Part I : Preliminaries (Thermodynamics and Kinetics)

Module 4: Driving force for diffusion

5.1 Motivation

A block of pure copper welded to pure nickel, if kept at 1000^0C, undergoes a transformation such that the composition becomes equal throughout the system. On the other hand, if a block with homogeneous composition (say, of 50 wt % nickel) is kept at a lower temperature of 200^0C or so, the compositional homogeneity is lost and it becomes a mechanical mixture of copper and nickel rich phases. Why?

5.2 Free energy minimation as the driving force for diusion

Consider the Cu-Ni phase diagram as shown in Fig. 20. Let we weld a block of copper to a block of nickel at keep it at 1000 C; let the overall composition be 50 wt.% nickel. The schematic free energy versus composition diagram at this temperamture is as shown in Fig. 21. Since the system prefers a complete solid solution and since the initial configuration is a mechanical mixture of pure copper and pure nickel, there is a driving force for the mechanical mixture to turn into a solid solution. In other words, like any spontaneous change, in this case too, the minimization of free energy will drive the process of compositional homogenisation. However, since copper and nickel are in the solid state, it takes a finite time to achieve the compositional homogenisation. This time needed for the homogenisation is decided by the kinetics of the diffusion process.

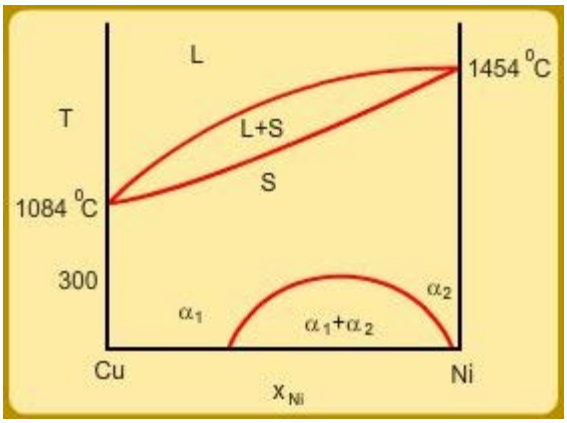

Figure 20: Schematic copper-nickel phase diagram.

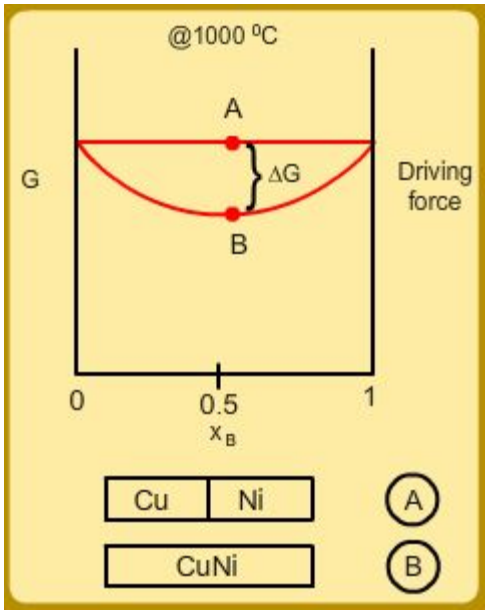

Figure 21: Free energy versus composition diagram at 1000 C.

In general, the process described above is true for almost all phase transformations. A study of the thermodynamics can only tell us whether a transformation is possible or not, and the driving force for the transformation when it is possible. However, how fast or slow the transformation is going to be is decided by the kinetics. In most of the transformations discussed in these notes, it is the kinetics of diffusion which decides the time taken for the completion of the transformation; further, as we describe later, the diffusion process is a thermally activated process; hence it is very sensitive to changes in temperature.

5.3 Tutorial problems and questions

1. Consider the block of uniform composition of 50 wt % nickel kept at 200^0. The low temperature section of the copper-nickel phase diagram is as shown in Fig. 22. Does the system undergo any phase transformation? If yes, show the driving force for the transformation.

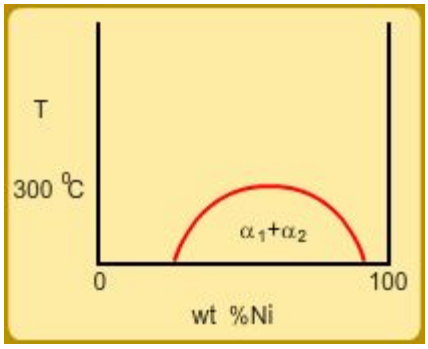

Figure 22: Schematic low temperature section of the copper-nickel phase diagram.

5.4 Solutions to the tutorial

The system will undergo unmixing. The driving force for unmixing is as shown in Fig. 23.

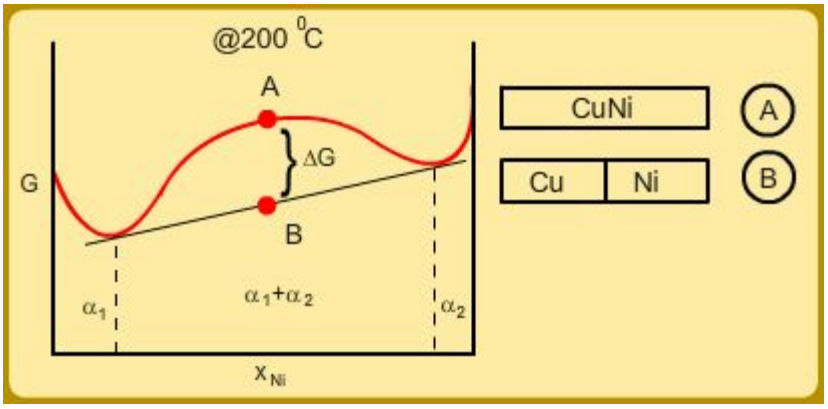

Figure 23: Driving force for unmixing in the copper-nickel system at low temperatures.

5.5 Supplementary information

Two systems will achieve thermal equilibrium when their temperatures are the same; till then, there will be exchange of energy. Similarly, two systems will change their volumes till their pressures are equal. In a similar fashion, the atomic flux and chemical potential are the complementary quantities; the atomic flux operates till the chemical potentials for both the species are the same in both the phases. This is shown in Fig. 24.

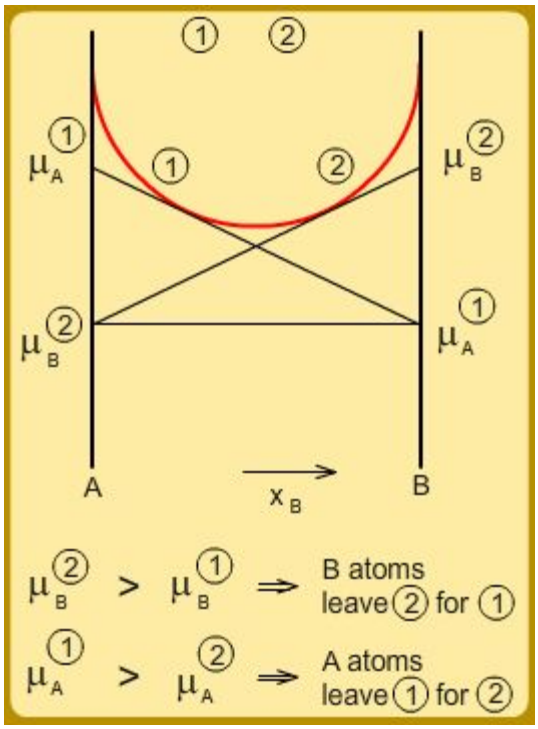

Figure 24: Chemical potential and atomicux.