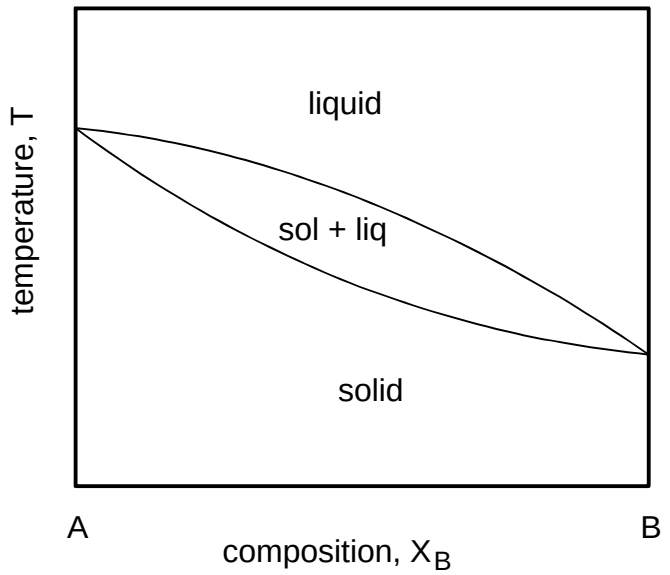
THE GIBBS FREE ENERGY BEHIND THE PHASE DIAGRAM OF A BINARY, ISOMORPHOUS SYSTEM



$G = H - TS$ (1)

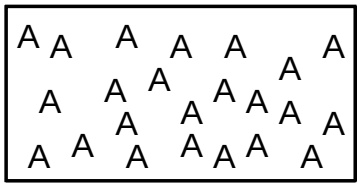
H = enthalpy
T = temperature
S = entropy

Define *molar* quantities:
g = G/mole
h = H/mole
s = S/mole

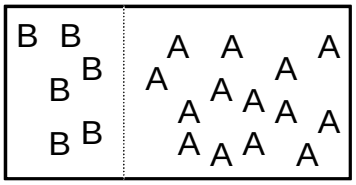
X_i = mole fraction of i
$= N_i / \Sigma N_i$

Consider the gibbs free energy of one mole of atoms (molar gibbs free energy), some of which are A atoms and some of which are B atoms. For the moment, let a partition sit between the two types of atoms. Consider $g(X_B)$, that is, g as we change the relative amounts of A and B.

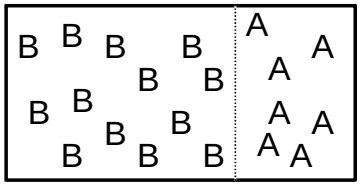
0% B (100% A)



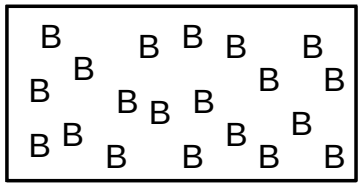
33% B



67% B



100% B

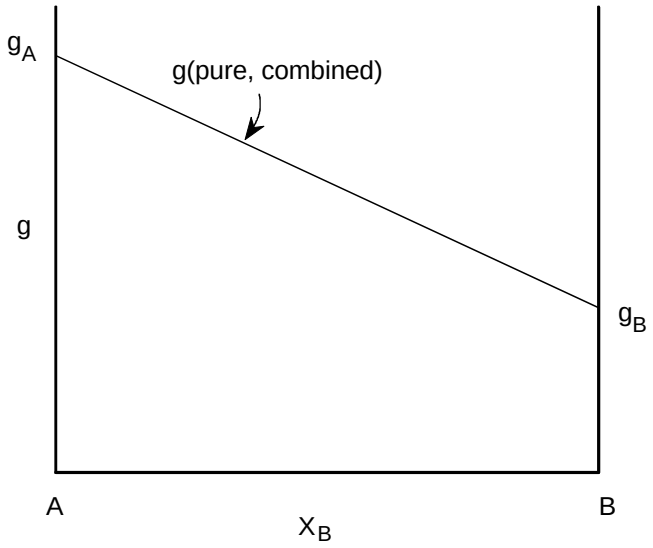


If the (molar) gibbs free energy of pure A is g_A, and that of pure B is g_B, then the (molar) gibbs free energy for the combination of pure components is

$$g\ (\text{pure, combined}) = g_A \bullet X_A + g_B \bullet X_B \qquad (2)$$

Note: the molar gibbs free energy of a pure element is often give the symbol μ_A^o, as it is equivalent to the chemical potential of the pure element.

As a function of composition, the gibbs free energy for the combination of pure A and pure B is a straight line connecting g_A and g_B, as shown below:



Now, let us remove the imaginary partition and let the A and B atoms mix. There should be some change in g due to this mixing, and it is given by

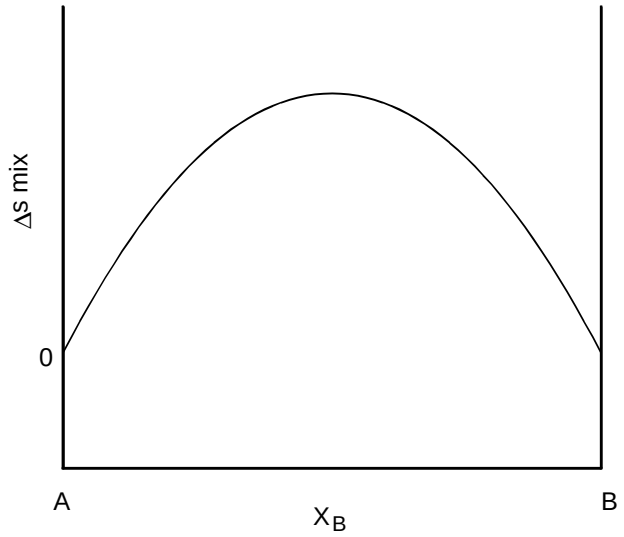
$$\Delta g^{mix} = \Delta h^{mix} - T\Delta s^{mix} \qquad (3)$$

The enthalpy term, Δh^{mix}, represents the nature of the chemical bonding, or, put in different words, the extent to which A prefers B, or A prefers A as a neighbor. (No social commentary implied).

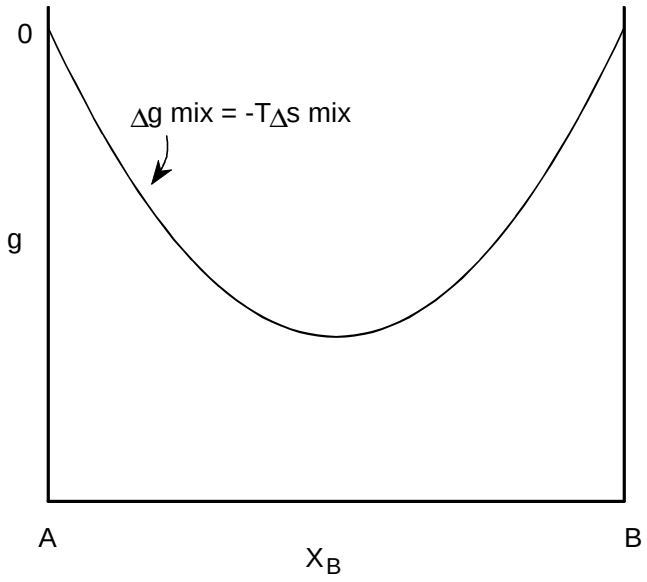
The entropy term, Δs^{mix}, signifies the increase in disorder in the system as we let the A and B atoms mix. It is independent of the nature of the chemical bonding.

We can approximate our isomorphous, binary system as an ideal solution. That is, A couldn't care less whether it is sitting next to another A to a B atom. This is much like our Ni-Cu system. Under these circumstances, $\Delta h^{mix} = 0$.

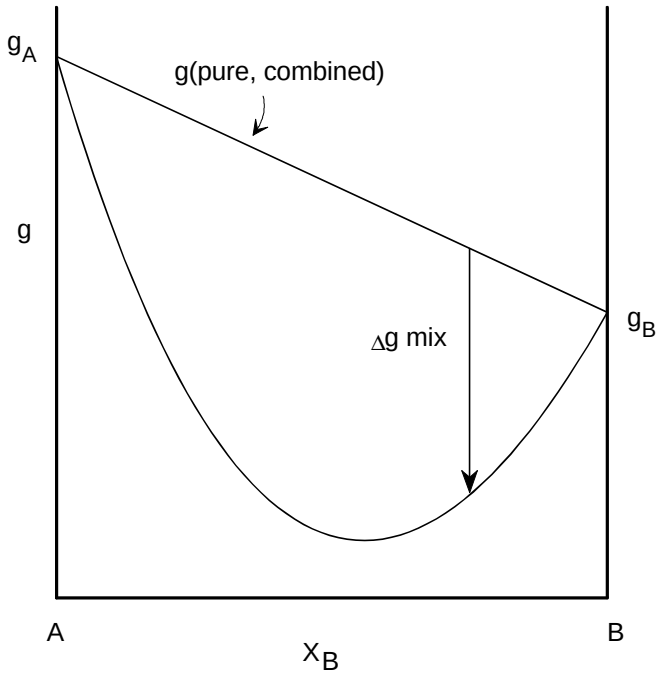
Let us qualitatively examine the entropy of mixing. If we have a system of pure A, and let the A atoms "mix" with one another, there is no increase in entropy because they were mixed to begin with. The same holds true for a system of pure B. If we have just one atom of B in a mole of A, removing the invisible partition hardly changes the amount of disorder. But, as we get to a 50:50 composition of A:B, the increase in entropy as we allow the system to mix is enormous. Therefore, Δs^{mix} has the following dependence on composition:



From that we can easily get the change in gibbs free energy due to mixing:

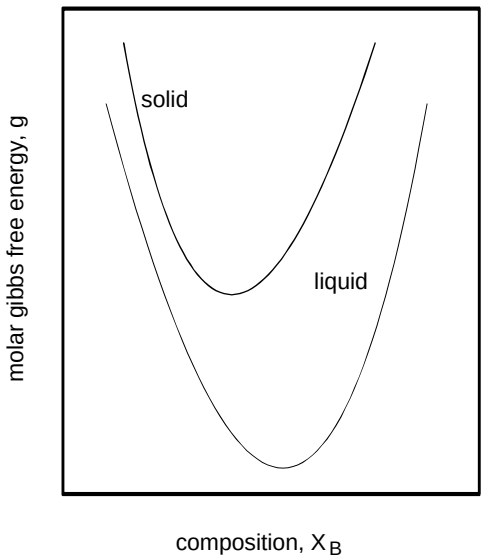


Now we sum g(pure, combined) and Δg^{mix} to get the total gibbs free energy of the solution as a function of composition:

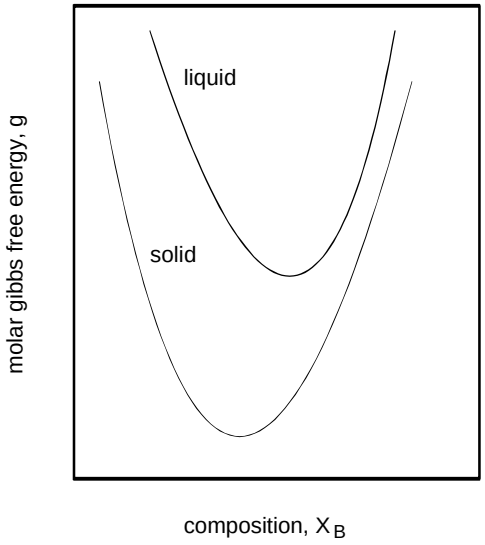


At this point we have the *general shape* of the $g(X_B)$ curves for phases in a binary system. This overall shape holds for both the solid and liquid phases, so long as both make ideal (or close to ideal) solutions. We are now ready to compare $g_{sol}(X_B)$ with $g_{liq}(X_B)$ for various temperatures, and examine how these correlate to the phase diagram.

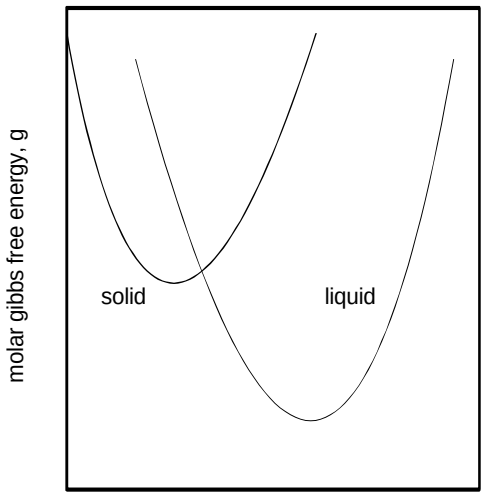
(1) *High temperature*: At temperatures above the melting points of both pure A and pure B, the **liquid** is the stable phase for all compositions. Therefore, $g_{sol}(X_B) > g_{liq}(X_B)$ and the gibbs free energy curves look like:



(2) *Low temperature*: At temperatures below the melting points of both pure A and pure B, the **solid** is the stable phase for all compositions. Therefore, $g_{sol}(X_B) < g_{liq}(X_B)$ and the gibbs free energy curves look like:



(3) *Intermediate temperature*: As the temperature is brought down from high to low, the $g_{sol}(X_B)$ starts to move below that of $g_{liq}(X_B)$. The minima in the two curves, in general, do not occur at the same point, so for some compositions, $g_{sol}(X_B) > g_{liq}(X_B)$, while for others $g_{sol}(X_B) < g_{liq}(X_B)$. Therefore, at temperatures between the melting points of pure A and pure B, the solid and liquid curves look like:

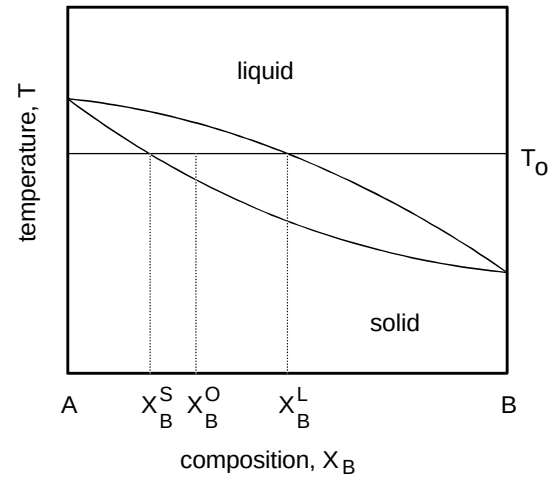


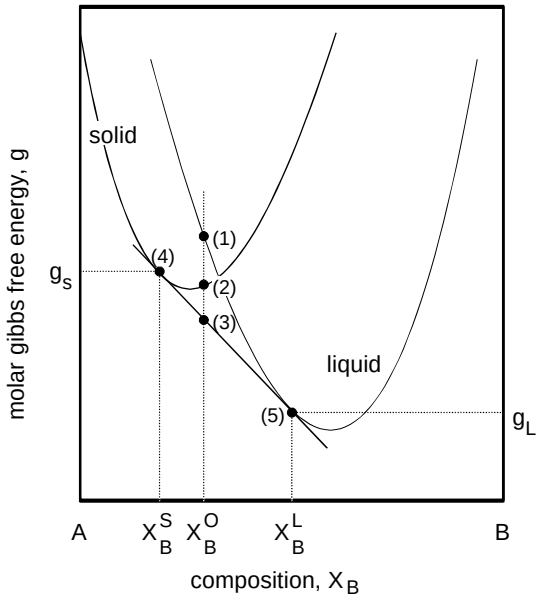
There are two reasons why the lines don't pass exactly over one another:

(1) the slope of the line g(pure, combined) will be different for the solid and liquid, because $g_A(\text{liquid}) \neq g_A(\text{solid})$ and $g_B(\text{liquid}) \neq g_B(\text{solid})$.

(2) no solution is really ideal, so the enthalpy of mixing needs to be taken into account.

What are these last pair of free energy curves telling us? They contain the information we need to show that we must pass through a two-phase, solid + liquid region as we cool from only liquid to only solid. To facilitate the discussion, let's redraw the last figure with a few points labeled, and compare it to the phase diagram, also redrawn with important points labeled.





Let's say we start out with a liquid of composition X_B^O and cool it to T_o. The gibbs free energy of the liquid would be given by point (1) on the $g(X_B)$ diagram. The system realizes it could lower its gibbs free energy by transforming to a solid. The gibbs free energy of that solid would be given by point (2) on the $g(X_B)$ diagram. But, how low can you go?

The system can, in fact, lower its free energy even further by splitting up into a solid of composition X_B^S and a liquid of composition X_B^L (shown on both diagrams). The gibbs free energy of the solid is given by point (4) on the $g(X_B)$ diagram and that of the liquid by point (5) on the same diagram. Now let's prove that the *phase separation* (into liquid + solid) does indeed lower g.

The gibbs energy of a system composed of a liquid and a solid is

$$g\ (\text{total}) = g_{liq} \bullet F_{liq} + g_{sol} \bullet F_{sol} \qquad (4)$$

where F_{liq} and F_{sol} are the mole fractions of liquid and of solid, respectively (these can be determined by the lever rule). This looks a lot like equation (2), if we simply notice that in the case of the pure components, the mole fraction of A is X_A and of B is X_B. Notice also that the line connecting points (4) and (5) acts like the line in the plot of the gibbs free energy of the *pure, combined* components as a function of composition. For example, let's say we had a system of overall composition X_B^S (at T_o). Then, we only have solid phase present, and the gibbs free energy is given by point (4) (in agreement with equation 4). If we has a system of overall composition X_B^L, then we only have liquid phase present and the total gibbs free energy is given by point (5), also in agreement with equation 4. If we had a system of a composition exactly in the middle of X_B^S and X_B^L, then half the moles of our system would be in the solid phase and the other half in the liquid phase. The gibbs free energy would be given by a point half-way between points (4) and (5), sitting precisely on the line that connects them. Similarly, any system with an overall composition that is between X_B^S and X_B^L and that undergoes the phase separation, will have a gibbs free energy on the line connecting points (4) and (5). So, for the composition X_B^O, splitting into a solid and liquid lowers the gibbs free energy to point (3). Et viola: a two phase region exists on the phase diagram because its the lowest gibbs free energy state!

MIT OpenCourseWare
http://ocw.mit.edu

22.14 Materials in Nuclear Engineering

Spring 2015

For information about citing these materials or our Terms of Use, visit: http://ocw.mit.edu/terms.