

MIXED SYSTEMS: EFFECT OF INTERACTION ENERGY AND THE SOLUBILITY GAP

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.58.

So far when we've examined the Gibbs free energy and entropy of a mixture of two pure substances, we've assumed that the interaction energy is the same between all molecules in the mixture, that is, that a species A molecule has the same interaction energy with another A molecule as it does with a B molecule (and likewise for B molecules).

To get an idea of how a difference in the interaction energies affects the phase transition of a mixture, we'll consider a simple model as follows. We have our usual two species A and B , and the potential interaction energy between two nearest-neighbour A s is the same as between two B s, and we'll call this energy u_0 . Between a nearest neighbour A and B , however, the energy is different, say u_{AB} . Further, suppose each molecule has n nearest neighbours, and any given molecule interacts only with its nearest neighbours. For a system composed of unmixed samples of A and B , with total number $N = N_A + N_B$, we can work out the total potential energy as follows.

Any particular molecule has n other molecules with which it interacts, so its total interaction energy is nu_0 . There are a total of N molecules, but if we simply multiply nu_0 by N , we are counting each interaction twice, so the total interaction energy is

$$U_{unmixed} = \frac{1}{2}Nnu_0 \quad (1)$$

Now suppose we mix the two populations thoroughly. Let x be the proportion of molecules that are of species B , so that $1 - x$ is the proportion for A . On average, an A molecule now has xn nearest neighbours of type B and $(1 - x)n$ of type A , so its interaction energy is now

$$U_A = xnu_{AB} + (1 - x)nu_0 \quad (2)$$

Similarly for type B :

$$U_B = (1 - x)nu_{AB} + xnu_0 \quad (3)$$

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To get the total energy, we multiply 2 by $N_A = (1-x)N$ and 3 by $N_B = xN$, add and divide by 2 to avoid double-counting:

$$U_{mixed} = \frac{1}{2}[xnu_{AB} + (1-x)nu_0](1-x)N + \frac{1}{2}[(1-x)nu_{AB} + xnu_0]xN$$

$$= x(1-x)nNu_{AB} + \frac{1}{2}\left((1-x)^2 + x^2\right)nNu_0 \quad (5)$$

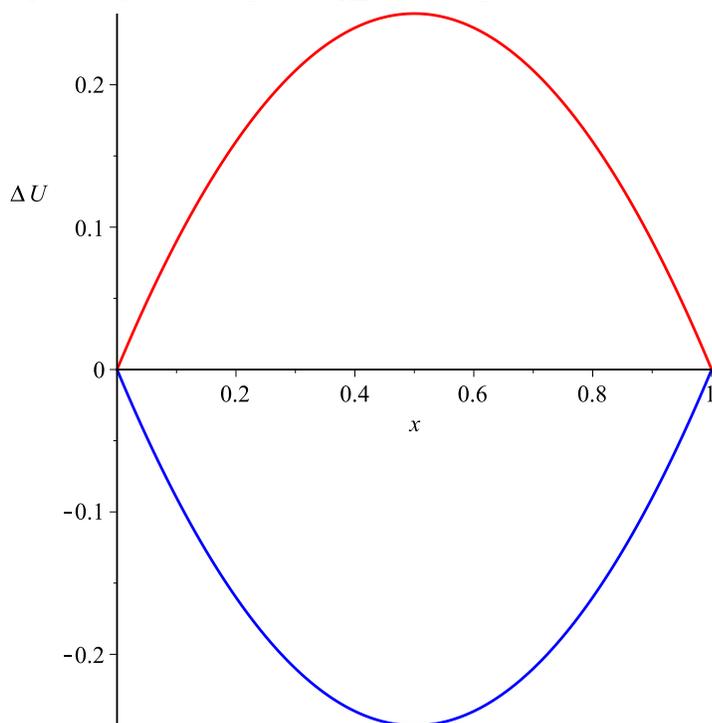
$$= x(1-x)nNu_{AB} + \frac{1}{2}[1 - 2x(1-x)]nNu_0 \quad (6)$$

We can now subtract 1 from this to get the energy change resulting from mixing:

$$\Delta U = U_{mixed} - U_{unmixed} \quad (7)$$

$$= x(1-x)nN(u_{AB} - u_0) \quad (8)$$

Depending on the sign of $u_{AB} - u_0$, a plot of ΔU looks like this:



The red line is for $u_{AB} - u_0 > 0$ and the blue line for $u_{AB} - u_0 < 0$. Note that the slopes of ΔU are finite at the endpoints:

$$\frac{d\Delta U}{dx} = (1-2x)nN(u_{AB} - u_0) \quad (9)$$

which is finite when $x = 0$ or $x = 1$.

As we saw earlier, the Gibbs free energy of an unmixed system is

$$G = (1 - x)G_A^\circ + xG_B^\circ \quad (10)$$

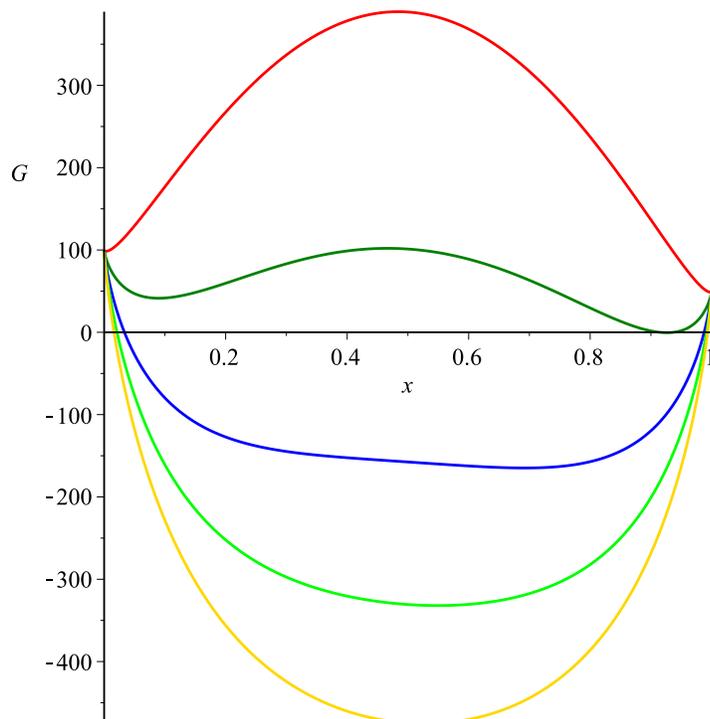
and the change in entropy due to mixing is

$$\Delta S_{mixing} = -Nk [x \ln x + (1 - x) \ln (1 - x)] \quad (11)$$

Combining this with 8 we get the Gibbs energy for our system, taking account of both the difference in interaction energy and the entropy of mixing:

$$G = (1 - x)G_A^\circ + xG_B^\circ + x(1 - x)nN(u_{AB} - u_0) + NkT [x \ln x + (1 - x) \ln (1 - x)] \quad (12)$$

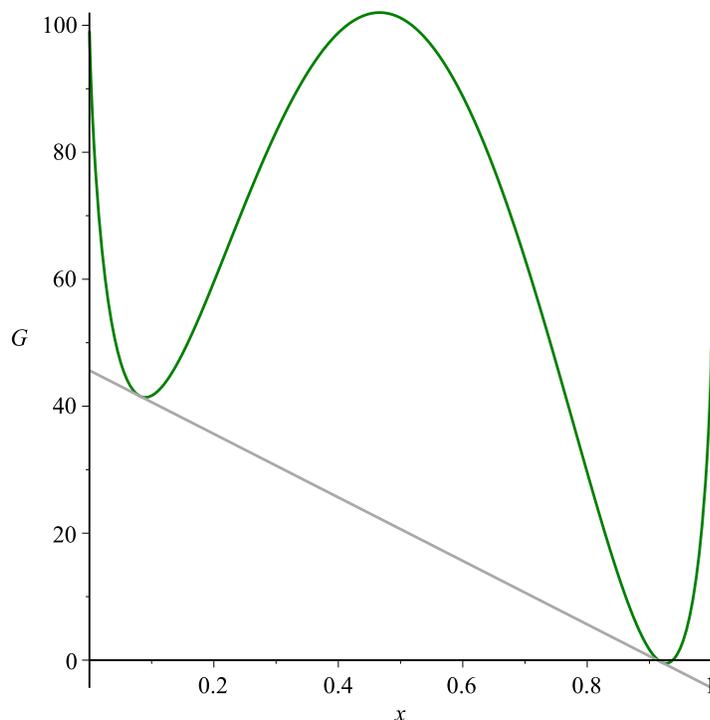
In order to plot the Gibbs energy, we need to plug in a few numbers. I'll take $G_A^\circ = 100$ J, $G_B^\circ = 50$ J, $N = 6.02 \times 10^{23}$, $n = 4$ and $u_{AB} - u_0 = 10^{-21}$ J. With these values, we can plot G for several temperatures:



From the top down, the red curve is for $T = 50$ K, dark green for $T = 100$ K, blue for $T = 144.928$ K (the reason for this peculiar value will be explained below), light green for $T = 175$ K and yellow for $T = 200$ K.

Note that the shape of the curve changes from concave down for low temperatures to concave up for high temperatures, with a combination of concavities for the intermediate temperature of $T = 100$ K (dark green curve). It's worth looking at this latter curve in more detail.

Suppose we expand the plot of this curve and draw the straight line (in grey) that is the lowest line that is tangent to the curve at two points:



The grey line represents a system consisting of two unmixed substances, one of which has $x = 0.081$ (the value of x at the left-most tangent point) and the other of which has $x = 0.919$ (the right-most tangent). For values of x between these points, the grey line represents a system which consists of two separate subsystems, one with mostly A molecules and the other with mostly B molecules. Since the Gibbs energy of the separated system is lower than that of a fully mixed system (represented by the green curve), the system will be found in this relatively unmixed state for these values of x . This is known as a *solubility gap*. By the way, note that these two unmixed subsystems are *not* pure systems, since they both contain molecules of both species. It's just that one subsystem consists of about 92% A molecules while the other consists of about 92% B molecules. As we vary x , the proportion of each of these two subsystems varies, but the composition within each subsystem remains the same: there is no mixing between them.

Returning now to the compound plot of G for various temperatures above, we note that the central maximum that is present in the dark green curve gets shallower until at some critical temperature it disappears and then as the temperature is increased further, it turns into a minimum. We can find this critical temperature as follows.

The two tangent points (where the grey line intersects the green curve above) can be found by taking the derivative of 12:

$$\frac{dG}{dx} = G_B^\circ - G_A^\circ + (1 - 2x)nN(u_{AB} - u_0) + NkT \ln \frac{x}{1-x} \quad (13)$$

The tangent points are defined by the condition that their slope is equal to that of an unmixed system, which is $G_B^\circ - G_A^\circ$, so the tangent points must satisfy

$$(1 - 2x)nN(u_{AB} - u_0) + NkT \ln \frac{x}{1-x} = 0 \quad (14)$$

One solution of this equation is always $x = 0.5$, since this makes both terms on the LHS zero. This corresponds to the maximum point on the green curve above. To find the two tangent points we'd need to solve the transcendental equation for x (which I did using Maple to get the plot above), but we actually don't need to do that to find the critical temperature. The key is to look at the *second* derivative at the maximum point. The second derivative is negative for a maximum and positive for a minimum, so the critical temperature (the highest temperature at which a solubility gap exists) is that value of T where the second derivative is zero. That is

$$\frac{d^2G}{dx^2} = -2nN(u_{AB} - u_0) + NkT \left(\frac{1}{x} + \frac{1}{1-x} \right) \Big|_{x=0.5} = 0 \quad (15)$$

$$T_c = \frac{n(u_{AB} - u_0)}{2k} \quad (16)$$

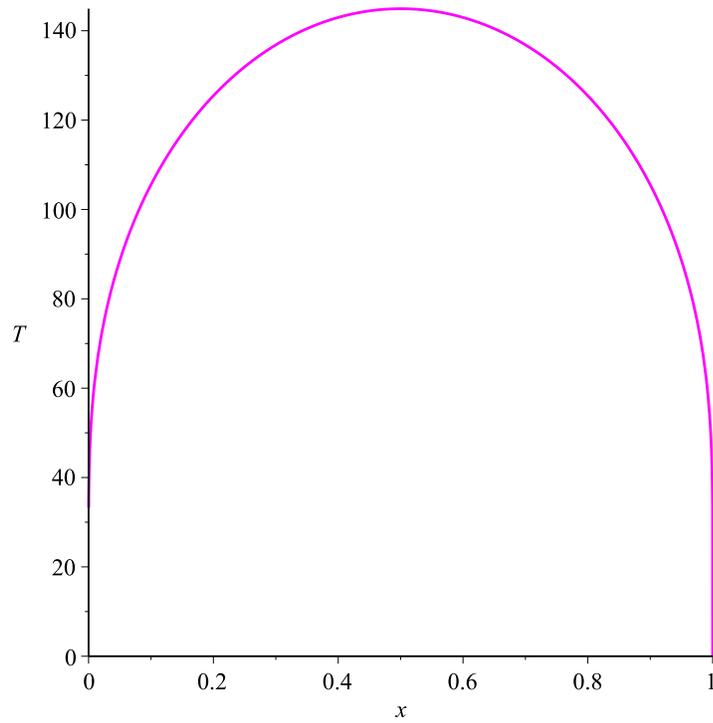
For the values we used above, $T_c = 144.928$ K, which explains why I chose this value for the blue curve above.

Finally, we can generate a phase diagram which shows the temperature at which a solubility gap appears. From 14, if a tangent occurs at a given value of x , the corresponding temperature must be

$$T = \frac{(1 - 2x)n(u_{AB} - u_0)}{k \ln \frac{1-x}{x}} \quad (17)$$

For the parameters we used above, a plot of this is as follows:

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For temperatures above the curve, full mixing occurs, while for temperatures below the curve, the system separates into two unmixed subsystems. The maximum on this curve occurs at $x = 0.5$ and $T = 144.928$ K, as above.