1. Introduction

Phase transformations are associated with changes of state or crystal structure in solids towards the equilibrium state under specific ambient conditions. The resultant microstructure enables division of phase transformations in solids into two categories:
a) The original phase disappears in full and it is replaced with another one,
b) The original phase develops a small fraction of one or more new phases (minor phases).

As far as the technology is concerned, phase transformations represent a very significant tool to enable a controlled process for changing of structural characteristics of materials as well as their end-use properties.

When studying phase transformations, we look deeper into the conditions, at which one phase transforms into another or even a mix of several phases. Phase transformations are driven by the fact that the initial structural condition of material is unstable when compared to the new condition. How do we measure the stability of phases? This question is addressed by ***thermodynamics***. For transformations occurring at constant temperature and pressure, the Gibbs free energy defines the relative system stability:

$$G = H - TS \tag{1.1}$$

Where H is enthalpy, T is the absolute temperature and S is the system entropy. Enthalpy is a measure of the heat content of the system defined by the following formula:

$$H = E + pV \tag{1.2}$$

Where E is the internal energy of the system (the sum of potential and kinetic energy of atoms in the system), p is the pressure and V refers to the system volume.

The system is in equilibrium when in the most-stable condition, i.e. there is no driving force towards changes. With constant temperature and pressure, the closed system (its weight and composition remain constant) will remain in stable equilibrium provided it reaches the minimum value of Gibbs free energy:

$$dG = 0 \tag{1.3}$$

For graphic depiction of the equilibrium state see Fig. 1.1. Various atomic configurations of the system are shown along the x-axis. The A configuration represents the ***stable equilibrium state.*** Nevertheless, the system could feature a few more configurations, e.g. B, located within the area of local minimum of the Gibbs free energy. Such configuration is defined as the

metastable equilibrium state. With respect to principles of thermodynamics, any reaction is possible when associated with a reduction of Gibbs free energy:

$$\Delta G = G_2 - G_1 \tag{1.4}$$

where G_1 refers to Gibbs energy in the initial state and G_2 is Gibbs energy found in the resultant state. Transformations can occur throughout a whole range of metastable conditions until the system reaches its stable equilibrium.

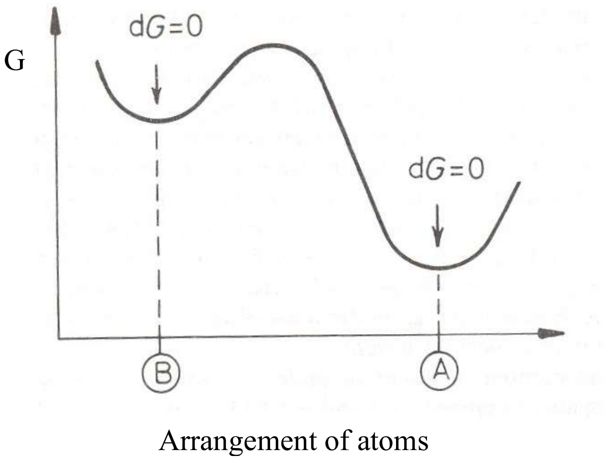

Fig. 1.1 Change of Gibbs free energy provoked by different arrangements of atoms. The A configuration represents a stable equilibrium the lowest G), whereas the B configuration matches the metastable condition

As far as technology is concerned, the vital factor here is the rate of phase transformations. This issue is addressed by ***kinetics***. Some life cycles of metastable conditions may be very short; other cases might show these periods as almost infinite. These differences are due to the maximum of Gibbs energy located between the metastable and stable conditions, respectively. The maximum represents an energy barrier reducing the rate of transformation. Fig. 1.2 shows the change of free energy per atom throughout the phase transformation, starting at the initial metastable condition towards the condition with reduced free energy. The driving force of transformation is then defined as follows: $\Delta G = G_2 - G_1$. Before the amount of free energy per atom drops from the level of G_1 to G_2, the relevant atom must undergo its activated condition matched by the amount of Gibbs energy expressed as $G_1 + \Delta G^a$. The energy shown in Fig. 1.2 represents energy averages related to a great number of atoms. A random thermal shift of atoms will induce change of energy per atom over time and it may be sometimes sufficient to enable the atom to achieve its activated state. This process is called the ***thermal activation***.

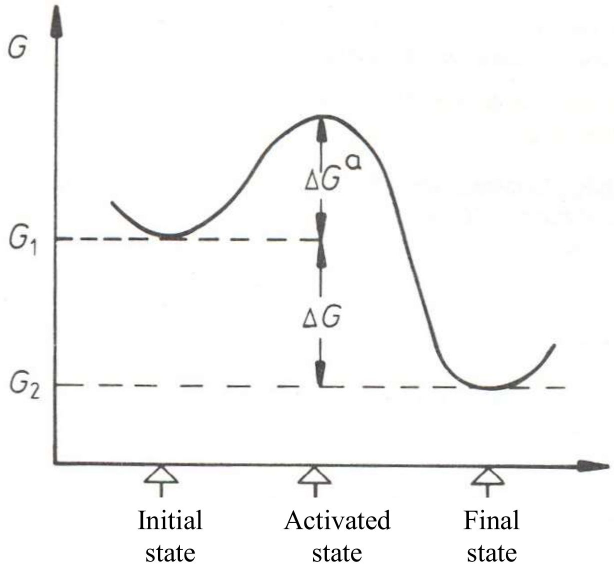

Fig. 1.2 Transfer from the initial state to the final state via the activated state having a greater energy

The theory of kinetics implies the apparent stage, when the atom reaches its activated stage, it is defined by the formula $\exp\left(-{\Delta G^a}/{kT}\right)$, where k refers to the Boltzmann's constant (k = $1.38 \cdot 10^{-23}$ J·K^{-1}) and ΔG^a is the activation energy barrier. The rate of transformation will depend on frequency of atoms when reaching the activated state:

$$velocity \propto exp\left(-\frac{\Delta G^a}{kT}\right) \tag{1.5}$$

This formula is called the ***Arrhenius rate equation***. It was initially determined on empirical basis using the observed temperature dependence of chemical reaction rate.