Colligative properties

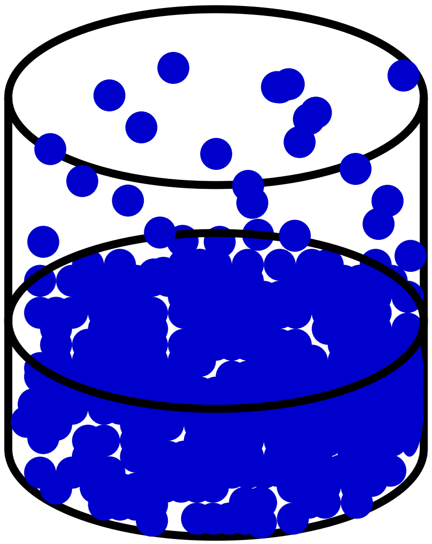
There are a number of properties of a dilute solution that depend only on the number of particles and not on their kind. Colligative properties include the lowering of the vapor pressure of a solvent and elevation of the boiling temperature by the addition of a nonvolatile solute, the depression of the freezing point of a solution by a solute, and osmotic pressure.

They all have a common treatment using the chemical potential of the pure substance compared to the chemical potential of the mixture. In this case the mixture consists of a non-volatile (solid) solute.

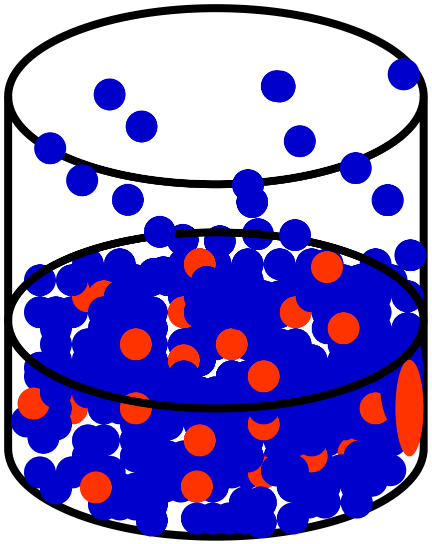
Vapor pressure reduction

The reduction of the vapor pressure is the most fundamental Colligative property, but it is often not discussed. A non-volatile solute will lower the vapor pressure by Raoult's law. The mole fraction of the solvent is lowered and the solute does not contribute to the vapor pressure because it is non-volatile.

P_1^*



$x_1 P_1^*$



P and T dependence of the chemical potential

We can think of the colligative properties as shifts from equilibrium values of either temperature or pressure. Therefore, the fundamental equations of these effects come from the temperature and pressure dependence of the chemical potential.

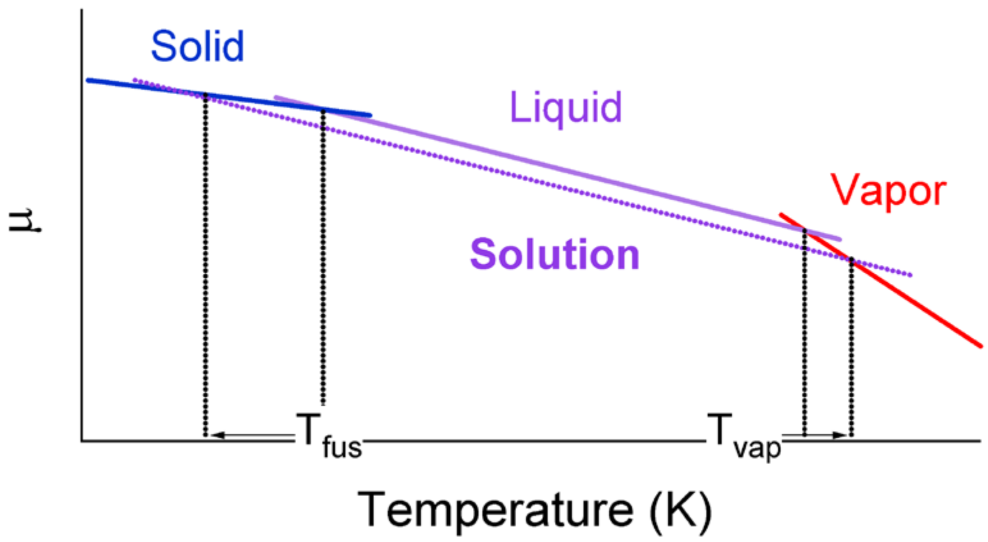
$$d\mu = \left(\frac{\partial \mu}{\partial P}\right)_T dP + \left(\frac{\partial \mu}{\partial T}\right)_P dT$$

$$V_m = \left(\frac{\partial \mu}{\partial P}\right)_T \qquad -S_m = \left(\frac{\partial \mu}{\partial T}\right)_P$$

$$d\mu = V_m dP + -S_m dT$$

Connection of freezing point depression and boiling point elevation

The diagram shows the chemical potentials of the three phases of a substance as a function of temperature. To understand this we will explore the meaning of the slope of these lines and the lowering of the chemical potential of the solution relative to the pure liquid.

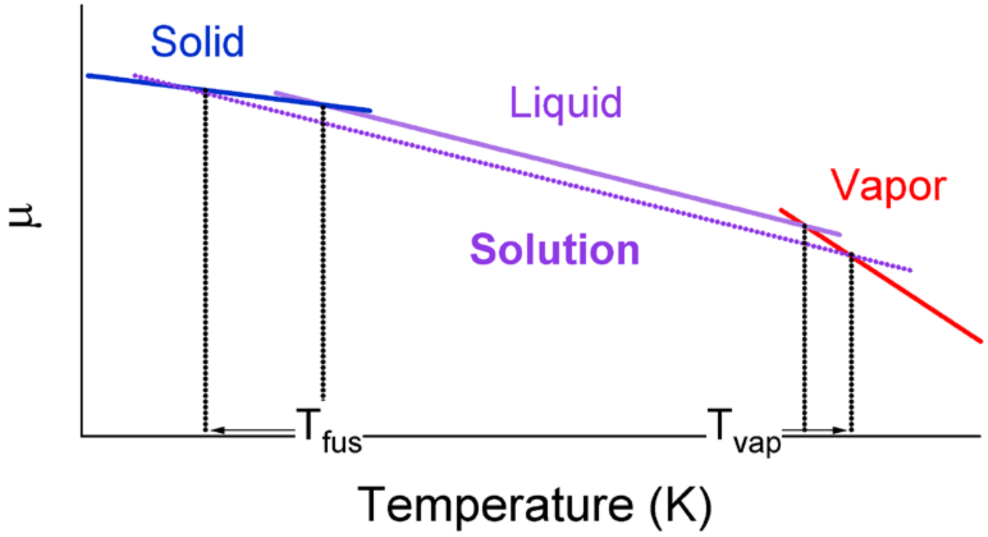


The slope is the negative entropy

The slope of this plot is equal to –S.

$$-S = \left(\frac{\partial \mu}{\partial T}\right)_P$$

Notice that the slope (and therefore entropy) increases as the system is transformed from solid → liquid → gas.
The slope is negative as the equation for the chemical potential Indicates.



Lowering of the chemical potential for a solution

When a solute is added to the pure liquid the chemical Potential decreases at all temperatures. This can be seen from

$$\mu_1 = \mu_1{}^* + RT ln x_1$$

Note the convention that component 1 is always the solvent and component 2 is the solute.