

Part I : Preliminaries (Thermodynamics and Kinetics)

Module 2: Gibbs free energy of a binary alloy

3.1 Motivation

Pure lead melts at about 327.5°C and pure tin melts at 232°C. However, an alloy of lead and tin known as solder alloy (consisting of 61.9% of tin by weight) melts at 183°C. Why?

3.2 Composition dependence of free energy in a binary alloy

Consider the free energy $G = U + PV - TS = H - TS$. In condensed systems (solids and liquids), $H \approx E$: see the tutorial at the end of this module. Hence, in the rest of this module, we assume $G = E - TS$.

Consider a binary alloy - an alloy consisting of two components. Let us consider a statistical model for the free energy of such an alloy (known as the regular solution model). Such a statistical picture, as we see later in this chapter, can explain many observed features of binary systems.

Let the two components of the binary alloy be labeled as A and B . Let N_A and N_B be the number of A and B atoms. Let $N_A + N_B = N_{Av}$, where N_{Av} the Avogadro number. Thus, the alloy composition is defined as $x_B = \frac{N_B}{N_{Av}}$.

Consider the free energy associated with the mixing of these two components. Since $G = E - TS$, one can define the the free energy of mixing $\Delta G^{mix} = \Delta E^{mix} - T\Delta S^{mix}$. Note $\Delta G^{mix} = G - (1 - x_B)G_A + x_B G_B$, where, G is the overall free energy after mixing the A and B atoms, and G_B and G_A are the molar free energies of pure A and B respectively. Let us consider the calculation of these two quantities, namely, internal energy ox mixing and entropy of mixing as a function of composition.

3.2.1 Congurational entropy of mixing

We assume that the only contribution to entropy is the configurational one. We also assume that the A and B atoms are randomly distributed on the given lattice sites. Under such assumptions, one can show (see the tutorial) that

$$S_{config}^{mix} = N_{Av} k_B \{(1 - x_B) \ln(1 - x_B) + x_B \ln x_B\} \quad (2)$$

where k_B is the Boltzmann constant, and $N_{Av} k_B = R$, the universal gas constant.

3.2.2 Internal energy of mixing

Let us assume that the internal energy in the given alloy is a result of pair-wise interactions between the atoms. There are three types of interactions, namely, AA and BB (the 'like' interactions), and AB (the 'unlike' interaction). If E_{AA} , E_{BB} and E_{AB} are the strengths of these interactions, and if we define ϵ as the difference in internal energy associated with replacing $N_{Av} k_B = R_{AA}$ and BB bonds by AB bonds, then, $\epsilon = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})$. It can be shown that under certain approximations (see [1]), the internal energy is

$$\Delta E^{mix} = \Omega(1 - x_B)x_B \quad (3)$$

where $\Omega = N_{Av} z \epsilon$ where z is the number of nearest neighbours in the given crystal structure of the alloy.

3.2.3 Gibbs free energy of mixing

Thus, putting together the two expressions above, one obtains the composition dependence of free energy as a function of temperature and composition as follows:

$$\Delta G^{mix}(T, x_B) = \Omega(1 - x_B)x_B + RT \{(1 - x_B) \ln(1 - x_B) + x_B \ln x_B\} \quad (4)$$

We can non-dimensionalise the above equation by dividing all the quantities by RT . Let $\Delta G' = \Delta G^{mix}/RT$ be the non-dimensional energy, and, let $\alpha = \frac{\Omega}{RT}$. Then,

$$\Delta G'(T, x_B) = \alpha(1 - x_B)x_B + \{(1 - x_B)\ln(1 - x_B) + x_B\ln x_B\} \quad (5)$$

One can consider three cases.

3.2.4 Case 1: $\alpha = 0$

In this case, the (normalised) free energy of mixing (which is the same as the entropy of mixing) is as shown in Fig. 5. Since this quantity is negative, it implies that when the A and B atoms mix, the overall free energy comes down, and hence the configuration of complete mixing is preferred.

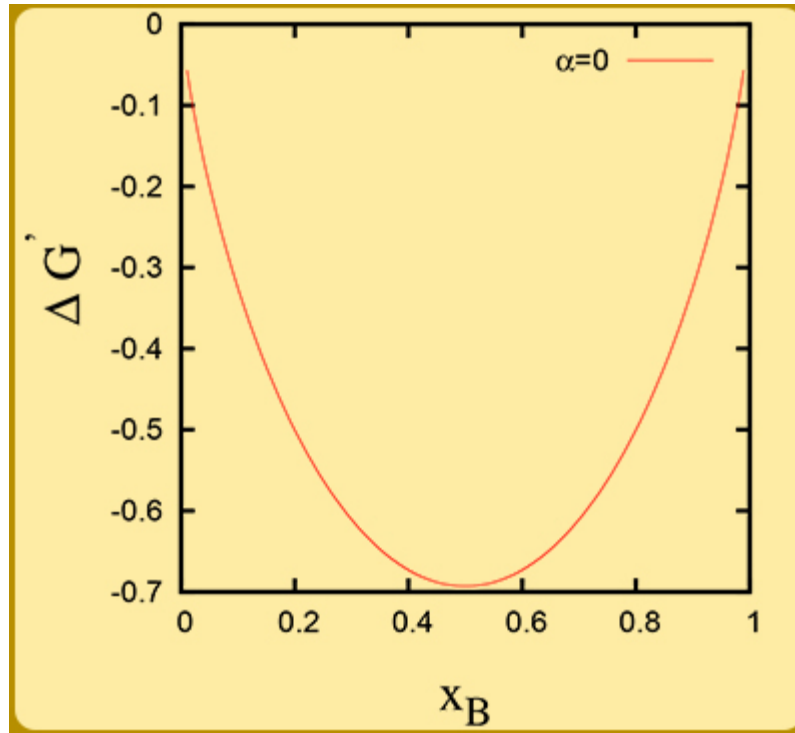


Figure 5: Normalised free energy of mixing as a function of composition when $\alpha = 0$.

Another way to understand this result is as follows: $\alpha = 0$ implies $\Omega = 0$ for $T \neq 0$; that is $\epsilon = 0$. This implies $E_{AB} = \frac{1}{2}(E_{AA} + E_{BB})$; that is, there is no internal energy cost associated with replacing, on the average the AA and BB bonds by an AB bond. In other words, the system does not distinguish between A and B atoms in terms of internal energy; hence, this case is also known as the ideal solution. The configurational entropy always prefers a mixed state (since that increases the overall entropy). Hence, the system always prefers to mix completely.

3.2.5 Case 2: $\alpha = -2.5$

In Fig. 6, we show the internal energy, entropy and free energy of mixing in this case. Here too we see that the overall free energy decreases when there is mixing. Hence the system would prefer mixing.

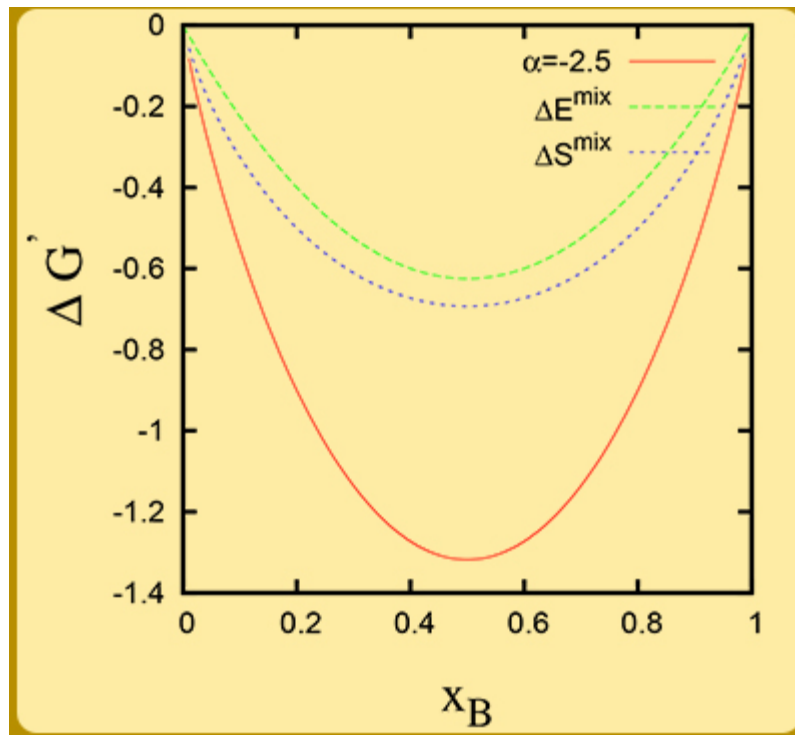


Figure 6: Normalised free energy of mixing as a function of composition when $\alpha = -2:5$.

Another way of understanding the result is as follows: $\alpha < 0$ implies $\Omega < 0$ for $T \neq 0$; that is $\epsilon < 0$. This implies $E_{AB} < \frac{1}{2}(E_{AA} + E_{BB})$; that is, the system prefers **AB** bonds over **AA** and **BB** bonds. The configurational entropy always prefers a mixed state (since that increases the overall entropy). Thus, there is a competition between the preference of internal configuration at low temperatures (where the contribution of internal energy of mixing is dominant) and at high temperatures (where the contribution of entropy of mixing is dominant). Thus, at very low temperatures, there is mixing at the atomic scale (which is known as ordering), while at high temperatures the mixing is truly random.

3.2.6 Case 3: $\alpha = 2:5$

In Fig. 7, we show the internal energy, entropy and free energy of mixing in this case. In this case, we see that the signs of internal energy of mixing and entropy of mixing are opposite. Hence, there are at least some composition range in which the system does not prefer to mix. This is much more clearly seen in Fig. 8 wherein we show only the free energy of mixing which contains regions of concavity wherein a mechanical mixture of two phases would have a lower free energy than the mixed one.

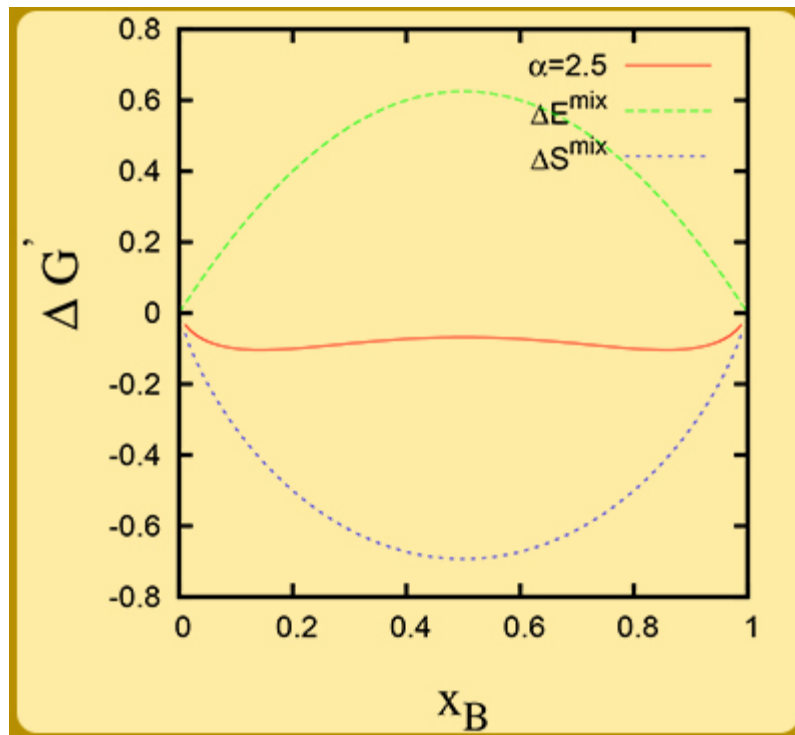


Figure 7: Normalised free energy of mixing as a function of composition when $\alpha = 2:5$.

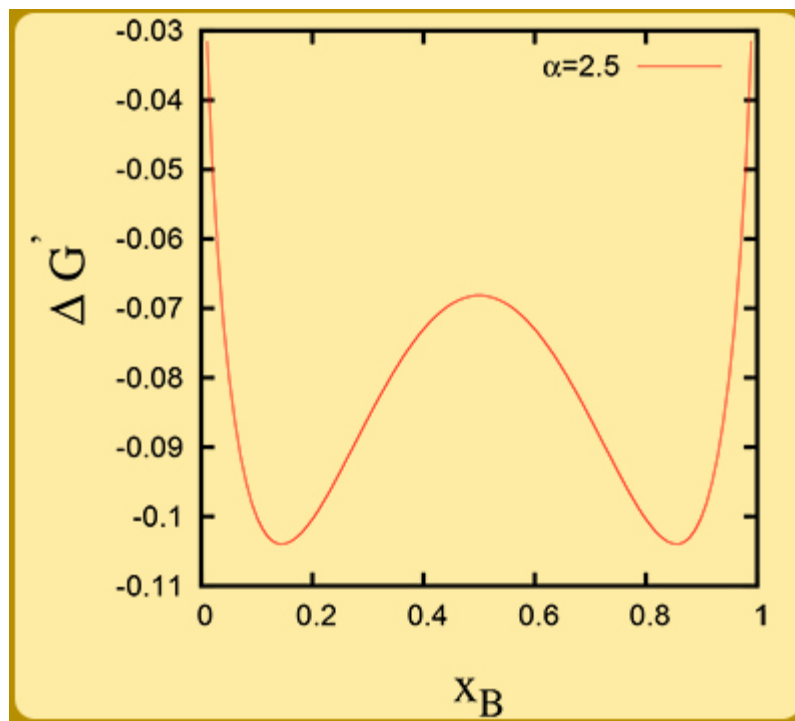


Figure 8: Detail of the normalised free energy of mixing as a function of composition when $\alpha = 2:5$.

Another way of understanding the result is as follows: $\alpha > 0$ implies $\Omega = 0$ for $\Omega > 0$; that is $\epsilon > 0$. This implies $E_{AB} > \frac{1}{2}(E_{AA} + E_{BB})$; that is, the system prefers AA and BB bonds over AB bonds. The configurational entropy always prefers a mixed state (since that increases the overall entropy). Thus, there is a competition between the preference of internal configuration at low temperatures (where the contribution of internal energy of mixing is dominant) and at high temperatures (where the contribution of entropy of mixing is dominant). Thus, at very low temperatures, there is unmixing at the atomic scale (which is known as phase separation), while at high temperatures the mixing is truly random.

Note that when the numerical value of Ω is small (say, 0.5), the overall free energy of mixing would still be

negative and hence mixing would be preferred: see Fig. 9. In fact, as we show in one of the later modules, that the critical value for α for phase separation to be dominant is 2 (See [1]).

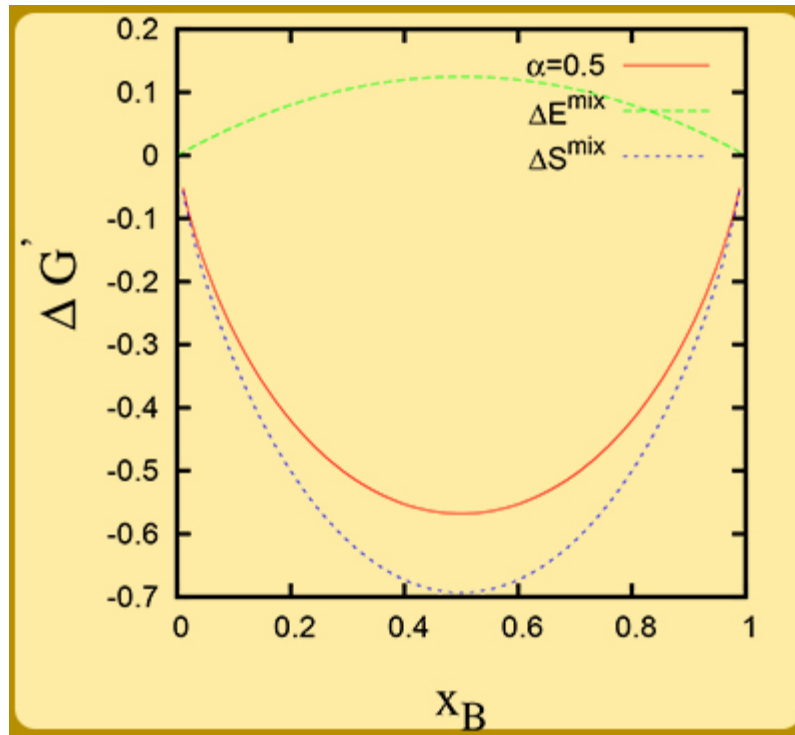


Figure 9: Detail of the normalised free energy of mixing as a function of composition when $\alpha = 0.5$.

3.3 Estimating the bond energies

When a pure material melts, the thermal energy given to the material is used to break the bonds. Hence, there is a direct relationship between melting point and the bond energy: higher the melting point, stronger the bonds. Keeping this in mind, we are now ready to answer the question posed in the motivation section of this module. An alloy of lead and tin melts at a lower temperature because the AB bonds in lead-tin system are weaker compared to lead-lead and tin-tin bonds. In other words, the lead-tin system prefers lead-lead and tin-tin bonds over lead-tin bonds. This is also seen in that there is phase separation in the lead-tin system. In a similar fashion, any system that undergoes ordering will have the melting point for the alloy to be higher than that of the pure components.

3.4 Tutorial problems and questions

1. Show that for condensed systems $H \approx E$.

Answer

The change in enthalpy due to a change in pressure from P_1 to P_2 is given by (See 1)

$\Delta H = \int_{P_1}^{P_2} V_m(1 - \alpha T)dP$ where α is the isobaric coefficient of thermal expansion and V_m is the molar volume.

Typically, most of materials are considered at 1 atmospheric pressure (which is a very small quantity by itself). Further, since the coefficient of expansion for condensed systems (liquids and solids) is very small, the total change in enthalpy due to pressure changes is very small. Hence, it can be neglected.

As an example, consider iron, for which $V_m = 7.1 \text{ cm}^3$, $\alpha = 0.3 \times 10^{-4} \text{ K}^{-1}$. Even an increase of pressure from 1 to 100 atmospheres at 298 K thus increases the enthalpy by about 70 J or so, which can be achieved just by increasing temperature by about 3 K.

2. Derive $S_{\text{config}}^{\text{mix}} = RT \{(1 - x_B) \ln(1 - x_B) + x_B \ln x_B\}$

Answer

$S_{config} = k_B \ln \omega$ where ω is the number of available states.

In the case of pure materials, there is only one state and hence $S_{config} = 0$. On the other hand, for N_A and N_B atoms of types **A** and **B** respectively places on a lattice of N_{Avog} sites,

$$\omega = \frac{N_A! N_B!}{N_{Avog}!}$$

Thus, $S_{config}^{mix} = k_B \ln \left[\frac{N_A! N_B!}{N_{Avog}!} \right]$

We can use Stirling's approximation which is valid for large $\ln n! = n \ln n - n$, and which states n .

Thus, $S_{config}^{mix} = k_B [N_A \ln N_A - N_A + N_B \ln N_B - N_B - N_{Avog} \ln N_{Avog} + N_{Avog}]$

But, $N_{Avog} = N_A + N_B$

Hence,

$S_{config}^{mix} = k_B N_{Avog} [(N_A/N_{Avog}) \ln N_A + (N_B/N_{Avog}) \ln N_B - ((N_A + N_B)/N_{Avog}) \ln N_{Avog}]$
where we have also multiplied and divided the quantity in the square brackets by N_{Avog} .

$S_{config}^{mix} = k_B N_{Avog} [(N_A/N_{Avog}) \ln(N_A/N_{Avog}) + (N_B/N_{Avog}) \ln(N_B/N_{Avog})]$

$S_{config}^{mix} = R[(1 - x_B) \ln(1 - x_B) + x_B \ln x_B]$.

Supplementary information

Note that the two assumptions made in the regular solution model are contradictory. We assume that the **A** and **B** atoms either have a preference for their own or the opposite kind of atoms (by assuming Ω to be non-zero) in the calculation of internal energy. On the other hand, we assume random placement while calculating the configurational entropy (as well as while calculating the probability of occupation of atoms to estimate the internal energy). However, if we assume non-random arrangement, we can not derive an analytical expression for the free energy, and, typically, one has to resort to numerical methods to evaluate the same. Because of the contradictory assumptions that we have made, the use of the regular solution model is restricted to systems in which $|\Omega|$ is small.