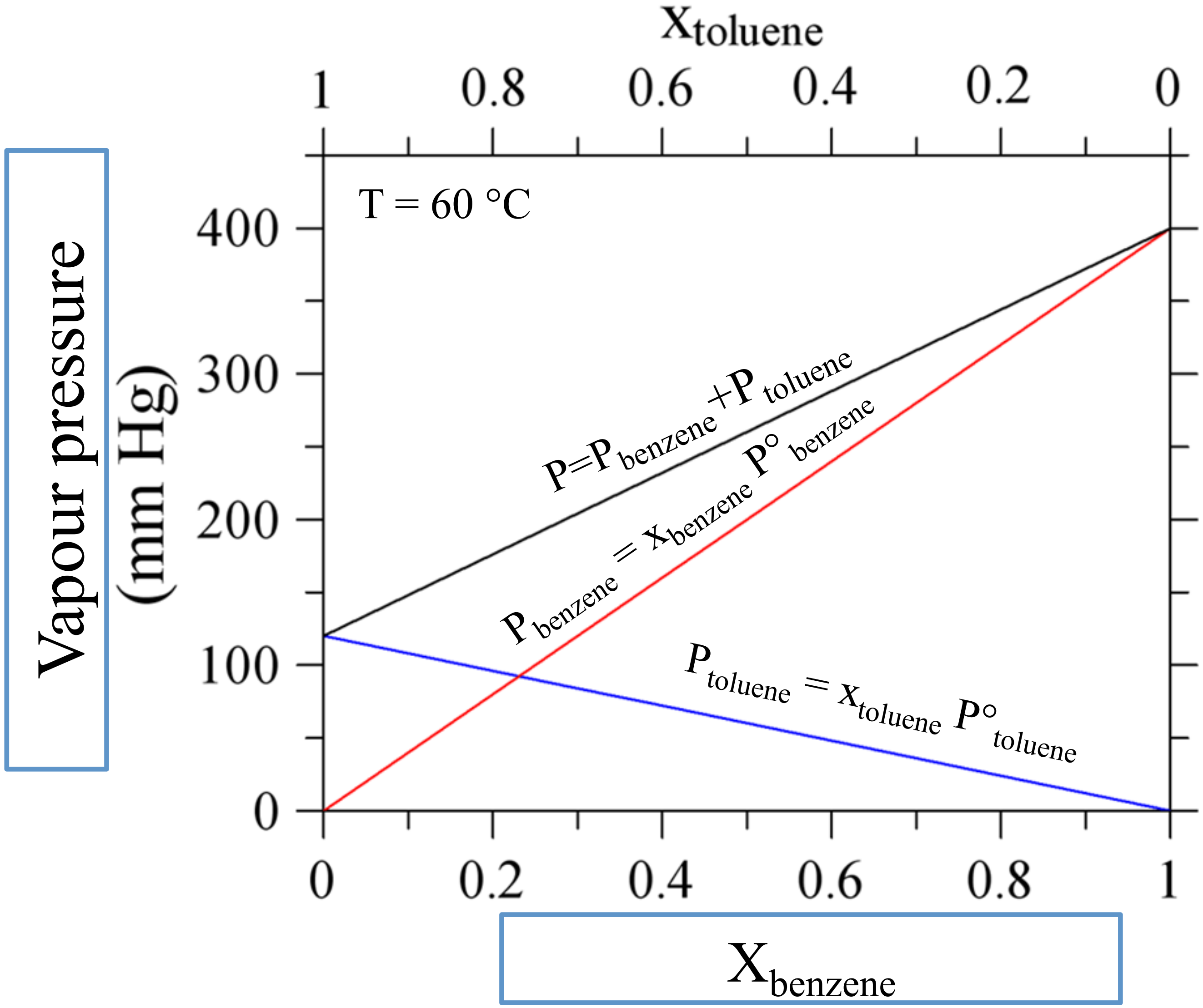
In the general case in which the solute is also volatile Raoult's law states that the vapor pressure of a solution P is the sum of the partial pressures of the components in equilibrium with the solution:

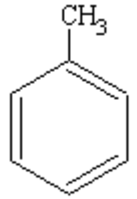
$$P = \sum_{i=1}^{n} P_i = \sum_{i=1}^{n} x_i P_i^0$$

For a solution made of two components (A e B)

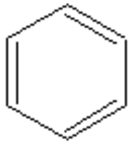
$$P = P_A + P_B = x_A P_A^0 + x_B P_B^0$$

Compounds whose mixtures follow Raoult's law usually have similar molecular structures, eg. Benzene (C_6H_6) and toluene (C_7H_8). In these solutions the interactions A-A and B-B interactions are virtually identical to A-B, and in the formation of the mixture thermal effects are not observed.



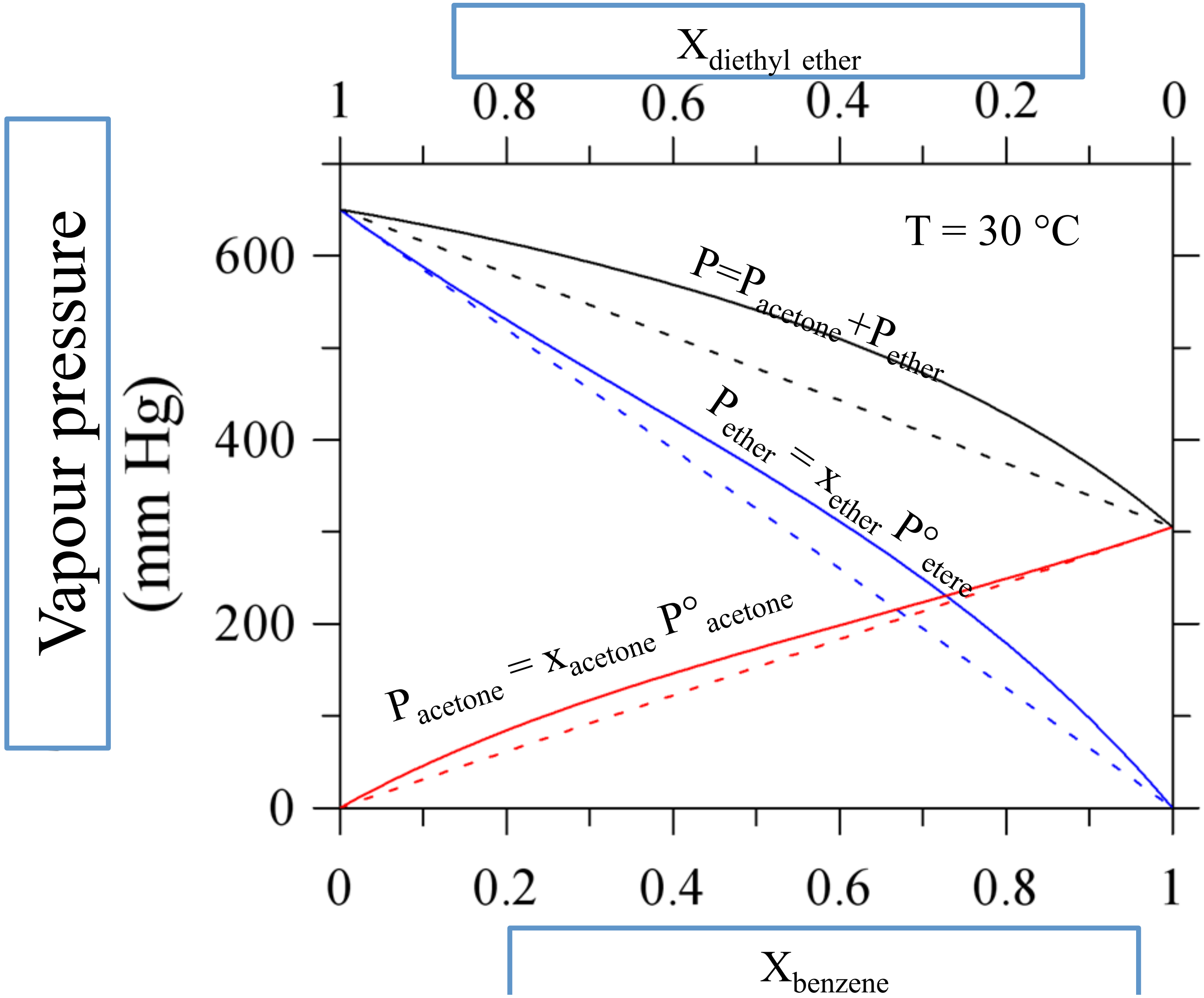


toluene

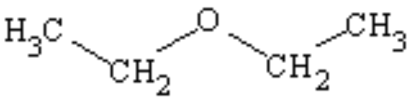


benzene

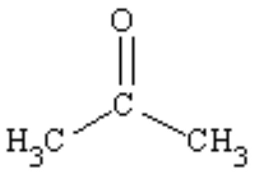
In most cases, however, solutions do not obey Raoult's law (except for dilute solutions). Positive deviations indicate that intermolecular attractions in pure components (A-A and B-B) are stronger than in the mixture (A-B), eg. diethyl ether ($C_4H_{10}O$) and acetone (C_3H_6O).



dashed lines= ideal behaviour

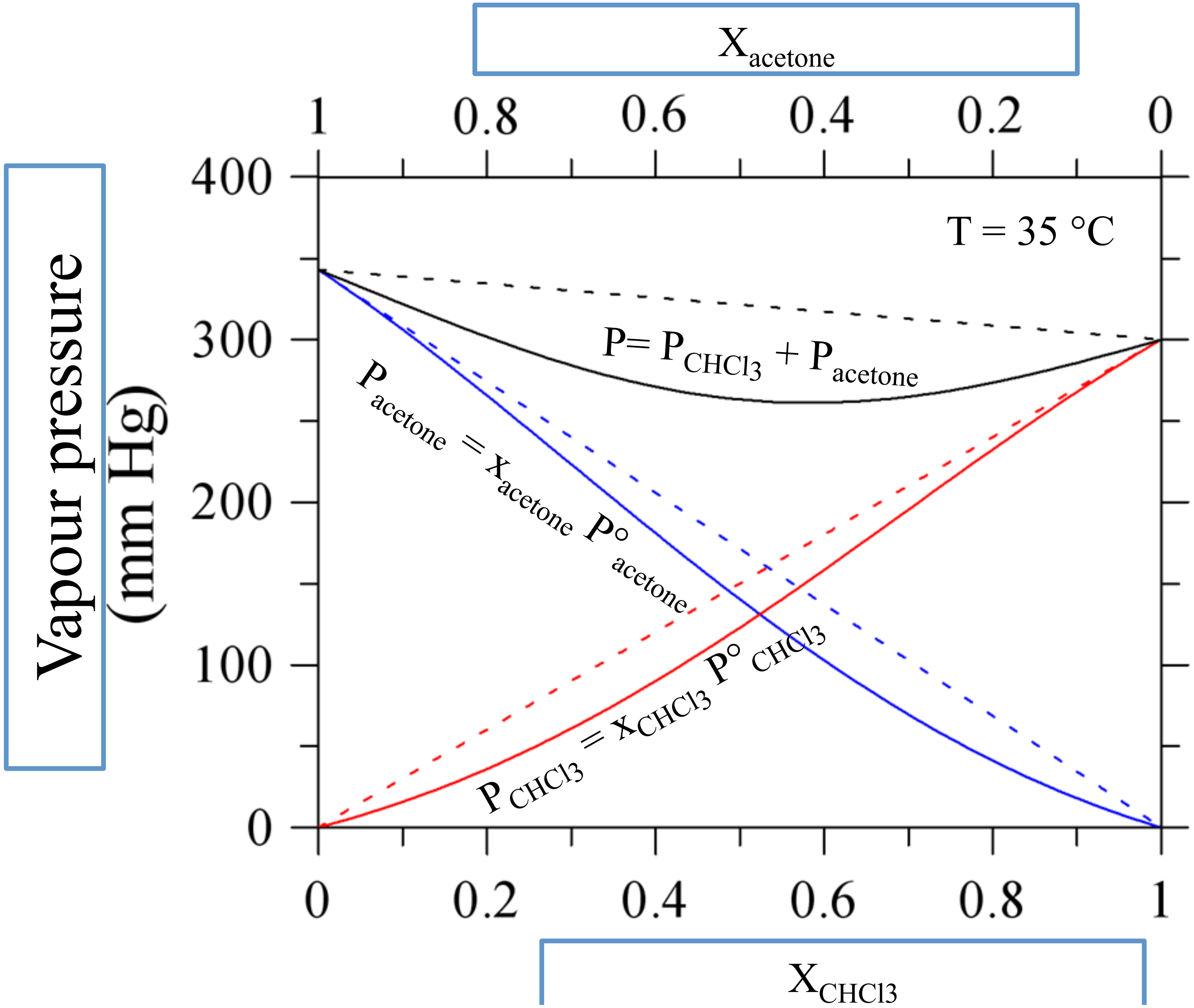


Diethyl ether

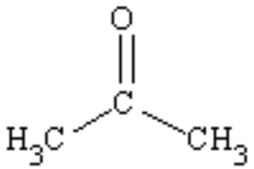


acetone

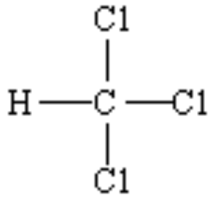
Negative deviations indicate that intermolecular attractions in pure components (A-A and B-B) are weaker than in the mixture (A-B), eg. diethyl ether ($C_4H_{10}O$) and acetone (C_3H_6O).



dashed lines= ideal behaviour

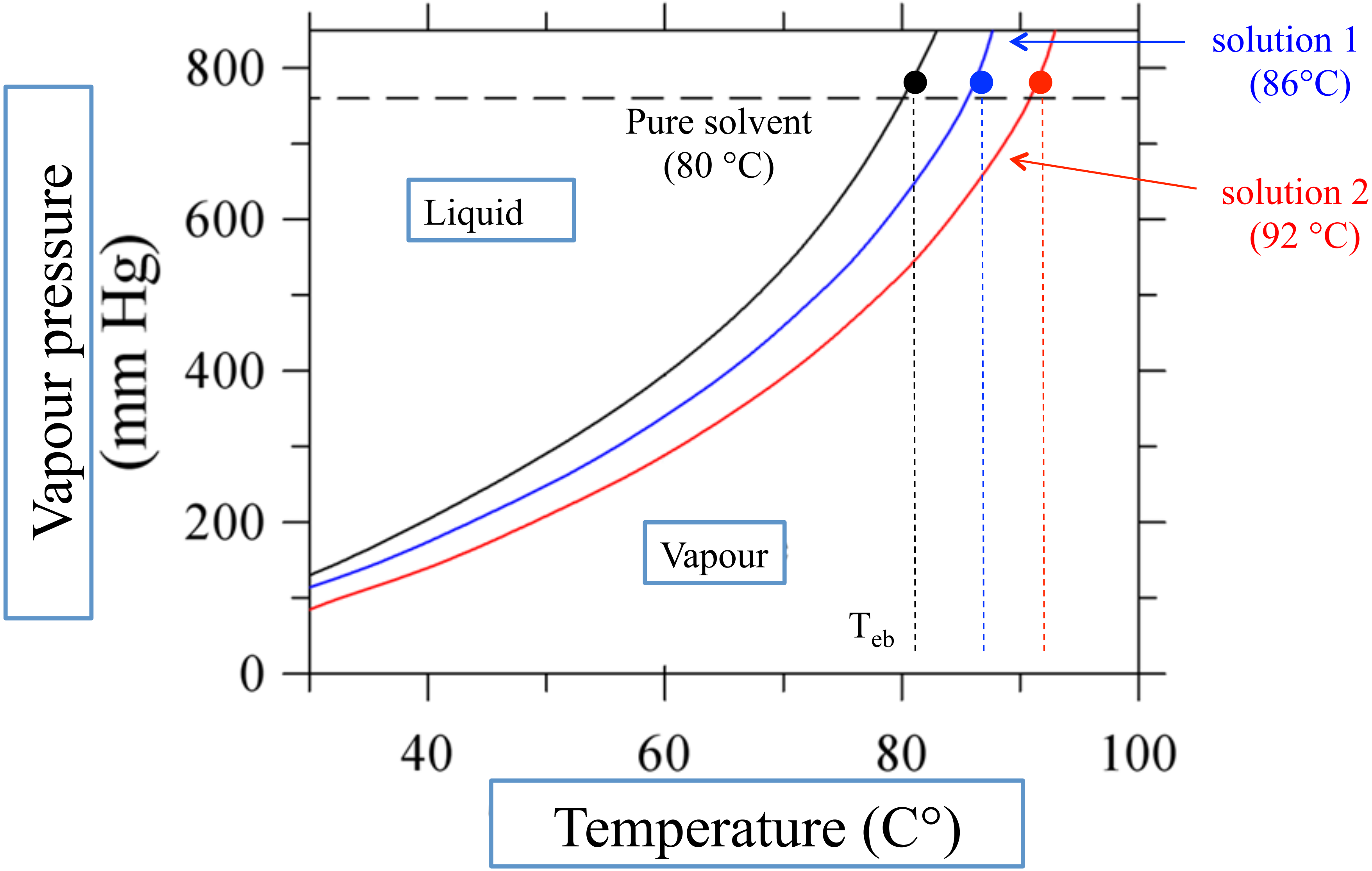


acetone



chloroform

An important consequence of Raoult's law is that the decrease in vapour pressure caused by the non-volatile solute causes an increase in the boiling point of the solution.



There is a simple relationship between the rise in boiling point and the concentration: the increse of the boiling point ΔT_{eb} is directly proportional to the molality of the solute.

$$\Delta T_{eb} = K_{eb} m$$

The constant K_{eb} (ebullioscopic constant) dipends on the nature of the solvent and it s units are °C / m (°C kg/mol).

solvent	T_{eb} (°C)	K_{eb} (°C/m)
H_2O	100	0.515
$CH_3CH_2OCH_2CH_3$	34.55	1.824
CS_2	46.23	2.35
C_6H_6	80.10	2.53
CCl_4	76.75	4.48
camphor	207.42	5.611

Another consequence of the presence of a solute in a solution is that the freezing point of the solution is lower than that of the pure solvent. For an ideal solution the freezing point depression (cryoscopy) is given by:

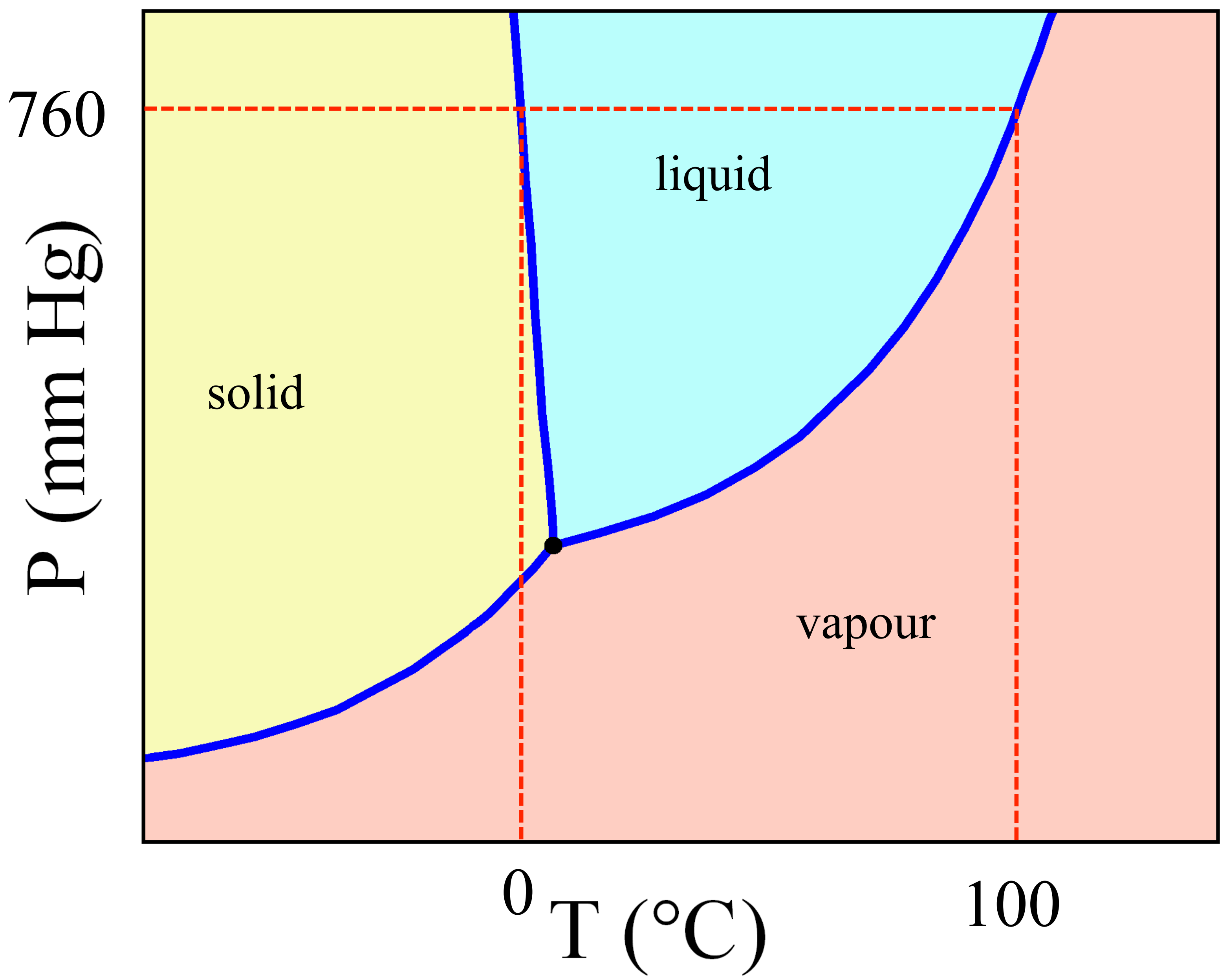
$$\Delta T_{cr} = K_{cr} m$$

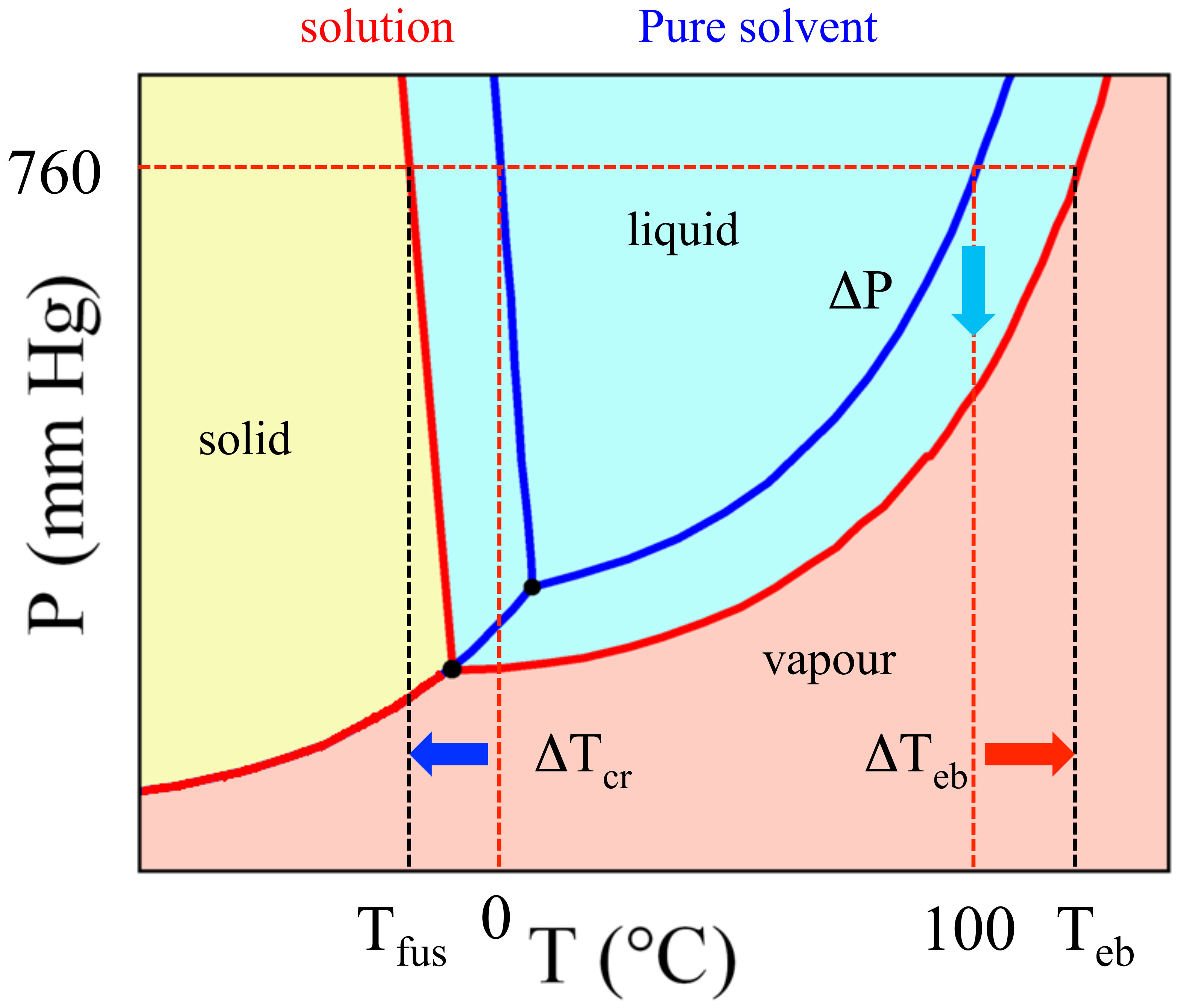
The proportionality constant K_{cr} (cryoscopic constant) depends on the solvent, its units are °C / m (°C kg/mol).

solvent	T_{fu} (°C)	K_{cr} (°C/m)
water	0.0	−1.853
Acetic acid	16.66	−3.90
benzene	5.53	−5.12
naftalene	80.29	−6.94
ciclohexane	6.54	−20.0
CCl_4	−22.95	−29.8
camphor	178.75	−37.7

State diagram of water

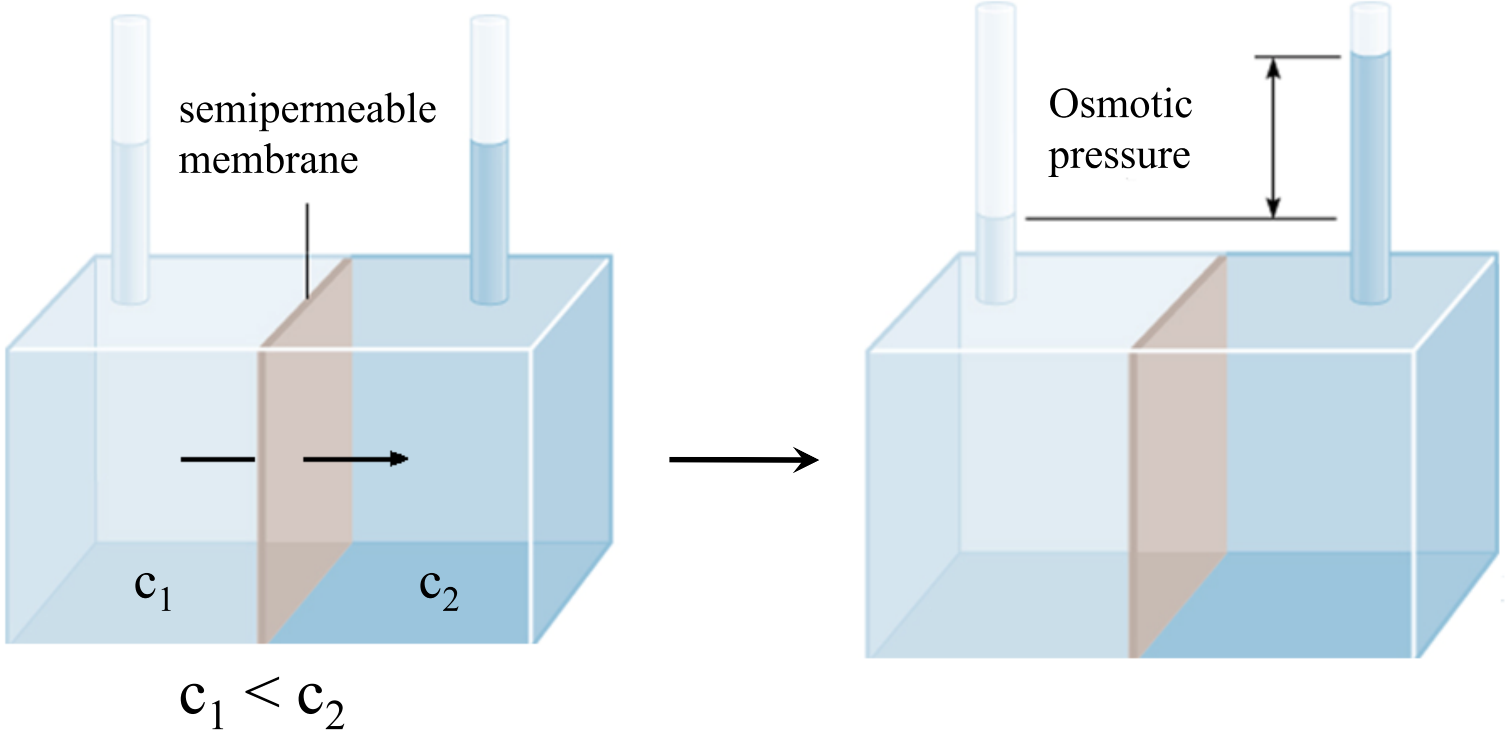
Pure solvent




solution
Pure solvent
760
P (mm Hg)
liquid
ΔP
solid
vapour
ΔT_{cr}
ΔT_{eb}
T_{fus}
0
T (°C)
100
T_{eb}

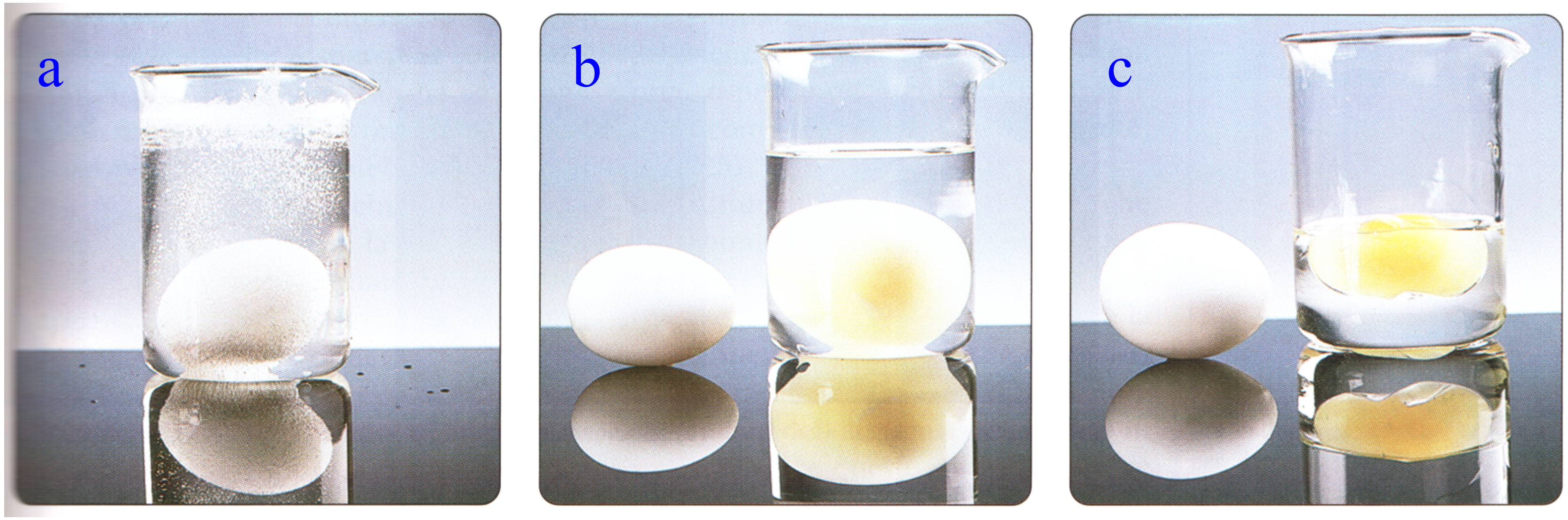
Osmosis and osmotic pressure

When two solutions with the same solvent but with different concentrations of solute are separated by a semipermeable membrane, the solvent moves from the less concentrated solution to more concentrated one in order to cancel the difference between the concentrations of the two solutions .



Osmosis is a selective flow of solvent through a semipermeable membrane and the osmotic pressure is the external pressure to be applied to prevent osmosis.

Osmosis



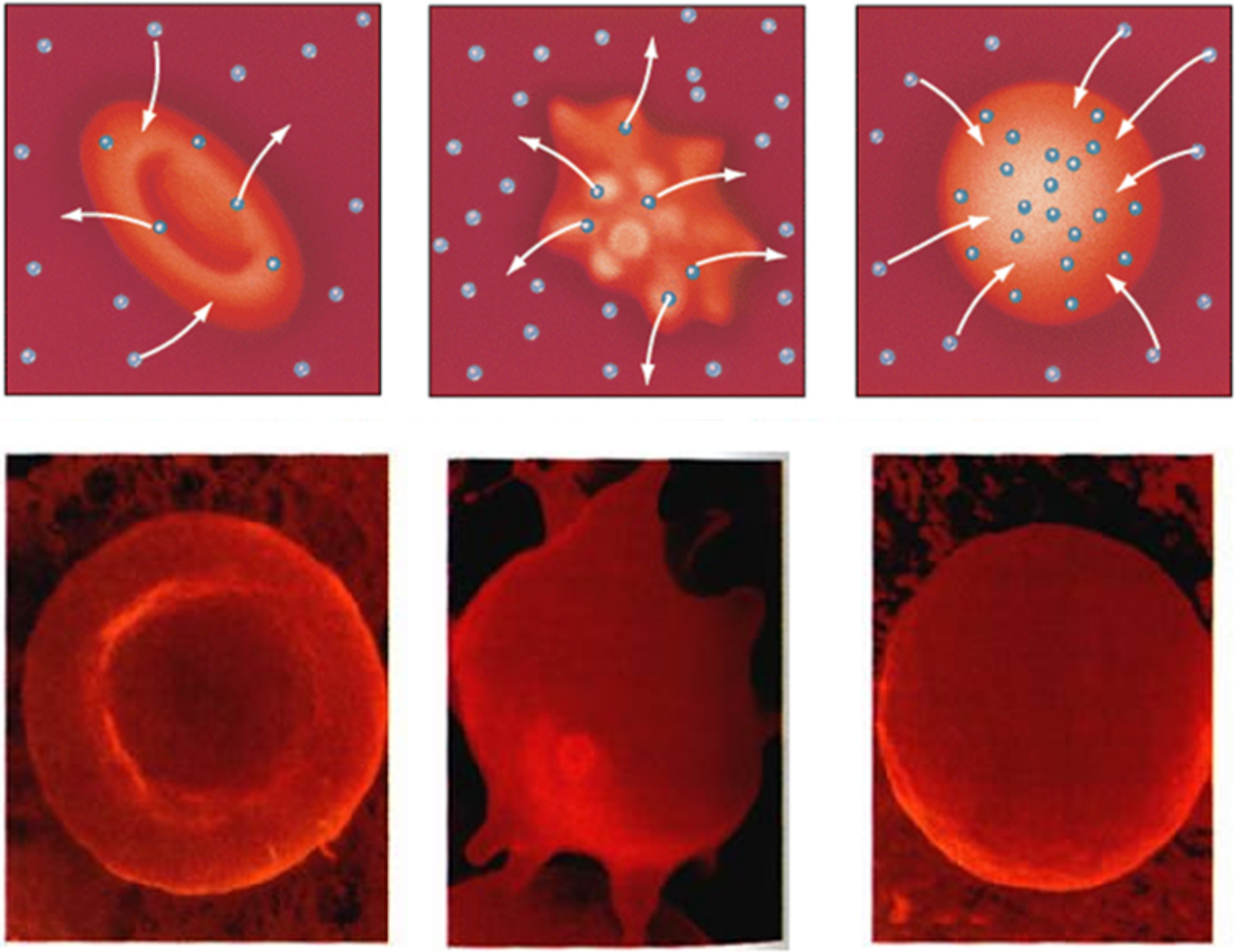
a) An egg is placed in a diluted CH_3COOH solution (vinegar). The acid reacts with $CaCO_3$, but the inner membrane is not affected.

$$CaCO_3\ (s) + 2\ CH_3COOH\ (aq) \text{->} Ca^{2+}(aq) + 2\ CH_3COO^-\ (aq) + CO_2\ (g) + H_2O\ (l)$$

b) If the egg is placed in pure water the membrane is swollen (hypotonic medium).

c) If the egg is placed in a very concentrate solution of sucrose (sugar) it shrinks (hypertonic medium).

Osmosis and red blood cells

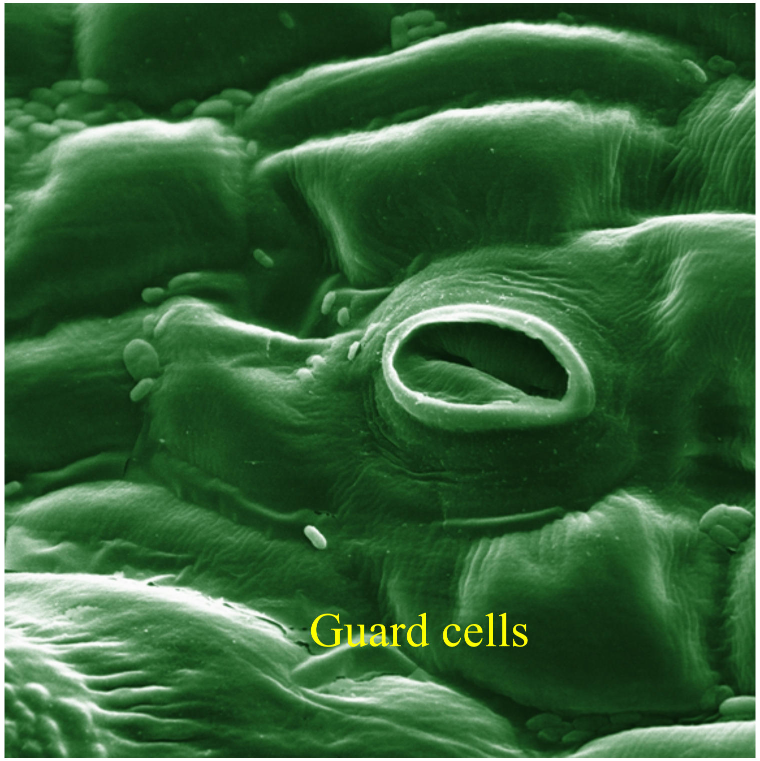


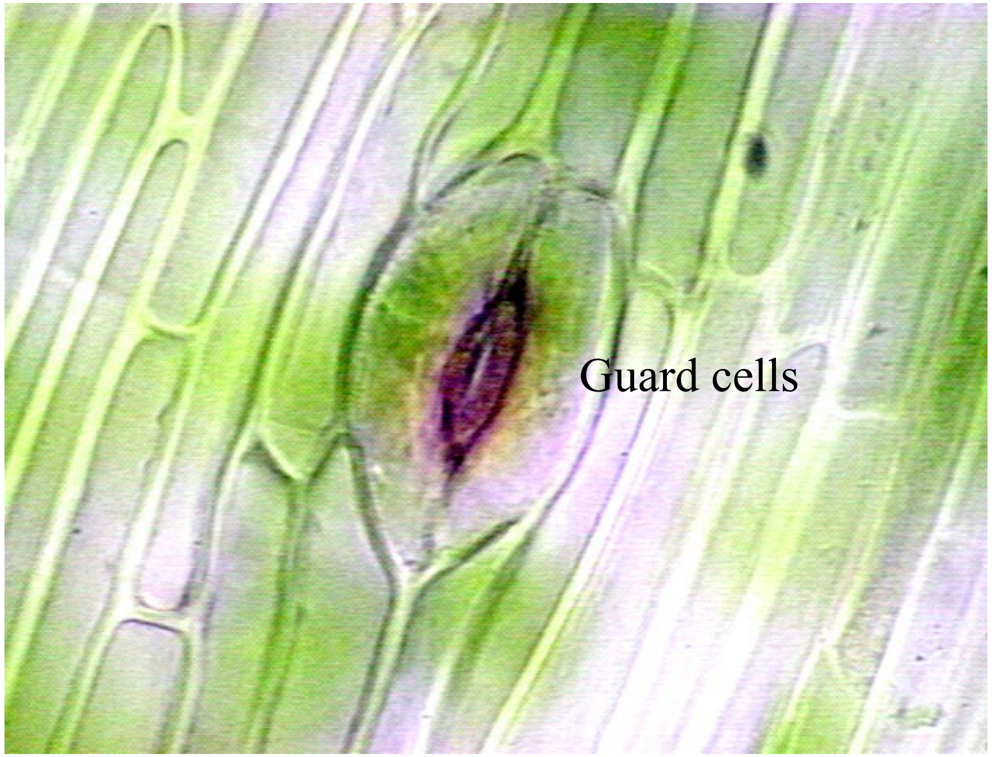
Isotonic solution

Hypertonic solution

Hypotonic solution

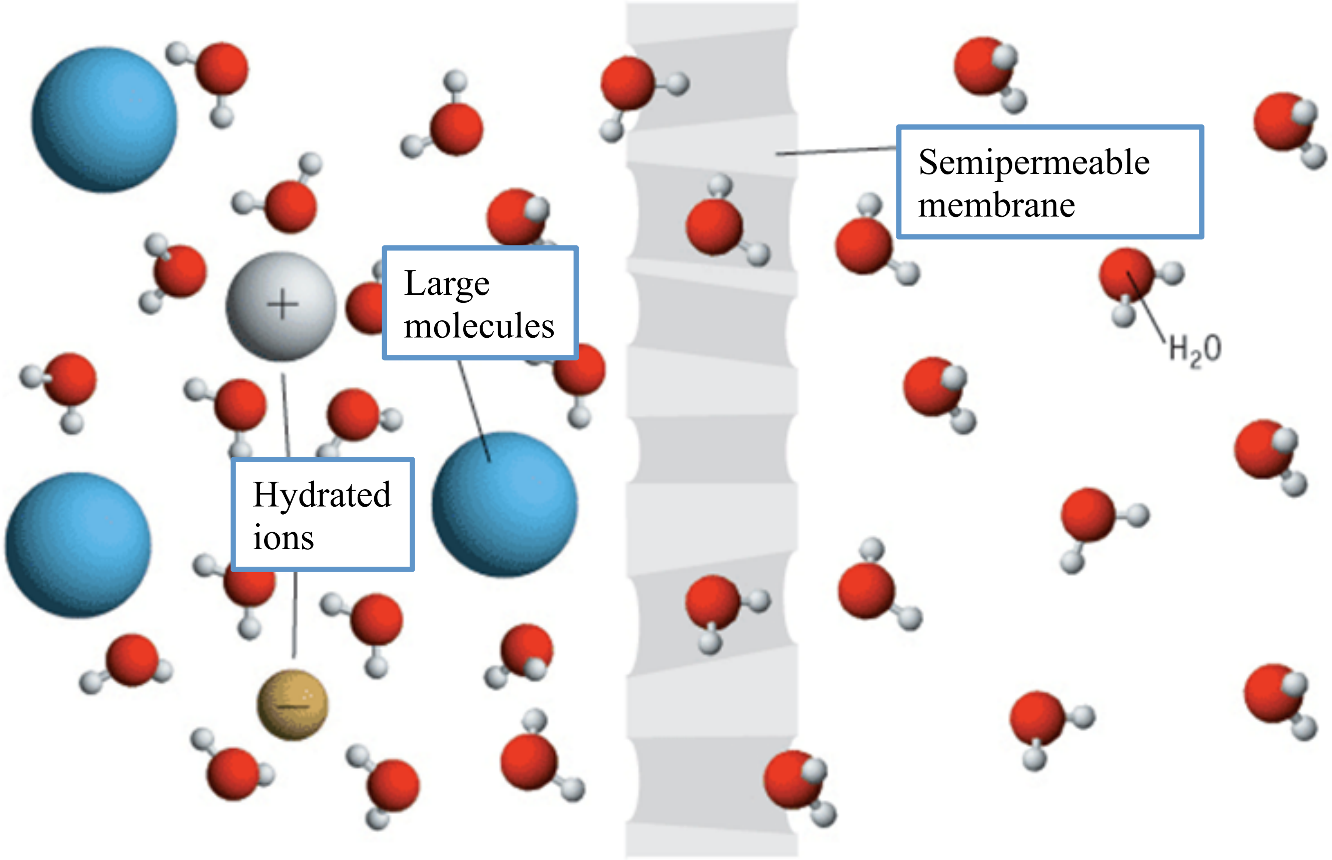
The opening /closing of stomata in plants is determined by changes in osmotic pressure



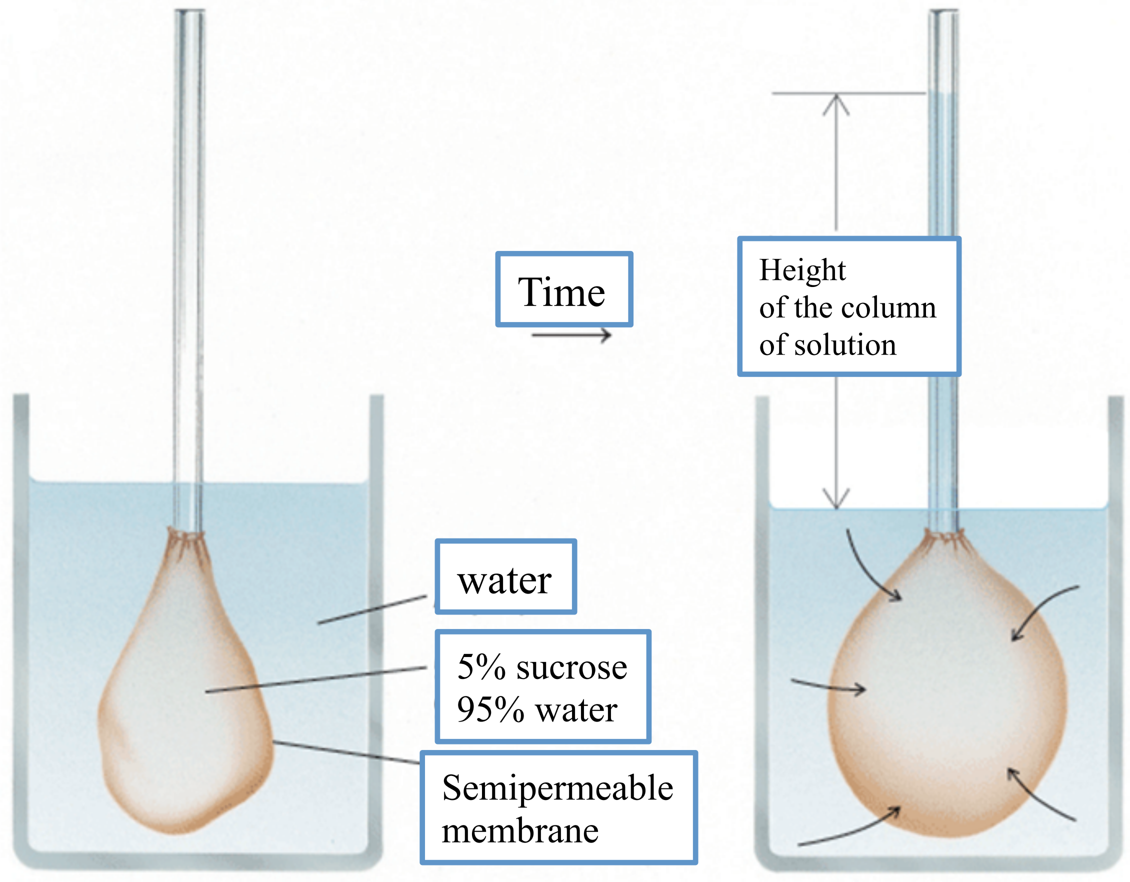


Semipermeable membranes

Osmotic flow through a membrane which is selectively permeable (semipermeable) towards H_2O. The substances dissolved (hydrated ions, large molecules), can not diffuse through the membrane. The membrane acts as a molecular sieve.



In this system, the number of solvent molecules per unit time that move through the membrane towards the solution is greater than the number of solvent molecules that cross it in the opposite direction.



The solute molecules inside the membrane do not cross it, but they impact on the membrane exerting a pressure.

The mechanism of the osmotic pressure can be visualized considering that the solute particles tend to disperse uniformly in the solvent, like a gas that occupies all the available space: the solute exerts pressure similar to gas pressure.

Indeed, according to measurements carried out in dilute solutions, osmotic pressure π and molar concentration c are linked by this relationship:

$$\pi = cRT$$

c = solute concentration in (mol/L)
R = gas constant (0.0821 atm L mol^{-1} K^{-1})
T = temperature (Kelvin)

This relationship is similar to the ideal gas state law ($PV=nRT$) with the osmotic π pressure instead of P p and $c = n/V$.

The colligative properties of solutions depend on the concentration of the solute but not on its nature. Therefore they do not depend on the type of particle but a are determined solely by the number of particles in solution. In the case of electrolytes is necessary to take into account the dissociation.

Colligative properties corrected for dissociation

$$\begin{cases} \Delta P_{solvent} = -i\, x_{solute} P^{o}_{solvent} \\ \Delta T_{eb} = i\, K_{eb} m \\ \Delta T_{cr} = i\, K_{cr} m \\ \pi = i\, cRT \end{cases}$$

$i = 1 + \alpha\,(\nu - 1)$ is the van't Hoff coefficient and α is the dissociation degree.

ν= number of particles or ions formed after dissociation

$$NaCl \longrightarrow Na^+ + Cl^- \qquad \nu = 2$$

$$MgCl_2 \longrightarrow Mg^{++} + 2\ Cl^- \qquad \nu = 3$$

$$Na_3PO_4 \longrightarrow 3Na^+ + PO_4^{3-} \qquad \nu = 4$$

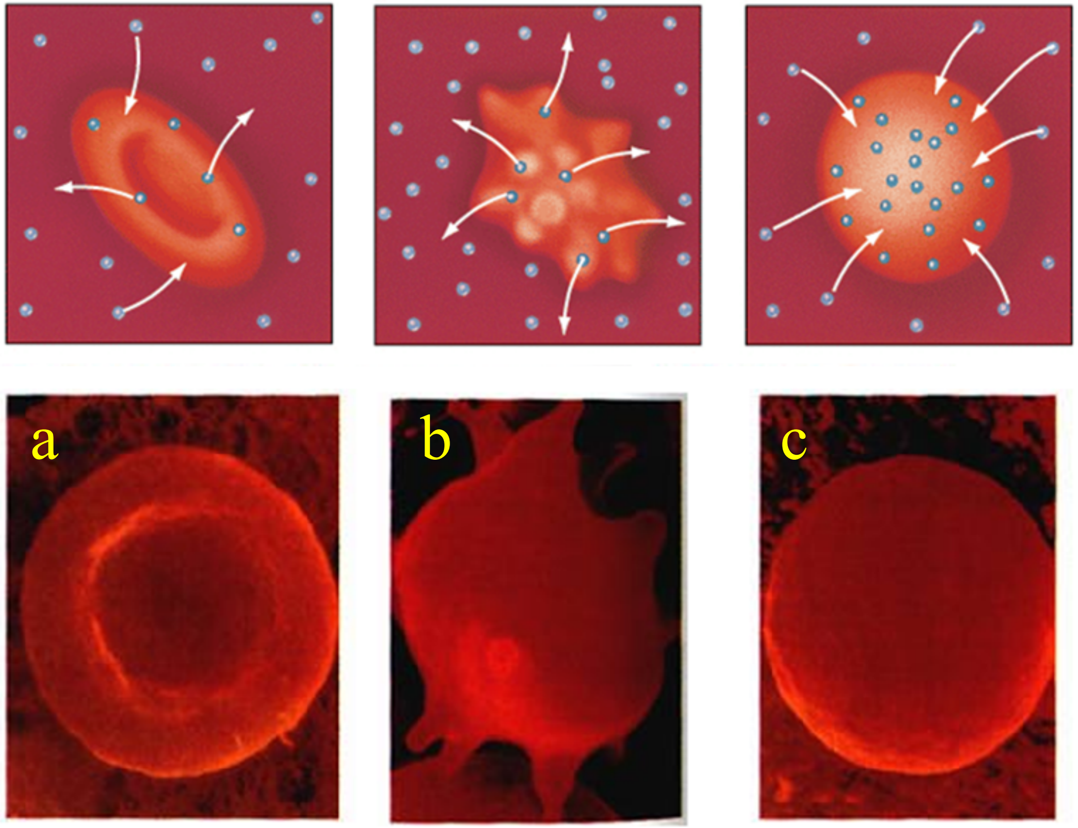
α = dissociated moles/total moles

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

$$\alpha = \frac{[CH_3COO^-]}{[CH_3COOH] + [CH_3COO^-]}$$

Patients at risk of dehydration, often need to take water and nutrients intravenously. Pure water can not be infused. The solution to be administered intravenously must have the same total concentration of solutes in the blood of the patient or to be isotonic.

Isotonic solution
0.9 % NaCl (w/v)
= 0.154 M



isotonic hypertonic hypotonic

a) Isotonic solution

$$\pi_{out} = \pi_{in}$$

b) Hypertonic solution

$$\pi_{out} > \pi_{in}$$

c) hypotonic

$$\pi_{out} < \pi_{in}$$