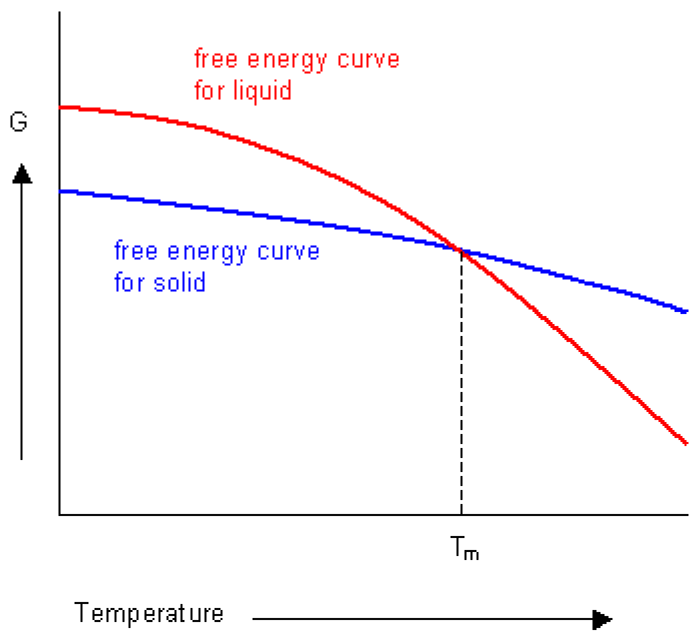
Phase diagrams and Solidification I:Free energy curves

For any phase the free energy, *G*, is dependent on the temperature, pressure and composition.

Pure Substances

For pure substances the composition does not vary and there is little dependence on pressure. Therefore the free energy varies greatest with temperature.

The phase with the lowest free energy at a given temperature will be the most stable. The curves for the free energies of the liquid and solid phases of a substance have been plotted below. It shows that below the melting temperature the solid phase is most stable, and above this temperature the liquid phase is stable. At the melting temperature, where the two curves cross, the solid and liquid phases are in equilibrium.



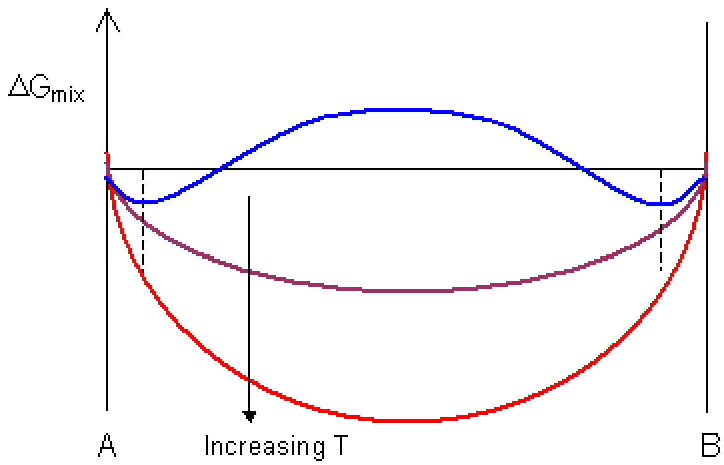
Solutions

Solutions contain more than one component and in these situations the free energy of the solution will become dependent on its composition as well as the temperature.

It is shown above that the free energy of mixing is:

$\otimes G_{mix} = \otimes H_{mix} - T\otimes S_{mix} = x_A x_B \Omega + RT\,(x_A \ln x_A + x_B \ln x_B)$

The shape of the $\otimes G_{mix}$ curve is dependent on temperature . For the curve shown below the value of $\otimes H_{mix}$ is positive, leading to a maximum on the curve at low temperatures. $\otimes G_{mix}$ is always negative for low solute concentrations as the gradient of $\otimes S_{mix}$ is infinite at $x_A = 0$ and $x_A = 1$.



At high temperatures there is a complete solution and the curve has a single minimum. At low temperatures the curve has a maximum and two minima. In the composition range between the two minima (denoted by the dashed lines) a mixture of two phases is more stable than a single-phase solution.

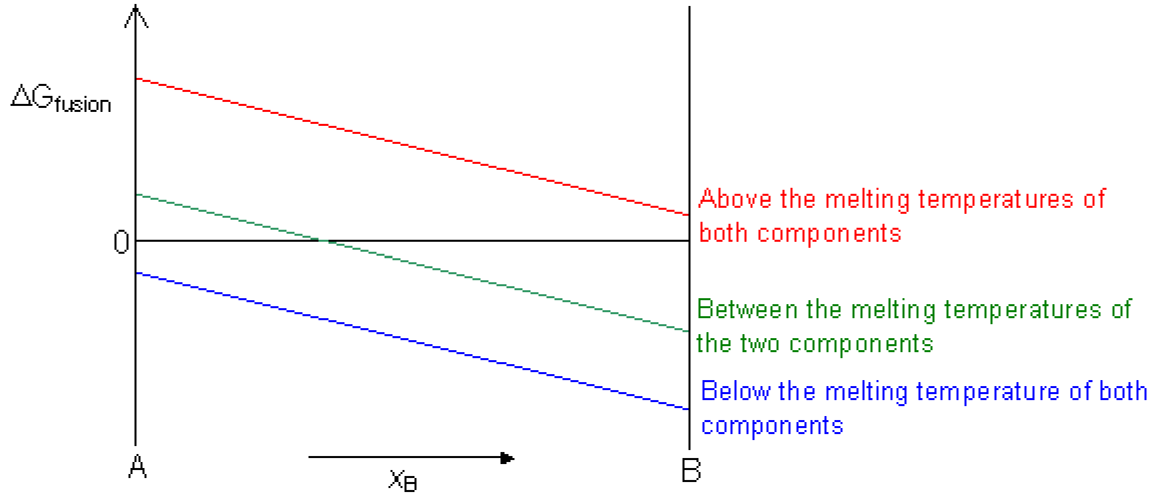
The free energy of a regular solid solution, $\otimes G_{sol}$, is the sum of the free energy of mixing $\otimes G_{mix}$ and the free energy of fusion $\otimes G_{fus}$.

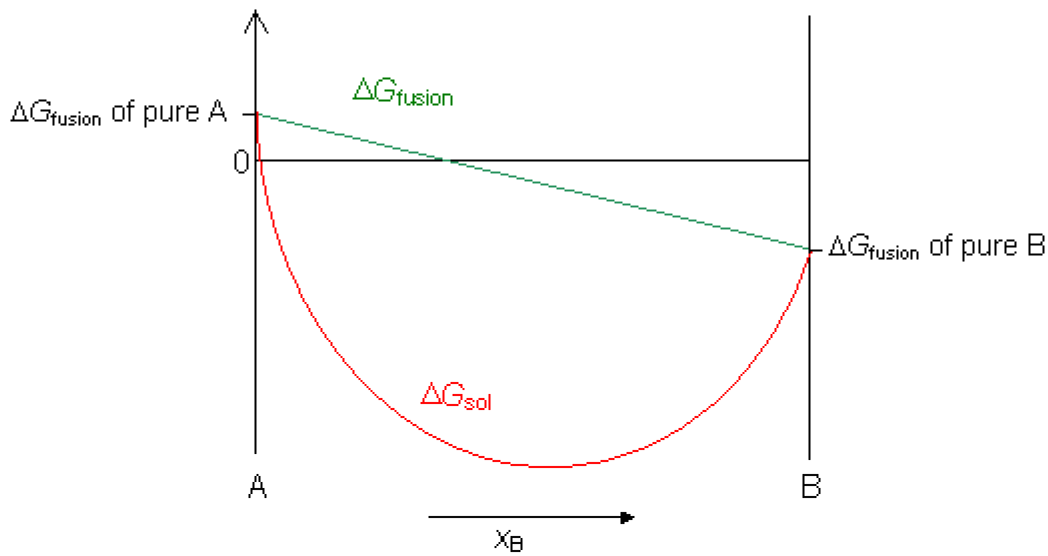
Free energy of fusion

When a liquid solidifies there is a change in the free energy of freezing, as the atoms move closer together and form a crystalline solid. For a pure component, this can be empirically calculated using Richard's Rule:

$\otimes G_{fusion} = - 9.5\,(T_m - T)$
T_m = melting temperature
T = current temperature
$\otimes G_{fusion} = 0$ at the melting temperature of the component.
$\otimes G_{fusion} < 0$ below the melting temperature of the component.
$\otimes G_{fusion} > 0$ above the melting temperature of the component.
In an alloy, if both the liquid and solid solutions are ideal then $\otimes G_{fusion}$ for the alloy can be interpolated between the values for the two components.
Now we can plot the free energy of a regular solid solution from the equation,

$\otimes G_{sol} = \otimes G_{mix} + \otimes G_{fusion}$





Source : http://www.doitpoms.ac.uk/tlplib/phase-diagrams/freeenergy.php