

CHAPTER 12  
DISSOLUTIONS.

## Treatment of dissolutions, activities ...

**Henry's Law** : it refers to the solute in a dissolution, while the **Law of Raoult** deals with *solvents*.

In the context of **ideal and non-ideal dissolutions**, changes in phases and laws of Henry and *Raoult* etzettera, we have:

Power of attraction between the solute and solvent species (to dissolve the solute):

$$| E_{\text{ion-dipole}} | > | E_{\text{ion-ion}} | \text{ and } | E_{\text{dipole-dipole}} |$$

In the case of water as a solvent, such a process is called *hydration*; This process is what happens in the ideal or real dissolutions or those that are under the rules of Raoult and that we will see next:

In the case of Raoult (solvent-solvent) we have the graph P vs X ( **composition or molar fraction** ), and at the ends only the true law is fulfilled since we find that it clears the ideal (it is natural that lines are assimilated Ideals and reals because the mixture is diluted, which implies a dissolution without interactions).

We can also sense, and we will see later, that if the dissolution of Raoult only contains 1 component then:

$P_{\text{solvent}} = 1 \cdot P^0_{\text{solvent}}$  where 1 = mol No. of solvent / n° mol of dissolution.

Retrieving the graph P vs X Raoult, we know that there are **positive and negative deviations** :

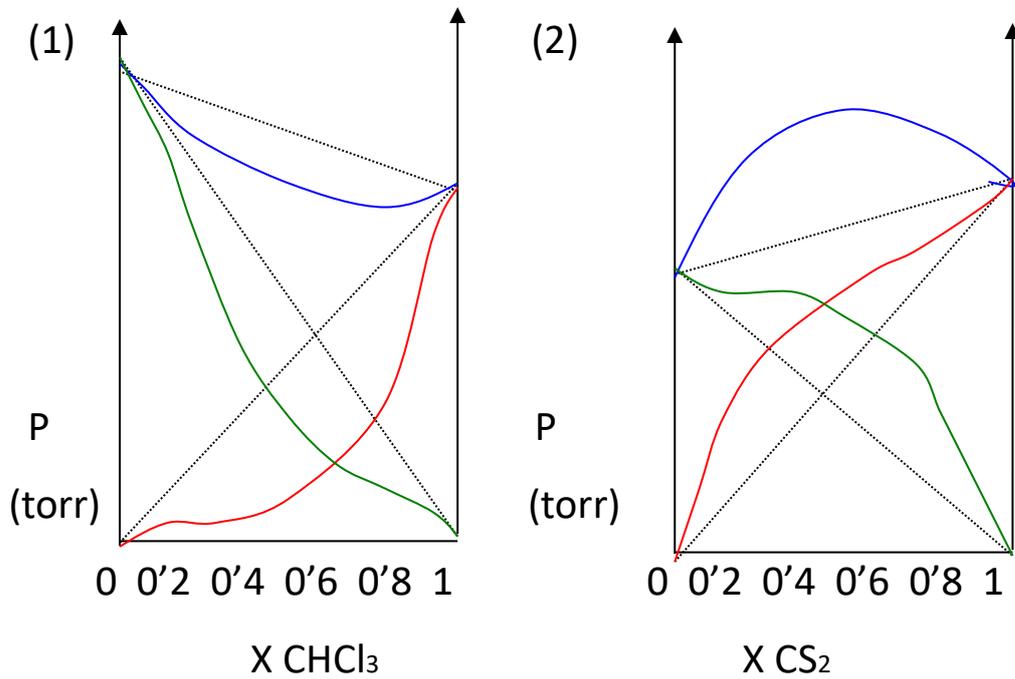
(1). Negatives involve attractions between solute-dissolvent molecules (for example, between polar molecules) which implies that there is a tendency to separate from the whole dissolution, so the steam pressure (Pv) of the whole dissolution is lower:

$$| E_{\text{stability of solute - solvent}} | > | E_{\text{stability of solute - solute}} |$$

Or

$$| E_{\text{stability of solute - solvent}} | > | E_{\text{stability of solvent - solvent}} |$$

Fig. 36:



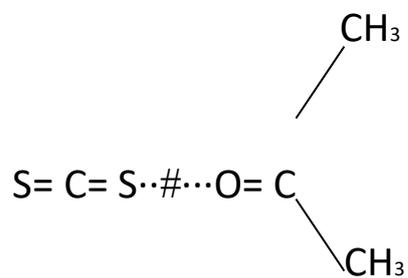
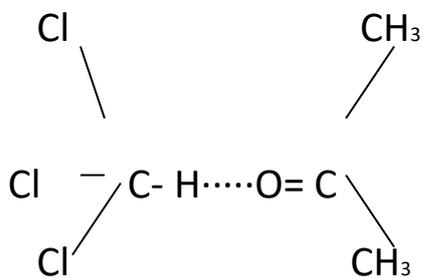
Where X represents the molar fraction.

Discontinuous line:  
ideal behavior

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Blue line:  $P_v$  of the dissolution  
Red line:  $P_v \text{ CHCl}_3$   
Green line:  $P_v$  acetone.

Blue line:  $P_v$  of the dissolution  
Red line:  $P_v \text{ CS}_2$   
Green line:  $P_v$  acetone



(2). In positive deviations we find that the attractions between polar and non-polar molecules (solute-solvent) are less strong, so there is no tendency to scape from the dissolution because  $|E_{stability\ of\ solute - solute}|$  and  $|E_{stability\ of\ solvent - solvent}|$  are superior to  $|E_{stability\ of\ solute - solvent}|$ .

Absorption of heat to maintain the dissolution altogether. They are energetically unfavourable.

; then the steam pressure increases to become steam as we see in the graph.

Now until tomorrow, but I do not go without mentioning *the Dalton Law*, which suggests that it is the touchstone of all this treatment:

$P_t = P_1 + P_2$ ; when the *equilibrium* between the 2 is reached, we find that  $P^0_1 = P^0_2$ , therefore  $P_t = X_1 \cdot P_1 + X_2 \cdot P_2$

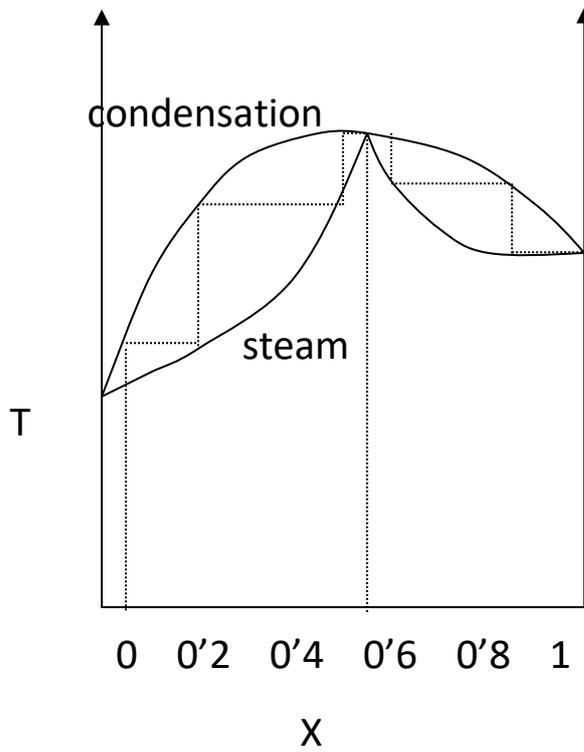
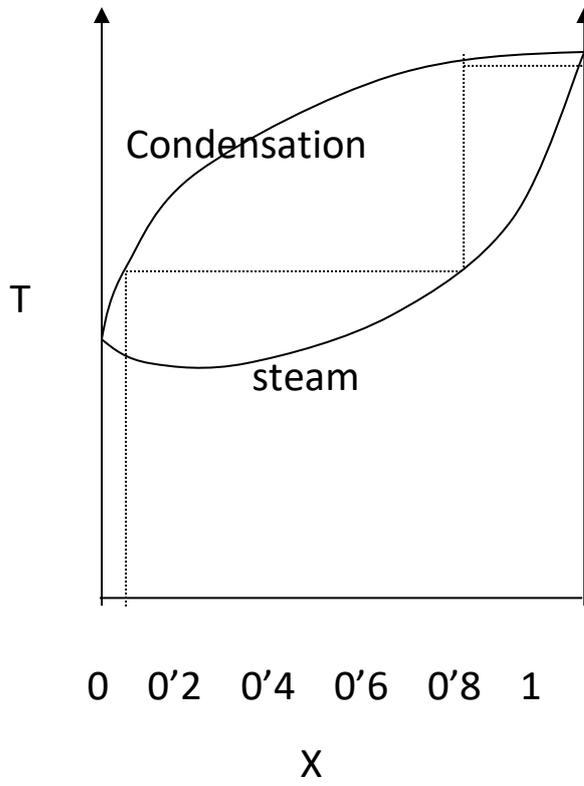
$P^0_1 (X_1 + X_2) = P_t$ , which indicates that  $P^0_1 = P_t$  and therefore:

$$X_1 = P_1 / P_t$$

$$\text{Last } X_a \cdot P_t = P_a$$

Now, define **Azeotrop** and the graph T vs X to illustrate it: when the steam and its dissolution have the same composition. (Fig.37)

Fig. 37:



AZEOTROP

I now deepen the subject of **solute-solute interactions** in ideal dissolutions: if the *dissolution is diluted*, there are no such interactions:

$[ ]^0 = \text{activity}$ .  $[ ]$ ; when “act” = 1 is that there is ideality, whereas when “act” is not equal to 1, ideality does not exist.

We can also see that “act” =  $P_s / P^0_s$   
“act”. it has no units

In this way we see that the  $P_i$  and the  $[ ]$  are proportional.  
 $P^0$  is based on *the standard or hypothetical state*, and we work with concentrations of up to 1 molal because, although it would be possible to use concentrations of  $10^{-4}$  m and that the lack of solute-solute interactions were fulfilled, we would work with *mass concentrations small*

$$P_{\text{solute}} = P^0_{\text{solute}} = k' \cdot 10^{-4} \text{ molal}$$



## Boiling point and freezing point:

As we can see, there is a relationship between  $\Delta T_e$  and the concentration ( [ ] ) of the solute (increase of the **boiling T** of the dissolution with respect to the *pure solvent* ).

So the rise of T boiling depends on whether the concentration also increases.

Therefore the equation that can be drawn from this is:

$\Delta T_e = K \cdot \text{Molality}$ , where **K is the constant regulatory**

*Molality* = moles of solute / 1000 grams of solvent

In fact the classic graph that represents the **P of steam** with respect to the T (remember that the Boiling temperature is obtained when the Pv of the *gas phase* is equal to the Pv of the *liquid phase* ) is a curve, but based on Linear differential equations are adding and fitting (based on approximations, which are assimilated to *ideal dissolutions*).

Molar fraction =  $X = n_2 / (n_1 + n_2)$  where  $n_2$  is the solute

In ideal dissolutions  $n_2 / n_1$  where it turns out that the solute is in small concentration.

$$\Delta P / \Delta T = k = \text{slope} \quad \Delta T \cdot k = \Delta P = k' \cdot X_{\text{solute}}$$

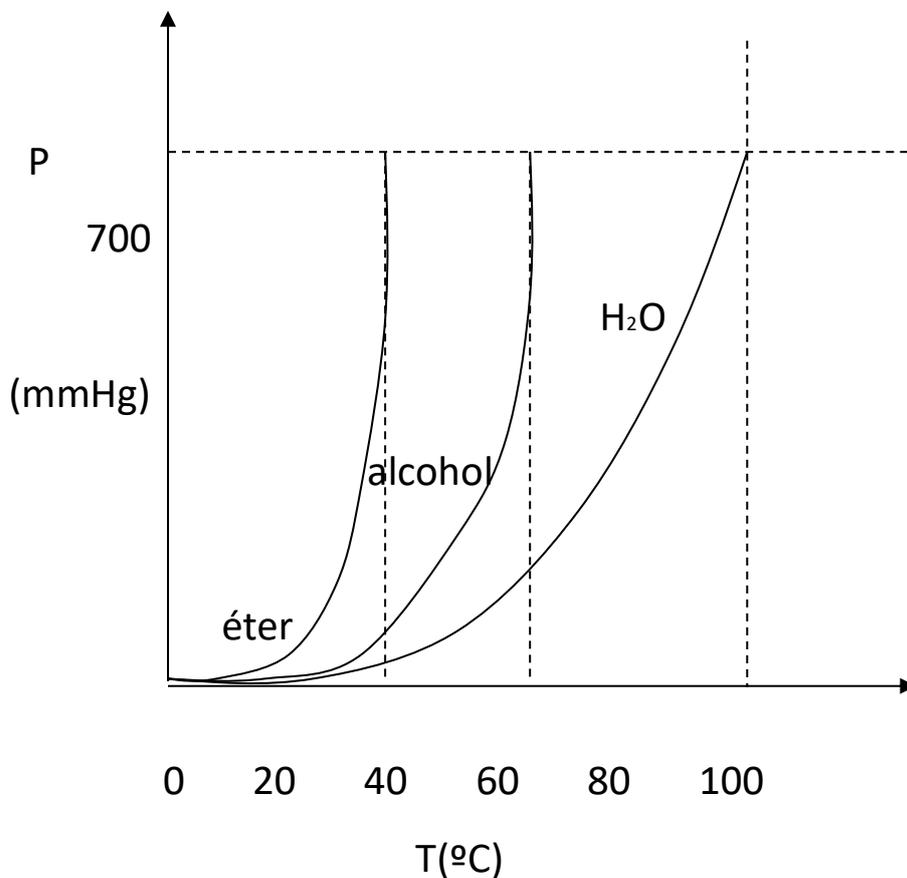
$$\text{Then } \Delta T = \frac{k'}{k} \cdot (n_2/n_1) \quad n_2/n_1 = \frac{\text{grs solut} / \text{PM}(\frac{\text{grs solute}}{\text{mols solute}})}{\text{grs solvent} / \text{PM}(\frac{\text{grs solvent}}{\text{mol solvent}})}$$

Where **K** is =  $k'/k$

## Steam pressures:

If  $P_{\text{atmospheric}} = P_v$ , then the temperature at which this happens is the  $T_{\text{boiling}}$  (fig.38: variation of the vapor pressure with the T)

Fig. 38:

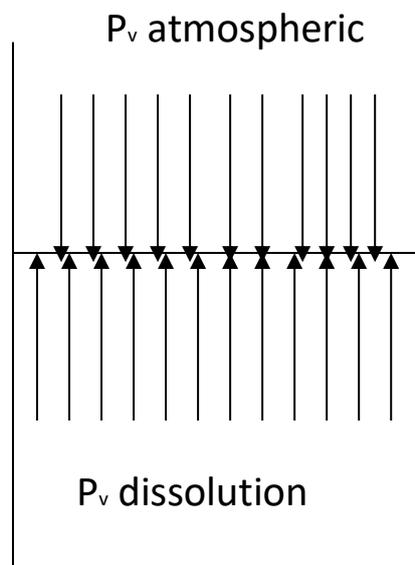


Also, when the pressure in a container is less than the atmospheric then the water or the liquid sprouts.

On the other hand, when we handle a *pressure cooker* where the  $P_{\text{inner}}$  is very high, to get to the boil it takes more and therefore it adds more to the food.

The number of molecules that pass into the gaseous state is equal to the number of molecules that pass into the liquid. Then the **surface tension** is broken. (fig.39).

Fig. 39:



The  $T$  boiling increases so does the  $E_c$  and this relationship also comes from the fusion of **Boyle's law** and **kinetic theory of kinetic energy**.

It is also necessary to keep in mind that **alcohol** has a low boiling point, therefore, the experience we are doing is as follows: dampen your hand with alcohol and it tends to evaporate, then it captures heat (physiological) and he gets it, and we can see this because his hand cools. If we do this with some other substance or liquid, if I do not have the  $P_{eb}$  bass, it would not make sense.