Lecture 3: Models of Solutions

List of Symbols

Symbol	Meaning
ΔG_M	Molar Gibbs free energy of mixing
ΔH_M	Molar enthalpy of mixing
ΔS_M	Molar entropy of mixing
$\Delta_e G$	Excess Gibbs free energy per mole of solution
$\Delta_e H$	Excess enthalpy per mole of solution
$\Delta_e S$	Excess enthalpy per mole of solution

Mechanical Mixtures and Solutions

Consider the pure components A and B with molar free energies μ_A^o and μ_B^o respectively. If the components are initially in the form of powders then the average free energy of such a mixture of powders is simply:

$$G\{\text{mixture}\} = (1 - x)\mu_A^o + x\mu_B^o \tag{1}$$

where x is the mole fraction of B. It is assumed that the powder particles are so large that the A and B atoms do not "feel" each other's presence via interatomic forces between unlike atoms. It is also assumed that the number of ways in which the mixture of powder particles can be arranged is not sufficiently different from unity to give a significant contribution to a configurational entropy of mixing. Thus, a blend of powders which

obeys equation 1 is called a *mechanical mixture.* It has a free energy that is simply a weighted mean of the components, as illustrated in Fig. 1a for a mean composition x.
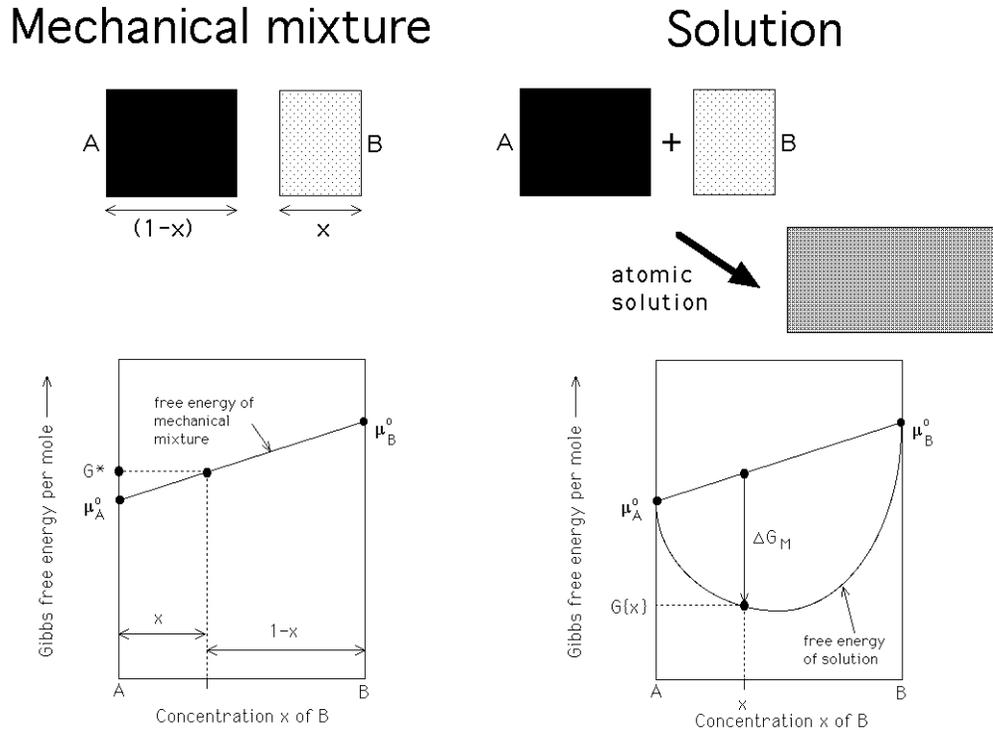

Fig. 1: (a) The free energy of a mechanical mixture, where the mean free energy is simply the weighted mean of the components. (b) The free energy of an ideal atomic solution is always lower than that of a mechanical mixture due to configurational entropy.

In contrast to a mechanical mixture, a *solution* is conventionally taken to describe a mixture of atoms or molecules. There will in general be an enthalpy change associated with the change in near neighbour bonds. We shall show later that much more probable arrangements of atoms become possible with intimate mixtures; this enters thermo-

dynamics via the configurational entropy, ensuring a reduction in free energy on mixing even when there are no enthalpy changes. The free energy of the solution is therefore different from that of the mechanical mixture, as illustrated in Fig. 1b. The difference in the free energy between these two states of the components is the free energy of mixing ΔG_M, the essential term in all thermodynamic models for solutions.

Ideal Solution

An ideal solution is one in which the atoms are, at equilibrium, distributed randomly; the interchange of atoms within the solution causes no change in the potential energy of the system. For a binary $(A\text{–}B)$ solution the numbers of the different kinds of bonds can therefore be calculated using simple probability theory:

$$
\begin{aligned}
N_{AA} &= z\frac{1}{2}N(1-x)^2 \\
N_{BB} &= z\frac{1}{2}Nx^2 \\
N_{AB} + N_{BA} &= zN(1-x)x
\end{aligned}
\tag{2}
$$

where N_{AB} represents both $A\text{–}B$ and $B\text{–}A$ bonds which cannot be distinguished. N is the total number of atoms, z is a coordination number and x the fraction of B atoms.

It is assumed that there is a random distribution of atoms in an ideal solution. There is no enthalpy of mixing since there is no change in energy when bonds between like atoms are broken to create those between unlike atoms. This is why the atoms are randomly distributed in the solution.

Configurational Entropy

Thus, the preparation of a binary alloy by this route would involve taking the two elemental powders (A and B) and mixing them together in a proportion whereby the mole fraction of B is x. The pure powders have the molar free energies μ_A^o and μ_B^o respectively, as illustrated on Fig. 1. The free energy of this mechanical mixture of powders is given by:

$$G\{\text{mixture}\} = (1-x)\mu_A^o + x\mu_B^o - T\Delta S_M \qquad (3)$$

where ΔS_M is the change in configurational entropy as a consequence of the mixing of the powders. We have assumed here, and shall continue to assume, that there is no change in enthalpy in the process since the atoms are indifferent to the their neighbours whatever they might be.

The change in configurational entropy as a consequence of mixing can be obtained using the Boltzmann equation $S = k \ln\{w\}$ where w is the number of configurations.

Suppose that there are m_A atoms per particle of A, and m_B atoms per particle of B; the powders are then mixed in a proportion which gives an average concentration of B which is the mole fraction x.

There is only one configuration when the heaps of powders are separate. When the powders are randomly mixed, the number of possible configurations for a mole of atoms becomes (see Appendix):

$$\frac{\left(N_a([1-x]/m_A + x/m_B)\right)!}{(N_a[1-x]/m_A)! \ (N_a x/m_B)!} \qquad (4)$$

The numerator in equation 4 is the factorial of the total number of particles and the denominator the product of the factorials of the A and

B particles respectively. Assuming large numbers of particles, we may use Stirling's approximation ($\ln\ y! = y\ln\ y - y$) to obtain the molar entropy of mixing as

$$\frac{\Delta S_M}{kN_a} = \frac{(1-x)m_B + xm_A}{m_A m_B}\ln\left\{N_a\frac{(1-x)m_B + xm_A}{m_A m_B}\right\}$$
$$- \frac{1-x}{m_A}\ln\left\{\frac{N_a(1-x)}{m_A}\right\} \quad (5)$$
$$- \frac{x}{m_B}\ln\left\{\frac{N_a x}{m_B}\right\}$$

subject to the condition that the number of particles remains integral and non–zero. This equation reduces to the familiar

$$\Delta S_M = -kN_a[(1-x)\ln\{1-x\} + x\ln\{x\}]$$

when $m_A = m_B = 1$.

Molar Free Energy of Mixing

The molar free energy of mixing is therefore:

$$\Delta G_M = N_a kT[(1-x)\ln\{1-x\} + x\ln\{x\}] \quad (6)$$

Fig. 2 shows how the configurational entropy and the free energy of mixing vary as a function of the concentration. ΔG_M is at a minimum for the equiatomic alloy because that is when the entropy of mixing is at its largest; the curves naturally are symmetrical about $x = 0.5$. The form of the curve does not change with temperature though the magnitude at any concentration scales with the temperature. It follows that at 0 K there is no difference between a mechanical mixture and an ideal solution.

The chemical potential per mole for a component in an ideal solution is given by:

$$\mu_A = \mu_A^o + N_a kT \ln\{1 - x\} \tag{7}$$

and there is a similar equation for B. Since $\mu_A = \mu_A^o + RT \ln a_A$, it follows that the activity coefficient is unity.
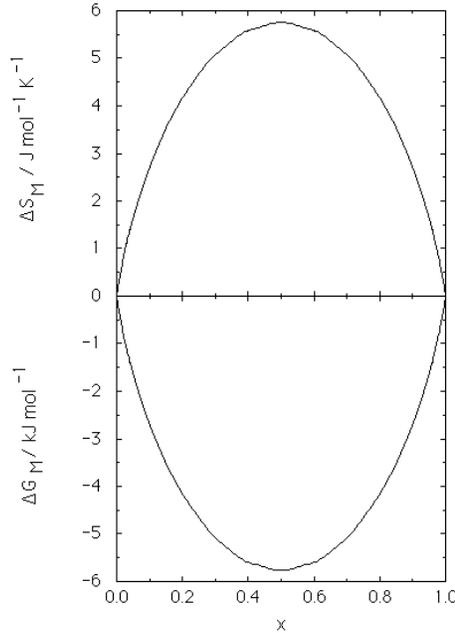

Fig. 2: The entropy of mixing and the free energy of mixing as a function of concentration in an ideal binary solution where the atoms are distributed at random. The free energy is for a temperature of 1000 K.

Regular Solutions

There are no solutions of iron which are ideal. The iron–manganese liquid phase is close to ideal, though even that has an enthalpy of mixing which is about $-860\,\mathrm{J\,mol^{-1}}$ for an equiatomic solution at 1000 K, which compares with the contribution from the configurational entropy

of about $-5800\,\mathrm{J\,mol^{-1}}$. The ideal solution model is nevertheless useful because it provides reference. The free energy of mixing for a non–ideal solution is often written as equation 7 but with an additional excess free energy term $(\Delta_e G = \Delta_e H - T\Delta_e S)$ which represents the deviation from ideality:

$$
\begin{aligned}
\Delta G_M &= \Delta_e G + N_a kT[(1-x)\ln\{1-x\} + x\ln\{x\}]\\
&= \Delta_e H - T\Delta_e S + N_a kT[(1-x)\ln\{1-x\} + x\ln\{x\}]
\end{aligned}
\tag{8}
$$

One of the components of the excess enthalpy of mixing comes from the change in the energy when new kinds of bonds are created during the formation of a solution. This enthalpy is, in the *regular solution* model, estimated from the *pairwise* interactions. The term "regular solution" was proposed to describe mixtures whose properties when plotted varied in an aesthetically regular manner; a regular solution, although not ideal, would still contain a random distribution of the constituents. Following Guggenheim, the term regular solution is now restricted to cover mixtures that show an ideal entropy of mixing but have a non–zero interchange energy.

In the regular solution model, the enthalpy of mixing is obtained by counting the different kinds of near neighbour bonds when the atoms are mixed at random; this information together with the binding energies gives the required change in enthalpy on mixing. The binding energy may be defined by considering the change in energy as the distance between a pair of atoms is decreased from infinity to an equilibrium separation (Fig. 3). The change in energy during this process is the binding energy, which for a pair of A atoms is written $-2\epsilon_{AA}$. It follows that when $\epsilon_{AA} + \epsilon_{BB} < 2\epsilon_{AB}$, the solution will have a larger than

random probability of bonds between unlike atoms. The converse is true when $\epsilon_{AA} + \epsilon_{BB} > 2\epsilon_{AB}$ since atoms then prefer to be neighbours to their own kind. Notice that for an ideal solution it is only necessary for $\epsilon_{AA} + \epsilon_{BB} = 2\epsilon_{AB}$, and not $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB}$.
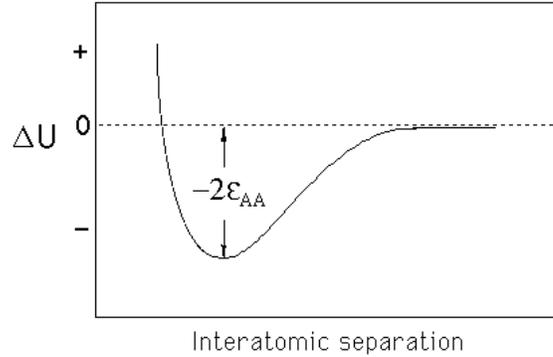

Fig. 3: Curve showing schematically the change in energy as a function of the distance between a pair of A atoms. $-2\epsilon_{AA}$ is the binding energy for the pair of atoms. There is a strong repulsion at close–range.

Suppose now that we retain the approximation that the atoms are randomly distributed, but assume that the enthalpy of mixing is not zero. The number of A–A bonds in a mole of solution is $\frac{1}{2}zN_a(1-x)^2$, B–B bonds $\frac{1}{2}zN_ax^2$ and A–$B + B$–A bonds $zN_a(1-x)x$ where z is the co–ordination number. It follows that the molar enthalpy of mixing is given by:

$$\Delta H_M \simeq N_a z(1-x)x\omega \tag{9}$$

where

$$\omega = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB} \tag{10}$$

The product $zN_a\omega$ is often called the regular solution parameter, which

in practice will be temperature and composition dependent. A composition dependence also leads to an asymmetry in the enthalpy of mixing as a function of composition about $x = 0.5$. For the nearly ideal Fe–Mn liquid phase solution, the regular solution parameter is $-3950 + 0.489T \, \mathrm{J\,mol^{-1}}$ if a slight composition dependence is neglected.

A positive ω favours the clustering of like atoms whereas when it is negative there is a tendency for the atoms to order. This second case is illustrated in Fig. 4, where an ideal solution curve is presented for comparison. Like the ideal solution, the form of the curve for the case where $\Delta H_M < 0$ does not change with the temperature, but unlike the ideal solution, there is a free energy of mixing even at 0 K where the entropy term ceases to make a contribution.
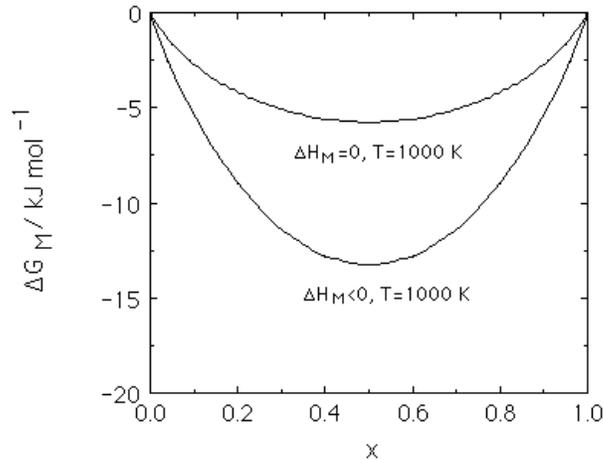

Fig. 4: The free energy of mixing as a function of concentration in a binary solution where there is a preference for unlike atoms to be near neighbours. The free energy curve for the ideal solution $(\Delta H_M = 0)$ is included for comparison.

The corresponding case for $\Delta H_M > 0$ is illustrated in Fig. 5, where it is evident that the form of the curve changes with the temperature. The contribution from the enthalpy term can largely be neglected at very high temperatures where the atoms become randomly mixed by thermal agitation so that the free energy curve has a single minimum. However, as the temperature is reduced, the opposing contribution to the free energy from the enthalpy term introduces two minima at the solute–rich and solute–poor concentrations. This is because like–neighbours are preferred. On the other hand, there is a maximum at the equiatomic composition because that gives a large number of unfavoured unlike atom bonds. Between the minima and the maximum lie points of inflexion which are of importance in spinodal decomposition, which will be discussed later. Some of the properties of different kinds of solutions are summarised in Table 1.

Type	ΔS_M	ΔH_M
Ideal	Random	0
Regular	Random	$\neq 0$
Quasichemical	Not random	$\neq 0$

Table 1: Elementary thermodynamic properties of solutions

Appendix: Derivation of equation 9

Energy, defined relative to infinitely separated atoms, before mixing:

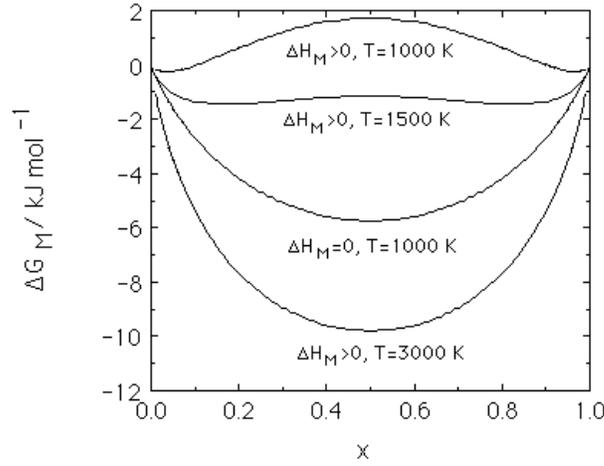$$\frac{1}{2} z N_a \left[(1-x)(-2\epsilon_{AA}) + x(-2\epsilon_{BB}) \right]$$

Fig. 5: The free energy of mixing as a function of concentration and temperature in a binary solution where there is a tendency for like atoms to cluster. The free energy curve for the ideal solution ($\Delta H_M = 0$) is included for reference.

since the binding energy per pair of atoms is -2ϵ and $\frac{1}{2}zN_a$ is the number of bonds. After mixing, the corresponding energy is given by:

$$\frac{1}{2}zN_a\left[(1-x)^2(-2\epsilon_{AA}) + x^2(-2\epsilon_{BB}) + 2x(1-x)(-2\epsilon_{AB})\right]$$

where the factor of two in the last term is to count AB and BA bonds. Therefore, the change due to mixing is the latter minus the former, *i.e.*

$$= -zN_a\left[(1-x)^2(\epsilon_{AA}) + x^2(\epsilon_{BB}) + x(1-x)(2\epsilon_{AB})\right.$$
$$\left. - (1-x)(\epsilon_{AA}) - x(\epsilon_{BB})\right]$$
$$= -zN_a\left[-x(1-x)(\epsilon_{AA}) + -x(1-x)(\epsilon_{BB}) + x(1-x)(2\epsilon_{AB})\right]$$
$$= zN_a(x)(1-x)\omega$$

given that $\omega = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$.

Appendix: Configurations

Suppose there are N sites amongst which we distribute n atoms of type A and $N - n$ of type B (Fig. 6). The first A atom can be placed in N different ways and the second in $N - 1$ different ways. These two atoms cannot be distinguished so the number of different ways of placing the first two A atoms is $N(N-1)/2$. Similarly, the number of different ways of placing the first three A atoms is $N(N-1)(N-2)/3!$

Therefore, the number of distinguishable ways of placing all the A atoms is

$$\frac{N(N-1)\ldots(N-n+2)(N-n+1)}{n!} = \frac{N!}{n!(N-n)!}$$

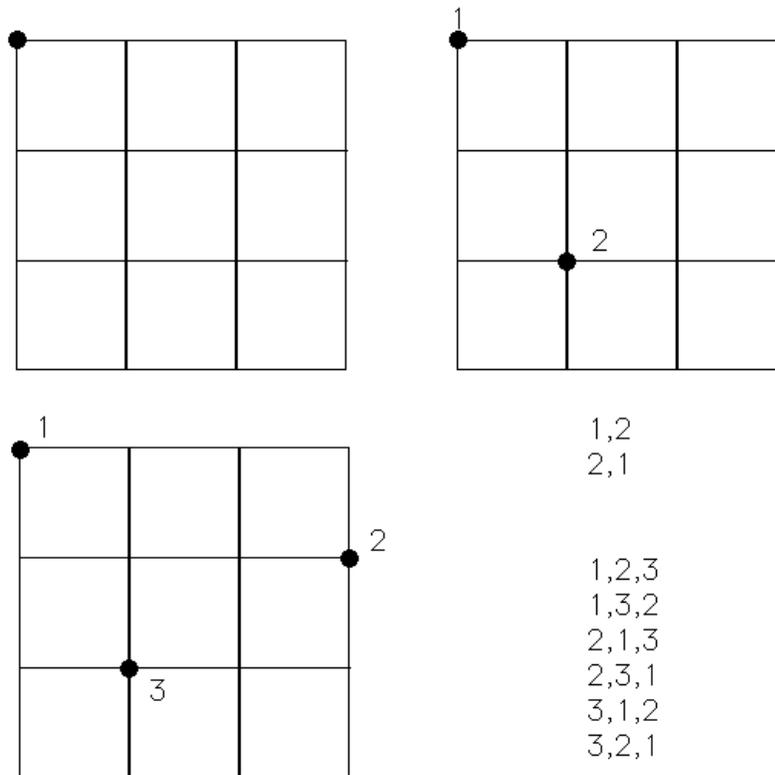Fig. 6: Configurations