Lecture 25: Ordering Transformation

Today’s topics

• Understanding of the concepts of “ideal solution”, “regular solution” and “real solution”, and comparison of the mixing thermodynamics between them regarding the free energy, enthalpy and entropy change.
• Understanding of ordered phase: how to define the short-range order (SRO) and long-range order (LRO).
• Ordering transformation: the way in which the degree of LRO and SRO decreases with temperature is different for different superlattices.

Before going through the Ordering Transformation, we need to understand the following basic thermodynamics about solid solutions


The simplest type of mixing, for which the enthalpy change of the mixing, $\Delta H_{\text{mix}}=0$; the resultant solution is said to be ideal, and the free energy change on mixing is only due to the change in entropy, $\Delta G_{\text{mix}}=\Delta H_{\text{mix}} - T\Delta S_{\text{mix}} = - T\Delta S_{\text{mix}}$.

Since $\Delta S_{\text{mix}} = -R(X_A\ln X_A + X_B\ln X_B)$, we have $\Delta G_{\text{mix}} = RT(X_A\ln X_A + X_B\ln X_B)$

Regular solution: (refs to the same Book above)

The ideal solution as defined above, $\Delta H_{\text{mix}}=0$ is almost impossible in practice, where the mixing is, however, either endothermic (heat absorbed, $\Delta H_{\text{mix}} > 0$) or exothermic (heat evolved, $\Delta H_{\text{mix}} < 0$). For a regular solution, where $\Delta H_{\text{mix}} \neq 0$, the free energy change of the mixing includes the $\Delta H_{\text{mix}}$ term, which in turn can be described by a so-called “quasichemical model” --- i.e., the heat of the mixing, $\Delta H_{\text{mix}}$ is only due to the bond energies between adjacent atoms. For this assumption to be valid, it is necessary that the volumes of pure A and B are equal and do not change during mixing so that the interatomic distance and bond energies are independent of
As shown in Figure 1.13 above (cited from the book above): the structure of a regular solid solution, where three types of interatomic bonds are present:

1. A-A bonds each with an energy $\varepsilon_{AA}$
2. B-B bonds each with an energy $\varepsilon_{BB}$
3. A-B bonds each with an energy $\varepsilon_{AB}$

Let's define zero energy to be the state where the atoms are separated to infinity, then $\varepsilon_{AA}$, $\varepsilon_{BB}$, $\varepsilon_{AB}$, are all negative in quantity (forming a bond is an exothermic process), and become increasingly more negative as the bonds become stronger. The internal energy ($E$) of the solution will be determined by the number of bonds of each type, $P_{AA}$, $P_{BB}$, $P_{AB}$,

$$E = P_{AA} \varepsilon_{AA} + P_{BB} \varepsilon_{BB} + P_{AB} \varepsilon_{AB}$$

Then, the change of internal energy on mixing ($\Delta H_{mix}$) can be expressed as

$$\Delta H_{mix} = P_{AB} \varepsilon$$

where, $\varepsilon = \varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2$, is the difference between the A-B bond energy and the average of the A-A and B-B bond energies.

For an ideal solution, $P_{AB} = N_0 z X_A X_B$ (bonds per mole),

where $N_0$ is the Avogadro constant, $z$ is the number of bonds per atom, $X_A$ and $X_B$ are the molar fraction of A and B atom, respectively.

Assuming $\varepsilon$ is not too different from zero (quite close to the situation of ideal solution), for a regular solution we can still approximately have: $P_{AB} = N_0 z X_A X_B$ (bonds per mole),

Now, let's define $\Omega = N_0 z \varepsilon$; $\Omega$ is interaction parameter

Then, $\Delta H_{mix} = P_{AB} \varepsilon = \Omega X_A X_B$

Therefore, for a regular solution, we have the free energy change of mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$
**Real solution:** (refs to the same Book above)

Considering the “quasichemical model” described above --- i.e., the heat of the mixing, \( \Delta H_{\text{mix}} \) is only due to the bond energies between adjacent atoms, or in other words, the volumes of pure A and B are equal and do not change during mixing so that the interatomic distance and bond energies are independent of composition.

However, the model is oversimplified for many systems in practice (i.e., the real solutions), and does not provide correct dependence of \( \Delta G_{\text{mix}} \) on composition and temperature. For the real solutions, it is simply not true to assume that a random arrangement of atoms (as shown in Figure 1.13 above) is the equilibrium (or the most stable arrangement); the calculated value of \( \Delta G_{\text{mix}} \) will not give the minimum free energy change.

The actual atomic arrangement for a real solution (as depicted in Figure 1.18) will be a compromise that gives the lowest internal energy (i.e., \(|\Delta H_{\text{mix}}|\) is maximized) consistent with sufficient entropy (or randomness, \( \Delta S_{\text{mix}} \)), so as to achieve the minimum \( \Delta G_{\text{mix}} \).

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**FIGURE 1.18**

Schematic representation of solid solutions: (a) ordered substitutional, (b) clustering

- When \( e < 0 \), A-B bonding is thermodynamically favorable (or atoms in solution prefer to be surrounded by atoms of the opposite type), the internal energy of the system is reduced (or \( \Delta H_{\text{mix}} \) becomes more negative) by increasing the number of A-B bonds, i.e., by **ordering** the two atoms as shown in Figure 1.18a.
- When \( e > 0 \), A-B bonding is not thermodynamically favorable (or atoms in solution prefer to cluster by themselves), the internal energy of the system can be reduced (or \( \Delta H_{\text{mix}} \) becomes more negative) by increasing the number of A-A and B-B bonds, i.e., by **clustering** the atoms into A-rich and B-rich domains, as shown in Figure 1.18b.
- Both the two situation above describe **substitutional** solid solution, for which the degree of **ordering** and **clustering** will decrease when temperature increases due to the increasing importance of entropy.

**Ordered phase:** (refs to the same Book above)

If the atoms in a substitutional solid solution are completely randomly arranged, each atom position is equivalent and the probability that any given site in the lattice will be occupied by an A atom will be equal to the fraction of A atoms in the solution \( X_A \), in the same way \( X_B \) for the B atoms. In such a case, the number of
A-B bonds, now marked as $P_{AB}$ (random), can be given following the same equation above:

$$P_{AB} \text{ (random)} = N_0 z X_A X_B \text{ (bonds per mole)}$$

If the real number of A-B bonds, $P_{AB}, > P_{AB} \text{ (random)}$, the solution is said to contain short-range order (SRO).

The degree of ordering can be quantified by defining a SRO parameter, “$S$”, as such

$$s = \frac{P_{AB} - P_{AB} \text{ (random)}}{P_{AB} \text{ (max)} - P_{AB} \text{ (random)}}$$

Where $P_{AB} \text{ (max)}$ and $P_{AB} \text{ (random)}$ refer to the maximum number of A-B bonds possible and the number of A-B bonds for a random solution, respectively.

Figure 1.19 shows the difference between random and short-range ordered solutions with total of 100 atoms ($X_A = X_B = 0.5$):

- Figure 1.19a, for a random solution, $P_{AB} = P_{AB} \text{ (random)} = 100$, then, $s = 0$.
- Figure 1.19b, for a short-range ordered solution, $P_{AB} = 132$, with $P_{AB} \text{ (max)} = 200$, we have $s = 0.32$.

![Figure 1.19](image)

**FIGURE 1.19**

(a) Random A–B solution with total of 100 atoms and $X_A = X_B = 0.5$. $P_{AB} \sim 100$, $S = 0$. (b) Same alloy with SRO $P_{AB} = 132$. $P_{AB} \text{ (max)} \sim 200$, $S = (132 - 100)/(200 - 100) = 0.32$.

In solutions with compositions that are close to a simple ratio of A:B atoms another type of order can be found as shown schematically in Figure 1.18a. This is known as long-range order (LRO). Now the atom sites are no longer equivalent, but can be labeled as A-sites and B-sites. Such a solution can be considered to be a different (ordered) phase separate from the random or nearly random solution.

An example of LRO is for Cu-Au alloy, as shown in Figure 1.20, where Cu and Au are both fcc and totally miscible:

- At high temperatures Cu and Au atoms can occupy any site and the lattice can be considered as fcc with a “random” atom at each lattice point as shown in Figure 1.20a.
At low temperatures, however, solutions with $X_A = X_B = 0.5$, form an ordered structure in which the Cu and Au atoms are arranged in alternate layers as shown in figure 1.20b. Now, each atom position is no longer equivalent and the lattice is described as a CuAu superlattice.

For alloys with the composition Cu$_3$Au, another superlattice is found as shown in Figure 1.20c.

Including the ordered lattice shown in Figure 1.20, there are five most common ordered lattices as summarized in Figure 1.22 along with their Strukturbericht notation and examples of alloys in which they are found.
Ordering Transformation:

It occurs when solution has a negative enthalpy of mixing, $\Delta H_{\text{mix}} < 0$.

Define long-range order parameter:

$$L = \frac{r_A - X_A}{1 - X_A} = \frac{r_B - X_B}{1 - X_B}$$

Where $X_A$ is molar fraction of A atoms; $r_A$ are probability of A lattice sites occupied by “right” A atoms; $X_B$ and $r_B$, similarly for B atoms.

- At $T=0$, $L=1$, complete order ($\Delta S = 0$), corresponding to the lowest internal energy, $\Delta G_{\text{mix}}$ minimized.
- As $T \uparrow$, $L \downarrow$, due to entropy contribution --- some atoms interchange positions by diffusion so that they are located on “wrong” sites. Entropy effects becomes increasingly more important.
- As $T > T_c$, $L = 0$, complete disorder.

Using the quasichemical model as described above for the “regular solution”, it is possible to calculate how $L$ changes with temperature for different superlattices as shown in Figure 1.20 for an example.
Schematic diagram showing the variation of long-range order parameter (L) with temperature for (a) CuZn-type and (b) Cu3Au-type alloy transformation.

From the Figure above we can see: the way in which L decreases to zero is different for different lattices.
- For the equiatomic CuZn alloy, L decreases continuously with temperature up to T_c
- For the Cu3Au alloy, L decreases only slightly up to T_c, and then abruptly drops to zero.