

## Lecture 2: Equilibrium between Solutions

### List of Symbols

<i>Symbol</i>	<i>Meaning</i>
$a$	Activity
$G$	Molar Gibbs free energy
$H$	Molar enthalpy
$S$	Molar entropy
$x$	mole fraction
$\Gamma$	Activity coefficient
$\mu_i$	Chemical potential per mole of element $i$ in solution
$x_i^{\gamma\alpha}$	Mole fraction of $i$ in $\gamma$ which is in equilibrium with $\alpha$

### Different Kinds of Equilibria

We discussed in the previous lecture the meaning of equilibrium (no perceptible change no matter how long one waits) and illustrated this by considering equilibrium between allotropes. The definition of equilibrium is in a sense subjective. Fig. 1 shows four cases which illustrate this. The first is where the ball is in a *universal minimum*, whatever *that* means. The second is probably representative of all practical equilibria, the state of metastable equilibrium. In both cases, an infinitesimal perturbation would tend to restore equilibrium. The third case is unstable equilibrium where an infinitesimal perturbation would lead to further

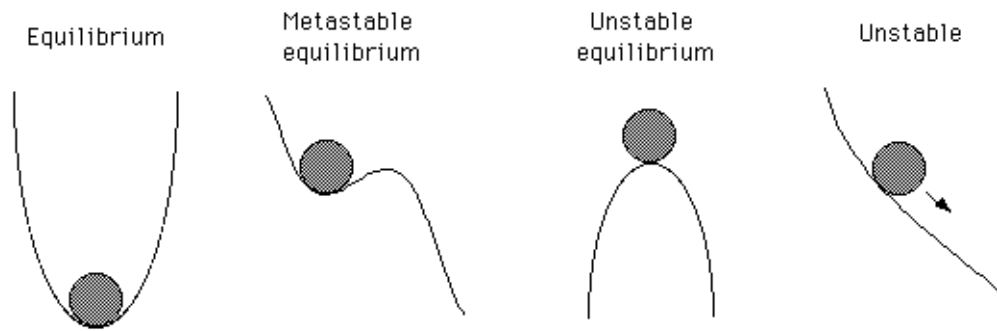


Fig. 1: Variety of state of mechanical equilibrium and of an unstable situation.

states of lower free energy. Finally, the case which does not correspond to equilibrium but is a process which is dissipating free energy.

## The Chemical Potential

We saw in the last lecture 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  $\alpha$ , the free energy will in general be a function of the mole fractions  $(1 - x)$  and  $x$  of  $A$  and  $B$  respectively:

$$G^\alpha = (1 - x)\mu_A + x\mu_B \quad (1)$$

where  $\mu_A$  represents the mean free energy of a mole of  $A$  atoms in  $\alpha$ . The term  $\mu$  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  $\alpha$  and  $\gamma$  in our binary alloy. They will only be in equilibrium with each other if the  $A$  atoms in  $\gamma$  have the same free energy as the  $A$  atoms in  $\alpha$ , 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  $\alpha$  which is in equilibrium with phase  $\gamma$  *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.

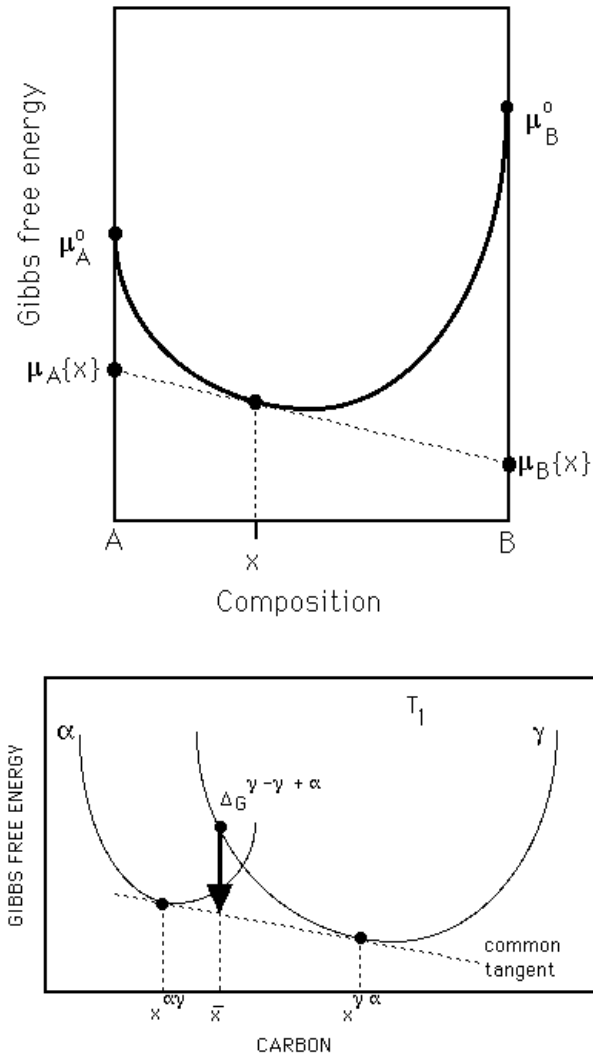


Fig. 2: (a) Diagram illustrating the meaning of a chemical potential  $\mu$ . (b) The common tangent construction giving the equilibrium compositions of the two phases at a fixed temperature.

### Activity

The chemical potential  $\mu_A^\alpha$  of the A atoms in the  $\alpha$  phase may be expanded in terms of a contribution from the pure component A and a concentration dependent term as follows:

$$\mu_A^\alpha = \mu_A^{o\alpha} + RT \ln a_A^\alpha$$

where  $\mu_A^{o\alpha}$  is the free energy of pure  $A$  in the structure of  $\alpha$ , and  $a_A$  is the *activity* of atom  $A$  in the solution of  $A$  and  $B$ .

The activity of an atom is like its effective concentration when it is in solution. For example, there will be a greater tendency for the  $A$  atoms to evaporate from solution, when compared with pure  $A$ , if the  $B$  atoms repel the  $A$  atoms. The effective concentration of  $A$  in solution will therefore be greater than implied by its atomic fraction, *i.e.* its activity is greater than its concentration. The opposite would be the case if the  $B$  atoms attracted the  $A$  atoms.

The atom interactions can be expressed in terms of the change in energy as an  $A - A$  and a  $B - B$  bond is broken to create  $2(A - B)$  bonds. An ideal solution is formed when there is no change in energy in the process of forming  $A - B$  bonds. The activity is equal to the mole fraction in an ideal solution (Fig. 3). If, on the other hand, there is a reduction in energy than the activity is less than ideal and vice versa.

The activity and concentration are related via an activity coefficient  $\Gamma$ :

$$a = \Gamma x \tag{2}$$

The activity coefficient is in general a function of the chemical composition of all the elements present in the solution, but tends to be constant in dilute solutions (*i.e.* in the Henry's law region).

In the above discussion, the activity of the solute was defined with respect to a Raoultian reference state, *i.e.*  $a = 1$  for  $x = 1$ . Other definitions are sometimes convenient.

Note that solutions where the enthalpy of mixing is positive tend to exhibit clustering at low temperatures whereas those with a negative

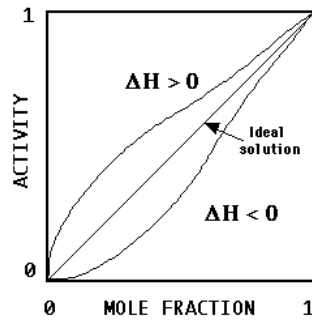


Fig. 3: The variation in Raoultian activity as a function of concentration in a binary solution. The ideal solution represents the case where the enthalpy of mixing is zero; the atoms are indifferent to the specific nature of their neighbours. The case where the activity is larger than the concentration is for solutions where the enthalpy of mixing is greater than zero, with like atoms preferred as near neighbours. When the activity coefficient is less than unity, unlike atoms are preferred as near neighbours, the enthalpy of mixing being negative.

enthalpy of mixing will tend to exhibit ordering at low temperatures. The effect of temperature is to mix all atoms since both clustering and ordering cause a reduction in entropy (*i.e.* a negative change in entropy). The product  $-T\Delta S$  (where  $\Delta S = S_{\text{ordered}} - S_{\text{random}}$  or  $\Delta S = S_{\text{clustered}} - S_{\text{random}}$ ) becomes increasingly positive at high temperatures, so much that it eventually overcomes the enthalpy effects and causes the mixing of all atoms. Some free energy of mixing curves are illustrated in Fig. 4 to illustrate this – we shall discuss these in more detail in the next lecture.

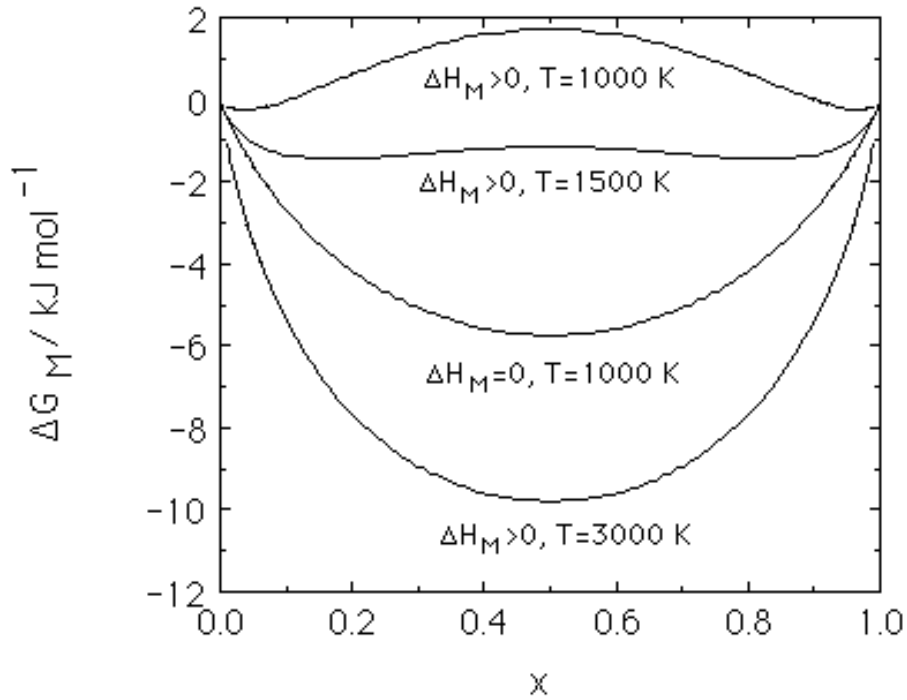


Fig. 4: Free energy of mixing plotted as a function of temperature and of the enthalpy  $\Delta H_M$  of mixing.  $\Delta H_M = 0$  corresponds to an ideal solution where the atoms of different species always tend to mix at random and it is always the case that  $\partial\mu_A/\partial C_A > 0$ . When  $\Delta H_M < 0$  the atoms prefer unlike neighbours and it is always the case that  $\partial\mu_A/\partial C_A > 0$ . When  $\Delta H_M > 0$  the atoms prefer like neighbours so for low temperatures and for certain composition ranges  $\partial\mu_A/\partial C_A > 0$  giving rise to the possibility of uphill diffusion.