Chapter 1

General thermodynamic aspects

I-1. Introduction

In a system at thermodynamic equilibrium, a phase is any part where the intensive quantities (such as temperature, pressure) are continuous functions of spatial coordinates. A phase change occurs when there is a discontinuity in at least one of these quantities. If all intensive parameters are homogeneous (independent of the specific point considered), the phase is considered homogeneous or uniform. In a solid or liquid substance, a phase can be defined as an arrangement of atoms, molecules, or particles, each arrangement corresponding to different properties of the solid or liquid material.

What is a phase transformation?

Phase transitions are physical phenomena that have been recognized for a long time. The experiment thus highlights phase transition phenomena (changes of state). For example, when a substance transitions from the liquid state to the solid state, it undergoes solidification. External manipulation of an intensive thermodynamic variable causes a phase transition.

At the microscopic scale, a phase transition begins to manifest itself through the phenomenon of nucleation. At the atomic or molecular level, the repulsive and attractive forces between atoms or molecules come into play in the processes of fusion and vaporization.

I-2. Kinetics of phase transformation

Phase equilibrium diagrams enable the determination, under equilibrium conditions, of the number, composition, and proportion of phases as a function of temperature and concentration. However, they do not provide information on the kinetics of phase transformations—that is, the time required to form new phases when there is a change in temperature or pressure conditions.

Any phase transformation involves the reorganization of atoms or molecules. The mobility of atoms or molecules in both the liquid and solid states governs the formation of microstructures. Therefore, diffusion, which is the migration of atoms or molecules in solid or liquid materials, determines the kinetics of numerous phase transformations.

In thermodynamics, if a system is in equilibrium at a specific temperature and pressure, its free energy G is at its minimum. When the system is not in equilibrium under the given conditions, it naturally tends to return to an equilibrium state. During this transformation, its free energy decreases: $\Delta G<0$.

Figure I-1 shows the variation of the free energy as a function of temperature T. It illustrates the transformation of iron from the α phase to the γ phase. This figure demonstrates that the free energy of a phase decreases as the temperature increases.

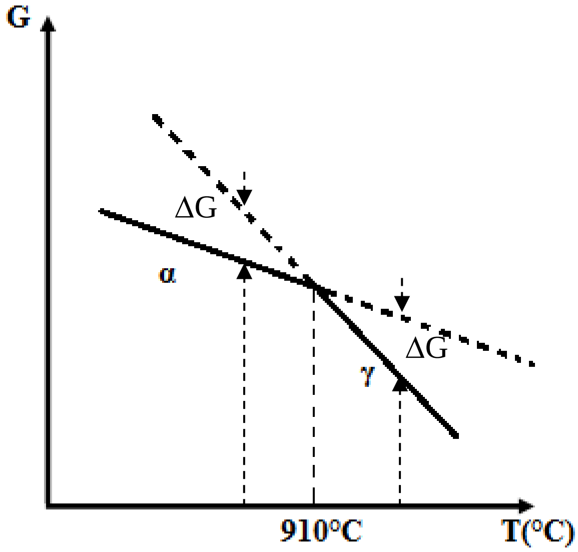


Fig. I-1- : Variation of the free energy as a function of the temperature T (example of the iron transformation from the α phase to the γ phase)

This is obvious because, by definition:

$$G = H - TS \tag{I-1}$$

Where H is the enthalpy, T the absolute temperature, and S the entropy of the system.

However, when a system returns to the equilibrium state, not all particles undergo the transformation simultaneously. Otherwise, at every moment, all particles would be in an intermediate configuration, and neither the initial nor the final configurations could coexist during the transformation. The atoms that undergo transformation at any given time are those with higher kinetic energy.

The fact that the final states of a transformation are equilibrium states allows the use of thermodynamic approaches to describe these states configurations. As a system transitions from the initial state to the final state, it passes through a continuous sequence of intermediate configurations. Among these intermediates, one is assumed to be the transition state, which is close to equilibrium and corresponds to unique values of the thermodynamic functions.

A phase transition occurs when a phase becomes unstable under specific thermodynamic conditions, which are described using intensive variables. Therefore, it is essential to describe the thermodynamic conditions that govern a phase transition if we aim to predict it.

I-3. Activated state

As an atom evolves from an initial equilibrium state to a final one, it passes through a continuous sequence of intermediate states. Since the free energies of the two extreme configurations have, by definition, minimum values (and two minima must be separated by a maximum), the free energy of an atom or a group of atoms during the transformation first increases to a maximum and then decreases to its final value. This process is illustrated in Figure I.2.

This figure shows the variation of G according to the position x. G_I represents the average free energy of an atom in the initial configuration, and G_F corresponds to the end of the transformation. $\Delta G = (G_F - G_I)$ is negative and serves as the driving force of the transformation.

Any atom with a maximum free energy G^*_A is unstable because it can either return to its initial state or progress towards a final state by reducing its free energy. The configuration associated with this peak in the free energy curve is typically referred to as the transient state, transition state, or activated state.

It is evident that a necessary condition for an atom to participate in the reaction is that it possesses sufficient free energy to reach the transient state, i.e., its free energy is at least equal to:

$$G_A = (G^*_A - G_I) \qquad \text{(I-2)}$$

G_A is known as the activation free energy for the reaction.

The additional free energy required for an atom to overcome the thermodynamic barrier of transformation is provided by fluctuations. The distribution of energy among a set of particles is non-uniform. At any temperature above 0°K, particles are in motion, and collisions resulting from this random motion lead to wide variations in the energy of individual particles over time. Consequently, at any given moment, the system exhibits a broad energy spectrum, with some particles having energy equal to or greater than G_A^* undergoing the transformation. Particles lacking sufficient energy must wait until they receive the necessary activation energy from thermal fluctuations. This phenomenon is known as *thermal activation*.

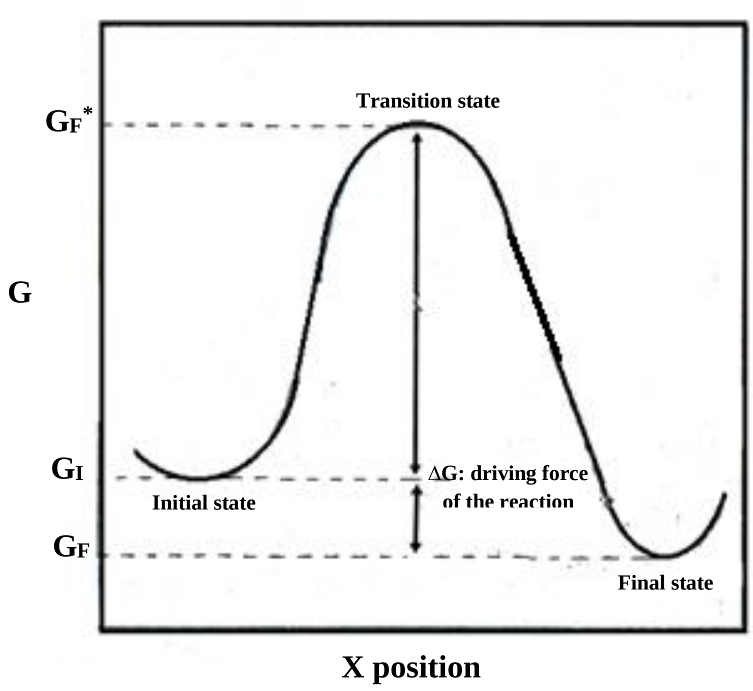


Fig. I-2- : Schematic variation of Gibbs free energy

I-4. Internal activation energy

Activation energy is the energy required by reactants to transition to another phase. On the other hand, the concept of an activated state naturally emerges from the equilibrium definition using G; it is often more convenient to study the thermodynamics of this state using an internal activation energy E_A and an activation entropy S_A. E_A and S_A are related by the following relationship:

$$G_A = E_A - TS_A \qquad \text{(I-3)}$$

The activation energy E_A is defined as the difference between the internal energy of an atom in the activated state and that of an atom in the initial state. The activation energy of a group of atoms can be subdivided into two parts:

a) The potential interaction energy of the atoms associated with the binding forces,

b) The kinetic energy due to the thermal vibrations of the particles.

Firstly, consider the interaction energy; equilibrium compels atoms to adopt positions of minimal potential energy in both the initial and final configurations. Thus, the potential energy of an atom during the transformation must evolve according to a curve akin to that shown in Figure I.2. However, a crucial distinction exists: E_F can be smaller or larger than E_I, while G_F is always less than G_I. If ΔE is positive, the reaction is endothermic; if ΔE is negative, it is exothermic. The potential energy of the transition state relative to that of the initial state is E_A[1].

As temperature increases, thermal energy causes all particles, including atoms, to exist at higher energy levels. At any given temperature, each atom within the system does not occupy the same energy level. Thermal fluctuations result in atoms distributing themselves among the available energy levels.

The activation energy value can assist us in estimating the relative rate of a reaction. A high activation energy value suggests a slow reaction because few reactants possess sufficient kinetic energy to surmount the barrier and produce new products. In contrast, a low activation energy value indicates a fast reaction.

I-5. Distribution of kinetic energy

Statistics aid in determining the most probable distribution of energy among the particles of a system. This distribution corresponds to the greatest number of possible arrangements because it can be achieved through the most numerous pathways. According to this hypothesis, calculations show that the fraction of atoms with thermal energy equal to or greater than a given value E_A at temperature T is:

$$\frac{n}{N} = \exp\left(-\frac{E_A}{K_B T}\right) \qquad \text{(I-4)}$$

Where K_B is the Boltzmann constant.

For an atom to transition from one phase to another, it must possess thermal or kinetic energy at least equal to the activation energy E_A.

We can then seek the expression for the rate of the single process, which constitutes the transition of an atom from the α structure to the γ structure (as in the case of iron), that is, the fraction of the total number of atoms reaching the final configuration per unit time dy/dt. Indeed, it is proportional to:

- The vibration frequency ν\nuν, which is assumed to be the same for all atoms, signifies that each atom encounters conditions conducive to undergoing the transition ν\nuν times per second.
- The probability that an atom has thermal energy at least equal to E_A during each vibration, that is:

$$P = \exp\left(-\frac{E_A}{K_B T}\right) \tag{I-5}$$

- The probability p that, when an atom has sufficient energy, it meets the geometric conditions required for the transformation. For example, in the case of iron, p will vary from 1/8 to 1/12 (because in the BCC and FCC systems, the number of neighboring sites of a given atom is 8 and 12, respectively). So:

$$\frac{dy}{dt} = p\nu \, exp\left(-\frac{E_A}{K_B T}\right) \tag{I-6}$$

I-6. Study of the reaction kinetics

Isoconversional analysis methods rely on accurately calculating the evolution of the activation energy E_A from kinetic data. Various linear integral methods proposed in the literature include:

- **KISSINGER-AKAHIRA-SUNOSE (KSA) method**

This method allows the estimation of E_A for a system from the following relation:

$$ln\frac{\beta}{T_p^2} = -\frac{E_A}{RT_p} + C \tag{I-7}$$

- **BOSWELL method**

It is based on the following linear expression, which enables the calculation of E_A across a series of temperature-scanning experiments:

$$ln\frac{\beta}{T_p} = -\frac{E_A}{RT} + C \tag{I-8}$$

❖ STARINK method

The method provides the following equation (I-9). According to Starink, the latter is significantly more efficient and yields better results compared to other linear integral methods.

$$ln\frac{\beta}{T_p^{1.92}} = -1.0008\frac{E_A}{RT} + C \qquad \text{(I-9)}$$

In the three methods:

C : constant which depends on the step of the reaction according to the kinetic model,

β: is the rate of heating,

Tp : the temperature of the maximum of the peaks

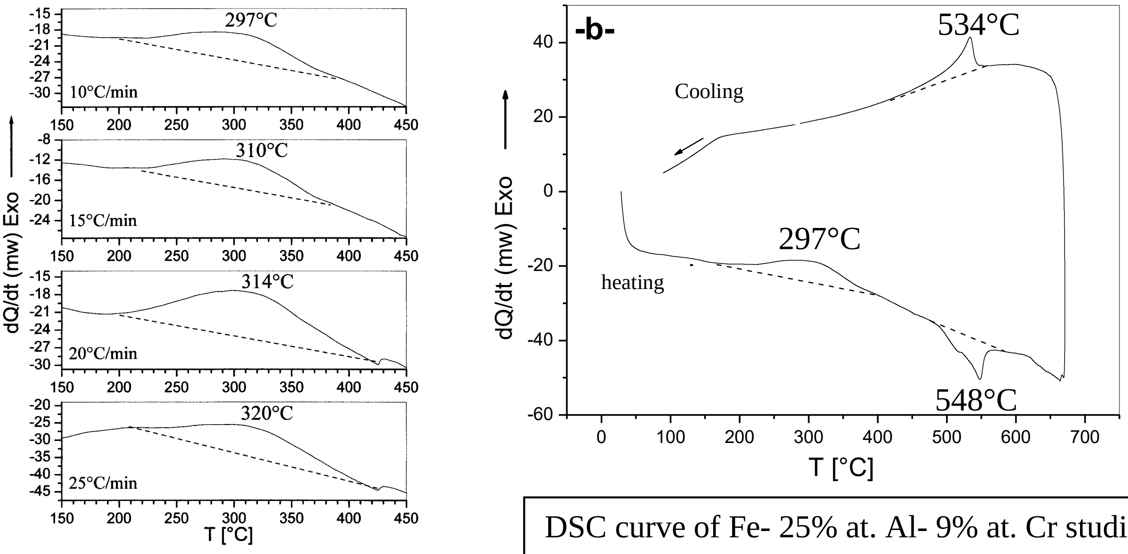
R = 8.314 J.mole^{-1} is the constant ideal gases.

Practice exercise

We consider an iron-based alloy with the addition of 9% at. Cr. The alloy is homogenized at 1000°C for 1 hour then water quenched. We want to determine the activation energy of the ordering process of the ordered phase Fe_3Al of $D0_3$ structure during heating of this alloy (the formation of Fe_3Al).

Figure 1 shows the differential scanning calorimetric analysis (DSC) test curves obtained with different heating rates. These curves show an exothermic peak around 300° C. which is linked to the formation of the ordered phase of $D0_3$ structure.

1. Based on the Starink method, give the variation curve of the straight line Y as a function of (1000 / Tm) for this alloy.
2. Deduce the activation energy value of of the ordered phase of $D0_3$ structure formed in this alloy.



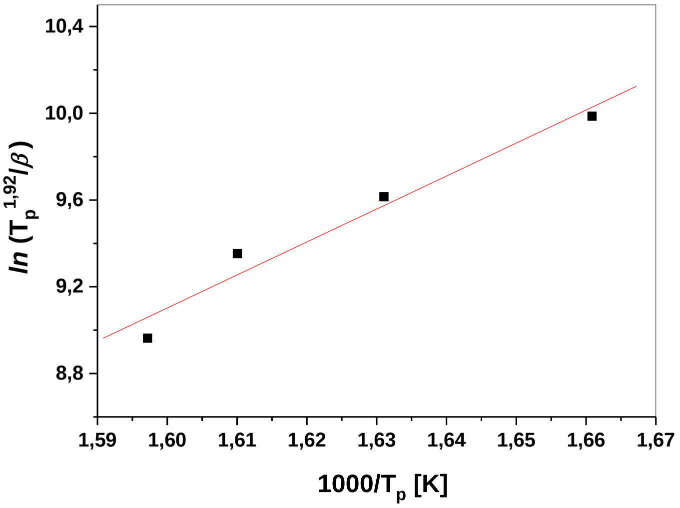
DSC curve of Fe- 25% at. Al- 9% at. Cr studied alloy obtained with a heating rate of 10°C/min

Figure 1

Answers

1- According to Starink equation (see course)

$$ln\frac{\beta}{T_p^{1.92}} = -1.0008\frac{E_A}{RT} + C$$



The slope of the line = 9.188

$E_{act} = \frac{9.188*1000R}{1.0008}$ = 18.22 Kcal/mol = 0.79 eV