Solutions and Colligative Properties

1. Concentration and units

Mixtures do not have a defined composition, so we need to define concentration to know the proportion between solute and solvent.

<u>**Concentration** is every magnitude that expresses the ratio between the amount of solute and solvent in a solution</u>. This can be solid in liquid, liquid in liquid, solid in solid (alloys), gas in liquid, solid in gas, liquid in solid, etc…

There are many different concentration units, each with their own *for and against*:

- **g/L (mass concentration)**: grams of solute per (divided by) litre of solution.

- **% (w/w)**: weight percentage of solute with respect to the total weight of the solution. <u>It is defined as the grams of solute in 100g of solution</u>. (it usually comes with the density of the solution).

- **M** or mol/L: **molarity** is the number of moles per litre of solution; this is by excellence the Chemistry unit.

- **m**: **molality** is defined as the number of moles of solute per kilogram of solvent.

- **x**: mole fraction (or molar fraction): is the number of moles of solute divided by the total number of moles of the solution. (In a more general basis, the mole fraction is the moles of target substance divided by total moles involved).

Richness: relative abundance of the component of interest in the sample.
Purity: percentage of the component of interest in the mixture.
"Per": divided by

2. Colligative properties of solutions

Colligative properties are those which depend on the concentration of the solution. These properties do not depend on the nature or type of solute but only on the amount of solute present in the solution. This is the reason why we will only consider non-dissociable solutes, in which the concentration directly indicates the number of particles of the solute.
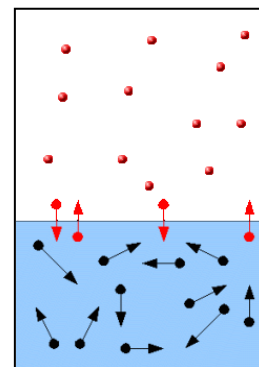

Figure 1. Vapour-liquid equilibrium is not a static situation but completely dynamic.

The colligative properties are four: vapour pressure lowering, freezing point depression, boiling point elevation and osmotic pressure.

1.-Vapour pressure lowering: RAOULT'S LAW

In 1887, **Raoult** found experimentally that partial vapour pressure of solvent, when in presence of a non-volatile solute, is directly proportional to the molar fraction of the solvent:

$$p = p_0 \cdot x_0$$

being:
p the vapour pressure of the solvent in the solution
p_0, that of pure solvent, and
x_0 the molar fraction of the solvent.
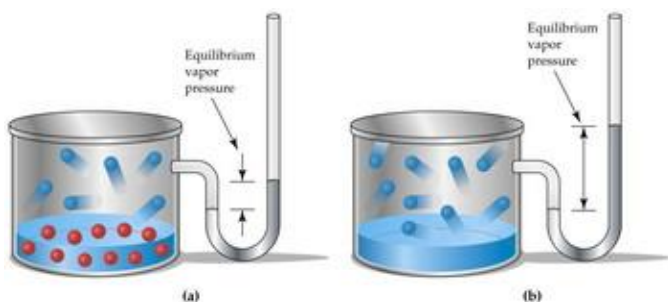
The variation in vapour pressure will therefore be:

Figure 2. The presence of a solute lowers down the vapour pressure of (a) a solution in comparison with (b) the pure compound, this is, less molecules evaporate to the gas phase.

The molar fraction of a pure solvent is logically 1 (moles of solute / total number of moles of the solution), therefore the vapour pressure will be that of the pure compound. If it is not pure, as it happens with solutions, the vapour pressure of the solvent dissolved in the solution can only be lower.

Example: The vapour pressure of pure water at 25°C is 23.8 torr. Calculate the vapour pressure when 50.0 g of glucose (mm=180 g/mol) is dissolved in 100 g of water at 25°C.

Solution: We need to first find the mole fraction of water. In order to do so you need to find out the moles of water and of glucose present in the solution.
The number of moles of each component is:

$n_{glucose}$ = 50.0 g x 1 mol/180 g = 0.278 mol
n_{water} = 100 g x 1 mol/18 g = 5.56 mol

The mole fraction of water is: X_{water} = 5.56 / (0.278)+(5.56) = 0.954

So, p = $p_0 \cdot x_0$ p = (23.8) x (0.954) = 22.70 torr

2. Freezing point depression

This is the lowering in the freezing point with respect to that of the pure solvent, given by:

$$\Delta T_f = K_f \cdot m$$

where ΔT_f is the depression in the freezing point, K_f, the cryoscopic constant, and **m,** the molality. For water K_f = 1.86 °C kg/mol.

3. Boiling point elevation

This is the increase in the temperature of the boiling point with respect to that of the pure solvent, given by:

$$\Delta T_b = K_b \cdot m$$

where ΔT_b is the elevation in the boiling point, K_b, the ebullioscopic constant of the solvent, and **m**, the molality. For water, K_b = 0.512 °C kg/mol.

(The previous expressions are only valid for non-dissociable, non-ionisable solutes. In the case of ionisable solutes the expression should be modified and the corresponding ionisation degree factor introduced).

HOMO FABER: Antifreezers

Man has learnt to explode on his own benefit the freezing-point depression in order to avoid dangerous winter situations. For example, cars have a water closed circuit to cool down engines while working. If outside temperatures go below 0 °C, this water could freeze, increasing its volume and pressing on every conduction, and could make the whole circuit explode. To prevent this circumstance, water is replaced by a very concentrated solution so that its freezing point is much lower than that of the water.

Another use of cryoscopy is the possibility of making ice disappear from roads by spreading salt. Salt dissolves in the very thin liquid film ice holds, producing salty water, which at 0 °C is liquid. As the resulting solution is very concentrated, ice tends to

melt in order to dilute it until there is no more ice or the solution is so diluted that its freezing points does not differ from that of the pure water, and it freezes. Anyway, when salty water freezes it forms a snow-like solid, not ice, so the slipping problem is overtaken.

4. Osmotic pressure

The level of liquid in two communicating vessels should reach the same height. However, if we locate a semi-permeable membrane in between, only the solvent will be able to go across the separation to the more concentrated solution, trying to balance both concentrations, and reaching so the equilibrium situation in which both solutions have the same vapour pressure. This process is called **osmosis**.

permeable: everything goes through   impermeable: nothing goes through   semipermeable: only solvent (water) goes through
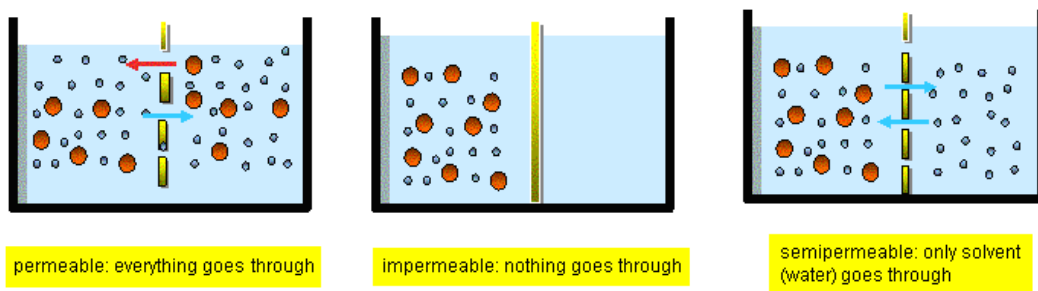
Figure 3. Types of membranes according to their permeability.

If we put the same level of solution and pure solvent in both branches of a U-tube, separated by a semi-permeable membrane in the middle, the osmotic process will make the branch with the solution go higher due to the transference of solvent from the other one, which will subsequently descend. This difference in height generates a hydrostatic pressure over the solvent through the membrane. This pressure is what we call **osmotic pressure**.
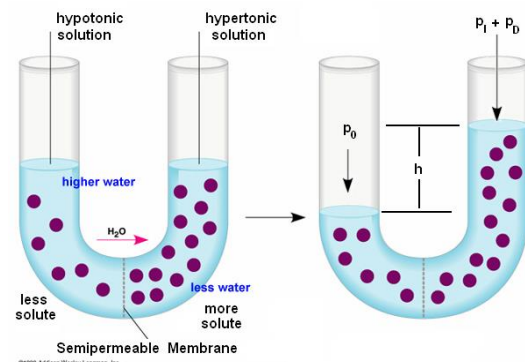

Figure 4. U-tube containing separated solutions of different concentration, causing a movement of solvent until hydrostatic pressure balances osmotic pressure.

$$p_D = p_0 x_D = p_0 \frac{n_D}{n_S + n_D} \quad ; \quad p_D + p_I = p_0$$

VAN'T HOFF had the idea of the particles of solute in the solution behaving similarly to an ideal gas, so the exerted pressure would be:

$$\pi \cdot V = n \cdot R \cdot T$$

where donde π is the osmotic pressure in atm, **V** is the volume of solution, **n**, number of moles of solute, **R**, the constant of gases and **T** the temperature in Kelvin. Working out π, and given that **n/V** is **M**, the molar concentration is:

$$\pi = (n/V)\cdot R\cdot T = M\cdot R\cdot T$$

As we have said that this is a hydrostatic pressure, then,
(you are not responsible for these two formulas)

$$\pi = \rho\cdot g\cdot h$$

$$\rho\cdot g\cdot h = (n/V)\cdot R\cdot T$$

Osmotic pressure on a solution is the pressure exerted by the solvent through the membrane, and balances the hydrostatic pressure corresponding to the difference in height between both columns.

Example: Estimate the osmotic pressure at 25 °C of a 0.010 M protein solution.

Solution: The molarity of the solution is M = 0.010 mol/L ; R = 0.082 L atm/mol K and the Kelvin temperature is 25 + 273 = 298 K. Now let's substitute these data into the equation:

$\pi = M\cdot R\cdot T$ $\pi = (0.010)$ x (0.082) x $(298) = 0.24$ atm

HEALTH AND SOCIAL EDUCATION: Physiological media

You may have wondered about what is contained in the hanging solutions we can see in hospitals. This is not medicine (although these can be dissolved in these bags to make easier their administration), but salt water.

But why salt water? Well, blood contains lots of different cells, mostly red blood cells; a red blood cell is made of a cytoplasm (quite a concentrated solution) separated from plasma by a membrane (which lets substances selectively go through, this is, semipermeable). If we put red blood cells in distilled water (*hypotonic* medium), water begins to get into the cell to try and dilute the inside solution, finally bursting the cell out. On the contrary, if we put the red blood cells in a very concentrated solution

Figure 5. Effect of the osmotic pressure on red blood cells in (a) isotonic, (b) hypotonic and (c) hypertonic medium.

(*hypertonic* medium), then the water goes out from the cells to try and dilute the surrounding solution, "drying out" themselves. In both cases the final result is the death of the cell, therefore showing how important is that the infused solutions have a con-
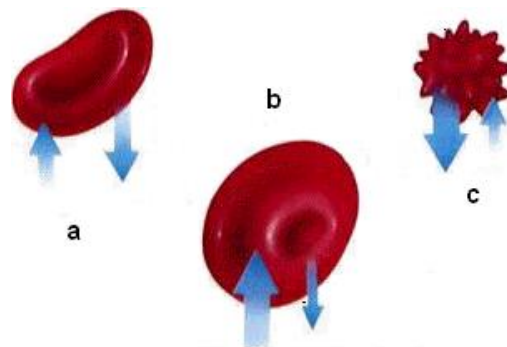
centration as similar as possible to that of the physiological medium, an *isotonic* solution.

Questions and problems

1. Determine the molarity of a sulfuric acid solution, obtained by addition of 196 g of the acid on water until 2 L of solution are obtained.

2. How many grams of potassium hydroxide will we have to weigh to obtain 250 cm^3 of 2 M solution?

3. Determine the molality of a solution of nitric acid, if 63 g of acid are added to 500 cm^3 of water.

4. Determine the mole fraction of each substance in the following solutions: a) 2 g of acetic acid in 15.6 g of benzene; b) 11.7 g of common salt in 144 g of water. MM of acetic acid: 60 g/mol ; MM of benzene: 78 g/mol.

5. The density of a hydrochloric acid solution is 1.101 g/mL and contains 19.91 % of HCl. Calculate its molarity, molality and molar fraction of HCl in the solution.

6. A solution is prepared by dissolving 9.75 g of iron(III) chloride in 500 mL of water. Let's assume the final volume of our solution is also 500 mL. Calculate: a) molarity, b) molality, c) molar fraction of each substance, d) number of moles of iron(III) chloride in 5 mL of solution.

7. Calculate how much ethanol would be needed per litre of water in order not to freeze above -4.8 °C.

8. Commercial sulfuric acid has a density of 1.8 g/mL and richness in weight of 98 %. Calculate its molarity and molality. What will be the corresponding vapour pressure of water for the solution at 20 °C? P_v(water, 20 °C)= 18 Torr.

9. 20.7 g of ethanol are dissolved in 100 g of water, resulting in a volume of 112 mL. Calculate the freezing and boiling points of the solution prepared. How much will the osmotic pressure be at 25 °C? MM of ethanol:

10. An aqueous solution of 9.2 g/L of a certain substance exerts an osmotic pressure of 0.474 atm at 0°C. Calculate the molecular mass of the solute.

11. How many grams of acetic acid should we dissolve in 250 mL of water in order to change its boiling point up to 101.3 °C? What would the corresponding freezing point? MM of acetic acid: 60 g/mol

12. When dissolving 5 g of a certain solute in 50 g of water, the resulting solution boils at 100.5°C. What is the corresponding molecular mass of the solute?

13. What is the vapour pressure of problem 11 at 20 °C? And what should it be at 100 °C? At what temperature will this solution boil?

14. Explain with your own words how antifreezers work.

Solutions

1) 1M

2) 28g

3) 2 m

4) a) 0.14 acid y 0.86 benzene, b) 0.024 NaCl and 0.976 H_2O

5) 6M, 6.81m, y 0.109

6) a) 0.12M, b) 0.12m, c) 2.16×10^{-3} y 0.99784, d) 6×10^{-4} mol, e) 3.6×10^{21} and f) 1.44×10^{22}.

7) 118.7 g

8) 18M, 500 m and 1.8 mmHg

9) -9.3, b) 102.6, c) 98.18 atm

10) 438

11) -4.65 °C

12) 104

13) 17.22, 0.957 atm, 101.3 °C

14) See text