Computation of Phase Diagrams (Revision) H. K. D. H. Bhadeshia

---

The Equilibrium State

Equilibrium is a state in which “no further change is perceptible, no matter how long one waits”. For example, there will be no tendency for diffusion to occur between two phases which are in equilibrium even though they may have different chemical compositions.

An equilibrium phase diagram is vital in the design of materials. It contains information about the phases that can exist in a material of specified chemical composition at particular temperatures or pressures. It carries information about the chemical compositions of these phases and the phase fractions. The underlying thermodynamics reveals the *driving forces* which are essential in kinetic theory. We shall begin the discussion of phase equilibria by revising some of the elementary thermodynamic models of equilibrium and phase diagrams, and then see how these can be adapted for the computer modelling of phase diagrams as a function of experimental thermodynamic data.

Allotropic Transformations

Consider equilibrium for an allotropic transition (*i.e.* when the structure changes but not the composition). Two phases α and γ are said to be in equilibrium when they have equal free energies:

$$G^{\alpha} = G^{\gamma} \tag{1}$$

When temperature is a variable, the transition temperature is also fixed by the above equation (Fig. 1).

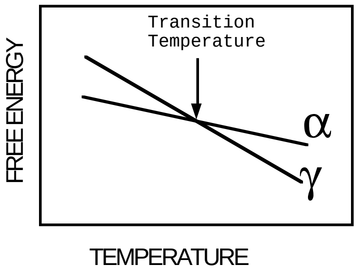

Fig. 1: The transition temperature for an allotropic transformation.

The Chemical Potential

We saw that equilibrium between allotropes occurs when their free energies are equal; there is no composition change during transformation. A different approach is needed when chemical composition is also a variable in discussing equilibrium. Consider an alloy consisting of two components A and B. For the phase α, the free energy will in general be a function of the mole fractions $(1-x)$ and x of A and B respectively:

$$G^{\alpha} = (1-x)\mu_A + x\mu_B \tag{2}$$

where μ_A represents the mean free energy of a mole of A atoms in α. The term μ is called the *chemical potential* of A, and is illustrated in Fig. 2a. Thus the free energy of a phase is simply the weighted mean of the free energies of its component atoms. Of course, the latter varies with concentration according to the slope of the tangent to the free energy curve, as shown in Fig. 2.

Consider now the coexistence of two phases α and γ in our binary alloy. They will only be in equilibrium with each other if the A atoms in γ have the same free energy as the A atoms in α, and if the same is true for the B atoms:

$$\mu_A^{\alpha} = \mu_A^{\gamma}$$
$$\mu_B^{\alpha} = \mu_B^{\gamma}$$

If the atoms of a particular species have the same free energy in both the phases, then there is no tendency for them to migrate, and the system will be in stable equilibrium if this condition applies to all species of atoms. Since the way in which the free energy of a phase varies with concentration is unique to that phase, the *concentration* of a particular species of atom need not be identical in phases which are at equilibrium. Thus, in general we may write:

$$x_A^{\alpha\gamma} \neq x_A^{\gamma\alpha}$$
$$x_B^{\alpha\gamma} \neq x_B^{\gamma\alpha}$$

where $x_i^{\alpha\gamma}$ describes the mole fraction of element i in phase α which is in equilibrium with phase γ *etc.*

The condition the chemical potential of each species of atom must be the same in all phases at equilibrium is general and justifies the common tangent construction illustrated in Fig. 2b.

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–B) solution the numbers of the different kinds of bonds can therefore be calculated using simple probability theory:

$$\begin{aligned} N_{AA} &= \frac{1}{2}N(1-x)^2 \\ N_{BB} &= \frac{1}{2}Nx^2 \\ N_{AB} &= N(1-x)x \end{aligned} \tag{3}$$

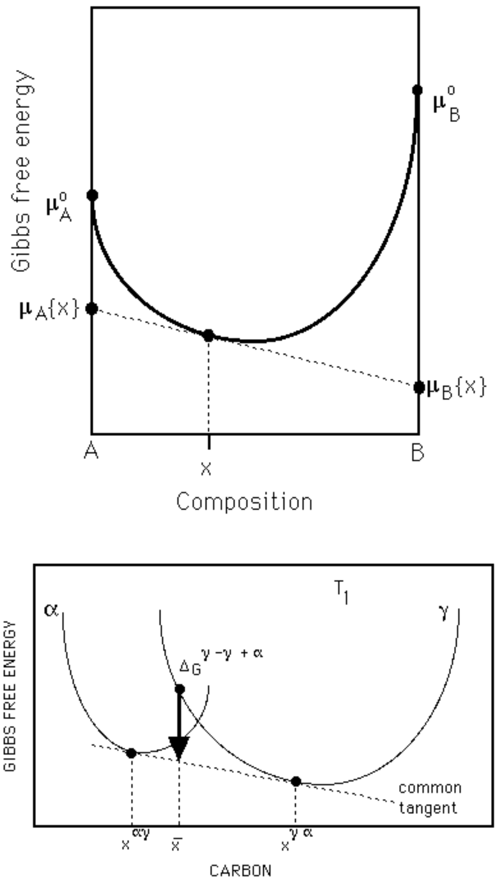

Fig. 2: (a) Diagram illustrating the meaning of a chemical potential μ. (b) The common tangent construction giving the equilibrium compositions of the two phases at a fixed temperature.

where N_{AB} represents both A–B and B–A bonds which cannot be distinguished. N is the total number of atoms and x the fraction of B atoms.

For an ideal solution, the entropy of mixing assumes a random distribution of atoms. 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. The molar free energy of mixing is therefore:

$$\Delta G_M = N_a kT[(1-x)\ln\{1-x\} + x\ln\{x\}] \tag{4}$$

Fig. 3 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 are naturally 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:

$$\mu_A = \mu_A^o + N_a kT \ln\{1-x\} \tag{5}$$

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.

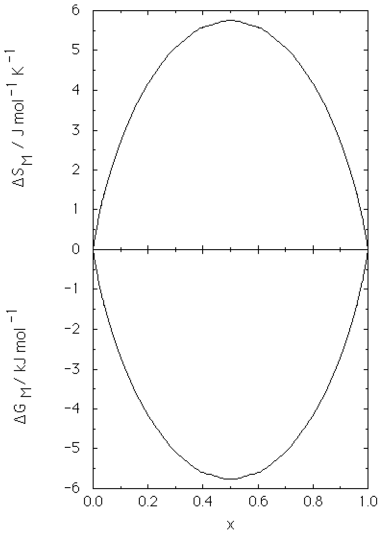

Fig. 3: The entropy of mixing and the free energy of mixing as a function of concentration in an ideal binary solution where the atoms are distributed at random. The free energy is for a temperature of 1000 K.

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 5 but with an additional excess free energy term ($\Delta_e G = \Delta_e H - T\Delta_e S$) which indicates the deviation from ideality:

$$\begin{aligned} \Delta G_M &= \Delta_e G + N_a kT[(1-x)\ln\{1-x\} + x\ln\{x\}] \\ &= \Delta_e H - T\Delta_e S + N_a kT[(1-x)\ln\{1-x\} + x\ln\{x\}] \end{aligned} \tag{6}$$

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 by Hildebrand (1929) to describe mixtures whose properties when plotted varied in an aesthetically regular manner; he went on to suggest that a regular solution, although not ideal, would still contain a random distribution of the constituents. Following Guggenheim (1935), 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. 4). 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 $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB}$ (Guggenheim, 1935),

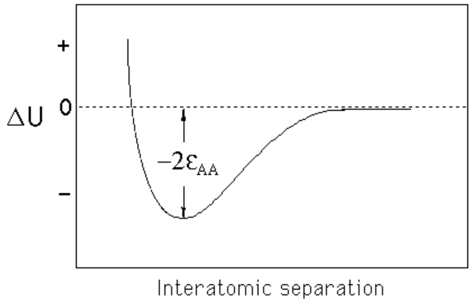

Fig. 4: Curve showing schematically the change in energy as a function of the distance between a pair of A atoms. $-2\epsilon_{AA}$ is the binding energy for the pair of atoms. There is a strong repulsion at close–range.

Suppose now that we retain the approximation that the atoms are randomly distributed, but 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 $\frac{1}{2}zN_a x^2$ and A–B bonds $zN_a(1-x)x$ where z is the co–ordination number. It follows that the molar enthalpy of mixing is given by:

$$\Delta H_M \simeq N_a z(1-x)x\omega \tag{7}$$

where

$$\omega = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB} \tag{8}$$

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. 5, 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.

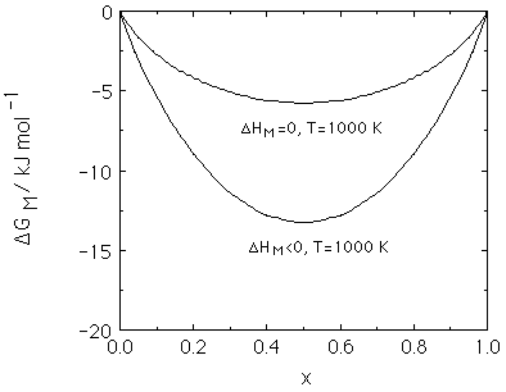

Fig. 5: The free energy of mixing as a function of concentration in a binary solution where there is a preference for unlike atoms to be near neighbours. The free energy curve for the ideal solution ($\Delta H_M = 0$) is included for reference.

The corresponding case for $\Delta H_M > 0$ is illustrate in Fig. 6, 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.

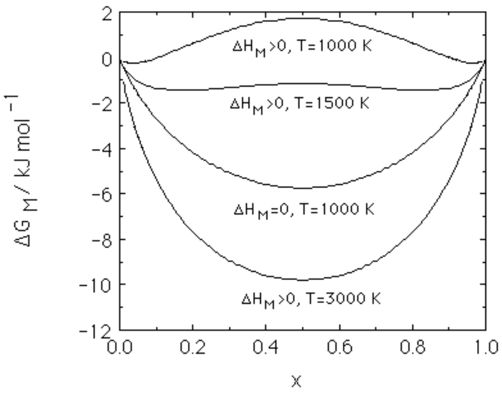

Fig. 6: The free energy of mixing as a function of concentration and temperature in a binary solution where there is a tendency for like atoms to cluster. The free energy curve for the ideal solution ($\Delta H_M = 0$) is included for reference.