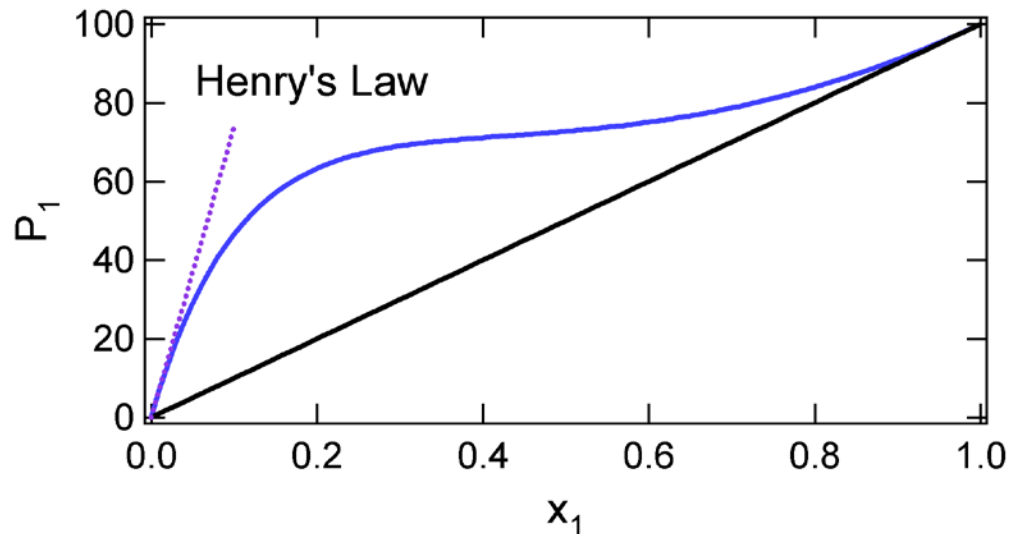# Non-ideal solutions

Many solutions are not ideal. For ideal solutions the role of intermolecular interactions can be ignored. This may be because they are small or because two components have the same interaction with each other that they have with themselves. In other words similar solvents will form ideal solutions. However, in many cases, intermolecular interactions cause deviations from Raoult's law. We can consider the "like" interactions between molecules of same species and "unlike" interactions between molecules of different species. If the unlike-molecule interactions are more attractive than the like molecule interactions, the vapor pressure above a solution will be smaller than we would calculate using Raoult's law. If the unlike-molecule interactions are more repulsive, then the vapor pressure is greater than for the ideal solution.

Non-ideal solutions

For the example shown in the plot above we have assumed that $P_1^* = 100$ torr. Note that as $x_1 \rightarrow 1$ the slope approaches the ideal slope obtained from Raoult's law. However, as $x_1 \rightarrow 0$ (and therefore $x_2 \rightarrow 1$) the slope is quite different from ideal behavior. Note that the slope has the value of the Henry's law constant $k_{H,1}$. This is depicted in the Figure below (purple line). The Henry's law value can be quite different from the ideal value.

Activity

The activity in non-ideal solutions corresponds to mole fraction in ideal solutions.

$$a_j = \frac{P_j}{P_j^*}$$

The activity replaces mole fraction in the expression for the chemical potential.

$$\mu_j^{soln} = \mu_j^* + RT \ln a_j$$

When considering a non-ideal solution the above expressions hold and thus the mole fraction x_j is no longer equal to P_j/P_j^*. However, as the mole fraction approaches unity (a pure substance) the solution becomes ideal.

Thus, as $x_j \rightarrow 1$, $a_j \rightarrow x_j$.

The activity coefficient

We can define an activity coefficient γ_1 such that

$\gamma_1 = a_1/x_1$.

The property of the activity coefficient is that it approaches a value of 1 (ideal behavior) as the composition approaches the pure solvent:

$a_1 \rightarrow x_1$ and $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$. Thus, the solution

This definition is based on a Raoult's law standard state, which is also known as a solvent standard state. The activities or chemical potentials are meaningless unless we know the standard state