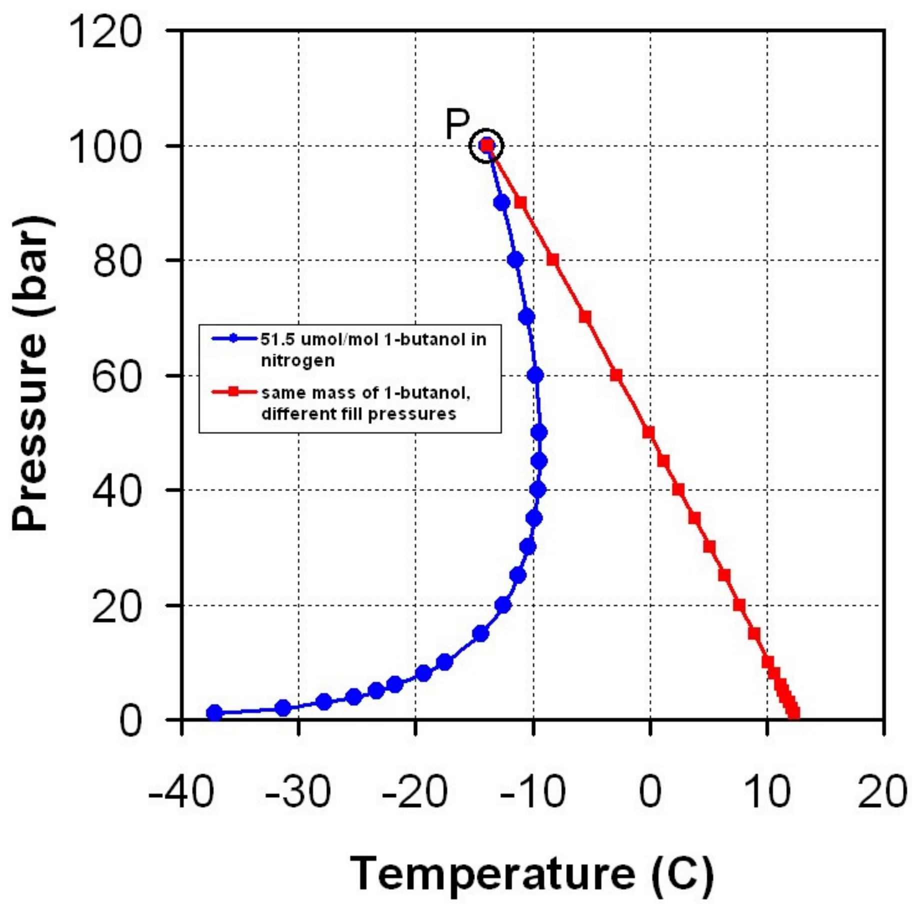
How can there be more vapour in a compressed mixture than in the vapour phase of a pure material?

In this discussion we take the example of a mixture of 51.5 μmol/mol of butanol in nitrogen.

The blue curve in the Figure is the dew curve of the mixture*. This is the temperature at which condensation would occur as a function of pressure for this particular mixture.



In order to illustrate how the condensation properties of such a mixture are related to the properties of the simple system of a vapour in equilibrium with its condensate, we consider a simple experiment in which nitrogen is added to pure butanol in a cylinder.

First, consider the behaviour of pure butanol in the container. The pressure of the butanol vapour as a function of temperature is described by the Antoine equation. If there is sufficient material within the cylinder to sustain the vapour pressure, then some of the butanol will exist in the liquid phase.

* All calculations of dew point in this note have been performed using the "Gas VLE" software.

Consider now the addition of 1 bar of pure nitrogen. For this example we have chosen the mass of butanol to be such that the amount fraction of butanol would now be 5150 μmol/mol. We can calculate the dew point for this mixture (at 1 bar) and it is plotted along the red line. The result shows a reduction in the dew point (*ie* the amount of condensate at constant temperature in the cylinder is reduced). This is because of the attraction (due to van de Waals forces) of the butanol molecules for the nitrogen molecules in the gas phase. This effect is larger for more polar molecules.

This effect continues as the amount of pure nitrogen is further increased and the dewpoint follows the red line. This calculation has been carried out using the mass of butanol required to give an amount fraction of 51.50 μmol/mol at 100 bar. This is indicated by the point P where the two lines meet.

If this cylinder is now vented to atmosphere slowly (so as to maintain isothermal conditions) the dewpoint of the mixture would follow the due curve. The mixture will never return to the start of the red line, since it will always stay at an amount fraction of 51.5 μmol/mol.

The effect described here is not the same as that leading to a pan of water boiling at 69 deg C on the top of Mount Everest where the atmospheric pressure is 0.26 bar. This concerns the variation of boiling point when the ambient pressure is close to the saturated vapour pressure. However, the effect described is the same as the observation that Henry's constant increases as the pressure of gas above a liquid is increased.

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