

## The Phase Stability in the Fe-B Binary System: Comparison between the Interstitial and Substitutional Models

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**Abstract.** In the present work, a thermodynamic study was carried out in order to analyze the thermodynamic stability of the  $\alpha-Fe$  and  $\gamma-Fe$  phases in equilibrium with the  $Fe_2B$  phase using the calculation of phase diagrams (Calphad) formalism. The two phases  $\alpha-Fe$  and  $\gamma-Fe$  are modelled as substitutional and interstitial solid solutions of boron. The expressions of the chemical potentials of  $B$  and  $Fe$  are derived in both phases to perform the thermodynamic calculations. A comparison is made between the results provided by the substitutional and interstitial models and good agreement is observed between these two models.

### Introduction

Thermodynamic information about the  $Fe-B$  system is required when developing B-containing alloys. For example, boron is a useful element that can improve the strength of many metals as iron and titanium based materials. Boron is also used for increasing the hardenability of steel and in the formation of a variety of amorphous alloys.

During the thermochemical process, boron combines with iron to form the intermetallic borides ( $FeB$  and  $Fe_2B$ ). To model the growth kinetics of the hard coatings composed of iron borides, it is necessary to determine the boron solubility in the  $Fe$  phase. Accordingly, the construction of a diffusion model requires knowledge of the thermodynamic description of the  $Fe-B$  system. In the literature, different diffusion models have been reported [1-5] which combine the thermodynamic description of the  $Fe-B$  system and the kinetics data. In this context, Ramdan et al. [6] have used an approach based on the Calphad Method [7] to model the growth kinetics of the  $Fe_2B$  phase using the phase-field method, where the Gibbs energies of the pure elements as a function of temperature are taken from the SGTE compilation by Dinsdale [8].

The purpose of this study was to compare the thermodynamic calculations from the interstitial model and those provided by the substitutional model using the Calphad formalism.

### The Calphad Approach

The analysis of the phase stability in the  $Fe-B$  system requires the use of Calphad formalism. It is known that the phase diagrams indicate the stable states to be expected as a function of the temperature and the composition at a fixed pressure. In particular, the authors Hallerans et al. [9] and Van Rompaey et al. [10] have studied in detail the  $Fe-B$  system using the Calphad approach. In the  $Fe-B$  binary phase diagram, six equilibrium phases are present: the liquid (L), the solid solutions of boron in the  $\alpha$ ,  $\gamma$  and  $\delta-Fe$  phases, the rhombohedral  $\beta$  phase as well as the intermetallic phases ( $FeB$  and  $Fe_2B$ ).

In the present work, the integral molar Gibbs energy ( $G_m^\Phi$ ) of the  $\Phi$  solid phase (where  $\Phi$  stands for the  $\alpha$ -Fe or  $\gamma$ -Fe phase) is presented according to the two formulations (interstitial and substitutional models).

### Interstitial Model

The solid phase  $\Phi$  was modelled as  $(Fe)_a(B,Va)_c$  for one mole on the basis of the two-sublattice model where the indexes a and c denote the stoichiometric coefficients of the  $\Phi$  phase. The Fe atoms occupy the first sublattice are fully filled by the Fe atoms whereas the second sublattice is occupied by boron atoms and vacancies (Va).

Thus, the vacancies in the interstitial sublattice may be regarded as additional components of the system. According to this model, the integral molar Gibbs energy ( $G_m^\Phi$ ) is given by:

$$G_m^\Phi = y_B^\Phi G_{Fe:B}^{0,\Phi} + y_{Va}^\Phi G_{Fe:Va}^{0,\Phi} + aRT(y_{Fe}^\Phi \ln(y_{Fe}^\Phi) + cRT[y_B^\Phi \ln(y_B^\Phi) + y_{Va}^\Phi \ln(y_{Va}^\Phi)] + y_B^\Phi y_{Va}^\Phi [L_0^\Phi + (y_B^\Phi - y_{Va}^\Phi)L_1^\Phi] + G_m^{\Phi,mag} \quad (1)$$

The composition-independent parameters  $L_0^\Phi$  and  $L_1^\Phi$  are defined as a function of temperature. They take into account the interaction between boron atoms and vacant interstitial sites. The magnetic contribution to the integral molar Gibbs energy is taken into account through the  $G_m^{\Phi,mag}$  term provided by Inden [11] and given by Eq. (2):

$$G_m^{\Phi,mag} = R.T.\ln(1 + \beta^\Phi).f(T/T_C^\Phi) \quad (2)$$

where  $R$  is the gas constant ( $= 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) and  $T$  is the absolute temperature.  $T_C^\Phi$  represents the Curie temperature in Kelvin for the  $\Phi$  phase, and  $\beta^\Phi$  is the average magnetic moment per atom. The indexes a and c denote also the number of interstitial sites per Fe atom, ( $a = c = 1$  for the  $\gamma$  phase, and  $a = 3$ ,  $c = 1$  for the  $\alpha$  phase). The quantity  $y_B^\Phi$  represents the atomic fraction of boron on the interstitial sublattice and is related to the atomic fraction  $x_B^\Phi$  as follows:

$$y_B^\Phi = \frac{ax_B^\Phi}{c(1 - x_B^\Phi)}, \quad y_{Fe}^\Phi = 1 \quad (3)$$

$$\text{And } y_B^\Phi + y_{Va}^\Phi = 1 \quad (4)$$

The partial molar Gibbs energy or the chemical potential of the iron element can be determined from Eq. (5):

$$\begin{aligned} \mu_{Fe}^\Phi &= \frac{1}{a} G_{Fe:Va}^{0,\Phi} + \frac{c}{a} RT \ln(1 - y_B^\Phi) + \frac{1}{a} [y_B^{\Phi^2} L_0^\Phi - (3y_B^{\Phi^2} - 4y_B^{\Phi^3}) L_1^\Phi] \\ &+ \frac{1}{a} (G_m^{\Phi,mag} - y_B^\Phi \frac{\partial G_m^{\Phi,mag}}{\partial y_B^\Phi}) \end{aligned} \quad (5)$$

In the same way, the chemical potential of boron can be derived as follows:

$$\begin{aligned} \mu_B^\Phi = & \frac{1}{c} (G_{Fe:B}^{\Phi,0} - G_{Fe:Va}^{\Phi,0} + L_0^\Phi - L_1^\Phi) + RT \ln\left(\frac{y_B^\Phi}{1 - y_B^\Phi}\right) - \frac{1}{c} [2y_B^\Phi L_0^\Phi - 6y_B^\Phi (1 - y_B^\Phi) L_1^\Phi] \\ & + \frac{1}{c} \frac{\partial G_m^{\Phi,mag}}{\partial y_B^\Phi} \end{aligned} \quad (6)$$

### Substitutional Model

In this model, the solid phase  $\Phi$  ( $= \alpha - Fe$  or  $\gamma - Fe$ ) belonging to the Fe-B system was modelled as  $(B,Fe)_a(V_a)_c$  for one mole. The expression of the integral molar Gibbs energy ( $G_m^\Phi$ ) can be written as follows:

$$\begin{aligned} G_m^\Phi = & x_B^\Phi G_{B:Va}^{0,\Phi} + x_{Fe}^\Phi G_{Fe:Va}^{0,\Phi} + aRT(x_{Fe}^\Phi \ln(x_{Fe}^\Phi) + x_B^\Phi \ln(x_B^\Phi)) + cRT(x_{Va}^\Phi \ln(x_{Va}^\Phi)) \\ & + x_B^\Phi x_{Fe}^\Phi L_0^\Phi + G_m^{\Phi,mag} \end{aligned} \quad (7)$$

with  $x_B^\Phi + x_{Fe}^\Phi = 1$  et  $x_{Va}^\Phi = 1$

The partial molar Gibbs energy of the *Fe* element can be calculated from Eq. (8):

$$\mu_{Fe}^\Phi = G_{Fe:Va}^{0,\Phi} + aRT \ln(1 - x_B^\Phi) + x_B^{\Phi^2} L_0^\Phi + (G_m^{\Phi,mag} - x_B^\Phi \frac{\partial G_m^{\Phi,mag}}{\partial x_B^\Phi}) \quad (8)$$

The partial molar Gibbs of *B* is then given by Eq. (9):

$$\mu_B^\Phi = G_{B:Va}^{0,\Phi} + aRT \ln(x_B^\Phi) + (1 - x_B^\Phi)^2 L_0^\Phi + G_m^{\Phi,mag} + (1 - x_B^\Phi) \frac{\partial G_m^{\Phi,mag}}{\partial x_B^\Phi} \quad (9)$$

### Results of the Thermodynamic Calculations and Discussions

To compute the boron solubility in the  $\Phi$  phase in equilibrium with the intermetallic boride  $Fe_2B$  using the Calphad method, the  $\Phi$  phase can be treated as regular or sub-regular solid solution. If we need to determine the boron solubility in the  $\Phi$  phase, Eq. (10) will be satisfied:

$$G_{Fe_2B}^0 = 2\mu_{Fe}^\Phi + \mu_B^\Phi \quad (10)$$

with  $G_{Fe_2B}^0 = H_B^{SER} + 2H_{Fe}^{SER} - 96363 + 481.992T - 79.04999T \ln(T) - 0.007071T^2 + (731991/T)$

$G_{Fe_2B}^0$  represents the Gibbs energy for one formula unit of the stoichiometric phase  $Fe_2B$  [10].

The terms  $H_B^{SER}$  and  $H_{Fe}^{SER}$  are the enthalpies at the reference state (for 298 K at 0.1 MPa) for boron and iron respectively, and are obtained from the SGTE database for pure elements [8]. Eq. (10) is not linear and has to be solved by the Newton-Raphson routine.

A computer program written in MATLAB version 6.5 was used to do the thermodynamic calculations. The calculations results using the Calphad method in the temperature range 800-1184.6 K are shown in Table 1. The  $\alpha - Fe$  phase exists at a temperature below 1184.6 K.

A comparison was made between the interstitial and substitutional models and it is concluded that the thermodynamic results in terms of the atomic fractions are very comparable.

Table 1. Comparison between the thermodynamic calculations from the both models regarding the boron solubility of boron in the  $\alpha - Fe$  phase.

T [K]	$x_B^\alpha$ ( substitutional model)	$C_B^\alpha$ ( interstitial model)
800	$2.49 \times 10^{-6}$	$2.97 \times 10^{-6}$
850	$4.30 \times 10^{-6}$	$4.85 \times 10^{-6}$
900	$6.98 \times 10^{-6}$	$7.48 \times 10^{-6}$
950	$1.07 \times 10^{-5}$	$1.10 \times 10^{-5}$
1000	$1.58 \times 10^{-5}$	$1.58 \times 10^{-5}$
1050	$2.25 \times 10^{-5}$	$2.50 \times 10^{-5}$
1100	$3.10 \times 10^{-5}$	$3.23 \times 10^{-5}$
1184.6	$4.96 \times 10^{-5}$	$4.68 \times 10^{-5}$

It is also possible to derive a relationship between the boron solubility in the  $\alpha - Fe$  phase and the temperature. Taking the interstitial model, the boron solubility (expressed in terms of the atomic fraction) in the  $\alpha - Fe$  phase was plotted versus reciprocal temperature as shown in Figure 1.

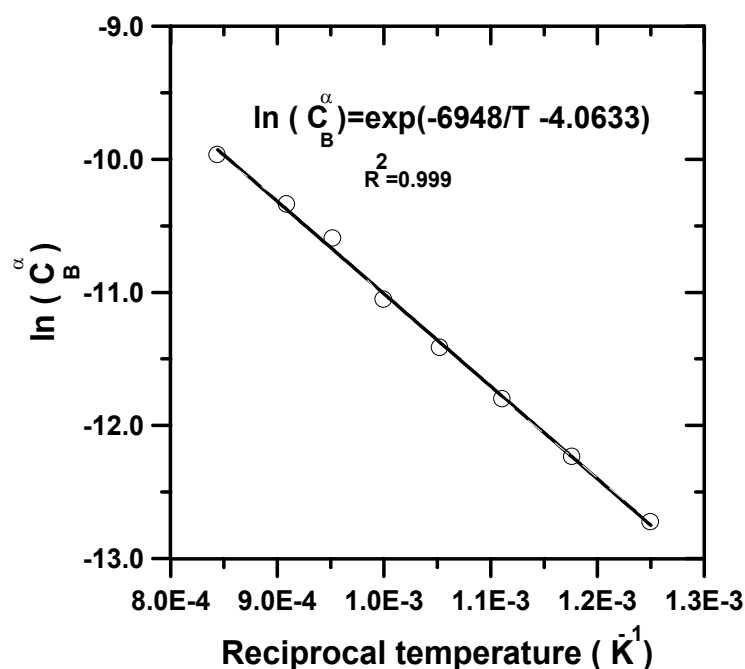


Fig. 1 The temperature dependence of the boron solubility in the  $\alpha - Fe$  phase.

The data obtained were fitted using an Arrhenius relationship. The resulted expression was given by Eq. (11) with a correlation coefficient equal to 0.999 and valid in the temperature range 900-1184.6 K.

$$C_B^\alpha = \exp(-6948/T - 4.0633) \quad (11)$$

Table 2. Comparison between the thermodynamic calculations derived from both models regarding the boron solubility in the  $\gamma - Fe$  phase.

T[K]	$x_B^\gamma$ (substitutional model)	$C_B^\gamma$ (interstitial model)
1184.6	$5.83 \times 10^{-5}$	$5.99 \times 10^{-5}$
1200	$6.31 \times 10^{-5}$	$6.57 \times 10^{-5}$
1220	$6.98 \times 10^{-5}$	$7.37 \times 10^{-5}$
1240	$7.69 \times 10^{-5}$	$8.22 \times 10^{-5}$
1260	$8.44 \times 10^{-5}$	$9.12 \times 10^{-5}$
1280	$9.24 \times 10^{-5}$	$10 \times 10^{-5}$
1300	$10 \times 10^{-5}$	$11 \times 10^{-5}$

The thermodynamic results obtained from the interstitial and substitutional models in the temperature range 1184.6-1300 K are gathered together in Table 2.

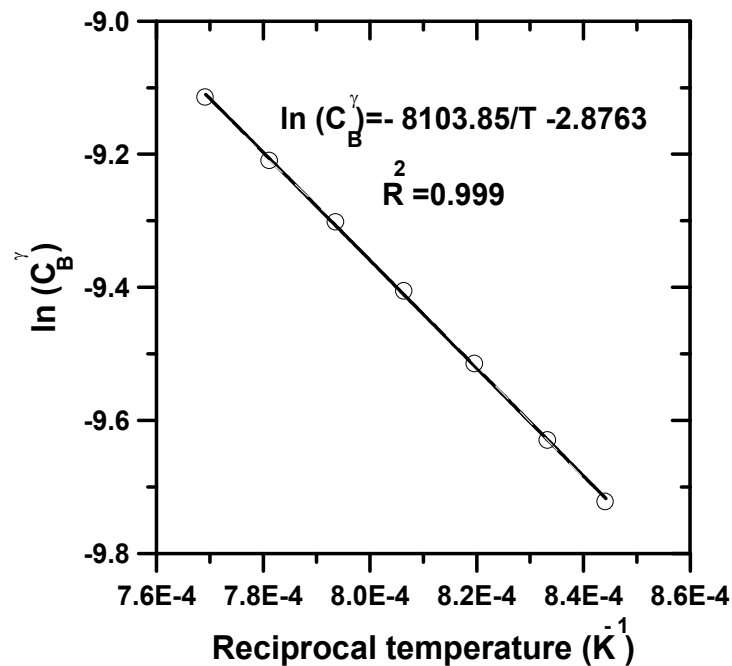


Fig. 2. The temperature dependence of the boron solubility in the  $\gamma - Fe$  phase.

A good concordance was obtained between these two models. For the interstitial model, the temperature dependence of the boron solubility in the  $\gamma - Fe$  phase was also fitted by an Arrhenius relationship given by Eq. (12) with a correlation coefficient equal to 0.999 (Figure 2).

$$C_B^\gamma = \exp(-8103.85 / T - 2.8763) \quad (12)$$

By adopting the interstitial model according to the Calphad method, it is interesting to study the effect of the boron composition on the thermodynamic stability of the  $\alpha - Fe$  and  $\gamma - Fe$  phases.

The value of the integral molar Gibbs energy for each phase was evaluated for different temperature using Eq. (1) and the results are displayed in Figures 3, 4 and 5 for boron contents 0.003, 10 and 16.20 wt.%.

For the very low solubility of boron content in the solid solution, the values of the integral molar Gibbs energies of  $\alpha$  and  $\gamma$  phases are found to be practically the same.

The very comparable values of the integral molar Gibbs energies between the  $\alpha - Fe$  and  $\gamma - Fe$  phases reported in Figure 3 correspond to the state of pure iron (since the boron content in the solid solution is extremely small).

In Figures 4 and 5, the existence of an inversion point due to the relative stability between the two phases  $\alpha - Fe$  and  $\gamma - Fe$  can be noted.

It is seen that the inversion point shown in Figures 4 and 5 is affected when increasing the boron content from 10 to 16.20 wt.%. The determined value of the inversion point corresponds to an energy of  $(-21.12 \text{ kJ/mol})$  at 732 K for a boron content of 10 wt.% while it has a value of  $(+1.12 \text{ kJ/mol})$  at 571 K, for a boron content of 16.20 wt.% (Figure 5).

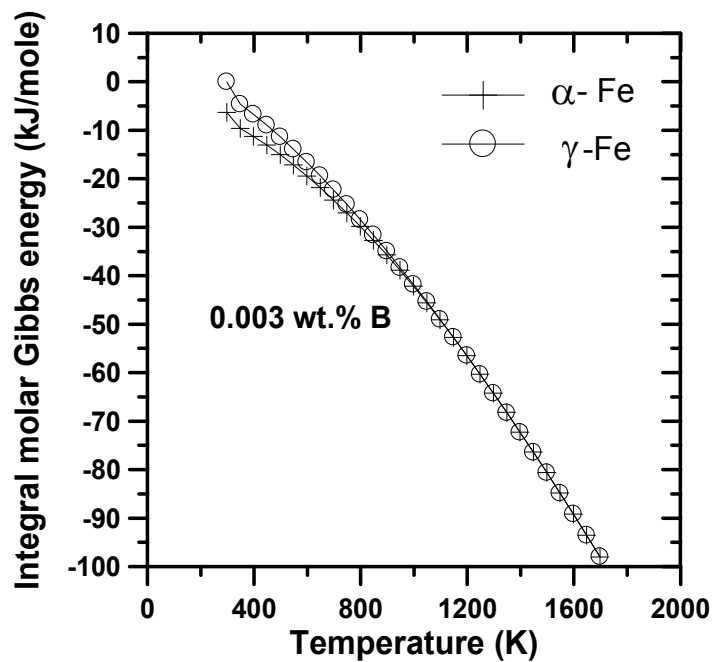


Fig. 3 Temperature dependence of integral molar Gibbs energies of  $\alpha$  and  $\gamma$  phases for a boron content equal to 0.003w.t.%.

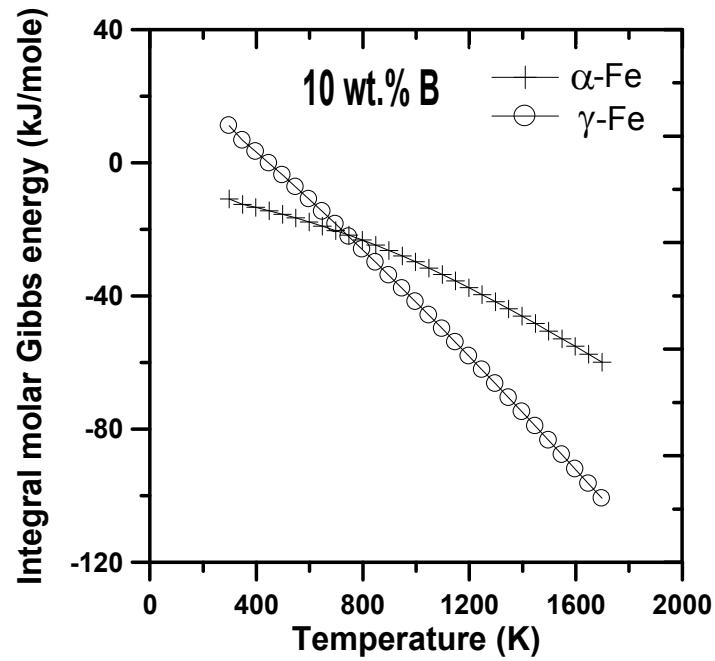


Fig. 4 Temperature dependence of the integral molar Gibbs energies of  $\alpha$  and  $\gamma$  phases for a boron content equal to 10 wt.%.

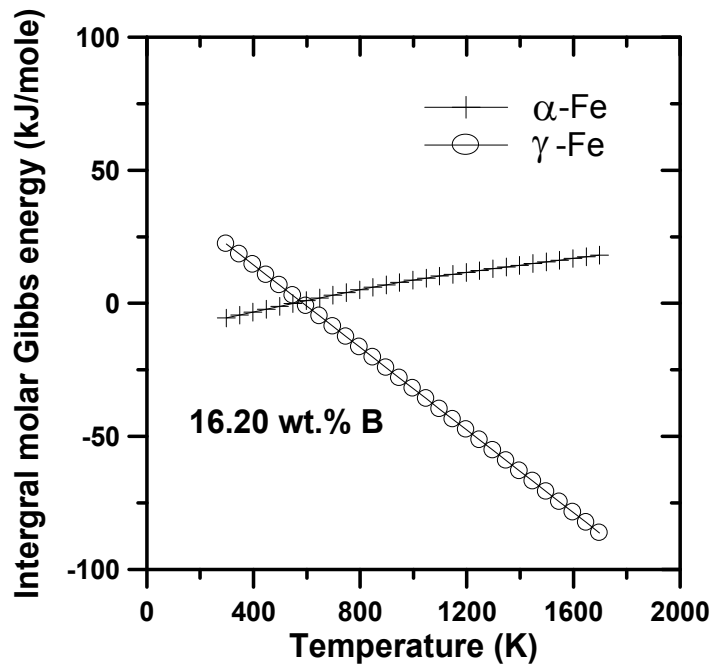


Fig. 5 Temperature dependence of integral molar Gibbs energies of  $\alpha$  and  $\gamma$  phases for a boron content equal to 16.20 wt.%.

### Alternative Approach to Study the Thermodynamic Equilibrium between the Fe Phase and the Fe<sub>2</sub>B Phase

The thermodynamic approach used by Huh et al. [12] was also applied by Ramdan et al. [6] to allow for the variation of the boron solubility in the Fe<sub>2</sub>B phase. In references [9, 10], the Fe<sub>2</sub>B iron boride has a fixed boron composition (0.33 at.% or 8.83 wt.% B). The integral molar Gibbs energy for the Fe<sub>2</sub>B phase is then described by a parabolic relationship in terms of the molar fraction of boron and its expression is given in Eq. (13):

$$G_m^{Fe_2B} = 3.6 \times 10^6 (x_B^{Fe_2B} - 0.33)^2 + G_{Fe_2B}^0 \quad (13)$$

An alternative expression of the integral molar Gibbs energy for the  $\gamma$ -Fe phase was also proposed by Ramdan et al. [6] as :

$$G_m^\gamma = y_B^\gamma G_{Fe:B}^{0,\gamma} + y_{Va}^\gamma G_{Fe:Va}^{0,\gamma} + RT(y_B^\gamma \ln(y_B^\gamma) + y_{Va}^\gamma \ln(y_{Va}^\gamma)) + 3.2 \times 10^6 (b - x_B^\gamma)^2 \quad (14)$$

where  $b$  is the boron concentration corresponding to a minimum of its internal molar Gibbs energy and  $b$  is taken to be equal to 0.1 in the present study.

The expression of  $G_{Fe:B}^{0,\gamma}$  was taken from the optimization of SGTE database by Van Rompaey et al. [10] :

$$G_{Fe:B}^{0,\gamma} = H_B^{SER} + H_{Fe}^{SER} + 45496 - 77.5T \quad (15)$$

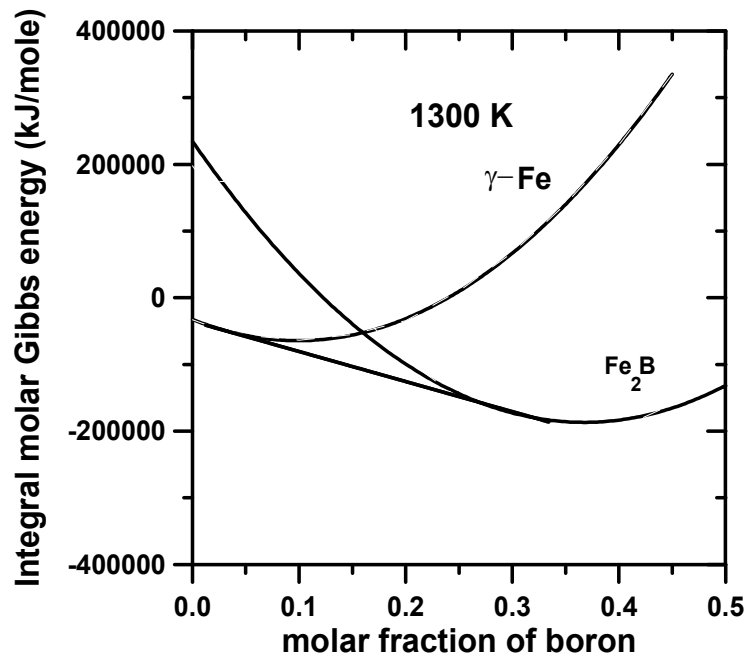


Fig. 6 Variation of the integral molar Gibbs energy versus the molar fraction of boron for the two phases  $\gamma$ -Fe and Fe<sub>2</sub>B.



In Figure 6, the variation of the integral Gibbs energy of each phase ( $\gamma-Fe$  and  $Fe_2B$ ) as a function of the molar fraction of boron is shown at a temperature of 1300 K. By applying the rule of the common tangent, it is possible to determine the boron solubility (in molar fraction) of the  $\gamma-Fe$  phase equal to  $1.228 \times 10^{-2}$  while the  $Fe_2B$  phase has a molar fraction of 0.3341.

The value of the boron solubility in the  $\gamma-Fe$  phase estimated by this thermodynamic approach is higher than that obtained from the Calphad method ( $= 1.08 \times 10^{-4}$  at 1300 K). It is concluded that this approach overestimates the boron solubility in the  $\gamma-Fe$  phase by a factor of 113.

## Conclusion

In this work, the boron solubility in the  $Fe$  phase was calculated using the Calphad method. The phases  $\alpha-Fe$  and  $\gamma-Fe$  were modelled as substitutional and interstitial solid solutions of boron. The expressions for the chemical potentials of  $B$  and  $Fe$  elements were derived in both phases to perform the thermodynamic calculations. Since the solubility of  $B$  in the  $Fe$  phase is extremely small, the choice of interstitial or substitutional model has only a very small effect on the thermodynamic calculations in terms of the boron solubility.

The second thermodynamic approach inspired from the works of Huh et al. [12] has overestimated the value of the boron solubility in the  $\gamma-Fe$  phase in equilibrium with  $Fe_2B$  at 1300 K.

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