

Part I : Preliminaries (Thermodynamics and Kinetics)

Module 1: Gibbs free energy and equilibria

Introduction

Phase transformations are ubiquitous; every one of us have kept water in the refrigerator to turn it into ice or added ice cubes to a drink to cool it (by transforming ice into water). In engineering materials, they are also of importance. In materials science, we are interested in phase transformations that can produce specific microstructures. Since microstructures determine many important properties of materials (mechanical strength, for example), phase transformations are one of the ways in which we produce materials which have specific properties (and hence applications). While the study of phase transformations in terms of the underlying thermodynamics and kinetics form the scientific aspect of formation of microstructures, the practical aspect of phase transformations is usually achieved using heat treatment (that is, specific cycles of heating and cooling).

In this course material, we begin with the thermodynamic and kinetic (specifically, diffusion) concepts needed to understand phase transformations. We primarily deal with solid-solid phase transformations. However, we do make occasional references to other types of phase transformations: for example, the liquid-solid transformation of melting and solidification is also discussed. We also discuss the structure and properties of defects – interfaces in materials. Most of the properties of materials are correlated with the microstructures, and interfaces are probably the most important microstructural features. Hence, an understanding of the effects of heat treatments (and resultant phase transformations) on the formation, removal and modification of interfaces is one of the most important learning outcomes of this course material. Finally, we deal with many different types of phase transformations, the mechanisms of transformations as well as case studies. In addition, we also discuss certain microstructural changes which are quite close in characteristics to phase transformations, though, they are not phase transformations per se.

The course material is organised into several small modules. Each modules conveys one idea; some are long enough to need a complete lecture while some others are suited for a tutorial session. Some modules are small enough to be taken up in twos and threes in a single lecture. There are also several self-assessment questions and assignments problems at the end of each modules (with solutions) so that any student can use these notes for self-study.

It is very difficult to discuss phase transformations without recourse to microstructures. Wherever possible, we have tried to use microstructures which are available under creative commons license, or which could be obtained under creative commons license. When it is not possible, we have tried to show the features schematically (with relevant references to textbooks and other scientific literature so that an interested reader may consult the same).

Thermodynamics

In this chapter, we discuss the types of equilibria, Gibbs free energy, binary alloys, binary alloy phase diagrams using free energy versus composition diagrams, and some laws and rules related to phase diagrams of relevance.

We assume that the user of this module has undergone a materials thermodynamics course. In this chapter, we only review certain concepts that are needed to study phase transformations (in a cursory manner, for the sake of completion). We direct the interested reader to Gaskell [1] for more details.

2 Gibbs free energy and equilibria

2.1 Motivation

Ice cube kept at 30°C spontaneously turns to water. Water kept in the freezer of a refrigerator (which is at about -15°C or so) becomes ice. Water taken to temperatures above 100°C or so, turns to water vapour. Thus, by changing the ambient temperature, it is possible to induce a phase transformation: solid (ice) to liquid (water) or liquid to solid or liquid to gas (water vapour) and so on. What determines (given a temperature) if water would stay a solid, liquid or vapour at that temperature or undergo a transformation of phase?

2.2 Equilibria: stable, metastable and unstable

Consider a Tanjore doll (roly-poly doll) with round bottom as shown in Fig. 1. When it stands as shown, its centre of gravity is close to the bottom. When it is pushed to lie down, the height of centre of gravity from the bottom increases. This leads to a increase in the potential energy (gravitational energy) of the system. Hence, the doll automatically comes back to the standing position. If we plot the gravitational energy for various angles of tilt of the doll, the curve looks as shown and the usual standing position of the toy is thus a position of minimum potential energy.

Consider the Gibbs free energy (G) defined as follows:

$$G = U + PV - TS = H - TS \quad (1)$$

where U is the internal energy, P is the pressure, V is the volume, T is the temperature, S is the entropy and H is the enthalpy [1]. In a material which is at a constant temperature and pressure, if we plot the Gibbs free energy as a function of different internal configurations, then, much like the Tanjore doll, the system chooses that configuration for which the Gibbs free energy is a minimum.

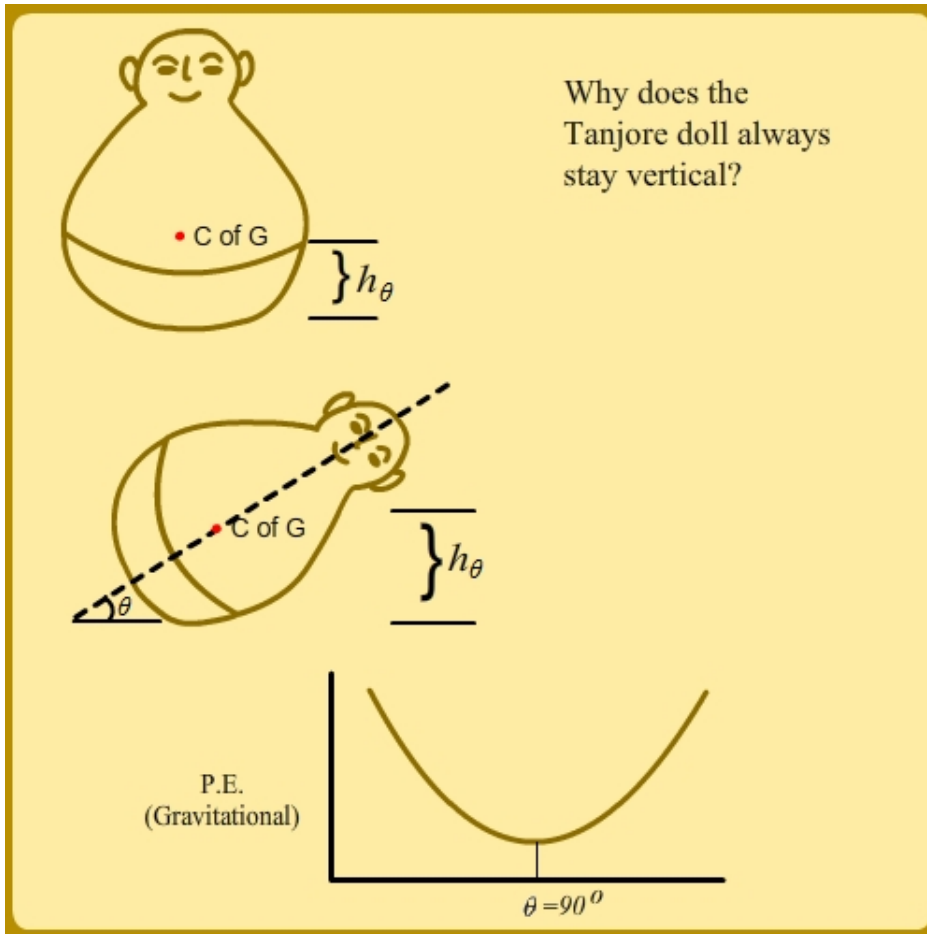


Figure 1: The Tanjore doll which always comes to the vertical position.

Now, let us consider a slightly more complicated mechanical system than the Tanjore doll: See Fig. 2. If the block is kept horizontally, the gravitational potential energy is the minimum. Any disturbance from this position takes the block back to horizontal position. However, there is another relatively stable position, namely vertical as shown. In this case also, any slight disturbances take the block back to the vertical position. However, if we stand the block on one edge as shown, any small perturbation will make the block reach the vertical or horizontal position. All these three configurations are known as equilibrium configurations for the block. The vertical position is known as the metastable equilibrium because even though the block prefers this position for small disturbances, larger disturbances push it to a different position. The horizontal position is known as the stable equilibrium because this is the minimum energy position and there are no other positions for which the gravitational potential energy is less than that for this position. Finally, a block standing on its edge is known as unstable equilibrium. At this position, it has the highest potential energy and any movement to the right or left decreases the potential energy. When placed in vertical position, if pushed to the right and left, the block comes back to the original position. This is because, as shown in the figure, the potential energy increases for small deviations from the given position. Such a state is known as metastable state. However, if the block is pushed to the peak point as shown, any small perturbation will make it fall down. Such a state is known as unstable state. Finally, when the block reaches the third position as shown, again, it is stable against perturbations and the potential energy is the lowest for this configuration. Such a configuration is known as stable configuration.

In materials also, an analogous situation with respect to internal atomic configurations and Gibbs free energy exist. Phase transformations take place when the internal configurations in a material correspond to the unstable or metastable equilibrium for the given parameters. Thus, to answer the question raised at the beginning of this module, when the temperatures are below 0°C , the solid form has a lower Gibbs free energy compared to the liquid and vaporous forms of water. In a similar manner, the Gibbs free energy for the liquid form is the lowest in the temperature range 0 to 100°C and that of vapour is the lowest above 100° . This automatically leads to the

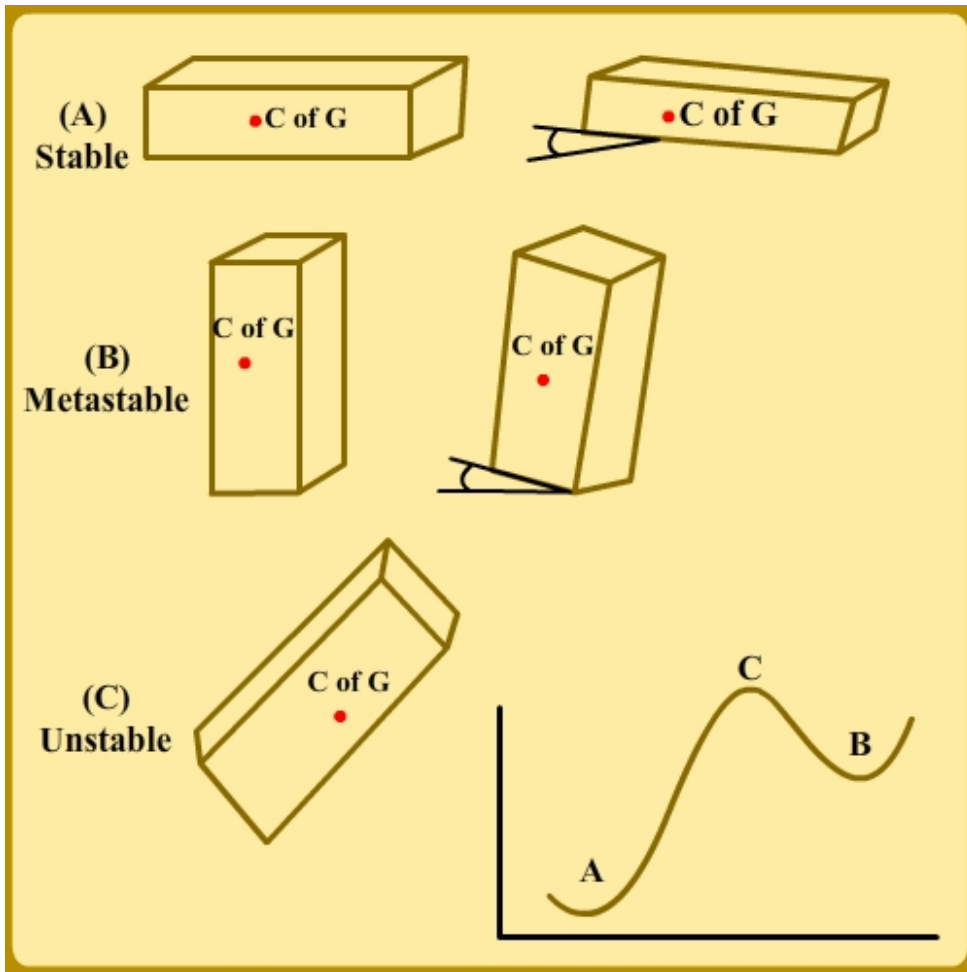


Figure 2: The stable, metastable and unstable equilibria.

definition of equilibrium transformation temperature (See Fig. 3): it is the temperature at which the two phases have the same Gibbs free energy and hence co-exist; below and above the temperature, one of the phases becomes the phase with the lower free energy and hence is preferred.

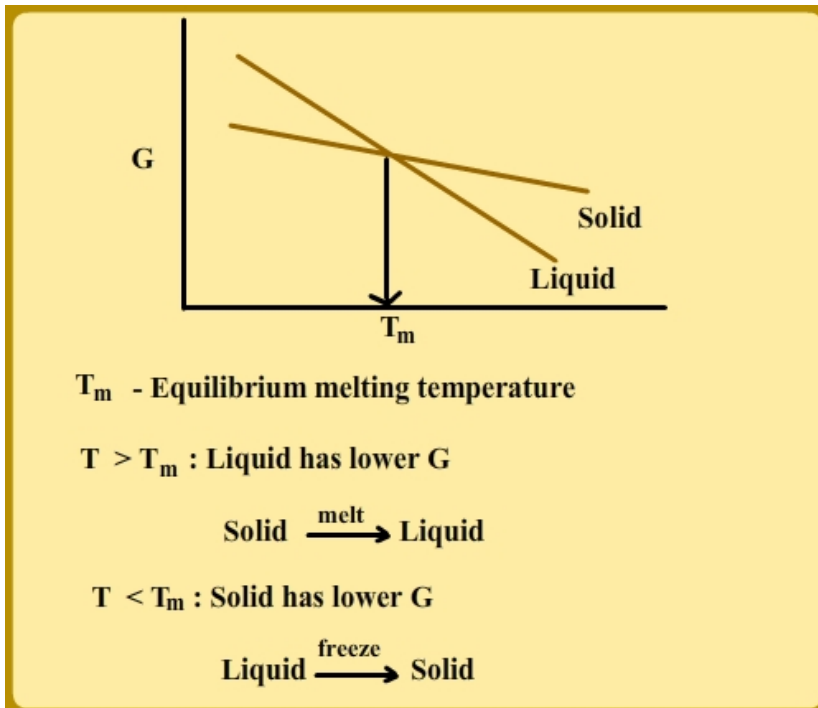


Figure 3: The definition of equilibrium transformation temperature.

The Gibbs free energy can be calculated given the C_p , the specific heat capacity at constant pressure [1].

2.3 Tutorial problems and questions

1. Calculate the increase in enthalpy and entropy for copper when it is heated from 300 to 600 K. The specific heat at constant pressure for

copper is described by the empirical relation $C_p = 22.61 + 6.27 \times 10^{-3}T$ J/mol/K and is as shown in Fig. 4.

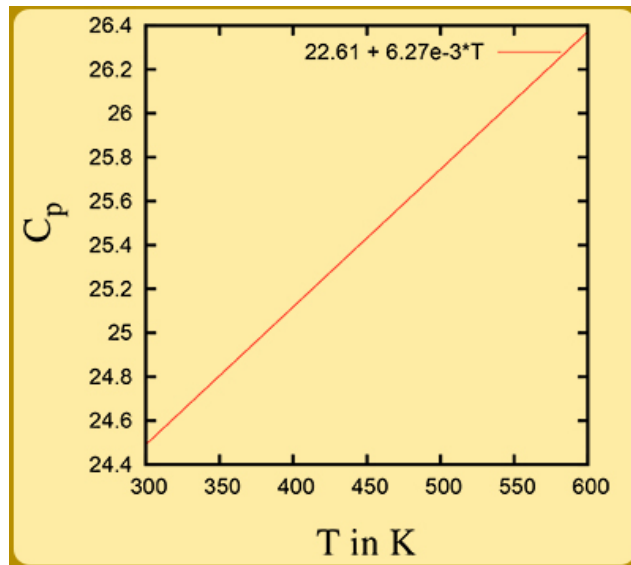


Figure 4: C_p as a function of temperature for copper in the temperature change 300 to 600 K.

2. At the equilibrium transformation temperature, the Gibbs free energies of the two phases are

2.4 Solutions to the tutorial

1. The change in enthalpy, $\Delta H = \int_{300}^{600} C_p dT$ and $\Delta S = \int_{300}^{600} \frac{C_p}{T} dT$. Hence, $\Delta H = 7629.45 \text{ J/mol}$ and $\Delta S = 17.55 \text{ J/mol/K}$.
2. Equal

2.5 Supplementary information

The stable, metastable and unstable equilibria are called equilibria because, as is clear from the figures, these points correspond to the extrema (minima in the case of stable and metastable equilibria and maxima in the case of unstable equilibria), and hence the first derivatives are zero at these extrema points.