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TRANSLATION

Thermodynamic Properties of the Wüstites W_i and W'_i from Thermogravimetric Data at Equilibrium

Pierre Vallet, Claude Carel*

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The present document is the result of the TRANSLATION into English of both French publications in Ref. [Ø] leading to the present Part 1 and Part 2 respectively.

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ABSTRACT of Part 1 – Equations $\log_{10}p_{O_2} = (a_i T^{-1} + b_i)x + c_i T^{-1} + d_i$ or $\log_{10}p_{O_2} = (a'_i T^{-1} + b'_i)x^2 + (c'_i T^{-1} + d'_i)x + e'_i T^{-1} + f'_i$ allows the best description of the thermogravimetric isotherms at equilibrium between oxygen with partial pressure p_{O_2} and solid wüstite W or W' with chemical formula FeO_x at temperatures T K $>$ or $<$ 1 184 , respectively. Coefficients a_i, b_i, c_i, d_i or $a'_i, b'_i, c'_i, d'_i, e'_i, f'_i$ were determined formerly for the wüstites W_i or W'_i respectively ($i = 1, 2, 3$). The analytical expression of the activities of oxygen and iron, the partial molar properties and the integral properties H°, S° and C_p° are set up by means of additional limit-relations adjusted for the equilibria of wüstite with γ - or α -iron. 69 equations, 4 figures, 1 Table.

KEY WORDS: thermogravimetry, haute temperature, equilibrium, activities, thermodynamic properties.

ABSTRACT of Part 2– The whole stability domain consists of 6 sub-domains which correspond to the 3 W_i and 3 W'_i , on both sides of the isothermal line at 1 184 K. The sub-domains are separated by arcs of hyperbola for the W_i , and arcs of more complicated curves for the W'_i . The experimental data (l'_o, l'_1, x_o, x_1 at T) on the external boundaries with α -, γ -iron and Fe_3O_4 are reexamined taking into account some restraints, in particular the accurate location of Chaudron's point, and the location at 1 184 K of the two equilibria W_3/Fe_3O_4 and W'_3/Fe_3O_4 , $x_{1(3)}=1.1353$ and $x_{1(3')} = 1.1277$ respectively. The assessment of the integration constants k_i, k'_i (T, P) ($k, k' = g, g', h, h', s, s'$) depends on the numerical adjustment of semi-empirical equations describing the α -Fe / W'_i and γ -Fe / W_i boundaries.

The integral properties $H^\circ_i, S^\circ_i, C_{p,i}^\circ$ are tabulated for the 3 W'_i and 3 W_i on the different boundaries, from 864.73 K (592°C : Chaudron's point) to 1 644 K (near melting). For a stable wüstite W'_1 then W_1 they are also tabulated, the composition being continuously that at the Chaudron's point $y_C = 0.934 5_4$ for $592 < \Theta ^\circ C < 1 371$. The isothermal decrease of the entropy is unexpectedly large with an increasing departure from stoichiometry, corresponding likely with an increase of the degree of ordering (point defects, clustering, percolation, superstructure). 30 equations, 3 figures, 7 Tables.

KEY WORDS: second order transitions, phase diagram, triple points, properties $H^\circ_i, S^\circ_i, C_{p,i}^\circ$, tabulations

Part 1. Formulations of the molar thermodynamic properties from data (T, p_{O_2}, x)

I. - INTRODUCTION

Since Darken and Gurry's key publication [1], numerous measurements have been published. It led to the evaluation of partial thermodynamic properties, mostly those of oxygen [2] to [21], and integral [1] [22] [23] [24] of the non-stoichiometric solid wüstite.

However, very few authors considered the necessary differentiation of distinct *behaviors* or *varieties* as they were first suggested in Paul Raccah's thesis in 1962 [25]. Experimentally traced again in 1966 by J. B. Wagner jr *et al.* [26], then in 1969 by Fender and Riley [27], they will be kept out enduringly by the scientific community. These latter authors never more envisaged the distinct behaviors although they continue working a long time on wüstite.

The present work follows the set of characterizing successive publications [28] [29] [30] [31] [32] between 1963 and 1979. The papers in Refs. [30] and [32] are based essentially on Raccah's equilibrium thermogravimetric measurements [25]. They retains the essential notations and conclusions, in particular the chemical formula written FeO_x for reasons of linearity of the graph $l'(x)$ for $x \in [1.045-1.212]$. The *three behaviors* or *varieties* are noted W_1, W_2 and W_3 above 911°C or 1 184 K, and W'_1, W'_2 and W'_3 below this temperature.

In addition to the Thermodynamic Tables [33] to [39] and classical references [40] to [43] used in the present work, the work of Spencer and Kubaschewski reviews the molar properties of iron oxides, in particular the wüstite, which was supposed to be unique and served as a reference [44].

II. – APPROXIMATION RELATING TO THE THREE WÜSTITES W_i .

II. 1. Oxygen activity

The gaseous molecular oxygen under one atmosphere can obviously be chosen as reference state as it will be the case in section II. 2. But the experimental reality shows that the decimal logarithm noted l' of the pressure p' of oxygen at equilibrium with wüstite varies about between -6. and -25. when p' is expressed in atmosphere. The resulting orders of magnitude for oxygen activity are rather not very easy to use. And so following Darken and Gurry [1], the oxygen reference state can be chosen as that in which it is in wüstite in equilibrium with α - or γ -iron under the pressure p'_o . So the value of x in the reference state is referred to by x_o .

Let us consider the reaction



in which \underline{O} denotes oxygen bonded with iron in wüstite according to the writing used for metal solutions. The oxygen activity being represented by a' , the application of the mass action law gives the following equation

$$a'^2 = Kp' \quad (2)$$

In the reference state where $p' = p'_o$ and $a' = 1$ it appears that

$$1 = K p'_o \quad (3)$$

By eliminating K between (2) and (3), it follows

$$a'^2 = p' / p'_o \quad (4)$$

This equation can be put in logarithmic form

$$2 \log a' = \log p' - \log p'_o \quad (5)$$

Using the abbreviated notation it follows

$$2 \log a' = l' - l'_o \quad (6)$$

We have shown previously [28] to [32] that for the wüstites W_i

$$l' = M_i(T) x + N_i(T) \quad (7)$$

so that equation (6) can be written as follows

$$2 \log a' = (x - x_o) M_i(T) \quad (8)$$

Finally, since $M_i(T)$ and $N_i(T)$ are linear functions of $1/T$, l' is completely developed according to

$$l' = (a_i T^{-1} + b_i) x + (c_i T^{-1} + d_i) \quad (9)$$

and equation (6) takes the form

$$2 \log a' = (x - x_o) (a_i T^{-1} + b_i) \quad (10)$$

When a wüstite changes into another, the temperature being constant, the coefficients a_i and b_i change but a' got the same value for both wüstites on the common boundary between their two domains.

The preceding equations are valid for the three wüstites W_i existing above 1 184 K with the appropriate coefficients (see Ref. [32], Table 1 p. 1186). For the three wüstites existing below 1 184 K, a more elaborate rectification of the thermogravimetric isotherms was given ([32], Table 2 p. 1187). This rectification is retained here in the continuation because it probably allows a better approximation in the calculations (see Part 2).

Equations (8) and (10) show that $\log a'$ is a linear function of x at a given absolute temperature T for a given wüstite W_i . If $\log a'$ is represented as a function of x , the isotherm of a single wüstite W_i is linear: this is the case for the isotherm at $T=1473$ K from x_0 to x_1 where the wüstite FeO_{xI} or W_1 is at equilibrium with the magnetite. If the isotherm includes the transition from one wüstite to another, it is formed by two consecutive linear segments. Figure 1 shows some isotherms supposing that the wüstite is in constant equilibrium with oxygen. Finally the each isotherm leaves the horizontal axis at an abscissa $x_{0(i)}$ where $a' = 1$.

The values of a' are in agreement with those given by Darken and Gurry [1] at high temperature.

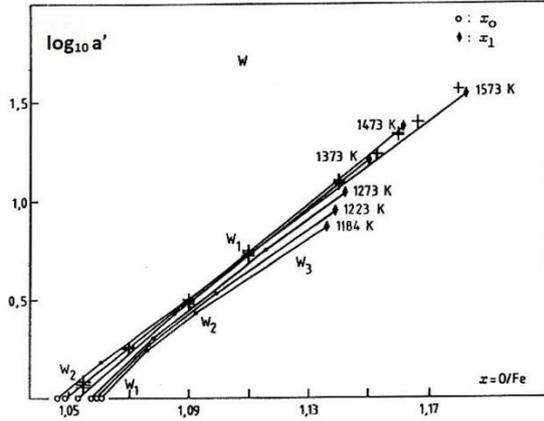


Fig. 1

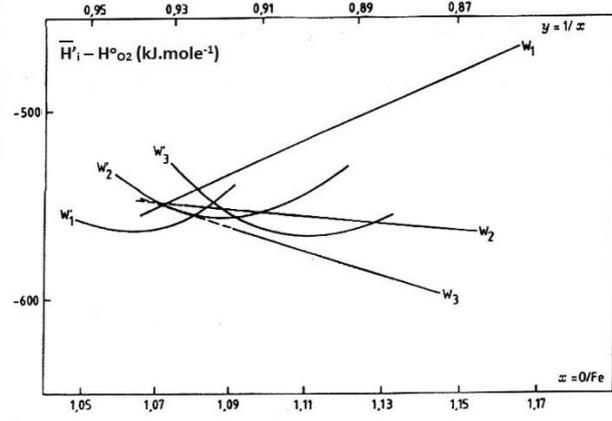


Fig. 2

Fig. 1. – Oxygen activity expressed by means of its decimal logarithm as a function of the composition parameter x at various temperatures above 1 184 K or 911 °C according to relation (10). Crosses + correspond to the results of Darken and Gurry [1].

Fig. 2. – Variations of $2(\bar{H}_O - \frac{1}{2}H^{\circ}_{O_2})_i$ as a function of composition for the 6 wüstites across the entire stability range according to relations (14) and (53). \bar{H}_O is the partial molar enthalpy of oxygen in wüstite.

II. 2. Partial molar properties of oxygen

(a) Partial molar free energy \bar{G}'_i

It might be possible to use directly the expression $\log a'$ provided by equation (10) in the form $\bar{G}'_i - \bar{G}'_i{}^{\text{ref}} = RT \text{Log } a'$, but $\bar{G}'_i{}^{\text{ref}}$ would correspond to the reference state used above and would have to be calculated*. It is much simpler to call on the very general equation by using the value of $\log p'$ as follows

$$\bar{G}'_i = 19.144 \ 64 \ T \ \log p' + G^{\circ}_{O_2} \quad (11)$$

for the wüstite i . This equation assumes \bar{G}'_i as evaluated in joule and p' in atmosphere. By replacing $\log p'$ by its expression (7), it results

$$\bar{G}'_i = 19.144 \ 64 \ T \ [M_i(T) x + N_i(T)] + G^{\circ}_{O_2} \quad (12)$$

or with the expression (9)

$$\bar{G}'_i = 19.144 \ 64 \ T \ [(a_i T^{-1} + b_i) x + c_i T^{-1} + d_i] + G^{\circ}_{O_2} \quad (13)$$

In these three equations, the reference state of oxygen is its usual state for which $p'_o = 1$ atm. Such a reference state of oxygen is purely fictitious as far as wüstite is concerned. It would correspond to $x = -N_i(T)/M_i(T)$, a value always higher than 1.5, even 2 at low enough temperatures, which would imply an oxidation state higher than that of Fe_2O_3 .

*NOTA : If the reference state is not molecular O_2 under 1 atmosphere but molecular O_2 for

$$p' = p'_o \text{ where } x = x_o \Rightarrow \bar{G}'_i{}^{\text{ref}} = 19.144 \ 64 \ T [M_i(T)x_o + N_i(T)] + G^{\circ}_{O_2}$$

By subtracting from (12), $N_i(T)$ disappears $\Rightarrow \bar{G}'_i - \bar{G}'_{i, \text{ref}} = 19.144\ 64\ T\ M_i(T) [x - x_0]$.

(b) *Partial molar enthalpy* \bar{H}'_i

Making explicit the derivative $[\partial(\bar{G}'_i/T)/\partial T^{-1}]_P$, it comes

$$\bar{H}'_i = 19.144\ 64(a_i x + c_i) + H^\circ_{O_2} \quad (14)$$

(c) *Partial molar entropy* \bar{S}'_i

Similarly the derivative $[\partial(\bar{G}'_i)/\partial T]_P$ leads to

$$\bar{S}'_i = -19.144\ 64(b_i x + d_i) + S^\circ_{O_2} \quad (15)$$

(d) *Partial molar heat capacity at constant pressure* $\bar{C}'_{P,i}$

$\bar{C}'_{P,i}$ is the derivative of \bar{H}'_i with respect to T . The first term of equation (14) does not affect this derivation because x is an independent variable, so that $\bar{C}'_{P,i}$ is reduced to C°_{P,O_2} . The same result divided by T would be obtained by deriving \bar{S}'_i with respect to T .

Figures 2 and 3 represent the variations of $\bar{H}'_i - H^\circ_{O_2}$ and $\bar{S}'_i - S^\circ_{O_2}$ as a function of composition independently of temperature, according to equations (14) and (15) for the W_i and (53) and (54) for the W'_i (see *infra* section V. 1).

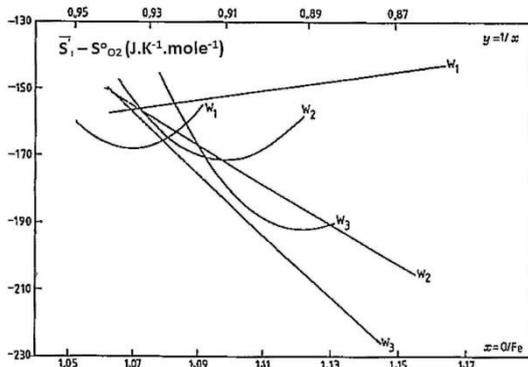


Fig. 3

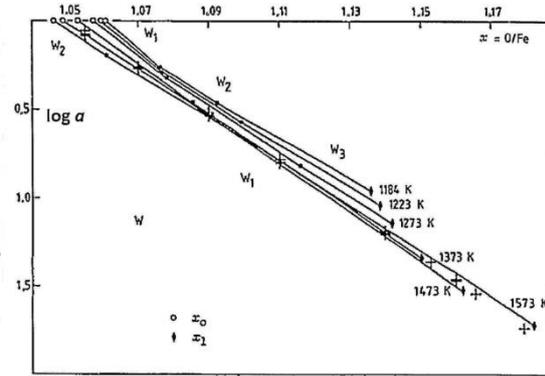


Fig.4

Fig. 3. – Variations of $\bar{S}'_i - S^\circ_{O_2} = 2(\bar{S}_O - 1/2.S^\circ_{O_2})_i$ for the 6 wüstites according to relations (15) and (54).

Fig. 4. – Iron activity represented according to relation (20), similarly to that represented for oxygen in Fig.1.

In the text afterwards, the activity a and the various partial molar properties of iron are designated by the same symbols as those used for oxygen, but without the accent. According to the chemical formula written FeO_x the ratio of the number of oxygen atoms to the number of iron atom is x .

II. 3. Iron activity

It can be calculated using Gibbs-Duhem's relationship, which here takes the form

$$d \log a = -x d \log a' \quad (16)$$

At constant temperature and total pressure P , equation (8) gives

$$2 d \log a' = M_i(T) dx \quad (17)$$

which allows immediately to write the following equation

$$d \log a = -\frac{x}{2} M_i(T) dx \quad (18)$$

easily integrated when noticing that on the boundary $W_i/Fe\gamma$ where $x = x_{0(i)}$ the iron activity is unity. Then it results the relation

$$\log a = -\frac{1}{4} (x^2 - x_{o(i)}^2) M_i(T) \quad (19)$$

or similarly to what was obtained for the oxygen

$$\log a = -\frac{1}{4} (x^2 - x_{o(i)}^2) (a_i T^{-1} + b_i) \quad (20)$$

As before, let us notice that when a wüstite changes to another at a given temperature, the coefficients a_i and b_i change but a got the same value on the boundary of their subdomains.

Equations (19) and (20), which are less simple than the corresponding equations (8) and (10), show that a parabolic arc is obtained as a representation of $\log a(x)$ for a given wüstite at constant temperature. Assuming a perfectly isothermal thermodynamic equilibrium, when one wüstite transforms to another, a parabolic arc transforms also to another on the common boundary of the two domains.

Fig. 4 depicts the variation of $\log a$ as function of x for various temperatures. The isotherms start from the point of the abscissa axis $x=x_{o(i)}$ where $\log a = 0$. The activity of iron in solid wüstite varies as much as that of oxygen at high temperatures: in the ratio 1 to about 0.019 at 1 300 °C. The direction of evolution is moreover reversed: when x increases, a' increases but a decreases. The values of a are in remarkable agreement with those given by Darken and Gurry [1] at high temperatures (1100-1350 °C).

II. 4. Partial molar properties of iron

The problem raised about oxygen does not exist for iron, because for $x=x_o$ on the iron/ wüstite boundary, the iron in wüstite is in equilibrium with solid iron (in fact the solid limit solution α - or γ Fe-O $_{\epsilon}$, $\epsilon \approx 10$ ppm at 1 200 K) and gaseous iron at temperature T under total pressure P.

(a) Partial molar free energy \bar{G}_i

There are two methods to calculate it. The first one needs the activity given above, the second uses the Gibbs-Duhem relation from \bar{G}'_i .

The first method uses the general relationship

$$\bar{G}_i = 19.144 \ 64 T \log a + G_{\gamma\text{Fe}}^{\circ} \quad (21)$$

Replacing $\log a$ by its expression (19), it results the relation

$$\bar{G}_i = -\frac{19.144 \ 64}{4} T (x^2 - x_{o(i)}^2) M_i(T) + G_{\gamma\text{Fe}}^{\circ} \quad (22)$$

or more with the expression (20) of $\log a$

$$\bar{G}_i = -\frac{19.144 \ 64}{4} T (x^2 - x_{o(i)}^2) (a_i + b_i T) + G_{\gamma\text{Fe}}^{\circ} \quad (23)$$

The second method based on the Gibbs-Duhem relationship leads to

$$d\bar{G}_i = -\frac{x}{2} d\bar{G}'_i \quad (24)$$

At constant T and P, equation (13) gives

$$d\bar{G}'_i = 19.144 \ 64 (a_i + b_i T) dx \quad (25)$$

so that equation (24) becomes

$$d\bar{G}_i = -19.144 \ 64 (a_i + b_i T) \frac{x}{2} dx \quad (26)$$

By integrating with respect to x , it results

$$\bar{G}_i = -\frac{19.144 \ 64}{4} (a_i + b_i T) x^2 + g_i(T, P) \quad (27)$$

in which $g_i(T, P)$ refers to a function of T and P independent of x , the expression of which is deduced from the comparison of equations (23) and (27), the term in x^2 being the same.

This comparison leads to the equation

$$g_i(T, P) = \frac{19.14464}{4} x_{o(i)}^2 (a_i + b_i T) + G_{\gamma\text{Fe}}^o \quad (28)$$

(b) *Partial molar enthalpy* \bar{H}_i

As in the case of oxygen, the most direct way is to derive \bar{G}_i/T with respect to $1/T$ at constant P. Equation (27) which does not contain $x_o(T)$ can be used. It results

$$\bar{H}_i = -\frac{19.14464}{4} a_i x^2 + h_i(T, P) \quad (29)$$

This equation could also be obtained in using Gibbs-Duhem relationship.

The function $h_i(T, P)$ is independent of x . To obtain its expression it is only to derive $g_i(T, P)/T$ given by equation (28) with respect to $1/T$, but remembering that x_o is a function of either $1/T$ or T . This derivation gives

$$h_i(T, P) = \frac{19.14464}{4} [a_i x_{o(i)}^2 + 2x_{o(i)}(a_i T^{-1} + b_i)(\partial x_{o(i)}/\partial T^{-1})_P] + H_{\gamma\text{Fe}}^o \quad (30)$$

The calculation of $(\partial x_o/\partial T^{-1})_P$ is obtained by deriving the two members of the equation giving x_o , namely

$$A_o T^{-1} + B_o = (a_i T^{-1} + b_i) x_{o(i)} + c_i T^{-1} + d_i = \log p'_o \quad (31)$$

The value of the coefficients A_o and B_o is determined when adjusting the equation of the boundary $\gamma\text{Fe}/W_i$ in accordance with an equation in the form

$$l'_o = A_o T^{-1} + B_o \quad (32)$$

(cf. Part 2, sections V. 1. to V. 3.). It results the equation

$$(\partial x_{o(i)}/\partial T^{-1})_P = (A_o - c_i - a_i x_{o(i)})/(a_i T^{-1} + b_i) \quad (33)$$

and any reductions made

$$h_i(T, P) = -19.14464 \left(\frac{a_i}{4} x_{o(i)}^2 + \frac{c_i}{2} x_{o(i)} \right) + \frac{19.14464}{2} A_o x_{o(i)} + H_{\gamma\text{Fe}}^o \quad (34)$$

Let us notice that the product $19.14464 A_o$ is none other than the enthalpy variation due to iron oxidation along the $\gamma\text{-Fe}/W_i$ (or $\alpha\text{-Fe}/W'_i$) boundary.

(c) *Partial molar entropy* \bar{S}_i

Here again, the simplest is to derive \bar{G}_i with respect to T, P being constant, *i.e.*

$$\bar{S}_i = \frac{19.14464}{4} b_i x^2 + s_i(T, P) \quad (35)$$

This equation could also be obtained by means of the Gibbs-Duhem relationship.

To obtain the function $s_i(T, P)$ which is independent of x , it is enough to derive the function $g_i(T, P)$ with respect to T by considering the function $x_{o(i)}(T)$ from (31), *i.e.*

$$s_i(T, P) = -\frac{19.14464}{4} [b_i x_{o(i)}^2 + 2x_{o(i)}(a_i + b_i T)(\partial x_{o(i)}/\partial T)_P] + S_{\gamma\text{Fe}}^o \quad (36)$$

where $(\partial x_{o(i)}/\partial T)_P$ is calculated from the equality (31), so it is

$$(\partial x_{o(i)}/\partial T)_P = (B_o - d_i - b_i x_{o(i)})/(a_i + b_i T) \quad (37)$$

It is obtained finally

$$s_i(T, P) = 19.14464 \left(\frac{b_i}{4} x_{o(i)}^2 + \frac{d_i}{2} x_{o(i)} \right) - \frac{19.14464}{2} B_o x_{o(i)} + S_{\gamma\text{Fe}}^o \quad (38)$$

As above the term $-19.14464 B_o$ represents the variation of entropy during the oxidation of iron to wüstite FeO_{x_o} along the boundary of the domain with iron.

(d) *Partial molar heat content at constant pressure* $\bar{C}_{P,i}$

That is the derivative of \bar{H}_i with respect to T. The first term of equation (29) being independent of T, only $h_i(T, P)$ is concerned in the derivation. It is thus obtained

$$\bar{C}_{P,i} = [\partial h_i(T, P) / \partial T]_P \quad (39)$$

So the derivation of equation (34) with respect to T only concerns $x_{o(i)}(T)$ and $H^\circ_{Fe}(T)$. The calculation gives

$$\bar{C}_{P,i} = -\frac{19.144\ 64}{2} [a_i x_{o(i)} + c_i - A_o]^2 / T(a_i + b_i T) + C^\circ_{P,\gamma Fe} \quad (40)$$

Deriving \bar{S}_i [equation (35)] with respect to T leads to $\bar{C}_{P,i} / T$, from which another expression is deduced, namely

$$\bar{C}_{P,i} = -\frac{19.144\ 64}{2} [T(B_o - d_i - b_i x_{o(i)})^2 / (a_i + b_i T)] + C^\circ_{P,\gamma Fe} \quad (41)$$

The two forms (40) and (41) are equivalent owing to equation (31). Their first term of complicated formalism is of rather low value with respect to $C^\circ_{P,Fe}$ as shown in the following Table.

TABLE I
Values of the first term in equation (40) for W_i and W'_i , and of $C^\circ_{P,Fe}$

T(K)	Wüstite i	x_o	A_o	First term (J.K ⁻¹ .mole ⁻¹)	$C^\circ_{P,Fe}$ (J.K ⁻¹ .mole ⁻¹)
1 600	W_2	1.045 7	-27 460.	-0.049	36.652
1 184	W_1	1.060 8	-27 460.	-4.523	34.041
1 184	W'_1	1.051 7	-27 318.4	-1.048	34.041
900	W'_1	1.065 5	-27 318.4	-2.232	43.848

Secondly, it is notable that the influence of the Λ point of α -iron is transferred automatically to $\bar{C}_{P,i}$. However, we can think that the variations of $\bar{C}_{P,i}$ with T will not be completely parallel to those of $C^\circ_{P,Fe}$ because of this first term in equation (40) whose variations are not simple. T not only appears explicitly in the equation (40), but x_o varies with T in W_i and W'_i . These considerations highlight in contrast the simplicity of $\bar{C}'_{P,i}$ which is equal to C°_{P,O_2} (see Section II. 2. d)).

These results will be reconsidered below.

III. – FORMULATION OF INTEGRAL PROPERTIES

They result immediately from the partial molar properties determined above, remembering that those of oxygen are related to one mole of di-oxygen while those of iron are related to one mole of iron atoms.

III. 1. Standard Free Energy G°_i

It is calculated by the general equation

$$G^\circ_i = \bar{G}_i + \frac{x}{2} \bar{G}'_i \quad (42)$$

by replacing \bar{G}_i and \bar{G}'_i by their expressions (27) and (13) respectively. The regrouping of the similar terms leads to

$$G^\circ_i = 19.144\ 64 [(a_i + b_i T) \frac{x^2}{4} + (c_i + d_i T) \frac{x}{2}] + g_i(T, P) + \frac{x}{2} G^\circ_{O_2} \quad (43)$$

III. 2. Standard Enthalpy H°_i

Applying similarly to the equation

$$H^\circ_i = \bar{H}_i + \frac{x}{2} \bar{H}'_i \quad (44)$$

by replacing \bar{H}_i and \bar{H}'_i by the expressions (29) and (14) respectively, it is obtained

$$H_i^o = 19.144\ 64 \left[a_i \frac{x^2}{4} + c_i \frac{x}{2} \right] + h_i(T, P) + \frac{x}{2} H^o_{O_2} \quad (45)$$

III. 3. Standard Entropy S_i^o

Similarly, the equation

$$S_i^o = \bar{S}_i + \frac{x}{2} \bar{S}'_i \quad (46)$$

leads, via equations (34) and (15), to equation

$$S_i^o = -19.144\ 64 \left[b_i \frac{x^2}{4} + d_i \frac{x}{2} \right] + s_i(T, P) + \frac{x}{2} S^o_{O_2} \quad (47)$$

III. 4. Molar heat capacity at constant pressure $C_{P,i}^o$

The general equation

$$C_{P,i}^o = \bar{C}_{P,i} + \frac{x}{2} \bar{C}'_{P,i} \quad (48)$$

is used, wherein $\bar{C}'_{P,i}$ is the same as C_{P,O_2}^o and where $\bar{C}_{P,i}$ is given by the equation (40) or (41). Using equation (40), we obtain the expression

$$C_{P,i}^o = - \frac{19.144\ 64}{2} \cdot \frac{(a_i x_{O(i)} + c_i - A_o)^2}{T(a_i + b_i T)} + C_{P,\gamma Fe}^o + \frac{x}{2} C_{P,O_2}^o \quad (49)$$

As shown in Table I (see section II. 4. (d)), the first term which is always negative is small compared to the last two. On the other hand, it refers to iron in wüstite, whereas oxygen seems to behave there as if it were alone. This feature can be related to the experimental fact that during the oxide formation it is iron which enters oxygen adsorbed at its surface, not oxygen which enters iron [45]. It was verified with Raccach in 1962 that from a cylindrical wire of iron with 0.5 mm diameter oxidized in a CO/CO₂ mixture at high temperature results a hollow cylinder, an oxide tube. A simple consideration of steric nature maybe allow to justify this fact. The average ionic radii are 1.40 Å, 0.76 Å and 0.63 Å for ions O²⁻, Fe²⁺ and Fe³⁺ respectively in octahedral site. The migration of iron towards the interstitial sites of the oxygen lattice appears to be easier than the reverse.

Equation (49) shows that the influence of the Λ point of α -iron already mentioned in respect with $\bar{C}_{P,i}$ finds oneself back in $C_{P,i}^o$, just as the primitive empirical equations had revealed [46]. Thus they find their theoretical justification (see Part 2, Tables VII and VIII, line at 1023 K).

Although the first term always negative in equation (49) is provided by iron at the energetic plan, it probably concerns the iron-oxygen bond in the oxide.

Finally let us note that $C_{P,i}^o$ is a linear function of x at a given temperature, just like the decimal logarithm l' of the oxygen pressure in equilibrium with the oxide FeO _{x} (see key equation (7)).

IV. – APPROXIMATION RELATING TO THE WÜSTITES W'_i

It was shown that for the three W'_i l' is best expressed by an equation of second degree in x [32]. Then the equation (9) can be replaced by

$$l' = (a'_i x^2 + c'_i x + e'_i) T^{-1} + b'_i x^2 + d'_i x + f'_i \quad (50)$$

The numerical value of the six coefficients of this equation was established for each of the three wüstites W'_i (see Réf. [32], Table 2 p. 1187).

So the preceding equations are complicated, but their setting up from each other remaining evidently the same, it seems enough sufficient to give the new expressions of the thermodynamic properties while keeping the same notations.

IV. 1. Oxygen activity and partial molar properties

(a) Activity a' : its expression is as follows

$$2\log a' = (a'_i T^{-1} + b'_i)(x^2 - x_{o(i)}^2) + (c'_i T^{-1} + d'_i)(x - x_{o(i)}) \quad (51)$$

(b) *Partial molar free energy* \bar{G}'_i : its expression is

$$\bar{G}'_i = 19.144 \ 64 \ T [(a'_i x^2 + c'_i x + e'_i) T^{-1} + b'_i x^2 + d'_i x + f'_i] + G^\circ_{O_2} \quad (52)$$

(c) *Partial molar enthalpy* \bar{H}'_i : it expresses as following

$$\bar{H}'_i = 19.144 \ 64 (a'_i x^2 + c'_i x + e'_i) + H^\circ_{O_2} \quad (53)$$

The variations of $\bar{H}'_i - H^\circ_{O_2}$ as function of x are given in figure 2.

(d) *Partial molar entropy* \bar{S}'_i : its expression is

$$\bar{S}'_i = -19.144 \ 64 (b'_i x^2 + d'_i x + f'_i) + S^\circ_{O_2} \quad (54)$$

The variations of $\bar{S}'_i - S^\circ_{O_2}$ as function of x are given in figure 3.

(e) *Partial molar heat capacity* $\bar{C}'_{P,i}$: it is identical to that obtained in section II, for the same reasons.

IV. 2. Iron activity and partial molar properties

(a) *Activity* a : it is given by the following relation

$$\log a = - \frac{x^3 - x_{o(i)}^3}{3} (a'_i T^{-1} + b'_i) - \frac{x^2 - x_{o(i)}^2}{4} (c'_i T^{-1} + d'_i) \quad (55)$$

(b) *Partial molar free energy* \bar{G}_i can be expressed in two forms. Either starting from $\log a$, it is obtained

$$\bar{G}_i = -19.144 \ 64 \left[\frac{x^3 - x_{o(i)}^3}{3} (a'_i + b'_i T) + \frac{x^2 - x_{o(i)}^2}{4} (c'_i + d'_i T) \right] + G^\circ_{\alpha Fe} \quad (56)$$

or using the Gibbs-Duhem equation, it results

$$\bar{G}_i = -19.144 \ 64 \left[(a'_i + b'_i T) \frac{x^3}{3} + (c'_i + d'_i T) \frac{x^2}{4} \right] + g'_i(T, P) \quad (57)$$

The comparison of the two equations gives $g'_i(T, P)$

$$g'_i(T, P) = 19.144 \ 64 \left[(a'_i + b'_i T) \frac{x_{o(i)}^3}{3} + (c'_i + d'_i T) \frac{x_{o(i)}^2}{4} \right] + G^\circ_{\alpha Fe} \quad (58)$$

(c) *Partial molar enthalpy* \bar{H}_i : its expression is

$$\bar{H}_i = -19.144 \ 64 \left(a'_i \frac{x^3}{3} + c'_i \frac{x^2}{4} \right) + h'_i(T, P) \quad (59)$$

The calculation gives the expression of $h'_i(T, P)$

$$h_i(T, P) = -19.144 \ 64 \left[a'_i \frac{x_{o(i)}^3}{6} + c'_i \frac{x_{o(i)}^2}{4} - \frac{x_{o(i)}}{2} (A_o - e'_i) \right] + H^\circ_{\alpha Fe} \quad (60)$$

(d) *Partial molar entropy* \bar{S}_i : its expression is

$$\bar{S}_i = 19.144 \ 64 \left(b'_i \frac{x^3}{3} + d'_i \frac{x^2}{4} \right) + s'_i(T, P) \quad (61)$$

the expression of $s'_i(T, P)$ being

$$s'_i(T, P) = 19.144 \ 64 \left[b'_i \frac{x_{o(i)}^3}{6} + d'_i \frac{x_{o(i)}^2}{4} - \frac{x_{o(i)}}{2} (B_o - f'_i) \right] + S^\circ_{\alpha Fe} \quad (62)$$

(e) *Partial molar heat capacity under constant pressure* $\bar{C}_{P,i}$: its expression is as following

$$\bar{C}_{P,i} = \frac{-19.144 \ 64}{2} \cdot \frac{T^{-1} (a'_i x_{o(i)}^2 + c'_i x_{o(i)} + e'_i - A_o)^2}{2a'_i x_{o(i)} + c'_i + T(2b'_i x_{o(i)} + d'_i)} + C^\circ_{P,\alpha Fe} \quad (63)$$

or equivalently

$$\bar{C}_{P,i} = \frac{-19.144\ 64}{2} \cdot \frac{T(b'_i x_{o(i)}^2 + d'_i x_{o(i)} + f'_i - B_0)^2}{2a'_i x_{o(i)} + c'_i + T(2b'_i x_{o(i)} + d'_i)} + C_{P,\alpha Fe}^0 \quad (64)$$

IV. 3. Integral properties of the wüstites W'_i

(a) Molar free energy G°_i :

$$G^{\circ}_i = 19.144\ 64 [a'_i \frac{x^3}{6} + c'_i \frac{x^2}{4} + e'_i \frac{x}{2} + T(b'_i \frac{x^3}{6} + d'_i \frac{x^2}{4} + f'_i \frac{x}{2})] + g'_i(T, P) + \frac{x}{2} G^{\circ}_{O_2} \quad (65)$$

(b) Molar enthalpy H°_i :

$$H^{\circ}_i = 19.144\ 64 (a'_i \frac{x^3}{6} + c'_i \frac{x^2}{4} + e'_i \frac{x}{2}) + h'_i(T, P) + \frac{x}{2} H^{\circ}_{O_2} \quad (66)$$

(c) Molar entropy S°_i :

$$S^{\circ}_i = -19.144\ 64 (b'_i \frac{x^3}{6} + d'_i \frac{x^2}{4} + f'_i \frac{x}{2}) + s'_i(T, P) + \frac{x}{2} S^{\circ}_{O_2} \quad (67)$$

(d) Molar heat content $C^{\circ}_{P,i}$: it is either

$$C^{\circ}_{P,i} = \frac{-19.144\ 64}{2} \cdot \frac{T^{-1}(a'_i x_{o(i)}^2 + c'_i x_{o(i)} + e'_i - A_0)^2}{2a'_i x_{o(i)} + c'_i + T(2b'_i x_{o(i)} + d'_i)} + C_{P,\alpha Fe}^0 + \frac{x}{2} C^{\circ}_{P,O_2} \quad (68)$$

or

$$C^{\circ}_{P,i} = \frac{-19.144\ 64}{2} \cdot \frac{T(b'_i x_{o(i)}^2 + d'_i x_{o(i)} + f'_i - B_0)^2}{2a'_i x_{o(i)} + c'_i + T(2b'_i x_{o(i)} + d'_i)} + C_{P,\alpha Fe}^0 + \frac{x}{2} C^{\circ}_{P,O_2} \quad (69)$$

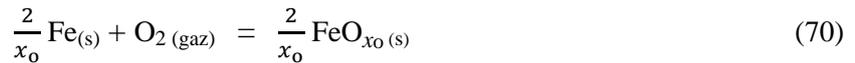
As for expression (49) obtained in section III.4., the first term although of rather complicated formalism takes a small value lower than $3 \text{ J.K}^{-1} \cdot \text{mole}^{-1}$. All the other considerations on the respective roles of iron and oxygen remain to be considered.

Part 2. Subdomains – Limit conditions - Numerical calculations - Tabulations

V. – ACCESS TO NUMERICAL VALUES

V. 1. General Considerations

The limit composition parameter x_o used above corresponds to the equilibrium represented by the chemicalwise equation



between oxygen under pressure p'_o and the wüstite W_i or W'_i on the boundary with γ - or α -iron respectively at given temperature T . Let ΔG°_o , ΔH°_o and ΔS°_o be the reference variations of free energy, enthalpy and entropy of reaction (70) such as

$$\Delta G^{\circ}_o = \Delta H^{\circ}_o - T\Delta S^{\circ}_o \quad (71)$$

It also arises the relation

$$\Delta G^{\circ}_o = 19.14464 T \log p'_o \quad (72)$$

According to equation (31), $\Delta H^{\circ}_o = 19.144\ 64 A_o$ and $\Delta S^{\circ}_o = -19.144\ 64 B_o$. This equation is also used to determine x_o , at least as a first approximation.

Similarly, but not involved in the previous equations, the composition parameter x_1 corresponds to the equilibrium represented by the chemicalwise equation



The limit composition x_1 on the boundary of the stability domain of W_i with magnetite Fe_3O_4 is defined by an equation similar to (31) such that

$$A_1 T^{-1} + B_1 = (a_i T^{-1} + b_i) x_1 + c_i T^{-1} + d_i = \log p'_1 \quad (74)$$

It is essential to note, when referring to the diagram provided earlier [29] [32], that x_o is only directly accessible for W_1 between 1 184 and 1 510 K, for W_2 between 1 510 and 1 643 K, and for W_3 between 1 643 and 1 644 K. The same applies to all the properties that explicitly depend on x_o .

The same can be said for W'_1 between 1 184 and 1 083 K, and between 1 073 and Chaudron's point C at 864.7 K, for W'_2 between 1 083 and 1 073, for W'_3 no temperature interval is convenient. So, it is necessary to overcome the difficulties resulting from these constraints.

V. 2. Equations of the boundaries with Fe and Fe3O4

Since 1979, multiple trials of sorting by statistical calculation and thermodynamic reasoning have led to the use of equations already published [32] only that one which concerns the boundary between W_i and γ -Fe, namely

$$l'_{oy} = -27\,460\,T^{-1} + 6.740\,1 \quad (75)$$

In a Note [47], it was suggested that the boundary W_i/Fe_3O_4 could be broken down into two distinct arcs. The first, above 1 160 °C or 1 433 K can be represented as first approximation by the equation

$$l'_1 = -35\,336.45\,T^{-1} + 14.844\,61 \quad (76)$$

the second, between 1184 and 1433 K, by the equation

$$l'_1 = -33\,385.61\,T^{-1} + 13.483\,31 \quad (77)$$

From then on, the four-term equation ((6) in Ref. [32]) encompassing the entire boundary $W-W'/Fe_3O_4$ disappeared. On the other hand, the extrapolation of equation (77) below 1 184 K is not satisfactory and does not agree well enough with the measurements of one of us slightly above point C [48]. This leads to look for an equation giving, at point D in Figure 1 of Ref. [32], the same pressure p'_1 as that calculated at 1 184 K by means of equation (77), i.e. $\log p'_1 = l'_1 = -14.714$. The linear equation in T^{-1}

$$l'_1 = -33.418.4\,T^{-1} + 13.511 \quad (78)$$

although it responds to this constraint, represents imperfectly the experimental results in the vicinity of point C, the confidence limit with which it allows the determination of l'_1 being $\pm 0.096\,6$ at the probability threshold of 0.05.

Therefore, it seems appropriate to propose a 3-terms equation

$$l'_1 = -40\,360.26\,T^{-1} - 6.597\,666\,\ln T + 66.063\,5 \quad (79)$$

which fits suitably l'_1 with a statistical confidence limit of $\pm 0.008\,7$.

The rectification of the boundary between α -Fe and W'_i is subject to greater constraints. It must cut the boundary between magnetite and W'_1 at Chaudron's point between 580 and 600 °C according to Bonneté and Païdassi's very accurate experiments on direct oxidation of iron [49]. In addition, it must meet specific requirements concerning the coefficients A_o and B_o of an equation of model (32).

Note: the equations of iron/wüstite and wüstite/magnetite published by Rizzo *et al.* (see Ref. [22], J. Electrochem. Soc. p. 273) locating the Chaudron's Point at $610 \pm 10^\circ\text{C}$ do not meet the first criterion.

The study of this boundary α -Fe/ W'_i has therefore been taken up again from a numerical point of view on the basis of the measures that can be considered as the safest, particularly the closest to point C. The 4-terms equation

$$l'_o = 83\,048.216\,T^{-1} + 218.983\,74\,\ln T - 0.107\,180\,43\,T - 1\,509.341\,7 \quad (80)$$

which can be proposed gives l'_o with a confidence limit of $\pm 0.017\,9$. When combining with equation (79), it gives point C at 874 K or 601 °C, temperature slightly too high.

However, it has the merit of presenting an inflection point at 1 021.6 K or 748.4 °C, about 20 ° below the Λ point of α -Fe (see Tables VII and VIII).

Under constant pressure P, the partial derivatives $[\partial l'_o/\partial T^{-1}]_P$ and $[\partial(Tl'_o)/\partial T]_P$ play the role in equation (32) of the two coefficients A_o and B_o respectively. Table II gives the value of these two quantities at three values of T.

TABLE II

Values of two partial derivatives for equation (80)

T(K)	1 184	1 021.6	873
$[\partial l'_o/\partial T^{-1}]_P$	- 25 977	- 28 805	- 26 439
$[\partial(Tl'_o)/\partial T]_P$	5.510 9	8.016 7	5.448 7

It is therefore understandable that the authors who represented l'_o by equations of type (32) obtained quite different coefficients A_o and B_o . However, the last experimental value of l' used to determine the equation (80) was obtained at 919 K or 646 °C, more than 50° above point C. Below 919 K the two-terms equation that is calculated with the four experimental values closest to point C

$$l'_o = - 28 370 T^{-1} + 7.581 7 \quad (81)$$

seems more likely, especially since it gives a Chaudron's point C at 864.73 K that is to say 591.6 °C.

V. 3. Selection of the coefficients A_o and B_o

As long as an external boundary of the stability domain can be represented by a law of model (32), the coefficients A_o and B_o are constant and immediately determined. On the contrary, if it is necessary to use a 3 or 4-terms equation, the coefficients become functions of T as discussed concerning previous equation (80). If such an equation were rigorously known, operations of derivation being themselves rigorous, the coefficients A_o and B_o would be exactly known at any temperature. Unfortunately, it cannot be said that this is the case, and the values of A_o and B_o such as those in Table II cannot be used.

The choice of suitable values of A_o and B_o is based on identity of the thermodynamic properties of the magnetite obtained at 1 184 K from either W_3 or W'_3 according to the calculation method below.

If Y refers to any extensive property, equation (73) allows the following relationship to be written

$$Y_{Fe_3O_4} = \frac{4-3x_1}{2} (\Delta Y + Y_{O_2}) + 3 Y_{FeO_{x_1}} \quad (82)$$

where ΔY represents the variation of Y during the reaction of equation (73). On the other hand, according to equation (74), $\Delta H^o_1 = 19.144 64 A_1$ and $\Delta S^o_1 = - 19.144 64 B_1$.

Concerning W_3 for which all the thermodynamic properties can be calculated at 1 184 K, the values $x_1 = 1.135 28$, $H^o_3 = -248 878 \text{ J.mole}^{-1}$ and $S^o_3 = 142.306 \text{ J.K}^{-1}.\text{mole}^{-1}$ are obtained. From equation (82), the values $H^o_{Fe_3O_4} = -927 842 \text{ J.mole}^{-1}$ and $S^o_{Fe_3O_4} = 424.332 \text{ J.K}^{-1}.\text{mole}^{-1}$ can be deduced for Fe_3O_4 at 1 184 K.

In order to change from W_3 to W'_3 at 1 184 K where $l'_1 = -14.714$ following equations (78) and (79), two distinct ways may be used. The first one is based on equation (7) of first-degree in x with all its consequences developed above (see Part 1 Sections I to IV). The second way is based on equation (50) of second-degree in x, with all its consequences. It is the second approximation, subject of Sections V.6. and V.7.

Let us say immediately that these two ways of calculating the properties of W'_i operate according to the same principles and lead on certain particular points to practically identical numerical results. However there is evidence overall that the second method is better concerning W'_i . It will be preferably used despite the obvious complication of numerical calculations.

So, using the six coefficients of W'_3 given previously (see Ref. [32] Table 2 p. 1 187), equation (50) at 1 184 K with the value of l'_1 referred above has a single acceptable root $x'_3=1.127\ 689$.

On the other hand, equation (78) leads to calculation of the reference enthalpy $\Delta H'^{\circ}_1 = -639.783$ kJ and entropy $\Delta S'^{\circ}_1 = -258.663$ J.K⁻¹ of reaction (73). By plugging all these values into preceding equation (82), the values $\Delta H'^{\circ}_3 = -246.499$ kJ.mole⁻¹ and $\Delta S'^{\circ}_3 = 142.394$ J.K⁻¹.mole⁻¹ are obtained successively.

Again at 1 184 K, for $x'_1 = 1.127\ 689$, equations (66) and (67) give respectively

$$H'^{\circ}_3 = 5\ 920.096 + h'_3 \text{ kJ.mole}^{-1} \quad (83) \quad S'^{\circ}_3 = 5\ 617.107 + s'_3 \text{ J.K}^{-1}.\text{mole}^{-1} \quad (84)$$

$h'_3 = 6\ 166.595$ kJ.mole⁻¹ and $s'_3 = -5\ 474.713$ J.K⁻¹.mole⁻¹ are then deduced.

It is explained below how the two differences $h'_1 - h'_3 = -377.578$ kJ.mole⁻¹ and $s'_1 - s'_3 = -278.832$ J.K⁻¹.mole⁻¹ are obtained. Together with the previous results, they give $h'_1 = -6\ 544.173$ kJ.mole⁻¹ and $s'_1 = -5\ 753.545$ J.K⁻¹.mole⁻¹ respectively. The first value plugged into equation (66) and the second value into equation (67) allow to calculate H'°_1 and S'°_1 respectively from the characteristic coefficients of W'_1 taken from the same Table 2 (p. 1187 in Ref. [32]). So, $H'^{\circ}_1 = -225.714$ kJ.mole⁻¹ and $S'^{\circ}_1 = 139.453$ J.K⁻¹.mole⁻¹ are obtained.

Using equation (80) which gives $l'_o = -16.429\ 2$ at 1 184 K, and from equation (50) relating to W'_1 , $x_{o(1')} = 1.049\ 504$ is obtained as the only acceptable root.

The relationship

$$\Delta Y_o = \frac{2}{x_o} (Y_{FeO_{x_o}} - Y_{Fe}) - Y_{O_2} \quad (85)$$

relating to equation (70) in which Y represents any extensive property and ΔY_o its standard variation allows then the calculation of $\Delta H'^{\circ}_o = -523.232$ kJ.mole⁻¹ and $\Delta S'^{\circ}_o = -126.849$ J. K⁻¹.mole⁻¹. These values give respectively $A_o = -27\ 330.5$ and $B_o = 6.625\ 8$.

Note that the first method of calculation based on equation (7) gives values that differ from the previous ones by only a few units of the third decimal order.

These values are used in the following to obtain the properties of the three W'_i . On the other hand, the resulting equation

$$l'_o = -27\ 330.5 T^{-1} + 6.625\ 8 \quad (86)$$

will not be used as it would give an unacceptable point C at 890.9 K or 617.7 °C.

V.4. Determination of the differences $[h_i(T, P) - h_j(T, P)]$

These differences are required since equation (34) is only working for the wüstite W_i actually in equilibrium with iron. For a wüstite W_j which does not have this privilege, h_j can only be known from h_i at the same temperature.

For this assessment, it can be used the fact that, on their mutual boundary, the enthalpy given by equation (45) has the same value for both wüstites W_i and W_j because it is a transformation of the second order. Into the equation

$$H_i = H_j \quad (87)$$

it only has to carry the value x_{ij} common to both wüstites. By laying down $a_i - a_j = \alpha$, $b_i - b_j = \beta$, $c_i - c_j = \gamma$, $d_i - d_j = \delta$, it is obtained on the boundary W_i/W_j

$$x_{ij} = \frac{\gamma + \delta T}{\alpha + \beta T} \quad (88)$$

which plugged into equation (87) gives a directly usable numerical equation

$$h_i - h_j = \frac{4.786\ 16}{\alpha} \cdot \left[\gamma^2 - T^2 \left(\frac{\alpha\delta - \beta\gamma}{\alpha + \beta T} \right)^2 \right] \quad (89)$$

These equations (88) and (89) apply to the W_i and W'_i in the case of the first approximation alone (see Ref. [32], coefficients in Table I, p. 1186). Two cases should be distinguished.

(a) Case of wüstites W_i : the following two equations are obtained

$$h_1 - h_2 = 310\ 137 - 275.609 \cdot \frac{T^2}{(56\ 322.3 - 38.550\ 9T)^2} \quad (90)$$

$$h_1 - h_3 = 439\ 535 - 3\ 889.35 \cdot \frac{T^2}{(79\ 992.3 - 55.745\ 0T)^2} \quad (91)$$

The denominator of the second term of these two equations is cancelled for $T=1\ 461$ and $1\ 435$ K respectively, each of these differences tending towards $-\infty$. In the conditions of use, this possibility is excluded.

For equation (90), even at the temperature of $1\ 447$ K (*cf.* Ref. [32], point F in the equilibrium diagram) below 14 K only to $1\ 461$ K, the second term is only $-1\ 985$ J.mole⁻¹, and at $1\ 510$ K (point G in the diagram), it is only -176 J.mole⁻¹. At temperatures either above $1\ 510$ K, or below $1\ 447$ K, this second term is much lower in absolute value (-19 J.mole⁻¹ at $1\ 644$ K, -3 J.mole⁻¹ at $1\ 184$ K).

The same applies to equation (91). At $1\ 310$ K (point E of the diagram), the term is -138 J.mole⁻¹, and it is only -28 J.mole⁻¹ at $1\ 184$ K.

It is understandable that the two differences $h_1 - h_2$ and $h_1 - h_3$ could be considered as constant in first approximation [50].

(b) Case of wüstites W'_i : relations of the same form as the two preceding ones could be established, but they would not relate to the approximation used for the W'_i (see equations (89) and (97)).

V. 5. Determination of the differences $[s_i(T, P) - s_j(T, P)]$

On the common boundary of the subdomains of W_i and W_{i+1} , equation (87) is accompanied by identity

$$S_i = S_j \quad (92)$$

which leads to the relationship

$$s_i - s_j = -\frac{4.789\ 16}{\beta} \cdot \left[\delta^2 - \left(\frac{\alpha\delta - \beta\gamma}{\alpha + \beta T} \right)^2 \right] \quad (93)$$

(a) Case of the W_i : the two relationships are obtained

$$s_1 - s_2 = 211.951 - \frac{(402\ 661)}{(56\ 322.3 - 38.550\ 9T)^2} \quad (94)$$

$$s_1 - s_3 = 305.270 - \frac{5.5811 \cdot 10^6}{(79\ 992.3 - 55.745\ 0T)^2} \quad (95)$$

The denominators of the second terms of these two equations are respectively the same as those of equations (90) and (91). The operating temperature intervals are therefore the same.

On the other hand, the absolute value of these terms being low or very low compared to the first terms, the differences $s_1 - s_2$ and $s_1 - s_3$ are almost constant.

(b) Case of the W'_i : the corresponding relationships will not be established.

V. 6. Second approximation in the case of the W'_i

The general principle of the calculations is the same as for the previous approximation. Outside the α -Fe/ W'_i boundary especially concerning W'_1 , so h'_1 and s'_1 , the same will be done using the common boundaries W'_i / W'_j . The previous notations must then be completed by $\varepsilon = e_i - e_j$ and $\varphi = f_i - f_j$.

So x_{ij} is given by the equation

$$(\alpha + \beta T) x_{ij}^2 + (\gamma + \delta T) x_{ij} + \varepsilon + \varphi T = 0 \quad (96)$$

which has only one acceptable root x_{ij} at a given temperature. Taking into account equation (66), the resulting equation is

$$h'_i - h'_j = -19.144\ 64 \left(\alpha \frac{x_{ij}^3}{6} + \gamma \frac{x_{ij}^2}{4} + \varepsilon \frac{x_{ij}}{2} \right) \quad (97)$$

Similarly, equation (67) allows the calculation of the difference $s'_i - s'_j$ given by the relationship

$$s'_i - s'_j = 19.144\ 64 \left(\beta \frac{x_{ij}^3}{6} + \delta \frac{x_{ij}^2}{4} + \varphi \frac{x_{ij}}{2} \right) \quad (98)$$

Thus $h'_1 - h'_2$ is $-946.428\ \text{kJ.mole}^{-1}$ at 1 184 and 923 K. It drops to $-946.445\ \text{kJ.mole}^{-1}$, its smallest value at 1 073 K. Similarly, $s'_1 - s'_2$ is $-809.641\ \text{J.K}^{-1}.\text{mole}^{-1}$ at 1 184 and 923 K, and drops to $-809.647\ \text{J.K}^{-1}.\text{mole}^{-1}$, its smallest value at 1 073 K.

Similarly $h'_2 - h'_3$ is $568.873\ \text{kJ.mole}^{-1}$ at 1 184 and 973 K, and drops to $568.866\ \text{kJ.mole}^{-1}$, its lowest value, at 1 050 K. Finally, $s'_2 - s'_3$ is $530.830\ \text{J.K}^{-1}.\text{mole}^{-1}$ at 1 184 and 973 K, and drops to $530.823\ \text{J.K}^{-1}.\text{mole}^{-1}$, its lowest value at 1 050 K.

These differences vary very little. For numerical calculations relating to the W'_i , the terms $h'_i - h'_j$ and $s'_i - s'_j$ can therefore be considered as constant for T when used to construct the lower part of Table III between 592 and 911 °C.

V. 7. Molar heat capacities under constant pressure

Equation (49) for W_i and equations (68) or (69) for W'_i involve $x_{o(i)}$. The calculation of $C_{p,i}$ therefore calls for the same precautions as that of h_i or s_i . The first term of these equations is therefore calculable only for the wüstite W_i or W'_i in equilibrium with iron and oxygen under pressure p'_o . At the transition of wüstite W_i to wüstite W_j on their mutual boundary, there is identity according to equation (87) between the constant pressure derivatives of H_i and H_j with respect to T. Thus, there is identity between $C_{p,i}$ and $C_{p,j}$ on the common boundary

$$C_{p,i} = C_{p,j} \quad (99)$$

It follows that the first term of equation (49) or that one of equations (68) or (69) is the same for the whole isotherm, and $C_{p,i}$ is a linear function of T throughout the isotherm: there is no discontinuity during the transformation of W_i into W_j .

Note: $C_{p,i}$ and $C_{p,j}$ can be calculated separately from H_i and H_j given by equation (45), and deriving them from T under constant pressure. If the difference $C_{p,i} - C_{p,j}$ is calculated when x has the common value x_{ij} given by equation (88), on the boundary W_i/W_j , zero will be found according to equation (99).

VI. – RESULTS – TABLES

VI. 1. General note

It is worth recalling that formula FeO_x was only used for convenience of calculation because the thermodynamic properties of wüstite are expressed in a simpler way than using the variable $y = x^{-1}$ [32]. It is obvious that wüstite having an iron deficiency and not an excess of oxygen compared to stoichiometric oxide, the formula Fe_yO is to be preferred. Therefore, after establishing the formalism according to the variable x , the numerical results are given essentially according to the variable y .

The extensive properties, whose values are tabulated, are by nature proportional to the mass of matter. Moving from the formula FeO_x , thus from the molar mass ($\text{Fe} + x \times \text{O}$), to the formula Fe_yO , *i.e.* to the molar mass ($y \times \text{Fe} + \text{O}$), it is easy to see that the latter is the quotient of the first by x . Therefore, when the value of any molar property is obtained with the variable x , to divide it by x gives the value corresponding to a mole of wüstite Fe_yO .

VI. 2. Description of Tables III to VIII

The next six Tables give the value of the various thermodynamic properties of wüstite at various Kelvin temperatures T ranging from 864.73 K of the Chaudron's triple point to 1 644 K near

melting. These values of T are integer multiples of 50 K or integer multiples of 50 °C: so, they end in 23 or 73.

The particular temperature of 1 184 K corresponding to the transition from α - to γ -Fe or from W_i to W'_i is usually shown twice, once about W_i , again about W'_i .

(a) Table III below

It gives the values of h_i and h'_i as well as s_i and s'_i for the calculation of a number of properties of either W_i or W'_i at various temperatures.

(b) Tables IV and V below

They give the values of H° and H'° , of S° and S'° at various temperatures either of the W_i in Table IV or the W'_i in Table V. The values of y are either $y_0 = x_0^{-1}$ on the iron/wüstite boundary, or $y_{ij} = x_{ij}^{-1}$ on the boundary W_i / W_j or W'_i / W'_j , or $y_1 = x_1^{-1}$ on the wüstite/magnetite boundary.

(c) Tables VI and VII

They give $C^\circ_{P,i}$ and $C'^\circ_{P,i}$ at various temperatures and y values either of W_i (Table VI) or W'_i (Table VII). The layout of these Tables is the same as that of Tables IV and V respectively.

(d) Table VIII

It is surprising that the thermodynamic data collections have adopted for the non-stoichiometric iron monoxide the typical composition such as $y = 0.947$ of the chemical formula $Fe_{0.947}O$. Indeed Tables IV and V show that the oxide with this composition is stable only between 1 644 and about 1 300 K on the one hand, between 1 184 and about 1 125 K on the other hand. Outside these temperature ranges the oxide $Fe_{0.947}O$ is not stable and decomposes into iron and oxygen.

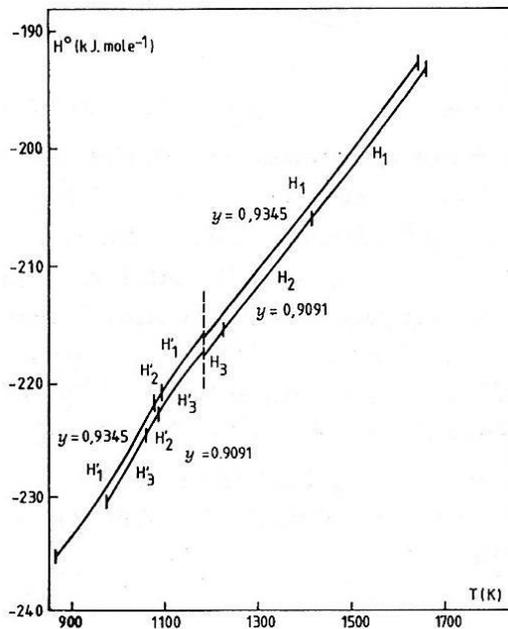


Fig. 5. Variations of the molar reference enthalpy H° of the wüstites whose composition is $x=1.100_0$ or $y=0.909_1$ from the boundary W'_3/Fe_3O_4 at 975 K until 1 643 K or 1 370 °C close to melting, and $x=1.070_1$ or $y=0.934_5$ from Chaudron's point with temperature 864.7 K or 591.5 °C to 1 644 K or 1 371 °C close by melting.

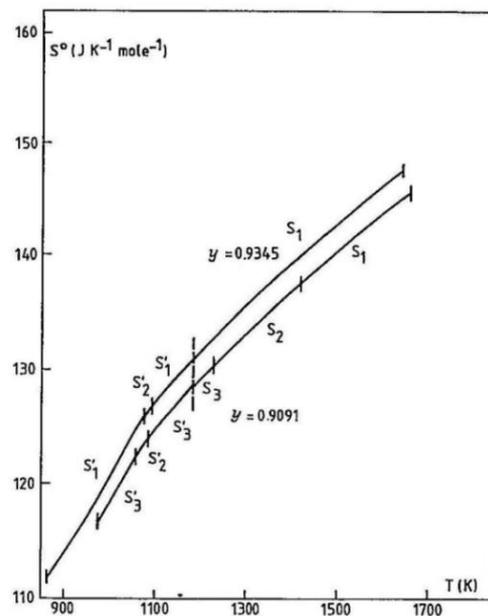


Fig. 6. Same variations for entropy S° .

TABLE III

Values of the integration constants h_i and h'_i (kJ.mole^{-1}), s_i and s'_i ($\text{J.K}^{-1}\text{mole}^{-1}$)

T(K)	W ₁		W ₂		W ₃	
	h_1	s_1	h_2	s_2	h_3	s_3
1 644	320.432	142.349	10.310	-69.594	-119.027	-162.884
1 623	319.659	141.876	9.541	-70.065		
1 600	318.815	141.350	8.703	-70.586		
1 573	317.815	140.721	7.715	-71.208		
1 550	316.962	140.172	6.881	-71.745		
1 523	315.932	139.503	5.907	-72.378		
1 500	315.057	138.920				
1 473	314.114	138.285				
1 450	313.308	137.732				
1 423	312.378	137.089	2.501	-74.674		
1 400	311.583	136.526	1.544	-75.352		
1 373	310.653	135.853	0.561	-76.063		
1 350	309.857	135.269	-0.252	-76.660		
1 323	308.939	134.583	-1.181	-77.354		
1 300	308.158	133.986	-1.967	-77.955	-130.885	-170.884
1 273	307.244	133.274	-2.884	-78.669	-132.031	-171.776
1 250	306.460	132.652	-3.670	-79.293	-132.907	-172.471
1 223	305.558	131.922	-4.574	-80.024	-133.868	-173.248
1 200	304.750	131.206	-5.383	-80.741	-134.706	-173.989
1 184	304.252	130.836	-5.881	-81.111	-135.218	-174.371

	W' ₁		W' ₂		W' ₃	
	h'_1	s'_1	h'_2	s'_2	h'_3	s'_3
1 184	-6 544 173	-5 753.545	-5 597 745	-4 943.904	-6 166 614	-5 474.734
1 173	-6 544 530	-5 753.854	-5 598 102	-4 944.213	-6 166 971	-5 475.043
1 150	-6 545 467	-5 754.651	-5 599 038	-4 945.010	-6 167 907	-5 475.840
1 123	-6 546 551	-5 755.638	-5 600 121	-4 945.995	-6 168 989	-5 476.824
1 100	-6 547 413	-5 756.375	-5 600 972	-4 946.721	-6 169 835	-5 477.548
1 073	-6 548 860	-5 757.710	-5 602 311	-4 948.053	-6 170 654	-5 478.299
1 050	-6 549 990	-5 758.790	-5 603 560	-4 949.147	-6 172 422	-5 479.970
1 023	-6 551 862	-5 760.601	-5 604 330	-4 950.960	-6 174 010	-5 481.789
1 000	-6 553 080	-5 761.802	-5 606 652	-4 952.161	-6 175 521	-5 482.990
973	-6 554 540	-5 763.276	-5 608 112	-4 953.635	-6 176 981	-5 484.465
950	-6 555 628	-5 764.410	-5 609 195	-4 954.769	-6 178 064	-5 485.599
923	-6 556 806	-5 765.685	-5 610 378	-4 956.044		
900	-6 557 786	-5 766.757				
873	-6 558 938	-5 768.054				
864.73	-6 559 062	-5 768.254				

TABLE V

Values of H° (kJ.mol^{-1}) and S° ($\text{J.K}^{-1}.\text{mole}^{-1}$) of wustites W'_i with the chemical formula Fe_yO

T(K)	$y_0=1/x_0$	Boundary $\alpha\text{-Fe}/W'_1$		Boundary W'_1/W'_2		Boundary W'_2/W'_3		Boundary W'_3/Fe_3O_4				
		H°	S°	H°	S°	H°	S°	H°	S°			
1 184	0.952 83	-215.07	132.87	0.926 35	-216.49	130.36	0.916 46	-216.99	129.40	0.886 77	-218.60	126.25
1 173	0.951 68	-215.66	132.31	0.926 47	-217.01	129.91	0.916 53	-217.51	128.96	0.887 62	-219.07	125.90
1 150	0.949 64	-217.07	131.01	0.926 81	-218.27	128.83	0.916 77	-218.76	127.90	0.889 44	-220.22	125.04
1 123	0.947 44	-218.69	129.46	0.927 73	-219.71	127.61	0.917 31	-220.21	128.63	0.891 66	-221.54	123.99
1 100	0.945 99	-219.99	128.26	0.930 92	-220.76	126.86	0.918 55	-221.33	125.71	0.893 68	-222.60	123.19
1 073	0.944 73	-221.89	126.45	0.919 74	-223.04	124.16						
1 050	0.943 99	-223.40	124.98	0.923 22	-224.38	123.09	0.911 59	-224.91	122.02	0.898 62	-225.54	120.76
1 023	0.942 96	-225.69	122.72	0.924 19	-226.54	121.05	0.913 94	-225.98	120.13	0.901 79	-227.29	118.95
1 000	0.942 25	-227.27	121.13	0.924 54	-228.06	119.58	0.914 52	-228.47	118.69	0.904 97	-228.90	117.78
973	0.941 00	-229.17	119.16	0.924 79	-229.87	117.75	0.914 85	-230.27	116.89	0.909 60	-230.49	116.41
950	0.939 68	-230.65	117.56	0.924 89	-231.27	116.30				0.915 10	-231.65	115.47
923	0.937 64	-232.31	115.69	0.924 99	-232.82	114.63						
900	0.936 39	-233.68	114.16							0.921 19	-232.96	114.32
873	0.934 96	-235.28	112.30									
864.73	0.934 54	-235.55	111.91									

TABLE VI

Values of $C_{P,i}^{\circ}$ ($J.K^{-1}.mole^{-1}$) of the wüstites W_i with the chemical formula Fe_yO

T(K)	$y_0 = 1/x_0$	$C_{P,i}^{\circ}$	$y = 1/x$	$C_{P,i}^{\circ}$	$y = 1/x$	$C_{P,i}^{\circ}$	$y_1 = 1/x_1$	$C_{P,i}^{\circ}$
	Boundary W3/ γ -Fe		Boundary W3/W2		Boundary W2/W1		Boundary W3/Fe3O4	
1 644	0.956 89	53.78	0.956 84	53.38	0.938 82	53.11	0.834 54	49.26
	Boundary W2/ γ -Fe							
1 623	0.956 63	53.51			0.939 58	52.89	0.837 76	49.15
1 600	0.956 32	53.33			0.940 67	52.76	0.841 28	49.13
1 573	0.955 95	53.11			0.942 53	52.63	0.845 40	49.10
1 550	0.955 62	52.93			0.945 02	52.55	0.848 91	49.08
1 523	0.955 21	52.71			0.950 34	52.53	0.853 03	49.05
	Boundary W1/ γ -Fe							
1 500	0.954 60	51.70					0.856 53	48.26
1 473	0.953 51	51.49					0.860 63	48.25
1 450	0.952 59	51.32					0.864 12	48.24
					Boundary W1/W2		Boundary W2/Fe3O4	
1 423	0.951 53	51.12			0.906 07	49.54	0.866 39	48.17
1 400	0.950 63	50.94			0.916 05	49.75	0.867 79	48.09
1 373	0.949 59	50.74			0.921 19	49.76	0.869 52	47.99
1 350	0.948 72	50.56			0.923 62	49.70	0.871 07	47.90
1 323	0.947 71	50.35			0.925 44	49.60	0.872 98	47.81
			Boundary W1/W2		Boundary W2/W3		Boundary W3/Fe3O4	
1 300	0.946 85	50.18	0.926 52	49.49	0.881 85	47.97	0.874 39	47.72
1 273	0.945 86	49.97	0.927 45	49.35	0.896 07	48.28	0.875 65	47.59
1 250	0.945 03	49.79	0.928 05	49.22	0.903 58	48.39	0.876 83	47.49
1 223	0.944 06	49.58	0.928 61	49.06	0.909 62	48.42	0.878 35	47.37
1 200	0.943 25	49.40	0.929 00	48.92	0.913 35	48.40	0.879 77	47.27
1 184	0.942 69	49.24	0.929 23	48.79	0.915 43	48.33	0.880 84	47.17

In its stable domain of existence, only the oxide Fe_yO with triple-point C composition $y_C = 0.934 54$ does not undergo any decomposition between its melting temperature around 1 650 K and the triple-point temperature. Hence Table VIII gives H° and H'° , S° and S'° , C_P° and $C_P'^{\circ}$ for W_i and W'_i respectively always at the same temperatures, for the corresponding value. This particular composition corresponds to that of wüstite in equilibrium with α -Fe and Fe3O4 at point C.

Finally, for this composition between 1 644 and 1 184 K, the wüstite is in the form of W_1 . Between 1 184 and 864.73 K, it is in the form of W'_1 with a brief passage in W'_2 around 1 080 K (see above Figs. 5 and 6 and Tables V and VII).

VI. 3. Phase diagram at thermodynamic equilibrium

Tables IV and V, equations (76), (77), (79), (75), (80), and (81) in section VI. 2., and the coefficients in Tables 1 and 2 in Ref. [32] p.1186 and 1187 are used to draw the 2D state diagram of wüstite in the form of $T(y)$ or $T(x)$. The slight changes that had to be made to the external boundaries α -Fe / W'_i and W'_i / Fe3O4 boundaries give a slightly different diagram from the one published for the first time in 1964 [29] then enhanced in 1979 concerning W' [32].

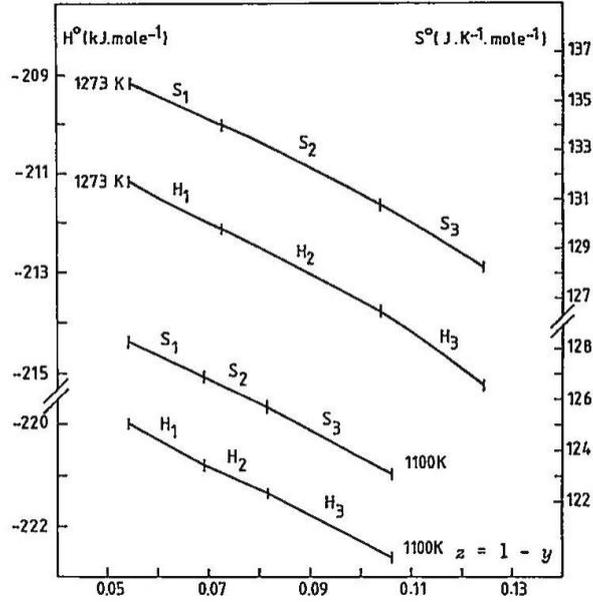


Fig. 7 – Variations of the reference enthalpy H_i° (H_i°) and entropy S_i° (S_i°) of one mole of wüstite $Fe_{1-z}O$ with the departure from stoichiometry, from the boundary with iron to that with magnetite (W_i at 1 273 K and W_i' at 1 100 K).

TABLE VII

Values of $C_{P,i}^{\circ}$ ($J.K^{-1}.mole^{-1}$) of the wüstites W_i with the chemical formula Fe_xO

T(K)	$y_0=1/x_0(1')$	$C_{P,i}^{\circ}$	$y = 1/x$	$C_{P,i}^{\circ}$	$y = 1/x$	$C_{P,i}^{\circ}$	$y_1= 1/x_1$	$C_{P,i}^{\circ}$
	Boundary α -Fe/ $W'1$		Boundary $W'1/W'2$		Boundary $W'2/W'3$		Boundary $W'3/Fe_3O_4$	
1 184	0.952 83	56.19	0.926 35	55.12	0.916 46	54.73	0.886 77	53.53
1 173	0.951 68	56.19	0.926 47	55.18	0.916 53	54.78	0.887 62	53.61
1 150	0.949 64	56.66	0.926 81	55.73	0.916 77	55.31	0.889 44	54.19
1 123	0.947 44	57.93	0.927 73	57.09	0.917 31	56.65	0.891 66	55.56
1 100	0.946 15	59.67	0.930 92	59.00	0.918 55	58.45	0.893 68	57.34
							Boundary $W'2/Fe_3O_4$	
1 073	0.944 73	62.44	0.919 74	61.25			0.895 94	60.12
							Boundary $W'3/Fe_3O_4$	
1 050	0.943 99	66.69	0.923 22	65.61	0.911 59	65.00	0.898 62	64.33
1 023	0.942 96	74.12	0.924 19	72.99	0.913 94	72.37	0.901 79	71.64
1 000	0.942 25	66.27	0.924 54	65.35	0.914 52	64.83	0.904 97	64.34
973	0.941 00	62.05	0.924 79	61.28	0.914 85	60.81	0.909 60	60.56
950	0.939 68	59.19	0.924 89	58.54			0.915 10	58.10
							Boundary $W'2/Fe_3O_4$	
923	0.937 64	56.68	0.924 99	56.15			0.921 19	55.99
							Boundary $W'1/Fe_3O_4$	
900	0.939 39	55.21					0.926 87	54.82
873	0.934 96	53.77					0.932 51	53.67
864.73	0.934 54	53.27					0.934 54	53.27

TABLE VIII

Values of H°_1 or $H^{\circ}'_1$ (kJ.mole^{-1}), S°_1 or $S^{\circ}'_1$, $C^{\circ}_{p,1}$ or $C^{\circ\prime}_{p,1}$ ($\text{J.K}^{-1}.\text{mole}^{-1}$) for wüstite W_1 or W'_1 with composition x_C or y_C of Chaudron's triple point between 864.7 and 1 644 K

T(K)	$x_C = 1.07005$			$y_C = 0.93454$		
	$H^{\circ} (\text{H}^{\circ})$	$S^{\circ} (\text{S}^{\circ})$	$C^{\circ}_p (\text{C}^{\circ}_p)$	$H^{\circ} (\text{H}^{\circ})$	$S^{\circ} (\text{S}^{\circ})$	$C^{\circ}_p (\text{C}^{\circ}_p)$
1 644	-206.19	158.04	56.66	-192.69	147.69	52.95
1 623	-207.38	157.36	56.39	-193.80	147.06	52.70
1 600	-208.87	156.56	56.21	-195.20	146.31	52.53
1 573	-210.20	155.95	56.00	-196.44	145.74	52.33
1 550	-211.35	154.76	55.82	-197.51	144.63	52.17
1 523	-213.07	153.74	55.60	-199.12	143.68	51.96
1 500	-214.39	152.87	54.56	-200.36	142.86	50.99
1 473	-215.86	151.87	54.39	-201.72	141.93	50.83
1 450	-217.12	151.01	54.24	-202.91	141.12	50.69
1 423	-218.58	150.00	54.07	-204.27	140.18	50.53
1 400	-219.82	149.12	53.92	-205.43	139.36	50.39
1 373	-221.27	148.07	53.74	-206.78	138.38	50.22
1 350	-222.51	147.16	53.58	-207.94	137.53	50.07
1 323	-223.95	146.08	53.40	-209.29	136.52	49.90
1 300	-225.18	145.15	53.25	-210.44	135.65	49.76
1 273	-226.66	144.03	53.06	-211.82	134.60	49.59
1 250	-227.84	143.06	52.90	-212.92	133.69	49.44
1 223	-229.26	141.91	52.71	-214.25	132.62	49.26
1 200	-230.50	140.83	52.55	-215.41	131.61	49.11
1 184	-231.31	140.20	52.39	-216.17	131.02	48.96
1 184	-231.19	140.13	59.34	-216.06	130.96	55.46
1 173	-231.76	139.84	59.39	-216.59	130.69	55.50
1 150	-233.13	138.67	59.97	-217.87	129.59	56.04
1 123	-234.73	137.23	61.40	-219.36	128.25	57.38
1 100	-236.02	136.09	63.30	-220.57	127.18	59.16
1 073	-237.98	134.30	66.30	-222.40	125.51	61.96
1 050	-239.55	132.81	70.83	-223.87	124.12	66.19
1 023	-241.92	130.51	78.77	-226.08	121.97	73.61
1 000	-243.57	128.89	70.49	-227.62	120.45	65.88
973	-245.53	126.90	66.07	-229.46	118.59	61.75
950	-247.05	125.32	63.10	-230.88	117.12	58.97
923	-248.72	123.52	60.51	-232.44	115.43	56.55
900	-250.13	121.98	59.00	-233.76	113.99	55.14
873	-251.77	120.12	57.51	-235.29	112.26	53.75
864.73	-252.05	119.75	56.99	-235.55	111.91	53.26

N.B.: between 1 644 and 1 184 K, W_1 is concerned only. Between 1 184 and 864.73 K, it is the case of W'_1 . In another part between about 1 089 and 1 075 K, W'_2 takes place briefly: see Figs 5 and 6. It can be neglected.

VI. 4. Relevance of the Tables

They result directly from the thermodynamic theory applied to the molar properties of wüstite. Equation (9) describing the experimental thermogravimetric isotherms is fundamental. The data are from the isotherms network established by P. Raccach [25] [29] [30].

Various sets of values of l' (T) on the boundaries α - γ -Fe/W-W' and W-W'/Fe₃O₄, and the thermodynamic properties of iron and oxygen extracted from the thermodynamic Tables in Refs. [33] to [39] are necessary additional data.

Along any isotherm, Tables IV and V show that H° or H'° decreases slightly from the fer/wüstite boundary to the wüstite/magnetite boundary. This phenomenon displayed in Fig. 7 appears as normal since the amount of iron bound to the same amount of oxygen decreases.

The parallel decrease in S° or S'° may be interpreted in part in the same way, but the fall in entropy is comparatively greater than the concomitant decrease in enthalpy. For example, at 1 273 K, from $y = 0.9459$ to $y = 0.8757$, the enthalpy variation is $-4\,050$ J. A decrease in entropy equal to $-4\,050/1\,273 = -3.18$ J.K⁻¹.mole⁻¹ could be expected. However, Table IV gives an entropy variation of -7.44 J.K⁻¹.mole⁻¹ which is slightly more than twice. Also at 1 000 K, where the variation of y is smaller, this parameter goes from 0.9423 to 0.9050, the variation of H° is worth $-1\,630$ J. One could have expected a variation of S° equal to -1.63 J. K⁻¹.mole⁻¹ whereas Table V gives -3.35 J.K⁻¹.mole⁻¹.

Tables IV and V are completed with $C_{P,i}$ across the whole stability domain, in Tables VI, VII and VIII. The anomalous behavior in C_P observed in the determination of this property is enhanced with coloring of line at 1 023 K in Tables VII and VIII.

Table VII shows that for a wüstite of a given composition, H° and S° increase constantly with temperature, which is normally expected (see Figs. 5 and 6 above).

Table VIII gathers some preceding remarks through the whole phase diagram and for the wüstites W'_1 and W_1 which got continuously the composition $y = 0.93454$ without phase change except the transformation $W'_1 \rightleftharpoons W_1$ in the vicinity of the temperature 1 184 K connected to the first order transformation α -Fe \rightleftharpoons γ -Fe. The corresponding narrow area in the phase diagram remains to be better characterized.

VII. – COMMENTS AND CONCLUSION

From a high departure from the stoichiometry, at least 4.3% (point J in the diagram) and at most 17.5% of missing iron atoms (point H) result point defects, mainly Fe³⁺ ions and vacancies in the metal lattice, whose properties remain to be specified [32], [51] to [58].

Hazen and Jeanloz [59] noted that Humphrey, King and Kelley [20] were the first to advance the need for order of vacancies. In 1960, with the neutron diffraction Roth was able to show that the point defects form clusters. He proposed a cluster (2/1) of two vacancies associated with one ion Fe³⁺ in tetrahedral or interstitial site [60].

For reasons of symmetry and stability, the basic tetrahedral cluster (4/1) being most often considered, the successive authors [60] to [71], [72] to [75] –it is not possible to cite all– who tried to find a definitive characterization of the cluster type(s) (vacancies / ion Fe³⁺) specific to wüstite, have been led for the most part to propose diverse classifications of sequences of clusters (4/1).

Authors have theoretically studied some of the first terms of possible cluster series, including the cluster (4/1), seeking to rank them in order of binding energy and hence stability. It was first used the Mott-Littleton model [76] [77] where the theory of the crystal field is applied to the 3d electrons of iron [78].

More recently, Anderson *et al.* [69] used a new approach that includes the 2s and 2p orbital energies of oxygen. Their conclusions (clusters (10/4), (13/5) and (16/7) of blende ZnS type), which would be validated by the success of the same model applied to spinels, would be in better agreement with the existence of the phases P' and P'' re-examined recently by Lebreton and Hobbs [68]. Other theoretical considerations in particular of models of the statistical thermodynamics may provide useful information on these clusters.

However that may be, it is now well established that a simple if not unique structural description cannot be suitable, especially since there are thermodynamically identified 'varieties'

which cannot not to correspond to different arrangements of the point defects, and their clusters. Successive variations of the cubic crystal parameter $a_i(T)$ and $a_i(x)$ confirmed as soon as 1964 this existence (see Refs. [31]). An indirect confirmation was found in the deepening of the reduction kinetics results under H₂/H₂O mixtures published in 1966 [79, 80].

Significant progress in the direct structural description by modeling linked to the varieties are owed to Men' *et al.* [73] [74] with the C(lusters) C(omponent) M(ethod). Gavarrri et al. [75] brought new interpretations of structural experimental results. It is also known that the complexity of clusters increases with the concentration of point defects, i.e. when the departure from stoichiometry increases, and that these clusters of one or more types forming mixtures behave differently for the three varieties, possibly encountered along an isotherm. It is also known that the clusters are blurred way ordered on the iron side, better and better ordered when approaching magnetite. From a structural point of view, these arrangements could be described in terms of tri-incommensurable modulations [81] [82].

Note: the formula $m-n = 4z p^3$, released for the first time by Gavarrri [71 b]) shows that for a single type of cluster (m/n) the repetition factor p of the supposed cubic superstructure with parameter pa can take a value characterizing an integer multiple of a translation vector only for a given value of the composition parameter z of the wüstite formulated Fe_{1-z}O. For any other value of z, the product pa is incommensurable to the lattice.

A characterization of the three W_i by new measurements of electrical conductivity and thermoelectric power, and a description of the transformation W₁ ⇌ (W₂ – W₃) in terms of semiconductor ⇌ metal Mott transition [77] are owed to Molenda, Stokłosa and Znamirovski [83] [84]. The analysis of the electrical conductivity at constant thermoelectric power, in terms of p-type conduction by small polarons regardless the composition [70], could then appear as contradictory.

The molar thermodynamic properties, in particular the entropy, given in this paper should be able to be linked to transitional phenomena from one variety to another, and to advance the physicochemical description of this complex ceramic material that is the wüstite.

(from French version on April and June , 1986, ¶.23 (3) and (6) in Ref. [Ø])

ENDNOTES

1 - The present paper will have formed in 2019 the base of a “**final paper**” (Ref. [85]) connecting tentatively phenomenological study and structural deviations from the NaCl structure of wüstite, due to clusters of point defects.

2 – The notation $x_{o(i)}$ appeared in the present English version corresponds to constant values of composition variable x on a boundary γ - or α -Fe/W₁ or W₁' at given temperature. In the equilibrium diagram in Ref. [29] p. 3681, continuous lines correspond to the stable boundaries γ - α Fe/W₁-W₁', dotted lines to the metastable boundaries γ -Fe/W₂ or W₃. The measure of the energy terms generally done in Joule.mole⁻¹ in chemistry could also be done in electronvolt when working at the electronic level for some characterizations of the complex nonstoichiometry [85].

3 – Epistemological truth - Max PLANCK (1858-1947, Nobel Price 1918) wrote (in his mother tongue): “Eine neue wissenschaftliche Wahrheit flegt sich nicht in der Weise durchzusetzen, daß ihre Gegner überzeugt werden und sich als belehrt erklären, sondern vielmehr dadurch, daß die Gegner allmählich aussterben und daß die heranwachsende Generation von vornherein mit der Wahrheit vertraut gemacht ist” in *Wissenschaftliche Selbstbiographie*, Barth, Leipzig, 1948, p. 22.

For an initial translation into English, see Max Planck Scientific Autobiography, F. Gaynor trans., Philosophical Library, New York 1949. For a first analyze of this famous often referenced Max Planck's sentence, see in Science, B. Barber, 134 (1961) p. 597.

For a translation into French, see Max Planck, Autobiographie scientifique, George André trad., Albin Michel, Paris, 1960, p. 84.

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