

*Chapter*

**I**

**General thermodynamic aspects**

## I-1. Introduction

In a system in thermodynamic equilibrium, a phase is any part whose intensive quantities (T, P...) are continuous functions of the coordinates of space. There is a phase change when there is a discontinuity of at least one of these quantities. If all the intensive parameters are homogeneous (independent of the considered point), the phase is considered homogeneous or uniform. A phase in a solid or liquid substance 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 known for a long time. The experiment therefore highlights phase transition phenomena (change of state). For example: a substance passes from the liquid state to the solid state it is *solidification*. Acting from the outside to modify an intensive thermodynamic variable, a phase transition is caused.

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 the atoms or molecules are brought into play in the phenomena of fusion and vaporization.

## I-2. Transformation kinetics

Phase equilibrium diagrams make it possible to determine, under equilibrium conditions, the number, composition and proportion of phases as a function of temperature and concentration. However, they do not give any information on the kinetics of phase transformations, i.e. on the time required to form new phases when there is a change in temperature or pressure conditions.

Any phase transformation requires a reorganization of atoms or molecules and it is the mobility of atoms or molecules in the liquid state and in the solid state that controls the formation of microstructures. So it is the phenomenon of diffusion, that is to say the migration of atoms or molecules in solid or liquid materials, which determines the kinetics of a large number of phase transformations.

In thermodynamics, if a system is in equilibrium at a given temperature and pressure, its free energy  $G$  is minimal. If the system is not in equilibrium, under the imposed conditions, it

tends to return to the state of equilibrium. Its free energy decreases during the transformation:  $\Delta G < 0$ .

The following figure I-1- shows the variation of the free energy as a function of the temperature T, it is an example of the transformation of iron from the  $\alpha$  phase to the  $\gamma$  phase, this figure shows that the free energy of a phase decreases with increasing temperature.

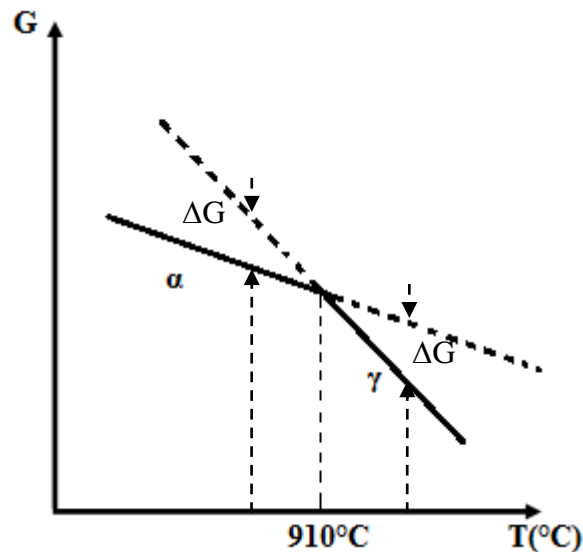


Fig. I-1- : Variation of the free energy as a function of the temperature T (example of the iron transformation from the  $\alpha$  phase to the  $\gamma$  phase)

This is obvious because, by definition:

$$G = H - TS \quad (I-1)$$

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 the particles would be in an intermediate configuration and neither the initial configuration nor the final configuration could coexist during the transformation. The atoms engaged in transformation at any given time are those that possess great kinetic energy.

The fact that the final states of a transformation are equilibrium states allows the use of thermodynamic approaches to describe the configuration of these states. When a system passes from the initial state to the final state it crosses a continuous sequence of intermediate

configurations, one of these intermediate states is assumed to be the transition state, it is a state close to equilibrium and it therefore corresponds to unique values of the thermodynamic functions.

A phase transition occurs when a phase becomes unstable under given thermodynamic conditions, described using intensive variables. It is therefore necessary to describe the thermodynamic conditions which preside over a phase transition if we want to predict it.

### I-3. Activated transition state

As an atom evolves from an initial equilibrium state to a final one, it passes through a continuous sequence of intermediate states. As the free energies of the two extreme configurations have, by definition, minimum values and two minimum 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 is illustrated in Figure I.2.

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

Any atom with the maximum free energy  $G^*_A$  is unstable because it can either return to the initial state or evolve towards the final state by decreasing its free energy. The configuration associated with this maximum of the representative free energy curve is assumed to be the transient state, or the transition state, or the activated state.

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

$$G_A = (G^*_A - G_I) \quad (I-2)$$

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

The additional free energy that allows the atom to overcome the thermodynamic barrier of transformation will be provided by fluctuations. The distribution of energy among a set of particles is not uniform. At any temperature above  $0^\circ\text{K}$ , the particles are in motion. The collisions that result from this random motion produce wide variations in the energy of individual particles and fluctuations over time in the energy of a given particle. At any moment therefore, the whole embraces an extended energy spectrum and some particles

which have energy much greater than or equal to  $G_A^*$  undergo the transformation. Those with insufficient energy must wait until they receive the necessary activation energy from thermal fluctuations. The phenomenon is known as *thermal activation*.

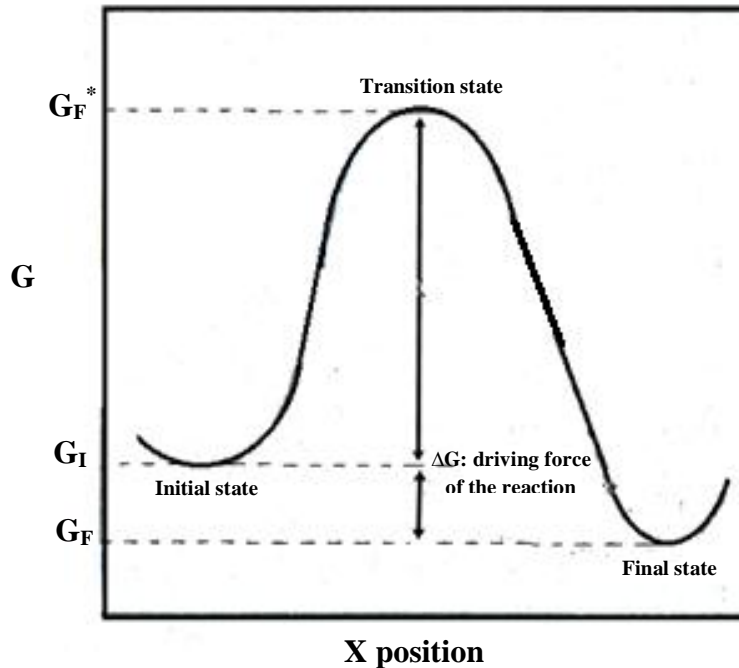


Fig. I-2- : Schematic variation of Gibbs free energy

#### I-4. Internal activation energy

Activation energy is the energy required by the reactors to transform to another phase. On the other hand, the concept of an activated state follows naturally from the definition of equilibrium 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 bound by the following relationship:

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

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 divided 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.

Consider first the interaction energy; equilibrium forces the atoms to occupy positions of minimum potential energy in both initial and final configurations. The potential energy of an atom during the transformation must therefore evolve according to a curve similar to that of figure I.2. But there is a crucial difference:  $E_F$  can be smaller or larger than  $E_I$  while  $G_F$  is always smaller than  $G_I$ . If  $\Delta E$  is positive, the reaction is endothermic, if  $\Delta E$  is negative, it is exothermic. The potential energy of the transition state compared to that of the initial state is  $E_A^1$ .

With regard to thermal energy, when the temperature rises, that of all the particles increases and the atoms exist at higher energy levels. At a given temperature, each atom in the system is not at the same level. Due to thermal fluctuations, the atoms distribute themselves between the allowed levels.

The activation energy value can help us to estimate the relative rate of a reaction. Indeed, a high activation energy value indicates a slow reaction. In the case of a slow reaction, few reactants have sufficient kinetic energy to cross the barrier and form new products. Conversely, a low activation energy value indicates a fast reaction.

### **I-5. Distribution of kinetic energy**

Statistics help to determine the most probable distribution of energy between the particles of a system. It is the one that corresponds to the greatest number of possible distributions because it is the one that can be obtained by the greatest number of possible means. From this hypothesis, it is shown that long enough calculations of the fraction of atoms which have a thermal energy equal to or greater than a given value  $E_A$  at the temperature  $T$  is:

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

Where  $K_B$  is the Boltzmann constant.

For an atom to pass from one phase to another, it must have a thermal or kinetic energy at least equal to the activation energy  $E_A$ .

We can then look for the expression of the rate of the single process which constitutes the passage of an atom from  $\alpha$  structure to the  $\gamma$  structure (case of iron), that is to say the

fraction of the total number of atoms which reach the final configuration per unit time  $dy/dt$ . Indeed, it is proportional to:

- The vibration frequency  $\nu$  which is assumed to be the same for all atoms; each atom finds, indeed,  $\nu$  times per second under the conditions where it is likely to undergo the transition.
- The probability that an atom has at each vibration a thermal energy at least equal to  $E_A$ , that is to say:

$$\exp\left(-\frac{E_A}{K_B T}\right) \quad (\text{I-5})$$

- The probability  $p$  that, when an atom has sufficient energy, it satisfies 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 CC and CFC system the number of neighboring sites of a given atom is equal to 8 to 12 respectively). So :

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

## I-6. Study of the reaction kinetics

Isoconversional analysis methods are based on the precision of the calculation of the value evolution of the activation energy  $E_A$  from kinetic data. The different linear integral methods proposed in the literature are:

### ❖ KISSINGER-AKAHIRA-SUNOSE (KSA) method

This method makes it possible to estimate  $E_A$  of a system from the following relation:

$$\ln \frac{\beta}{T_p^2} = -\frac{E_A}{RT_p} + C \quad (\text{I-7})$$

### ❖ BOSWELL method

It is based on the following linear expression which makes it possible to calculate  $E_A$  for a series of experiments in temperature scanning:

$$\ln \frac{\beta}{T_p} = -\frac{E_A}{RT} + C \quad (\text{I-8})$$

❖ **STARINK method**

The method which gives the following equation (I-9). According to Starink, the latter is much more efficient and gives good results compared to other linear integral methods:

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

In the three methods:

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

$\beta$ : is the rate of heating,

$T_p$  : the temperature of the maximum of the peaks

R = 8.314 J.mole<sup>-1</sup> is the constant ideal gases.

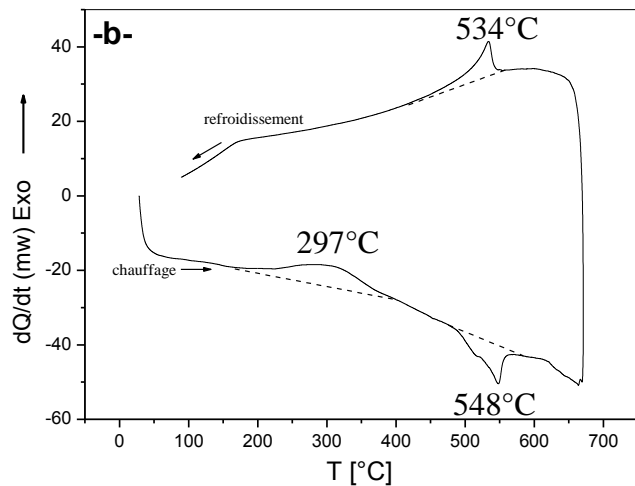
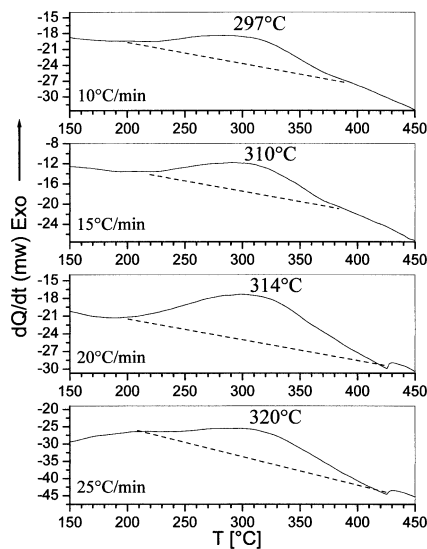


**Practice exercise**

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<sub>3</sub>Al of D0<sub>3</sub> structure during heating of this alloy (the formation of Fe<sub>3</sub>Al).

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<sub>3</sub> 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<sub>3</sub> 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