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# A review about wüstite $\text{Fe}_{1-z}\text{O}$ , pseudo-phases and defect clustering

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## Abstract

Thermodynamic properties and structural aspects of the non-stoichiometric wüstite  $\text{Fe}_{1-z}\text{O}$ , and its modifications - the so-called pseudo-phases - as functions of composition  $z$  and equilibrium temperature are reviewed from 1960 to present (159 references). The focus is first put on the complexity of the equilibrium phase diagram. The first order transition  $W \rightleftharpoons W'$  is specified on the boundary iron/wüstite close to 1185 K. Transitions correlated to the modifications  $W_i$  at  $T(W) > 1185$  K and  $W'_j$  at  $1185\text{K} < T(W') < T(W)$  ( $i$  and  $j = 1,2,3$ ) are re-examined. Structural determinations based on point defects and their clustering are recalled. A series of equilibria are developed, trying to justify the stabilization of the pseudo-phases, which can be interpreted in terms of transformation of defect clusters, or their mode of distribution (percolation, superstructure) including changes in electronic charge carriers

## Résumé

Une mise au point bibliographique des propriétés thermodynamiques et structurales de la wüstite non stœchiométrique  $\text{Fe}_{1-z}\text{O}$  et de ses «modifications» ou pseudo-phases, est faite, de 1960 à ce jour (159 références). L'attention est d'abord portée sur la complexité du diagramme de phases à l'équilibre. La transition du premier ordre  $W \rightleftharpoons W'$  est précisée sur la frontière fer/wüstite au voisinage de 1185 K. Les transitions dues à l'existence des variétés  $W_i$  à  $T(W) > 1185$  K et  $W'_j$  à  $1185\text{K} < T(W') < T(W)$  ( $i$  et  $j = 1,2,3$ ) sont reconsidérées, de même que les déterminations structurales relatives aux défauts ponctuels et à leurs amas. Des équilibres sont envisagés, qui tentent de caractériser la stabilité des pseudo-phases. Celles-ci peuvent être interprétées en termes de transformation ou de mode de distribution des amas de défauts (percolation, surstructure) en incluant des changements dans les porteurs de charges électroniques.

**Key-words:** wüstite, iron-oxygen phase diagram defect clusters, point defects, , pseudo-phases, transitions, percolation, superstructure, defect equilibria

## I – Introduction

The non-stoichiometric iron monoxide  $\text{Fe}_{1-z}\text{O}$  is the main constituent of traditional blast furnace slags. Historically this oxide was the subject of numerous studies in the general context of improving the metallurgy of iron, but also for its use in the fields of recycling of industrial waste, catalysis and nanoparticles.

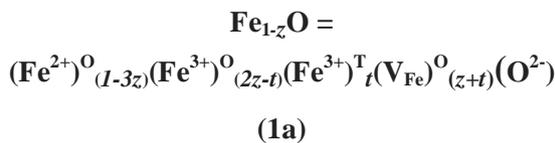
The oxide  $\text{Fe}_{1-z}\text{O}$ , also written presently  $\text{Fe}_y\text{O}$  or  $\text{FeO}_x$ , is named by means of its German mineralogical appellation « wüstit ». This oxide is in a steady state, between Chaudron's point not far from 600 °C (21Cha) and the melting temperature around 1400 °C (45Dar), under an equilibrium oxygen pressure in the range  $10^{-25}$  to  $10^{-6}$  bar. This oxide is a berthollide with a large iron deficiency, which is expressed by the nonstoichiometry

departure  $z \in [0.04 - 0.18]$  around 1400 °C and  $\cong [0.065]$  near 600 °C.

A succession of reviews or equivalent papers on the non-stoichiometric wüstite was published in the past

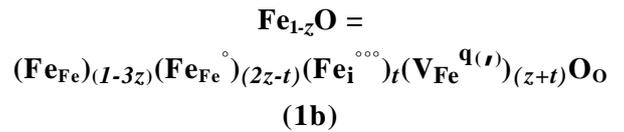
Goodenough (R-71), Per Kofstad (R-72), Vallet (R-72), Burgmann (R-75), N. A. Gokcen (R-75) Men' *et al.* (R-77), Spencer and Kubaschewski (R-78), Bauer and Pianelli (R-80), (R-Toft Sørensen (R-81), Hazen and Jeanloz (R-84), Gleitzer and Goodenough (R-85), N. A. Gokcen (R-86), Lykasov *et al.* (R-87), Mrowec and Podgoreka (R-87), Tomlinsom *et al.* (R-90), Long and Grandjean (R-91), Sundman (R-91), Wriedt (R-91), Collongues (R-92), T. Bak *et al.* (R-97), Gleitzer (R-97), Smyth (R-2000), Desré and Hodaj (R-10), Worrall and Coley (R-13)

Multiple studies have addressed the nature of the point defects (iron vacancies and interstitials), and the concept of defect clustering was systematically developed with a large variety of structural models. The NaCl face centered cubic structure of wüstite is characterized by high rate of iron vacancies, and the existence of a certain proportion of iron ions occupying interstitial sites. The crystallographic determinations showed that these defects were not disordered in the lattice. Diverse models of clusters of iron vacancies and interstitials were proposed. Given all the data acquired to date, a more accurate chemical formula (1a) can be expressed using classical ionic notations as follows



In this expression, the ionic species  $(\text{Fe}^{2+})^{\text{O}}$ ,  $(\text{Fe}^{3+})^{\text{O}}$ ,  $(\text{Fe}^{3+})^{\text{T}}$  and  $(\text{V}_{\text{Fe}})^{\text{O}}$  are characterized by

fractions  $(1-3z)$ ,  $(2z-t)$ ,  $t$  and  $(z+t)$  successively for one atom of ionized oxygen  $\text{O}^{2-}$ . Iron vacancies on octahedral sites are assumed to be neutral and noted  $\text{V}_{\text{Fe}}$  in a first simplified approach. The superscripts O and T  $((\text{---})^{\text{O}}$  and  $(\text{---})^{\text{T}}$ ) designate respectively octahedral and tetrahedral sites of the NaCl structure, and the subscripts  $z$  and  $t$  are respectively the fractions of iron vacancies and  $\text{Fe}^{3+}$  occupying tetrahedral sites. Because it simplifies the structural description of defects, the oxygen site is assumed to be fully occupied (no significant amount of oxygen vacancies). Adopting the international notation of Kröger and Vink, the formula (1a) is written as follows:



In this expression, iron vacancies can be charged with  $q=2$  or  $q=1$ , or neutral with  $q=0$ . The electrical compensation would be due to electrons jumping in the conduction band, or interacting with holes in the valence band. It should be recalled that the band gap of wüstite was recently evaluated at about 1.0 eV at 25 °C, which means that a large population of electrons in conduction band and/or holes in valence band can be expected at high temperature, depending on the oxygen partial pressure (12Sch).

In this review, we present a historical recall of observations and concepts on wüstite at equilibrium and on quenched samples. Then, we try to show how the complex non-stoichiometry of wüstite could be better described using mixtures of point defects and their associations or clusters.

**TABLE I.1 - Notations and symbols presently used**

	Formal ionic notations	Kröger and Vink notations
$\text{Fe}^{2+}$ in octahedral site of the fcc NaCl-structure	$[\text{Fe}^{2+}]^{\text{O}}$ or $\text{Fe}^{2+}$	$[\text{Fe}_{\text{Fe}}^{\times}]$ or $\text{Fe}_{\text{Fe}}$
$\text{Fe}^{3+}$ in octahedral site of the fcc NaCl-structure	$[\text{Fe}^{3+}]^{\text{O}}$ or $\text{Fe}^{3+}$	$[\text{Fe}_{\text{Fe}}^{\circ}]$ or $\text{Fe}_{\text{Fe}}^{\circ}$
$\text{Fe}^{3+}$ in tetrahedral site of the fcc NaCl-structure	$[\text{Fe}^{3+}]^{\text{T}}$ or $\text{Fe}_i^{3+}$	$[\text{Fe}_i^{\circ\circ}]$ or $\text{Fe}_i^{\circ\circ}$
Iron ( $\text{Fe}^{2+}$ ) vacancy in octahedral site		$[\text{V}_{\text{Fe}}^{\text{q}(\circ)}]$ (q-times charged)
Iron ( $\text{Fe}^{2+}$ ) vacancy in octahedral site		$[\text{V}_{\text{Fe}}^{\prime\prime}]$ (doubly charged)
Iron ( $\text{Fe}^{2+}$ ) vacancy in octahedral site		$[\text{V}_{\text{Fe}}^{\prime}]$ (singly charged)
Iron ( $\text{Fe}^{2+}$ ) vacancy in octahedral site		$[\text{V}_{\text{Fe}}]$ (neutral)
Oxygen on its site	$\text{O}^{2-}$	$[\text{O}_{\text{O}}^{\times}]$ or $\text{O}_{\text{O}}$
Electrons and holes	$e^- ; h^+$	$e' ; h^{\circ}$
	Other notations	
Partial pressure $p(\text{O}_2)$ / $\log_{10}(p(\text{O}_2))$ Partial pressure $p(\text{Fe gas})$	$p' // l'$ $p$	
$\text{Fe}_{1-z} \text{O} // \text{Fe}_y \text{O} // \text{FeO}_x //$	$x = 1/(1-z) = 1/y$	
3D-superlattices	<p>→ <math>(k_1.a \times k_2.a \times k_3.a)</math> with <math>k_1, k_2, k_3</math>, intergers or not <math>\geq 1</math> (for a non cubic superlattice with 3 different cell parameters)</p> <p>→ <math>(k.a)</math> with <math>k_1 = k_2 = k_3</math> (for a cubic superlattice)</p>	
References	<p>(21Cha) = article, 1921, Chaudron Gleiter (R-97) = Review article, 1997, Gleitzer (R-75Bur) = Burgmann Review in 1975</p>	

## II –The complex behavior of wüstite

### II.1. Some historical marks (1921-1961)

**1** - In 1921, G. Chaudron (21Cha) at work in H. Le Chatelier's lab determined experimentally with a very high accuracy at that time the drawing of the external boundaries ( $\log p(\text{O}_2)$ ,  $1/T$ ) of the stable domain of ferrous oxide considered as the daltonide 'FeO'. The invariant point C at the intersection of the two boundaries where three solid phases (Fe,  $\text{Fe}_3\text{O}_4$ , 'FeO') coexist at equilibrium at 570 °C is named Chaudron's point.

**2** - In 1933, Jette and Foote demonstrated by means of measurements of the cell parameter and density after quenching that wüstite was an iron deficient solid solution: an iron vacancy being 'a group FeO substituted by O'. They deduced for the ionic compound that a missing  $\text{Fe}^{2+}$  was necessarily compensated by the oxidation of two other  $\text{Fe}^{2+}$  giving rise to electron holes  $\text{Fe}^{3+}$  (36Jet).

**3** - In 1945-46, Darken and Gurry studied carefully the phase diagram when determining chemically the composition after slow quenching from  $T = 1100, 1200, 1300$  and  $1400^\circ\text{C}$ . The boundaries with iron and magnetite were specified. The

corresponding lines until Chaudron's point were thus obtained from a distant extrapolation. The authors determined the molar partial and integral thermodynamic properties (45- 46Dar).

**4** - In 1951 - 52, Todd and Bonnickson, and Humphrey *et al.* (51Tod) (52Hum) determined the values of entropy respectively 59.4 and 57.5 J.K<sup>-1</sup>. mole<sup>-1</sup> differing in 1.9 units for the same quenched wüstite Fe<sub>0.947</sub>O. The former determinations considered a calculated configurational entropy of 1.72 J. K<sup>-1</sup> on the assumption of a random distribution of iron vacancies. They deduced that the lacunary iron lattice envisaged by Jette and Foote (36Jet) was ordered.

**5** - Brynstad and Flood observed that some (electron holes) Fe<sup>3+</sup> are necessarily located in tetrahedral sites written [Fe<sup>III</sup>O<sub>4</sub>] (58Bry).

**6** - In 1960, when using neutron diffraction analyses, Roth determined the proportion of Fe<sup>3+</sup> occupying the tetrahedral sites of the fcc structure and concluded to the formation of clusters (2:1) constituted of two iron vacancies and one tetrahedral site occupied by a cation Fe<sup>3+</sup>, also named Frenkel cluster (60Rot). In 1969, Tarte *et al.* will also show directly by I.R. spectroscopy the existence of these Fe<sub>i</sub><sup>ooo</sup> ions.

**7** - Using the formalism of the mass action law initially proposed by Carl Wagner *et al.* (36-52Wag), Brynstad and Flood (58Bry), then Smyth ((61- R-00Smy) resorted to the simplifying expression linking the composition *z* to the oxygen partial pressure  $z \propto p^{1/5}$  to describe the defect structure of Mn<sub>1-z</sub>O and Fe<sub>1-z</sub>O when using experimental compositional data available by Darken and Gurry (45Dar).

## II.2 Modifications or pseudo phases evidenced in phase diagram

### 1 - Raccah -Vallet's team

During the years 1962-65, three supposed « allotropic varieties » or « modifications » noted Wi (i=1,2,3) named later « subphases » then « pseudo-phases » by other authors were evidenced by Vallet *et al.* (62Rac1) (63- 65Val, 65Kle) from experimental Raccah's thesis measurements. A

first layout of the corresponding phase diagram was proposed in the coordinates (Θ°C, *x*) (64Val). Raccah's results were re-interpreted by Kléman (65Kle).

It can be noted that the term pseudo-phase will be used in this review to design a structural and/or electrical configuration of wüstite, and that the term boundary will be used -except external limits of the whole domain- to design the separation between two domains in which each major pseudo phase should be stabilized. It should be also noted that such a boundary could designate a line of equimolar composition of defect populations.

During their thermogravimetric and thermodynamic studies, Vallet *et al.* (64- 65- 70- 751- 752- 79- 86- 89Val) established correlations between mass variation *i.e.* departure from stoichiometry expressed by *x* in FeO<sub>*x*</sub> (*y* = 1/*x* in Fe<sub>*y*</sub>O, *z*=(*x*-1)/*x*) in Fe<sub>1-z</sub>O), temperature *T* and oxygen partial pressure *p'* under equilibrium. They described the phase diagram of wüstite FeO<sub>*x*</sub> above 911°C (See below domain of W) through the following three equations connecting log(*p'*), noted *l'*, with the composition *x* and temperature *T*, and expressing the three behaviors of pseudo-phases W1, W2 and W3 (See (89Val): Table 1 p. 210), successively:

$$l' = (46753.4T^{-1} - 7.3781)x + (-78825.3T^{-1} + 16.0613) \quad (\text{II-2a-W1})$$

$$l' = (-9568.9T^{-1} + 31.1728)x + (-18413.3T^{-1} - 25.2569) \quad (\text{II-2b-W2})$$

$$l' = (-33238.9T^{-1} + 48.3669)x + (6883.9T^{-1} - 43.5669) \quad (\text{II-2c-W3})$$

To better relate nonstoichiometry and equilibrium pressure *p'* (*in* relationships II-2a, II-2b and II-2c) to the presence of defects (mainly cation vacancies and interstitials), we have expressed *l'* as a function of *z* instead of *x*, then we have reported log *z* values as a function of *l'*. It should be recalled that these relationships derive from the general expression of equilibrium constants *K*(*T*) linking the composition *z* to the oxygen partial pressure *p'*. A basic situation can be proposed as follows:



$$\text{with } [h^\circ] = q \cdot [V_{Fe}^{q(\prime)}] = q \cdot z \quad (\text{II- 3a})$$

$$K(T) = \{[O_O] \cdot [V_{Fe}^{q(\prime)}] \cdot [h^\circ]^q\} / (p')^{1/2} \quad (\text{II- 3b})$$

$$K(T)^2 = C^2 \cdot z^5 / p' \rightarrow$$

$$\log z = (1/s) \cdot l' + (1/s) \log(K/C)^2 \quad (\text{II- 3c})$$

where C depends on q.

In this type of equations, the activity  $[O_O]$  of oxygen on its site cfc will be taken equal to 1 because no significant amounts of vacancies can be considered on the oxygen lattice. The equilibrium constants depend on the values 2,1,0 of q. The three hypothetical corresponding values of exponent s should be 6, 4, 2 (more likely close to these values, taking into account the various approximations). In the remainder of this Review, exponent s will be characteristic of specific equilibrium equation connecting the fractions of point defects between them (See below § IV).

It should be noted that these effective relationships are not strictly linear. They assume the existence of three domains allowing comparison with classical models of defect equilibria. In each domain, a unique model of defect equilibrium is supposed to be valid, which is not exact because of a continuous evolution of interactions between defects, as composition and temperature vary in the phase diagram.

### Fixed temperature and variable composition

To evidence different behaviors or transitions in Figure II-1 below, we represent the relation  $\log z$

vs  $l'$  in the specific case of Vallet *et al.* data [89Val] as obtained at 1000°C (T=1273 K) by transformation of the initial relations (II-2a, b, c) above. It results:

$$\log z = 0.2036 l' + 1.7511 \rightarrow s = 4.9 (\pm 0.1)$$

$$(\text{II-4a-W1})$$

$$\log z = 0.1369 l' + 0.8352 \rightarrow s = 6.7 (\pm 0.12)$$

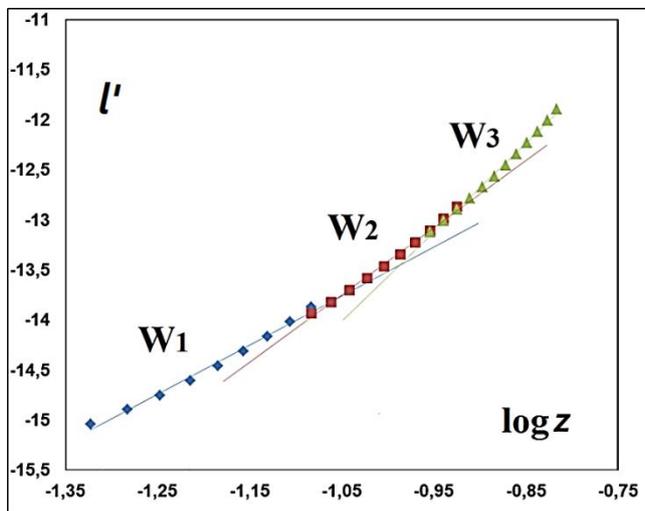
$$(\text{II-4b-W2})$$

$$\log z = 0.1124 l' + 0.5246 \rightarrow s = 8.9 (\pm 0.15)$$

$$(\text{II-4c-W3})$$

From the three segments observable on the curve in Fig. II-1, we could derive the three values  $s(W1) = 4.9$ ,  $s(W2) = 6.7$ ,  $s(W3) = 8.9$ . These values are similar to the ones found by Toft Sørensen (85Sor), Rekas and Mrowec (87Rek).

In reality, there is no reason for observing linear relationships considering the probable existence of mixtures of defects, and of their continuous evolution conditioned by the changes in charge of  $V_{Fe}^{q(\prime)}(q=0,1,2)$



**Fig. II-1 - The logarithm of oxygen partial pressure  $p'$  vs the logarithm of composition  $z$  (in  $Fe_{1-z}O$ ), derived from the data by (89 Val) a 1273 K. Three slopes can be determined giving rise to the three values of exponent s.**

### Fixed composition $z$ and variable temperature

For a fixed value  $x = 1.13$  ( $z = 0.115$ ), we report in Figure II-2 the experimental values of  $l'$  versus  $1/T$  following the data of Vallet *et al.* (89Val).

Three quasi linear domains can be distinguished suggesting the existence of three Gibbs energies of reaction  $\Delta G(\text{reaction})$  in relation with the equilibrium constant  $K(T)$ , with the classical relationship  $\Delta G(\text{reaction}) = \Delta H - T\Delta S = -RT \ln K$ . The linear correlations are

$$l' = -2.5994(10^4 \cdot T^{-1}) + 7.724 \quad (\text{II-5a-W1})$$

$$l' = -2.9226(10^4 \cdot T^{-1}) + 9.9684 \quad (\text{II-5b-W2})$$

$$l' = -3.0676(10^4 \cdot T^{-1}) + 11.088 \quad (\text{II-5c-W3})$$

Using the simplified relationship without activity coefficients (61Smy):

$$K(T)^2 = C^2 \cdot z^s / p' \quad (\text{II-3c})$$

we can derive the following relations for the fixed value  $z = 0.115$

$$\Rightarrow \text{Log } K = (s/2) \cdot \log z - \frac{1}{2} l' + \log C = - (2/2.3026) \Delta G/RT \quad (\text{II-6c})$$

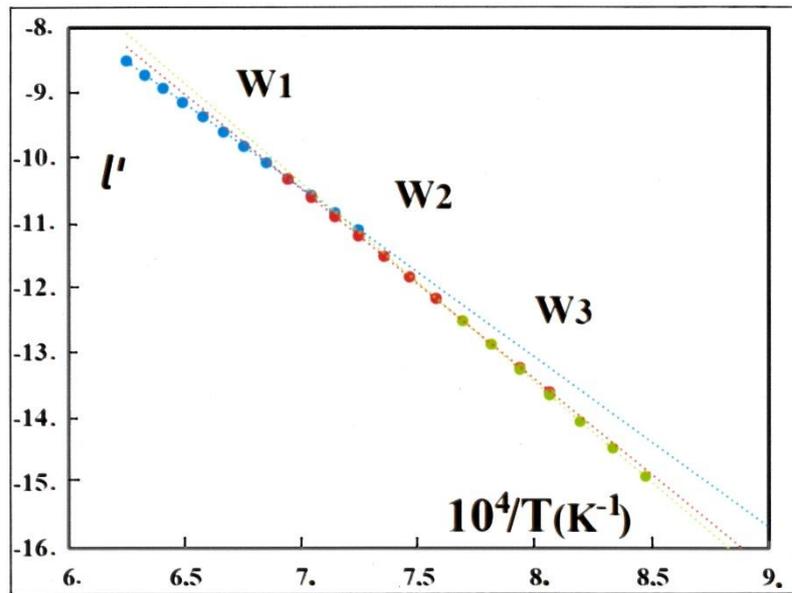
$$\Rightarrow dl' / d(1/T) = (2/2.3026) \Delta H/R \quad (\text{II-7c})$$

From this last relationship, we can determine three values of enthalpies linked to the changes in slopes and attributable to the so-called pseudo-phases

$$\text{W1: } \Delta H_1/R = -25526 \text{ K} \rightarrow \Delta H_1 = -2.20 \text{ eV}$$

$$\text{W2: } \Delta H_2/R = -29322 \text{ K} \rightarrow \Delta H_2 = -2.52 \text{ eV}$$

$$\text{W3: } \Delta H_3/R = -31008 \text{ K} \rightarrow \Delta H_3 = -2.67 \text{ eV}$$



**Fig. II-2 - Variation of  $l'$  vs  $1/T$  for a fixed value  $z = 0.115$ : three quasi linear correlations corresponding to the initial determinations in the three domains W1 (high T), W2 (intermediate T) and W3 (low T) give rise to three activation energies.**

At the same time, a qualitative dilatometric study under  $\text{CO}_2/\text{CO}$  indicated weak changes of slopes in curves  $\Delta l(T)$  with intersections located on the boundary W2/W3 (64Car). In addition, several correlations between the cubic cell parameter obtained after quenching or *in situ* and the composition  $x$  in  $\text{FeO}_x$  led to a possible separation in three pseudo phases or subdomains (65- 76Car) of the equilibrium phase diagram.

In the equations above, we have neglected the activity coefficients, assuming that the ionic interactions were constant as  $z$  varied. Another point of view could have been to consider that a significant evolution could be observed in these activity coefficients associated with fractions of point defects «i» at equilibrium (the activity  $a_i$  being proportional to the molar fraction  $[i]$  :  $a_i = \gamma_i \cdot [i]$ ). In the case of ionic solids, these activity coefficients  $\gamma_i$  are generally used to express deviations from ideal models of isolated defects at

equilibrium. Nowotny and Rekas (89Now) assumed the existence of only one hypothetical specific model, the cluster(4:1)<sup>5-</sup> (i.e. five times negatively charged). A mean  $\gamma_{\pm}$  coefficient was expressed in a simplified form resulting from the Debye-Hückel model, in its limited development, and in the case of purely ionic interactions. Such theoretical variations of activity coefficients as a function of  $z$  would correspond to a continuous description across the wüstite phase diagram, which is not the case because of the pseudo phases.

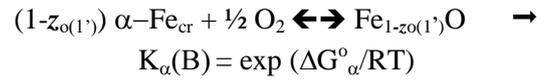
### The abnormal behavior close to 1184/1185 K. Suggested diagram

A splitting of the phase diagram was first proposed by (70Val), then more precisely described (75-Val1 and Val2). It concerned the two subdomains of phases W' and W, on each part of the first order transformation  $\alpha\text{-Fe} \rightleftharpoons \gamma\text{-Fe}$ , each other being constituted of three pseudo-phases W'<sub>j</sub> and W<sub>i</sub> respectively. Because the properties of W and W' are distinct, the boundary with iron of the stability domain are also distinct. That is the reason of the existence of points A and B at the lower and upper end respectively of the corresponding curves in the phase diagram (see: (86Val) Tables IV & V). Limit compositions on these boundaries  $y_{\alpha(1)} = 0.9427$  or  $z_{\alpha(1)} = 0.0573$ , and  $y'_{\alpha(1')} = 0.9528$  or  $z_{\alpha(1')} = 0.0472$  of W1 and W'1 in equilibrium with  $\gamma\text{Fe-O}_e$  and  $\alpha\text{Fe-O}_e$ , were firstly proposed at points A and B respectively, both supposed at 1184 K, which cannot strictly occur.

In an extended careful review, **Wriedt (R-91Wri)** emphasized *the extraordinary aspect of the continuous isothermal nature [at 1184 K] of the W'1/W1, W'1/W2, W'2/W2, W'3/W2 and W'3/W3 sub-boundaries, and their relationship, if any, to the  $\alpha$ - $\gamma$  Fe transformation*. This pending question was put until the 80s.

Let us recall the basic equations governing the various equilibria between gases and solids (See equilibrium diagram in Fig. II-3). At the two boundaries involving  $\alpha\text{-Fe}_{\text{cr}}$  or  $\gamma\text{-Fe}_{\text{cr}}$ , equilibria can be expressed:

- on boundary  $\alpha\text{Fe}/\text{W}'1$  from point B to point C:

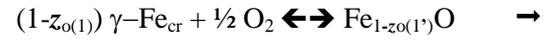


$$K_{\alpha,\text{gas}} = p_{\alpha}(\text{Fe}_{\text{gas}})$$



$$K_{(\alpha,\text{gaz})} = \exp(-\Delta G^{\circ}1_{(\text{gas})}/RT) = 1 / (p_1(\text{Fe}_{\text{gas}}) \cdot p'_{\alpha}{}^{1/2})$$

Similarly on boundary  $\text{Fe}\gamma/\text{W}1$  from point A to melting:



$$K_{\gamma}(\text{A}) = \exp(\Delta G^{\circ}\gamma/RT)$$



$$K_{\gamma,\text{gas}} = p_{\gamma}(\text{Fe}_{\text{gas}})$$



$$K_{(\gamma,\text{gaz})} = \exp(-\Delta G^{\circ}2_{(\text{gas})}/RT) = 1 / (p_2(\text{Fe}_{\text{gas}}) \cdot p'_{\gamma}{}^{1/2})$$

At the arbitrarily unique temperature of 1184 K, it should thus be necessary to apply two different partial pressures  $p_1$  and  $p_2$  of  $\text{Fe}(\text{gas})$ , at equilibrium with the solid, at A and B points. Obviously, at this unique  $\alpha \rightleftharpoons \gamma\text{Fe}$  equilibrium temperature, it exists only one value of the pressure  $p(\text{Fe}_{\text{gas}}) = 3.005 \times 10^{-11}$  atm. Thus, the A and B points cannot be at the same temperature.

NOTA: If T(A) and T(B) differ from a typical value of 4° (See reference (86Sjö) below), for example T(A) = 1191 K and T(B) = 1187 K, the partial pressures of iron are necessarily  $p(\text{A}) = p_1 = 3.692 \times 10^{-11}$  atm and  $p(\text{B}) = p_2 = 3.220 \times 10^{-11}$  atm ((82Pan) p. 153)((86Des) p.967-83). Thus, the differences between the two partial pressures  $p(\text{Fe})$  would be of the order of  $0.4 \times 10^{-11}$  atm. The corresponding partial pressures of oxygen are  $p'(A) = 4.829 \times 10^{-17}$  atm and  $p'(B) = 4.229 \times 10^{-17}$  atm, i.e. a difference of  $0.6 \times 10^{-17}$  atm. The compositions  $z_{\alpha}(\text{A}) = 0.0571$  and  $z_{\alpha}(\text{B}) = 0.0468$  would correspond to a gap of ~0.01 in composition.

Thus, in the case of the points A and B differing in temperatures T (A) and T (B), it must be taken into account that the compositions  $z_{\alpha}(\text{A})$  and  $z_{\alpha}(\text{B})$ , the partial pressures  $p'(\text{A})$  and  $p(\text{A})$ ,  $p'(\text{B})$  and  $p(\text{B})$  are necessarily different. Finally, a small difference in temperatures, probably a few degrees, should be determined experimentally in order to adjust this set of parameters determining the phase diagram (See Fig.II-3).

In this situation, the bottom line in Table IV (86Val) should be changed into a value of T(A) higher than 1184/1185 K, and the head line of Table V (86Val) in a value of T(B) also higher

than 1185 K but lower than T(A) by (see (86Val) p. 723 and 724).

### What about the isotherm at 1185 K?

Some experimental confirmations of this hypothetical separation were present in the literature. Several of them are indicated below.

- **Löhberg and Stannek** separated the pre-exponential term  $a$  and the energy term  $b = \Delta G/RT$  of an expression of Boltzmann type  $p_{\text{H}_2\text{O}}/p_{\text{H}_2} = a \cdot \exp(b \cdot z)$  expressed as a function of  $T^{-1}$  into two segments (See (75Lö) Fig. 8 and 9) intersecting in the vicinity of the  $\alpha \rightleftharpoons \gamma$  Fe transition temperature.
- Similarly, **Mrowec et al.** separated the determination of the self-diffusion coefficient of iron in wüstite as function of  $T^{-1}$  from their own results and several sets from the literature (See (81Jan) Fig. 7 p. 99). The intersection occurs for  $T^{-1} = 8.28 \cdot 10^{-4} \text{ K}^{-1}$  i.e. at 935°C of segments  $D_{\text{Fe}}$  vs  $T^{-1}$  attributed to  $W$  and  $W'$ .
- **Jacobsson and Rosén** (81Jac), **Guillemet and Per Gustafson** (85Gui), **Sjödén et al.** (86Sjö), **Grønvold et al.** (93Gro) published new experimental thermodynamic data of highly improved accuracy about the molar thermodynamic properties of iron and wüstite.
- **Sundman** in an assessment of the whole Fe-O system (R-91Sun) made particularly a modeling of the 'pure iron corner' (solid solutions  $\gamma\text{Fe-O}_\varepsilon$  and  $\alpha\text{Fe-O}_\varepsilon$ ) for which the assessment of **Spencer and Kubaschewski** (R-78Spe) shall also be referenced.
- A departure from a monotonous variation of the electromotive force (e.m.f.) of galvanic cells, near the  $\alpha \rightleftharpoons \gamma$  Fe transition, was evidenced from (81Jac) measurements at the iron/wüstite

electrode, in several galvanic cells, by **Sjödén et al.** (86Sjö). These latter published numerous determinations of the e.m.f. between 866.7 and 1339.3 K, measured in a galvanic cell equipped with a negative electrode constituted of the redox couple Fe/Fe<sub>y</sub>O (86Sjö). An anharmonic transitional zone between two separate continuous variations, not in continuation of each other, can be identified in the temperature range [1186-1194 K].

### Consequences concerning the Fe-O phase diagram.

The  $\alpha \rightleftharpoons \gamma$  Fe first order transition in the 'pure iron corner' of phase diagram Fe-O is insufficiently documented. On the left side in Figure II-3, are reported literature data concerning the domain of this transition (67Swi) (R-78Spe) (R-91Sun).

The temperature of the strictly pure  $\alpha\text{-Fe} \rightleftharpoons \gamma\text{-Fe}$  transition is tabulated at  $1184 \pm 3 \text{ K}$  in the data base NIST-Janaf ((98Cha) and 2011). At present, it is generally taken at 1185 K (point  $\emptyset$  in Fig. II-3).

The transition enthalpy is known with a 20% dispersion from assessed and experimental data, (See (85Gui): Table 3 p. 604). Very few experimental studies are available concerning the peritectoid invariant [ $\alpha\text{Fe-O}_\varepsilon$ ,  $\text{Fe}_{1-z}\text{O}$ ,  $\gamma\text{Fe-O}_\varepsilon$ ] close to the temperature of the pure  $\alpha\text{-Fe} \rightleftharpoons \gamma\text{-Fe}$  transition (67Swi). Sundman (R-91Sun) took up the molar fractions ( $\cong \varepsilon$  at point P,  $\varepsilon'$  at point b in Fig. II-3) of dissolved oxygen  $N_{\text{O}} = x/(1+x) = 16 \times 10^{-6}$  and  $6.8 \times 10^{-6}$  in  $\alpha$ - and  $\gamma$ -Fe respectively at 1185 K or 912 °C (Fig. II-3).

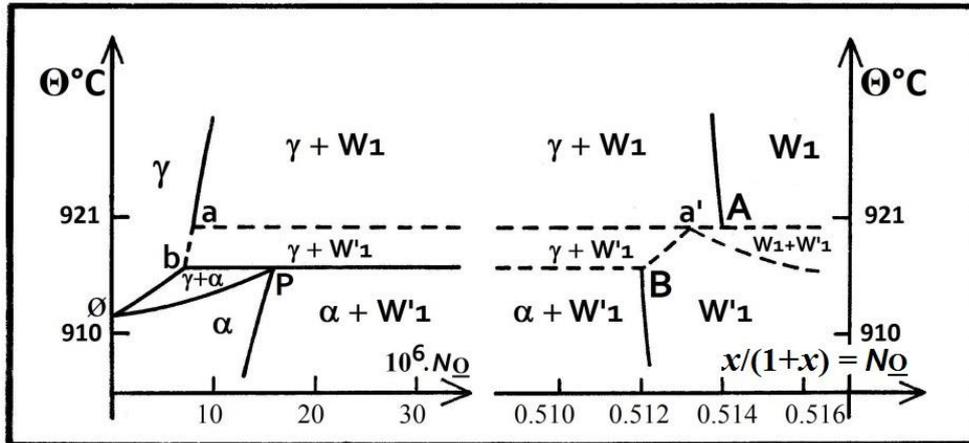


Fig. II-3 - 'Pure iron' corner. Equilibrium diagram between  $W_1$  and  $W'_1$  and 'pure iron', with both limit points A and B of  $\gamma$ -Fe/ $W_1$  and  $\alpha$ -Fe/ $W'_1$  boundaries. Compositions  $N_O = x/(1+x)$  of A and B are arbitrarily taken at 1184 K following ((86Val) Tables IV & V). Dashed lines correspond with hypothetical limits.

The separation of the boundary iron/wüstite into parts  $\gamma$ Fe- $O_\epsilon$ / $W_1$  from point A and  $\alpha$ Fe- $O_\epsilon$ / $W'_1$  from point B could arise distinctly in the temperature range characterized in (87Sjö) paper, following the phase diagram in right part of Fig. II-3. Two types of two-phase domains ( $\gamma + W'_1$ ) and ( $W_1 + W'_1$ ) have been necessarily added at the same time as an invariant point  $a'$  ( $W'_1, \gamma, W_1$ ). The right part of the diagram is in relation with the left part due to the existence of some symmetrical elements. Today, the location of points A and B remains to be determined precisely. New experiments would of course be necessary to confirm the preceding suggestions.

For the subdomain of  $W'$  below 911 °C, the information equivalent to that of  $W$  above 911 °C is of a more complicated access ((See (65Val) Fig. 6 and 7 p. 12 and 13). The two parts of the thermogravimetric isotherms are slightly curved.

Empirical relationship associated with the three  $W'_j$  requires a curvature term. The analytical expression was taken as follows:

$$l' = (a'_j T^{-1} + b'_j) x^2 + (c'_j T^{-1} + d'_j) x + (e'_j T^{-1} + f'_j) \quad (\text{II-4-(} a'_j - f'_j))$$

The coefficients ( $a'_j - f'_j$ ) are also given in ((89Val) Table 1 p. 210).

The above sets of numerical relations  $l'$  as functions of  $x$  and  $T^{-1}$  allowed determining transition lines or boundaries between domains of the pseudo phases  $W_1, W_2$  and  $W_3$  from  $\gamma$ -iron to magnetite between 1185 and around 1400 °C, and  $W'_1, W'_2$  and  $W'_3$  from  $\alpha$ -iron to magnetite between 1185 °C and 592 °C, at point C, as drawn in Figure II-4.

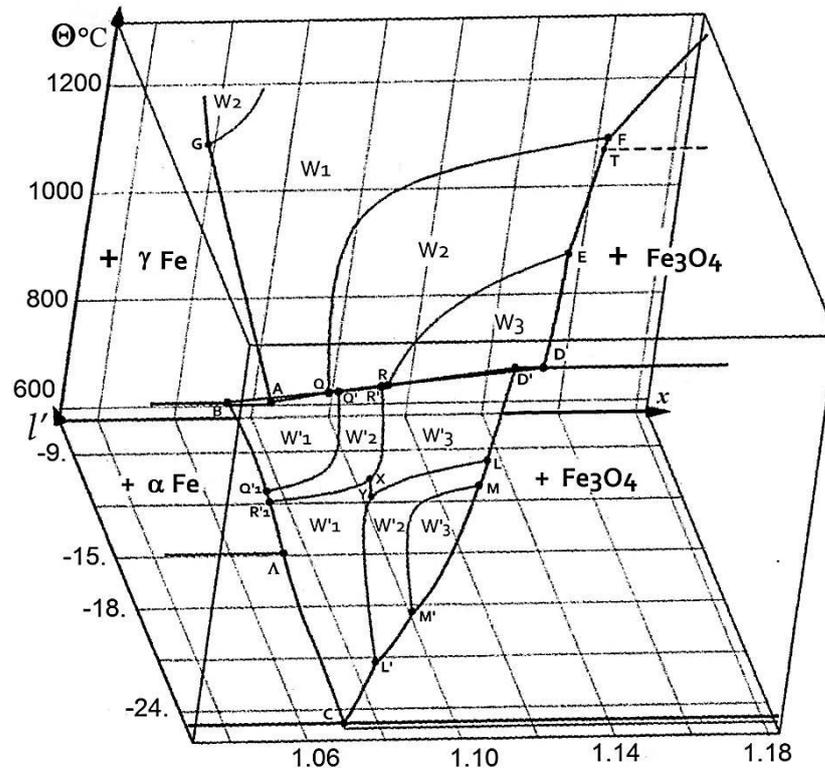


Fig. II-4 –Phase diagram  $\Theta(l', x)$  of solid wüstite  $\text{FeO}_x$  under equilibrium following Raccach-Vallet-Carel (64-89Val): upper temperature 1250 °C, lower one 592 °C at point C; coordinate  $l'$  for  $\log_{10}p(\text{O}_2)$ . Points noted by a capital letter are tabulated in (79Val), except point  $\Lambda$  in (86Val) and T in (87Val).

## 2 – First evidences of phase modifications or pseudo-phases in the literature

### Wagner jr's team

In the course of thermodynamics - defect structure approaches by Carl Wagner (36- 52Wag), Wagner jr's team identified some *unexpected changes in the slopes of  $\log \sigma$  vs.  $\log p_{\text{O}_2}$*  of the electrical conductivity at equilibrium (See (66Gei) Table IV p. 955 ; also Annexe 1 a-), at controlled T and  $p(\text{O}_2)$ . They stated that there is a *correlation between the estimated composition of the break of (their) curves and the compositions corresponding to Raccach et al. transitions*. So, for the first time out of Vallet's group, they experimentally identified the transitions  $W_i/W_j$  when using their own thermogravimetric measurements at equilibrium under  $\text{CO}_2/\text{CO}$  (67Swa). Their further studies will concern transport phenomena in the bulk and on the surface, principally in relation with the p to n transition.

### Fender's team

From numerous accurate electromotive force measurements in galvanic cells, Fender and Riley (69Fen) brought out of Vallet and Associates the second experimental confirmation of the likely existence of three pseudo-phases, and the location of the boundaries of the subdomains in the range 700-1350 °C. Their plot of the equilibrium diagram is in fairly agreement with that of Vallet *et al.* (See Annex 1, Fig. A1-1).

Fender and Riley (69Fen), then later Vallet and Carel (86Val) assessed the partial molar properties of solution of oxygen ( $\Delta \bar{H}_{\text{O}} \equiv \bar{H}_{\text{O}} - \frac{1}{2}H^{\circ}_{\text{O}_2}$ ,  $\Delta \bar{S}_{\text{O}} \equiv \bar{S}_{\text{O}} - \frac{1}{2}S^{\circ}_{\text{O}_2}$ ) as functions of  $y \in [0.945 - 0.853]$  for the three pseudo phases  $W_i$  named also  $w\text{I}$ ,  $w\text{II}$  and  $w\text{III}$  (See (69Fen) Table I p. 796, and in Fig. II-6 below). The following relations were drawn up by (86Val):

$$\Delta \bar{H}_{\text{O}} = 19.14475(a_i \cdot x + c_i), \quad \Delta \bar{S}_{\text{O}} = -19.1447(b_i \cdot x + d_i) \quad (\text{II-5})$$

for the 3  $W_i$  ( $i=1,2,3$ ) at  $T > 1184$  K;

$$(\Delta \bar{H}_O)' = 19.14475 (a'_j x^2 + c'_j x + e'_j), \quad (\Delta \bar{S}_O)' = -19.14475 (b'_j x^2 + d'_j x + f'_j) \quad (\text{II-6})$$

for the 3 W<sup>j</sup> (j=1,2,3) at T < 1184 K.

The coefficients a<sub>i</sub> - d<sub>i</sub> given in § II.2. above 1184 K are those in the initial relation

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

Coefficients (a'<sub>j</sub> - f'<sub>j</sub>) below 1184 K are given in (89Val, See Table 1 p. 210).

Relations (II-5) for the W<sub>i</sub>, and (II-6) for the W<sup>j</sup> are independent of T, in accordance with the

property of regularity of the solid solution wüstite identified in (62Rac1).

### 3 - Converging point Ω

Among numerous sets of determination of ΔH<sub>O</sub>, directly evaluated or analytically derived such as (69Fen), (70Mar) or (63- 64- 86Val) respectively, some of them are represented in Figure II-5.

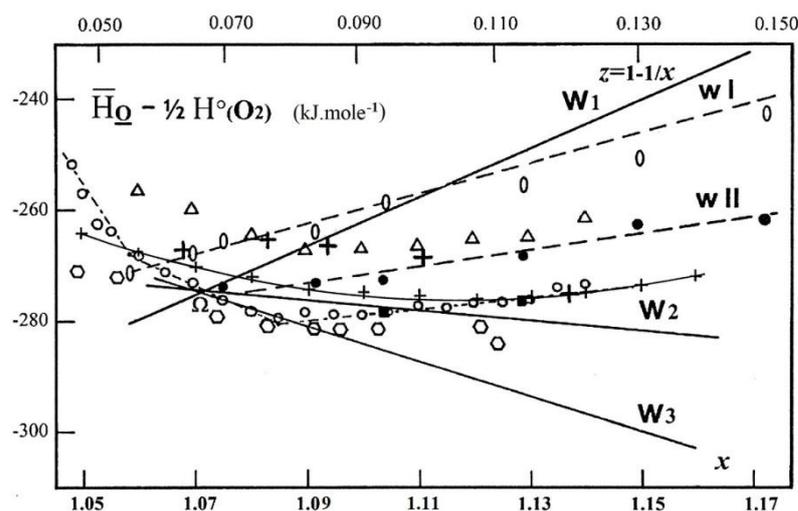


Fig. II-5 - ΔH<sub>O</sub> from some authors.

— : Derived by Vallet & Carel (86Val) for the W<sub>i</sub> (i=1-3) *i.e.* at T ∈ [1193-1523 K] from thermogravimetry + CO<sub>2</sub>/CO; ○-○: w I, ●-●: w II, and ■: w III (two points only) by Fender and Riley (69Fen) for the three w I (I=I-III) from emf at T ∈ [1023-1623 K]; dash-dot line ○-...-○: Gerdanian *et al.* (70Mar) from calorimetry at 1348 K under vacuum (+ δn<sub>O2</sub>); +: Asao *et al.* (70Asa) from emf at T ∈ [873-1273 K]; Δ: Takayama and Kimizuka (80Tak) from thermogravimetry + CO<sub>2</sub>/H<sub>2</sub> at T ∈ [1373-1673 K]; ◊: Barbero *et al.* (81Bar) from emf at T ∈ [823-1323 K]; †: Lykasov *et al.* (82Lyk) (R-87Lyk) emf data at T ∈ [873-1373 K].

A convergence in the vicinity of the common intersection point Ω at x = 1.0713 (±0.001) of the straight lines from relations (II-5) is globally noticed. Contrary to this contrived amalgam process, the next numerical adjustments are related principally to the initial Raccah's results (62Rac3) (65Val) which form a numerous and coherent set at

equilibrium, and for which it exists now a systematic interpretation by Vallet's group (86-89Val).

The graphical representation of the relations (II-5) and (II-6) for the isotherms at 1000 and 820 °C respectively is given in Fig. II-6.

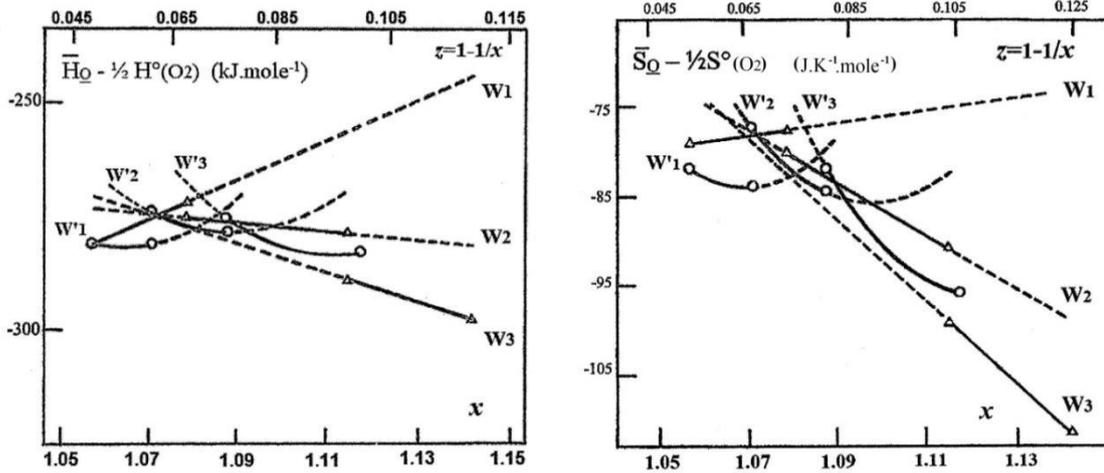


Fig. II-6- Partial molar enthalpy ( $\bar{H}_Q - \frac{1}{2}H^{\circ}(O_2)$ ) and entropy ( $\bar{S}_Q - \frac{1}{2}S^{\circ}(O_2)$ ) of solution of oxygen through the stability field of wüstite whatever the temperature. Continuous lines are in stability domains at 820 °C (W'i) and 1000 °C (Wi), dashed lines in extrapolated or metastable zones.

**The isotherm at 1000 °C:** the three Wi's are represented by linear successive segments. For the two transitions  $W_i \rightarrow W_j$  at decreasing iron content, a jump is observed toward the *lower* molar heat and entropy of solution which are exothermic and -entropic. For  $x_{1/2} = 1.078$ :  $\delta(\Delta\bar{H}_Q) = -3.5$  kJ,  $\delta(\Delta\bar{S}_Q) = -2.3$  J.K<sup>-1</sup>, and  $x_{2/3} = 1.1154$ :  $\delta(\Delta\bar{H}_Q) = -10.5$  kJ,  $\delta(\Delta\bar{S}_Q) = -8.3$  J.K<sup>-1</sup>.

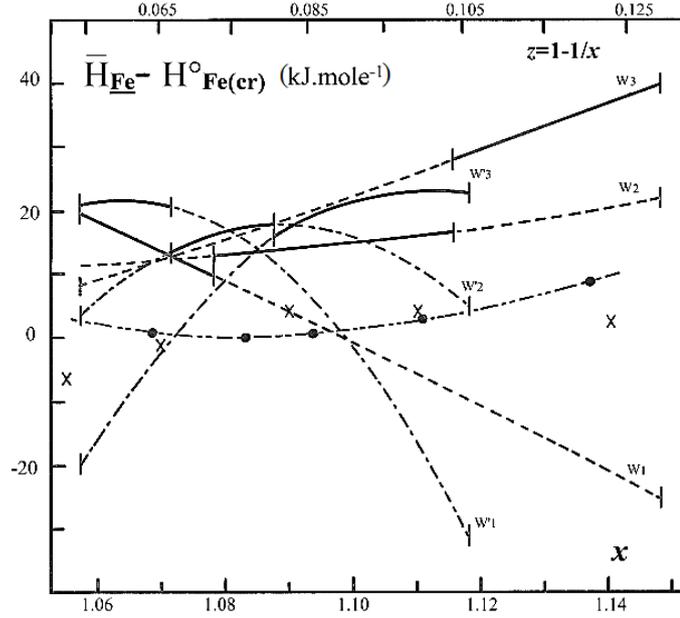
Above 1184 K, the exothermic  $\Delta\bar{H}_Q$  for W1 increases with  $x$  and  $z$  at the time of  $\underline{Q}$  dissolution. For each  $\underline{Q}$  a vacancy and electronic hole(s) are created (See below  $\frac{1}{2} O_2 \leftrightarrow O + V_{Fe}^{q(1)} + q h^{\circ}$ , eq.(11)) at the same time as the clustering is in progress. For W3 it is decreasing with  $x$ , probably because of the long-range ordering. For W2,  $\Delta\bar{H}_Q$  varies intermediately between W1 and W3, which corresponds to the observation by (69Fen) that W2 would be a solid solution of W1 and W3.

Below 1184 K, the variations are no more linear because the slight curvature of the isotherms  $l' = f(x)$  was expressed by a parabolic term (See (79-86- 89Val)). The variations are weaker for the three W'j. Nevertheless, an approximate convergence of parabolas  $\Delta\bar{H}_Q(x)$  is observed for  $x = 1.0852$  or  $y =$

$1-z = 0.9215 (\pm 0.004)$ , which is not so precisely defined in W' as it is in W, and at a composition different from that of point C ( $y = 0.935$ ).

**Isotherm at 820 °C:** the three W'i are represented by parabolic lines. A jump (weaker in amplitude than the one at 1000 °C) is observed toward the *higher* values for the exothermic transitions  $W'_i \rightarrow W'_j$ ,  $x_{1/2} = 1.071$ :  $\delta(\Delta\bar{H}_Q) = +10.9$  kJ,  $\delta(\Delta\bar{S}_Q) = +6.3$  J.K<sup>-1</sup> and  $x_{2/3} = 1.1154$ :  $\delta(\Delta\bar{H}_Q) = +2.9$  kJ,  $\delta(\Delta\bar{S}_Q) = +2.7$  J.K<sup>-1</sup>.

The Gibbs - Duhem relation leads to the iron solution property  $\Delta\bar{H}_{Fe}$  from  $\Delta\bar{H}_Q$  (Fig. II-7). In the domain of W, exothermic transitional jumps are observed toward the *higher* values for the two transitions  $W_i \rightarrow W_{i+1}$  at equilibrium. At 1000 °C, the transition W1/W2 ( $x_{1/2} = 1.0782$ ) is characterized by  $\delta(\Delta\bar{H}_{Fe})_{1/2} = 3.25$  kJ.mole<sup>-1</sup>,  $\delta(\Delta\bar{S}_{Fe})_{1/2} = 2.56$  J.K<sup>-1</sup>.mole<sup>-1</sup>, the transition W2/W3 ( $x_{2/3} = 1.1164$ ) is characterized by  $\delta(\Delta\bar{H}_{Fe})_{2/3} = 12.06$  kJ.mole<sup>-1</sup>,  $\delta(\Delta\bar{S}_{Fe})_{2/3} = 9.47$  J.K<sup>-1</sup>.mole<sup>-1</sup>. In the domain of W' the equivalent jumps are exothermic as shown in Fig. II-7 drawn for transitions at 820 °C.



**Fig. II-7- Variations of the partial molar enthalpy ( $\bar{H}_{Fe} - H^{\circ}_{Fe(cr)}$ ) vs  $x$  for the isotherms at 1000 °C ( $W_i$ ) and 820 °C ( $W'_j$ ). For comparison: ●- -●:  $\Delta\bar{H}_{Fe}$  from e.m.f. measurements at 1000 °C by Asao *et al.* [(70Asa) Table 3 p. 75]; ×: Darken and Gurry determinations [(45Dar) Table X p. 1408 ].**

At increasing iron deficiency, the partial molar enthalpy of iron solution  $\Delta\bar{H}_{Fe}$  is decreasing for  $W_1$  and increasing for  $W_3$  as opposite to  $\Delta\bar{H}_O$ . The five determinations of Asao (70Asa) at 1000°C are distributed on a curve noticeably parallel to the set of the successive segments concerning  $W_1$ ,  $W_2$  and  $W_3$ .

For the first time, the 3 ‘varieties’  $W_i$  of solid wüstite were defined in (63Val). Equations  $x_{i/i+1}(T)$  of the lines -the so-called boundaries- separating the areas of stability of the single phases  $W_i$  and  $W_{i+1}$  were then adjusted. Analytically their equations are

$$x_{i/i+1} = \frac{[(c_{i+1} - c_i) + T.(d_{i+1} - d_i)]}{[(a_i - a_{i+1}) + T.(b_i - b_{i+1})]}$$

Numerically, they are

$$x_{1/2} = (60412.0 - 41.3182T) / (56322.3 - 38.5509T) \quad (II-8)$$

and

$$x_{2/3} = (25297.2 - 18.310T) / (23670.0 - 17.1941T) \quad (II-9)$$

A metastable boundary can also be envisaged:

$$x_{1/3} = (85709.2 - 59.6282T) / (79992.3 - 55.7450T) \quad (II-10)$$

The authors (63Val) remarked that *the corresponding terms in numerator and denominator [of equations (II-8), (II-9) and (II-10)] are not far from proportionality following the same ratio, close to 1.07:  $(c_{i+1} - c_i) / (a_i - a_{i+1}) = (d_{i+1} - d_i) / (b_i - b_{i+1}) \cong 1.07$* , also close to Chaudron’s point composition. It results that ‘*the three oxygen pressures  $p'_1$ ,  $p'_2$  and  $p'_3$  at equilibrium with  $W_1$ ,  $W_2$  and  $W_3$  respectively are nearly identical for  $x \cong 1.07$ ’ at a given temperature, for examples  $p' = 8 \cdot 10^{-17}$ ,  $4 \cdot 10^{-15}$ ,  $8 \cdot 10^{-11}$  atm. whatever being  $i$  at 1184, 1273, 1573 K respectively. It is the reason why the property  $\Delta\bar{H}_O$  ( $= -274.8 \text{ kJ.mol}^{-1}$ ) of equation (6-h) is shared by the three  $W_i$ ’s with the same composition  $x \cong 1.07$  under the same equilibrium oxygen potential. That explains also why the oxygen partial molar properties vs  $x$  converge at point  $\Omega$ . The iron partial molar properties also converge for  $\Delta\bar{H}_{Fe} = +87.8 \text{ kJ.mol}^{-1}$  at 1000°C.*

At invariant point C ( $\alpha$ -Fe,  $W'_1$ ,  $Fe_3O_4$ ) of abscissa  $x_C = 1.070_0$ , these properties are merged ( $\Delta\bar{H}_O = -290.4 \text{ kJ.mol}^{-1}$ ,  $\Delta\bar{H}_{Fe} = +21.4 \text{ kJ.mol}^{-1}$ ) (86Val).

It is noticeable that a common *kinetical origin*  $\omega$  is characterized by  $x = 1.070 \pm 0.001$  in W' (See Annex 2 « Kinetics at 850 °C by (10Wor) »).

#### 4 - The triple point out of equilibrium (W1, W2, W3)

"Point 8 (W1, W2, W3)" (See (64Val) Table III p. 3681) was determined at intersection of the extrapolated boundaries W1/W2 and W2/W3 at temperature 302 °C and composition  $y = 0.9322$ , directly below point  $\Omega$  (See Fig. 6) and point C with  $y_C \cong 0.935_0$ . Manenc *et al.* observed a disproportionation near 300 °C in a gap of miscibility by slow drop in temperature (64Her, 68Man). Fender and Riley remarked about wII that "This behavior of  $[\partial \Delta \bar{G}_Q \text{ vs } 1-x]/\partial T$  in wII region is characteristic of a two-phase system above its critical temperature (...) Extrapolation into a metastable  $Fe_{1-x}O$  phase indicates that phase separation into wI and wIII [not explicitly demonstrated] would occur near 315 °C" (69Fen).

As soon as 1977, **Andersson and Sletnes** (77And) studied at the same time the ordering and the preceding behavior below 300 °C in reference with the spinodal decomposition (71Mor) by electron diffraction and microscopy (dark field images). Typical patterns were attributed to the phase P' (periodicity of  $2.6a_0$ ), in the composition interval  $y (Fe_yO) \in [0.95-0.92]$ . After heat treatment for 20 mn at 300 °C, a tetragonal or orthorhombic symmetry would be observed "also from the shape of the ordered P'-type regions". For compositions less than  $y = 0.91$  in  $Fe_{0.91}O$ , the more ordered structure identified as P'' was observed even after quenching. Its parameters would be  $a=b=c=5a_0$ .

These different observations would indicate that W2 could be a solid solution of W1 and W3 (See (R-10Des) p. 91-96), which also seems to be showed in the numerical determinations of  $[\Delta \bar{H}_{Fe}(x)]_i$  below.

#### 5 -Trends to disorder-order in the subphases at increasing z

The difference  $[\Delta \bar{H}_{Fe}(x)]_i^e$  between the partial molar property of iron in  $(FeO_x)_i$  and  $FeO_{x_{o(i)}}$  on the boundary with Fe was early envisaged as a property of "excess type" in order to tentatively

establish links between thermodynamic and structural properties (65Kle).

The corresponding formalism previously established for  $[\bar{H}_Q(x)]_i, [\bar{H}_{Fe}(x)]_i, [\bar{S}_Q(x)]_i$  and  $[\bar{S}_{Fe}(x)]_i$  (See Figs. II-7 and II-8 above) becomes simply

$$[\Delta \bar{H}_Q(x)]_i^e = [\bar{H}_Q(x) - \bar{H}_Q(x_o)]_i = 19.14475(a_i/2(x-x_{o(i)})) \quad (II-11)$$

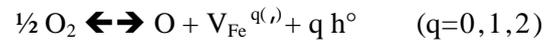
$$[\Delta \bar{S}_Q(x)]_i^e = [\bar{S}_Q(x) - \bar{S}_Q(x_o)]_i = -19.14475(b_i/2(x-x_{o(i)})) \quad (II-12)$$

$$[\Delta \bar{H}_{Fe}(x)]_i^e = [\bar{H}_{Fe}(x) - \bar{H}_{Fe}(x_o)]_i = -19.14475(a_i/4(x^2 - x_{o(i)}^2)) \quad (II-13)$$

$$[\Delta \bar{S}_{Fe}(x)]_i^e = [\bar{S}_{Fe}(x) - \bar{S}_{Fe}(x_o)]_i = 19.14475(b_i/4(x^2 - x_{o(i)}^2)) \quad (II-14)$$

When changing the coefficients  $a_i, b_i$  and  $x_{o(i)}$  on the  $\gamma$ -Fe/ $W_{o(i)}$  boundary to their numerical values at 1273 K, the Table II above is yielded in  $J.mole^{-1}$  and  $J.K^{-1}.mole^{-1}$  for  $\bar{H}$  and  $\bar{S}$  respectively.

The term  $[\Delta \bar{H}_{Fe}(y)]_i^e$  is determined from the corresponding term for oxygen Q by means of the Gibbs-Duhem relation. Its sign as well as the one of its derivative  $\partial/\partial x$  is the sign of  $-a_i$ . So, this term corresponds to the energetic effect  $\delta U$  on the iron lattice, in the interaction between  $1/2 O_2$  and a mole of  $FeO_x$  to which it is added, at constant iron content. For each additional Q, a vacancy and zero, one or two electronic hole(s) are created following:



The numerical values of  $[\Delta \bar{H}_{Fe}]_i^e$  in Table II show that :

- for W1, the internal energy  $U_m$  of iron lattice (the term  $P\Delta V_m$  is negligible compared to the contribution  $\Delta U_m$  in  $\Delta H_m$ ) decreases as z increases, which could correspond to the exothermic formation energy of clusters (m:n) that are thus favored (See Gokcen (R-75Gok) p. 241-44 , Gokcen (R-86Gok) p. 43-49, Desré and Hodaj (R-10Des) pp.57-58, 76-83);
- oppositely, W3 would be characterized by an increase in the lattice energy, which would correspond to the completion of the cluster percolation and the formation of the

superstructure (2.55a x 2.55a x 2.55a) calls P'' •  
by Manenc (63-68Man) and HREM  
characterizes by (74Iij);

probably because W2 would be a solid solution  
of W1 and W3, the variation of  $U_m$   
is intermediate (See (69Fen) and in Fig. II-8  
above).

**TABLE II.1 - Variations of the four "excess properties" (relations (II-11 to 14 below) at 1273 K**

FeO <sub>x</sub> /Fe <sub>1-z</sub> O	$x=1.0950$ or $z=0.0868$	$x=1.1420$ or $z=0.1243$
W1: $a_1= 46753.4$ $b_1= -7.3781$ $x_{o(1)}= 1.0572^*$ $z_{o(1)}= 0.0541$	$[\Delta\bar{H}_O]_1^e$ $[\Delta\bar{H}_{Fe}]_1^{e**}$ 16.90 -18.19 $[\Delta\bar{S}_O]_1^e$ $[\Delta\bar{S}_{Fe}]_1^{e**}$ 2.67 -2.87	$[\Delta\bar{H}_O]_1^e$ $[\Delta\bar{H}_{Fe}]_1^e$ 37.94 -41.72 $[\Delta\bar{S}_O]_1^e$ $[\Delta\bar{S}_{Fe}]_1^e$ 5.99 -6.58
W2: $a_2= -9568.9$ $b_2= 31.1728$ $x_{o(2)}= 1.0522$ $z_{o(2)}= 0.0496$	$[\Delta\bar{H}_O]_2^e$ $[\Delta\bar{H}_{Fe}]_2^e$ -3.92 4.21 $[\Delta\bar{S}_O]_2^e$ $[\Delta\bar{S}_{Fe}]_2^e$ -12.78 13.76	$[\Delta\bar{H}_O]_2^e$ $[\Delta\bar{H}_{Fe}]_2^e$ -8.23 9.03 $[\Delta\bar{S}_O]_2^e$ $[\Delta\bar{S}_{Fe}]_2^e$ -26.80 29.41
W3: $a_3= -33238.9$ $b_3= 48.3669$ $x_{o(3)}= 1.0482$ $z_{o(3)}= 0.0460$	$[\Delta\bar{H}_O]_3^e$ $[\Delta\bar{H}_{Fe}]_3^e$ -14.90 15.97 $[\Delta\bar{S}_O]_3^e$ $[\Delta\bar{S}_{Fe}]_3^e$ -21.68 23.24	$[\Delta\bar{H}_O]_3^e$ $[\Delta\bar{H}_{Fe}]_3^e$ -29.85 32.69 $[\Delta\bar{S}_O]_3^e$ $[\Delta\bar{S}_{Fe}]_3^e$ -43.44 47.57

\* For  $x= x_{o(i)}$ , all terms are equal to zero. \*\* The terms  $[\Delta\bar{H}_O]_i^e$  and  $[\Delta\bar{H}_{Fe}]_i^e$   
are expressed in  $\text{kJ}\cdot\text{mol}^{-1}$ , and the terms  $[\Delta\bar{S}_O]_i^e$  and  $[\Delta\bar{S}_{Fe}]_i^e$  in  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

Such trends were previously discussed by Fender  
and Riley (See (69Fen) p. 797) when considering  
 $\Delta\bar{G}_O$  and  $\Delta\bar{H}_O$ .

The positive and negative values of the term  
 $[\Delta\bar{S}_O]_i^e$  would correspond mainly to a vibrational  
entropy change (R-00Smy), without transpositional  
mixing effect (69Lyk). In the case of the  
disordered pseudo-phase W1, their variations  
would indicate a weak increase with  $z$  of the  
vibration frequency of the  $O$  lattice. In the case of  
the ordered pseudo-phase W3, they would suggest  
a strong decrease with  $z$  of this vibration  
frequency. These entropy variations could be  
related to the increasing frequency of the Fe-O  
bond because of an increased ordering (i.e. the  
presence of larger clusters and/or an increasing  
degree of percolation of them), involving a  
superstructure resulting from the percolation  
completion. The pseudo-phase W2 would appear at  
the starting of the percolation of clusters: at this  
stage, the lattice would become more rigid.

**6 - Burgmann** (R-75Bur) gathered some  
experimental results about the three  $W_i$ , the  
electrical conductivity and the transition p-to-n.  
Because of his own work concerning pyrrhotine  
Fe<sub>1-z</sub>S (68Bur), and numerous analogies with  
wüstite, he tentatively described the defect  
structure in terms of clusters (See (R-75Bur) Fig. 5  
p. 173). He proposed a conduction model  
involving the formation of an acceptor band or of  
new states produced by the interaction of defects as  
 $z$  increases. The lattice contraction reduces the gap  
between the valence and conduction bands,  
inducing a p to n transition for compositions  $z=$   
 $1/12 = 0.083$  at 900 °C and  $z = 1/13 = 0.076$  at  
1300 °C (See (R-75Bur) Fig. 5 p. 173 and Hillegas  
and Wagner jr (68Hil)). Such an overlap was  
envisaged later by Molenda (87Mol).

#### Manenc's phases.

Using X-ray diffraction, J. Manenc (63- 68Man)  
characterized the phases, (rapidly) quenched into  
water, that he named P and P'. For an iron rich

wüstite ( $z < 0.08$ ), vacancies and ions  $\text{Fe}^{3+}$  seems to be randomly distributed. This was the phase P characteristic of the weakly lacunary NaCl-type structure alone. Other diffraction patterns of more iron deficient samples ( $0.08 < z < 0.11$ ) had additional reflections corresponding to a cubic cell with a repeating distance  $2.6a_0$ . Diffuse trails parallel to  $\langle 100 \rangle$  directions connected these reflections. That was the phase P' alloyed with P, and individually observed only in "oxygen rich" samples. Iron vacancies would be ordered in them. Diffraction on a heated single crystal such as  $z = 0.08$  proves that the superstructure exists in the range  $800\text{ }^\circ\text{C} - 1000\text{ }^\circ\text{C}$  when  $z = 0.11$ . The phase P'' is observed in wüstite such as  $z \cong 0.10$  near  $300\text{ }^\circ\text{C}$ , when slowly cooling, at the threshold of disproportionation giving Fe and  $\text{Fe}_3\text{O}_4$ . New superstructure lines are then characteristic of a commensurate 5X cubic cell. The most iron deficient samples are constituted of this phase only.

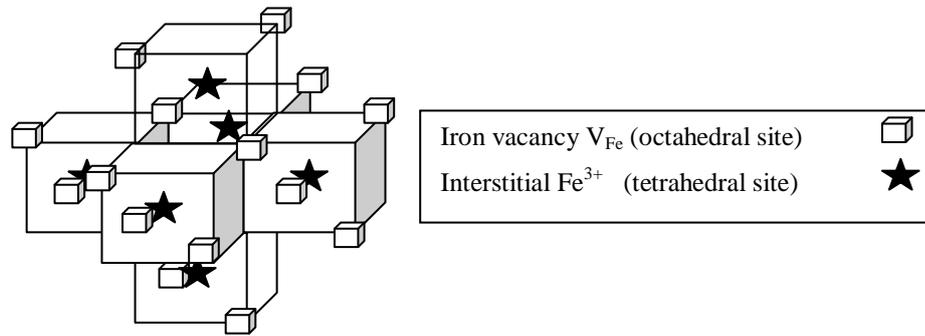
**Greenwood-Howe's** Mössbauer spectra were interpreted in modeling the asymmetrical doublet allowing evidencing "*slightly differing defect structures anticipated by Vallet & Raccach (65Val), and Fender & Riley (69Fen) at high temperature*" (72Gre). The quenching process would produce nuclei leading to Manenc phases P, P', P'' [(P+P') for  $z \in [0.05-0.08]$ , (P') for  $z \in [0.08-0.10]$ , and (P'') for  $z > 0.10$ ] below point C, detectable by fine variations of quadrupole splitting resulting from cubic symmetry distortions. These latter are evaluated for "single cluster" (4:1) and Koch and Cohen "four-fold cluster" (13:4). From a sample such as  $z \cong 0.05$ , the disproportionation would give rise to  $\text{Fe}_{0.918}\text{O}$  (defect rich phase P') and  $\text{Fe}_{0.976}\text{O}$  (defect poor phase P) because of a mixture of clusters (13:4) and (4:1).

Among numerous Mössbauer studies reviewed by Long and Grandjean (R-91Lon), let us reference Checherskaya *et al.* (72Rom) (73Che), Hryniewicz *et al.* (72Hry), Pattek-Janczyk *et al.* (86Pat). The latter authors modeled the asymmetric doublet with "a singlet" bearing on the contribution of the  $\text{Fe}^{3+}$  in tetrahedral sites, and

two "crossed doublets" everyone bearing on a contribution of the octahedral  $\text{Fe}^{3+}$ . They attributed the maximum observed in the variation of the quadrupole splitting to the p-n transition by (62Tan). That would be the transition « metal  $\leftrightarrow$  Mott insulator » identified by Molenda *et al.* (87Mol).

**Goodenough's** modeling was proposed as soon as 1971. Considering the relations  $z \propto (p')^{1/s}$  (61Smy) associated with thermogravimetry analyses, and  $\sigma \propto (p')^{1/s}$  corresponding to conductivity from Wagner jr *et al.* (66Gei), the result  $s=6$  in W1 subdomain above  $1060\text{ }^\circ\text{C}$  could characterize a statistical distribution of vacancies and electronic holes ( $\text{Fe}^{3+}$ ), possibly corresponding to Manenc's phase P (68Man). Below  $1060\text{ }^\circ\text{C}$ , the modifications in s values with  $4 < s < 6$  could correspond to an increasing association between vacancies and holes. In the W2 domain, triplets  $\text{Fe}^{3+} - \text{V}_{\text{Fe}} - \text{Fe}^{3+}$  would be partly ordered, improving Madelung energy. Numerous clusters (4:1) which could cooperatively form a superstructure in the quenched wüstite by Koch & Cohen (69Koc) would correspond to W3. A mapping of transfers of iron ions, and electronic exchanges is proposed, needing *small polarons* between charge carriers related to energy differences between the top of the valence band and an acceptor level (R-71Goo). Later, this author with Gleitzer (*See Section III §9 below*) will consider again the wüstite in the point of view of its electronic properties and crystallographic structure (85Glei).

**Zvintchuk's team.** Tchiong Tki Khong *et al.* (73Tch), in collaboration with J. Manenc, studied samples of wüstite of composition  $z \in [0.065-0.108]$  quenched from  $1100\text{ }^\circ\text{C}$ . Electron diffraction allowed evidencing three 'forms' I, II and III corresponding to the modifications wI, wII and wIII of the phase diagram by Fender and Riley (69Fen). They described a (16:6) defect complex of point symmetry  $m\bar{3}m$ , formed of six tetrahedral corner sharing clusters (4:1), distributed on the six faces of an empty cube. This cluster is represented on Figure II-8. An obvious correspondence of phases P, P', P'' with the three Wi is specified.

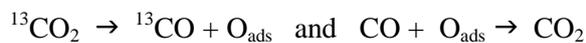


**Fig. II-8 –The m3m cluster (16:6) of <110> type corresponding to  $(z+t)/t = 2.66$ , from Tchieng Tki Khong *et al.* (73Tch)**

**7 - Kinetic transitions.** More than 40 years after Vallet *et al.* (63- 64- 65Val), Wagner jr *et al.* (66Gei) and Fender & Riley (69Fen), **Worral and Coley** (10Wor) evidenced kinetic transitions evidently related to the pseudo phases. Following the process initiated by Temkin *et al.* (59Str) at the surface of iron oxides, then applied by Grabke (65Gra), Belton *et al.* (81Cra), Sano *et al.* (96Mor), later Zhang *et al.* (12Hu) (13Zha), Worral and Coley studied the kinetics of the change in the equilibrium of  $CO_2/CO$  mixtures in which a measured proportion of  $^{13}CO_2$  species was introduced. In such a condition, a specific equilibrium of the carbon isotopes is established following the equation of exchange:



which can be envisaged as the sum of the two half-reactions



These half-reactions reflect oxygen exchange on the surface, and would be conditioned by the electronic structure in the bulk.

The apparent rate constant is expressed as function of oxygen activity following

$$k_a = k_0 \cdot a_O^{-m} \quad \text{or} \quad \log k_a = -m \cdot \log a_O + \log k_0$$

The variation of  $\log k_a$  with the activity  $a_O$  defined as being the ratio  $p(CO_2)/p(CO)$ , can be described by three successive linear segments at 995 °C, with  $m = 0.51$  (w1), 0.66 (w2), 1.03 (w3) by ((10Wor), Fig. 8 and equations [36]-[38]).

The authors observed only one transition attributed to two pseudo phases w'1-2 and w'3 along the isotherm at 850 °C, because no change was observed in the vicinity of the forecasted boundary w'1/w'2. The only observed transition appears as a discontinuity at the location of the transition W'2  $\leftrightarrow$  W'3 forecasted for  $x = 1.090$  at equilibrium.

Nevertheless, they admitted that three pseudo-phases w'1, w'2 and w'3 probably existed, but two of them could not be separated, because they were undetectable by electrical conductivity (66Gei), and their kinetics analyses, or maybe '*obscured by the scatter*'. Finally, Worral and Coley declared that, in their study, transitions at 850 °C and 995 °C were observed (except W'1/W'2) '*correspond(ing) exactly with the proposed pseudo-phase boundaries*' in quite good agreement with the phase diagram by Vallet and Carel (89Val).

Because of the identity of coefficients  $m$  in the correlations concerning  $W_i$  and  $W'_j$  of identical rank they attributed in their following paper (R-13Wor) three predominant clusters (7:2) type II to w1 and w'1, (12:4) type II to w2 and w'2 and (16:5) type I to w3 and w'3.

NOTA: In Annex 2, a graphical and numerical re-analyze of Fig 9 by ((10Wor) p. 821) shows a possible separation of three sets of the data at 850 °C which can likely correspond to the three  $W'_j$ , provided that some data or groups of them are located in a subdomain not corresponding to the previous stable one.

## 8 - Takayama and Kimizuka's phase modifications

Using thermogravimetric analyses under equilibrium oxygen pressure  $p'$  defined by CO<sub>2</sub>/H<sub>2</sub> mixtures, Takayama and Kimizuka (80Tak) observed significant modifications in curves representing  $\log x$  vs  $l'$  in FeO<sub>x</sub> as display in Fig. II-9, where the composition parameter is  $z$ .

The authors concluded to a transition between « pseudo phases » (See (80Tak) Table I and Annex 1 d-). Their conclusion agreed with the one of Bransky and Hed in the same domain of temperature (68Bra) (See also Annex 1 b-), but disagreed with results of Fender and Vallet, particularly with the latter whose isotherms have no break above 911 °C.

Typical changes in slopes are clearly observed from their data. To illustrate their results, we have

transformed their representations for one temperature T=1250 °C. For this temperature, their data were interpreted in terms of only two relations

- For low  $x$  values ( $x = 1/(1-z)$ ):  
 $l' = M_1 \cdot x + B_1 = 28.512 x - 41.366$
- For high  $x$  values:  
 $l' = M_2 \cdot x + B_2 = 23.288 x - 35.715$

The new representations  $l'$  vs  $\log z$  are represented in Fig. II.9. Two coefficients  $s$  might be defined in a first step, using the hypothesis of a transition implying two pseudo-phases proposed by the authors (80Tak):  $s$  close to 4 and  $s$  close to 7.5. However, three correlations could be defined from this representation as following

$$l' = 4.4539 \log z - 5.5685, \quad l' = 6.1378 \log z - 3.6876, \quad l' = 9.5059 \log z - 0.5046.$$

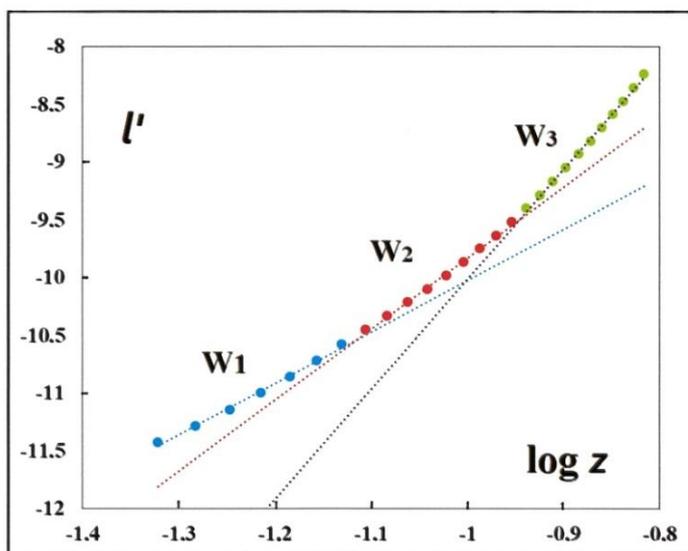


Fig. II-9 - Variation of  $l'$  vs.  $\log z$  for Fe<sub>1-z</sub>O at 1250 °C. Three sets of data can be defined as three linear relations.

From these relationships, it is possible to derive the three  $s$  values 4.5 (low  $z$ ), 6.1 (intermediate  $z$ ) and 9.5 (high  $z$ ). A first domain for low  $z$  values gives a first coefficient  $s = 4.5$ . A second domain appears as being nonlinear, with an average slope giving  $s=7.5$ . However, due to the curvature of the representation it might be possible to interpret this nonlinear domain in terms of two linear domains with two coefficients  $s = 6.1$  and  $s = 9.5$ . These

two last coefficients are quite close to the ones obtained from the Vallet *et al.*' data.

## 9- Percolation. Electrical transitions.

In an extensive review about electric properties, Gleitzer (R-Gle) points out that the electric conductivity of wüstite “cannot be understood without percolation models which take into account the cluster populations as function of

temperature and oxygen activity". Because of this common stress, the characterization of the p-n transition and that of the electronic structure are not easy to correlate. Because the percolation process is characterized experimentally by a brief steep variation of the studied property at a threshold composition, the curves of the electrical conductivity vs composition (63Ari) (66Gei) (67Koz) can be interpreted in terms of upgradable clusters and long-range ordering in the subdomains of W1, W2 and W3.

In a lower section (See § IV, Fig. IV-1), we give a schematic representation of a statistical distribution of clusters with two types of percolation modes through the phase diagram. This could structurally justify the singularities of the integral and partial thermodynamic properties (See above in Fig. II-9, II-2, II-1, II-8, II-7). It could justify also the distinct rate constants observed in kinetic processes (See above § II-Kinetic transitions (10Wor) and Annex 2, below in § 4- Precedent and new graphical modeling's in Fig. IV-1).

## The p-n transition

**Tannhauser** (62Tan) observed a thermoelectronic p to n transition around 1300 °C by thermal e.m.f. analyses of a highly nonstoichiometric wüstite. More precisely with Bransky (67Bra), the change in sign of the Seebeck effect is observed near O/Fe ~1.09 or  $z \sim 0.083$  for polycrystalline samples at  $T \in [1010-1310^\circ\text{C}]$  and near  $z \sim 0.066$  at 910 °C (See below Figure II-10). They formalized the Seebeck coefficient  $\alpha$  following (63Hei) in the case of completely ionized vacancies when the 'hopping process' is predominant.

$$\alpha = k/e(A/kT + \ln(c_o-c)/c)$$

$c$  = 'concentration' of charge carriers,  $c_o$  = concentration of available sites for the charge carriers.

The same formalism was used by **Lafollet and Duquesnoy** (77Laf) in the case of non-location of the charge carriers, and the wüstite considered as an intrinsic semiconductor, *i.e.* doped by its own impurities. They modeled  $\alpha = 0$  for  $z = 0.104$  at 1100 °C, and  $z = 0.108$  at 1000 °C (See in Fig. II-10).

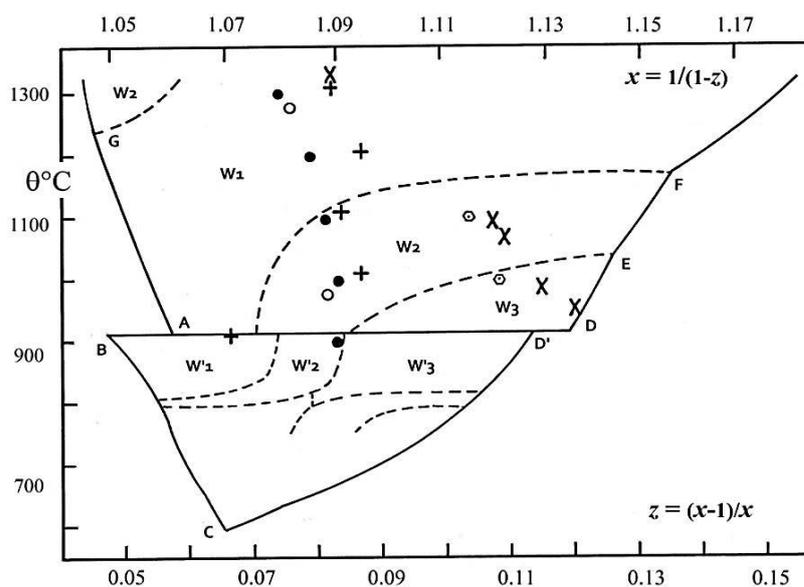


Fig. II-10 - Some determinations of the p-n transition by thermal e.m.f..

X : G. H. Geiger *et al.* (66Gei) not corrected for platinum ; + : I. Bransky and D. S.Tannhauser (67Bra) ; O : W. J. Hillegas jr and J. B. Wagner jr (67Hil) ; ⊙ : P. Lafollet and A. Duquesnoy (77Laf) by modeling ; ● : E. Gartstein and T. O. Mason (82Gar) by re-examination of W. J. Hillegas jr's thesis (1968).

Like in previous researches, Hodge and Bowen (81Hod) stated that the experimental change of sign from positive to negative of the thermal electromotive force occurred as  $z$  values were increasing or temperatures decreasing. Their model envisaged principally the cluster (4:1) and the electron holes trapped in octahedral sites adjacent to the cluster vacancies. The thermally activated hopping of these holes would permit continuous paths through the crystal because of the high point defect concentration between the zones separating the clusters.

The superimposition of the two kinds of p-n and  $W_i/W_{i+1}$  transitions, almost independent, and function of  $z$  respectively, was still referenced in Burgmann Review (R-75Bur).

In their studies on electrical conductivity of samples of  $Fe_{1-z}O$ , **Ariya and Bratch** (63Ari) and **Kozheurov and Mikhailov** (67Koz) observed modifications in the relationships  $\sigma \propto (p')^{1/n}$ , closely related to the relationships  $z \propto (p')^{1/n}$ , where their coefficient  $n$  ( $= s$ ) varied in such a way that three subdomains could be defined. They found an increase of the conductivity following two steps from  $z \cong 0.048$  to 0.079, then 0.097, from Fe/W- to W/Fe<sub>3</sub>O<sub>4</sub> boundaries.

Following **Molenda et al.** (87Mol1,2), the conductivity should be the sum of an « extrinsic conductivity »  $\sigma_y$  related to the nonstoichiometry and an intrinsic component  $\sigma_0$  non-envisaged until now, independent of the defect concentration *i.e.* of  $p'$ . Charge transport at high temperature would occur simultaneously in the valence and conduction bands, and the dopant acceptor band due to  $Fe^{3+}$  in octahedral and tetrahedral sites. Near the composition  $z \approx 0.08$ , the acceptor band overlaps with the valence band giving rise to a broad metallic band close to the thermoelectric transition « p to n'' » for  $z \approx 0.09$ , and corresponding to the stability limits of W1 and W2-3. Experimental details can be found in Fig.2 p. 519 and Fig. 4 by ((87Mol); *See Annex1 e-*) where successive segments corresponding to the Raccah-Vallet' isotherms are observable.

More recently, **Toroker and Carter** (12Tor) examine the possible means of improving the conductivity of  $Fe_{1-z}O$  by doping the p or n conduction mode with the technical aim of stabilizing the nanoscale fabrication of wüstite, then adapting this latter to a more efficient solar light conversion. The authors list the procedures allowing the calculation of Marcus theory parameters for « clusters models » with hydrogen dopant and substitutional dopants  $Cu^+$ ,  $Li^+$  and  $Na^+$ . They conclude that « *iron vacancies drastically limit the hole conductivity* » while Li, H and Na dopants improve it. So, it should be interesting to suppress the formation of vacancies by « alloying FeO », and amplify at the same time the p-type conductivity.

## 10 - Other kinetical and diffusional works.

**Desmarescaux and Lacombe** (63Des) studied the **self-diffusion** of iron using isotopes  $^{55}Fe$  and  $^{59}Fe$ . They stated that  $D_{Fe}$  increases with  $z$  at given temperature  $T$ , and decreases with  $T$  at fixed  $z$ . They deduced that self-diffusion proceeded following a vacancy mechanism especially noticeable as  $T$  is higher. At lower temperatures, less free vacancies and more complex vacancy-electron holes (the clusters) would exist. The number of vacancies associated to  $Fe^{3+}$  cations would increase with  $z$ .

**Landler et Komarek** (66Lan) followed by thermogravimetry the isothermal kinetics of mass loss *vs* time  $\Delta M(t)$  in  $H_2/H_2O$  mixtures by reduction of polycrystalline samples. Following their calculations, coefficients of self- and chemical iron diffusion decreased at increasing  $z$  for  $T \in [800 - 1050 \text{ } ^\circ C]$  because of « *the increased freezing due to repulsive interaction of the vacancies* ». This observation would correspond in majority to the formation of clusters, and their ordering in the bulk (*See p. 14-15 above Excess molar partial properties*).

Considering the relationship  $\log(\Delta M/\Delta M_0) = n \log t + k$  in which  $\Delta M_0$  is the total mass loss, their reduction kinetics at 950, 1000 et 1050  $^\circ C$  can be separated into three regimes II, III, IV, which might correspond to W3, W2, W1 (*See Annex 2, Fig. 1*). At 1000  $^\circ C$ , the calculated mean values of

n are -0.3, -0.49, -0.72, respectively (67Car). A brief anharmonic sequence is observed at the transition between a reduction process to another. The activation energies  $E_{II} = 182.8 \text{ kJ.mole}^{-1}$  and  $E_{III} = 126.8 \text{ kJ.mole}^{-1}$  for the reduction sequences likely characterizing W2 and W3 could correspond to an increase of clustering of defects in agreement with other observations by (63Des) at this date.

Similarly, successive different sequences of reduction by  $\text{H}_2\text{O}/\text{H}_2$  gas mixtures with such transitional anomalies can be observed (*See c- in Annex 1*) by **Rieke and Bohnenkamp** (66Rie).

**Rickert and Weppner** (74Ric) used an original method by combining a solid galvanic cell for the ionic conduction by  $\text{O}^{2-}$ , through a wüstite sample having the other face in contact with a platinum foil. The diffusion is studied *in situ* during the relaxation from a composition to another one imposed by controlled impulsions of electrical potential. The main result is that the chemical diffusion coefficient increases with the departure of stoichiometry *i.e.* the vacancy concentration, which is in agreement with Landler and Komarek (66Lan) not with any other authors. Transitional anomalies are clearly noticed (*See* (74Ric) Fig. 6 and 7 p.1856, and Fig. 8 p.1857).

## 11 - Relationships between defect structures and phase diagram

Let us reference authors who tried to solve the key challenge initiated by Carl Wagner from 1930 of linking more tightly thermodynamic properties and defect structure, such as partial molar properties or the equilibrium constant K of formation of the cluster. Kinetics (diffusional) relations were also developed.

**Per Kofstad and Hed** (68- R-72Kof) remarked that  $x$  or  $z$  increases at constant  $p'$  as  $T$  decreases, which is in contrast with other oxides, and likely due to a complex defect structure. They emphasized that all the iron vacancies would be doubly charged is *doubtful*. The electron holes associated to a vacancy should jump into only one of the 12 next nearest octahedral neighbors ( $\text{Fe}_{\text{Fe}}^{\circ}$ ) and one tetrahedral site ( $\text{Fe}_i^{\circ\circ}$ ). Most of octahedral vacancies would be singly charged. A modeling is

thus elaborated from the Roth complex ( $[\text{V}_{\text{Fe}}^{m(\prime)} - \text{Fe}_i^{n(\bullet)} - \text{V}_{\text{Fe}}^{p(\prime)}]^{q(\prime)}$ :  $n=2,3$ ,  $(m, p)=0,1,2$ . In

the relationship  $\sigma \propto p'^{1/s}$ , the  $s$  value is found to be larger than the one in the similar relationship connecting  $z$  to  $p'$  because vacancies might be neutral.

**Toft Sørensen** in a book devoted to nonstoichiometric oxides (R-81Sor), then with El Sayed Ali (85Sor), tentatively identified the defect structure of the *subphases*. They resorted to thermogravimetric data [ $l' - z$ ] at 1000 - 1300 °C by Bransky and Hed (68Bra) exclusively. They considered three main defects {double charged vacancy  $\text{V}_{\text{Fe}}''$ , tetrahedral complex defects (4:1) $^{(m)-}$  and (6:2)} as defined by Catlow *et al.* (75- 80Cat). They selected the defect cluster differently ionized which led to a linear plot of  $l'$  vs  $\log y$  ( $\equiv z$ ) with minimal slopes  $1/s$  in relation  $z \propto (p')^{1/s}$ . A second criterion concerns the so-called exclusion envelope, *i.e.* the long-range order as a layer structure or a close packing one. They localized in the *wüstite equilibrium area*  $T(z)$  according to  $\Delta T$  layers, above 1300 °C, between 1300 and 1200 °C, and below 1200°C respectively the predominant defect (4:1) plus a layer structure, (4:1) plus a close packing, (6:2) plus a layer structure. Iron vacancies  $\text{V}_{\text{Fe}}''$  are present in addition on the right side of a line at composition  $z$  close to 0.09 (*See* (85Sor) Fig. 7 p. 20 ). The pseudo-phases of Fender (69Fen) and Vallet (70Val) are thus *roughly depicted and structurally characterized*.

Also in the 80ies, **Men and Carel** applied the C(luster) C(omponent) M(ethod) to model wüstite solid solution (82Men<sub>1</sub>) (83Men<sub>1,2</sub>) (85Men). The « cluster components » were defined from crystallographic positions forming unit blocks in the general spinel structure. For example, three cluster components ①, ② and ③ and their concentration as function of  $z$  allowed to build the lattice of the wüstite  $\text{Fe}_{1-z}\text{O}$ , and to model some of its physical properties, taking into account the pseudo-phases (Fig.II-11).

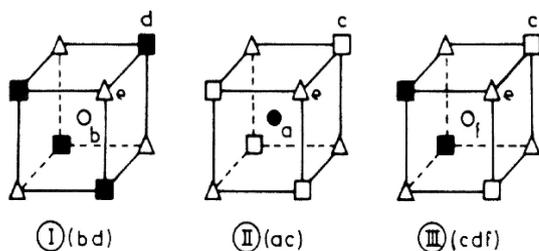


Fig. 3. Structural unit blocks S.S. ; ■: (16d) positions, □: (16c) positions, ○: (8b) positions, ●: (8a) positions, ⊙: (48f) positions, △: (32e) positions, (ref. 2, see Table 7.1. p. 186).

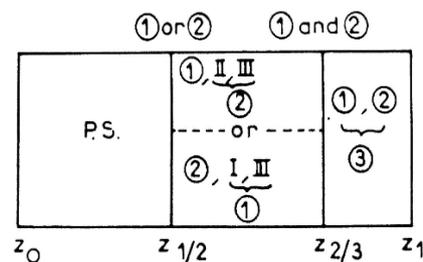


Fig. 4. Short range order in wüstite in terms of S.S. ① and C.C. ① in the three sub-domains of the wüstite homogeneity range. C.C. 1 : I-6III, C.C. 2 : II - 6III, C.C. 3 : I - 6III - II. In the subdomain ( $z_0, z_{1/2}$ ): II and III increase, I decreases; in ( $z_{1/2}, z_{2/3}$ ): II and III decrease, 1 or 2 increases; in ( $z_{2/3}, z_1$ ): 1 and 2 decrease, 3 increases.

According to Men and Carel (83Men1)

**Fig. II-11 – The three pseudo phases from  $z_0$  on the Fe/W1 boundary to  $z_1$  on the W3/Fe3O4 boundary described with the help of three cluster components ①, ②, ③.**

**Rekas & Mrowec** (87Rek) worked *On defect clustering in the wüstite phase* using a collection of data ( $z, \log p'$ ) from the literature (45- 46Dar) to (80Tak). They envisaged all the defect clusters suggested by Catlow and Fender (75Cat) *i.e.* (4:1), (6:2), (8:3), (10:4), (12:4) and (16:5) with several ionization degrees including the highest one. Elaborate calculations of the equilibrium constants led them finally to the assessment of the enthalpy and entropy of formation of all these ionized clusters, then to  $\Delta\bar{H}_O$ , independently of  $z$  and  $T$ , and  $\Delta\bar{S}_O$  for  $z \in [0.055-0.145]$  in the wüstite. They concluded that the (4:1) cluster is the most likely and that the ionization degree increased with temperature to reach the maximum value (5-) at 1573 K.

**Nowotny and Rekas** (89Now) tentatively described the *Defect structure and thermodynamic properties of the wüstite phase ( $Fe_{1-y}O$ )*. They looked for the clustering of point defects (iron vacancies and electron holes) across the whole domain by means of the Debye-Hückel theory, that allows to use a product  $\gamma \cdot [x_i]$  in place of  $[x_i]$  particularly for  $i = h^{\bullet}$ . In fact, the activity coefficients are confused with the sole mean coefficient  $f_{\pm}$  determined as function of the ionic force of the solution (not of its square root). They modeled the interactions during the formation of the cluster (4:1) in taking into account activity instead of concentration. Sets of data ( $z, \log p'$ ) and

( $\Delta\bar{H}_O, z$ ) are gathered from the literature. They evaluated the enthalpy and entropy of formation of a (4:1)<sup>5-</sup> cluster at  $-396.7 \text{ kJ.mol}^{-1}$  and  $267.4 \text{ J.K}^{-1}.\text{mole}^{-1}$ , respectively. It would be the constitutive module of more extended clusters (89Now). A numerical expression of the equilibrium constant of the cluster formation is determined across the whole domain independently of the existence or not of pseudo-phase transitions.

As soon as 1975, **Catlow & Fender** (75Cat) try the access to the defect structure by means of large computing calculations of the binding energies following the Born model. They envisaged theoretically the clusters unity (4:1), edge-sharing (6:2) and (8:3), corner sharing (16:5) precursor of  $Fe_3O_4$ . The location (zone  $z, T$ ) of these clusters was qualitatively suggested, but not in relation with the pseudo phases known by (69Fen). Catlow *et al.* (79Cat) assessed the formation energy and the relative stability of the clusters by means of the Mott-Littleton method. The cluster (12:4) type  $\langle 110 \rangle$  by Lebreton and Hobbs (83Leb) was considered as being the most stable extended cluster after the (6:2) and (8:3) ones. In a reviewing paper (87Cat), four classes of clusters are then defined

- 1- corner-sharing (4:1) clusters (7:2), (16:5);
- 2- edge-sharing clusters (6:2), (8:3), (12:4) by (83Leb);

- 3- ZnS blende like cluster (10:4) (86Grim) (87Gav);
- 4- the cluster (13:4) by (69Koc) and its incomplete sub-unit (5:2) cluster adjusted from diffraction data under equilibrium at 900 °C by (86Gart) following a simulation of order parameters (clustering similar to P'').

The author remark that the (10:4) blende ZnS cluster envisaged by Grimes *et al.* (84And) (86Grim) would not be the most likely because it was characterized without taking into account the geometric relaxation in the crystal.

**Tomlinson and Catlow** (89Tom) tried to relate the structural modeling of the short range order, and the macroscopic variation of  $z$  as a function of  $p'$ , adjusted by *mass-action treatment*. The « *binding energy per vacancy* » (See (89Tom) Table 2 p. 66) led the authors to order the clusters as following:

$[(8:3)^+1, -2.24 \text{ eV}]$ ,  $[(12:4), (6:2), (16:5)^-1, (12:5)^-1, (13:4)^-2, (4:1)^-1, (10:4)^-4, -2.22 \text{ to } -1.68 \text{ eV}]$ , then  $[(5:2 \text{ M}), -1.24 \text{ eV}]$  and  $[(5:2 \text{ G}), -0.71 \text{ eV}]$ .

They proposed a mixture of clusters  $[(12:4), (6:2), (4:1)]$  for the incommensurate « subphase P' ».

**R. W. Grimes *et al.*** (84And) (99Min) envisaged the structure and stability of clusters with different coordination types. A generalized crystal field is envisaged for d electrons of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  including the energy of orbitals 2s and 2p of the oxygen. Their computing of the binding energy per vacancy preferentially places the clusters  $\langle 110 \rangle$  ZnS blende and  $\langle 111 \rangle$  spinel type stackings. It rules out the clusters (8:3) (10:4) based on  $\langle 100 \rangle$  stacking of (4:1) units, and the Koch and Cohen (13:4) cluster. Within the lower field of stoichiometry (P' phase) smaller clusters could coexist such as (4:1), (6:2), (7:2)  $\langle 110 \rangle$  and (10:4) ZnS blende type, (7:2)  $\langle 111 \rangle$  spinel type. Larger clusters from the (12:4) type  $\langle 110 \rangle$ , (18:6), (16:5) spinel type  $\langle 111 \rangle$ , (16:5) type  $\langle 110 \rangle$  and (16:7)  $\langle 110 \rangle$  ZnS blende type clusters could be convenient at higher nonstoichiometry (P'' phase). The clusters should be neutral to be in agreement with experimental data.

NOTA: The classification of the clusters became more complicate because of the increasing number of propositions in the literature. Initially, the criterion of corner or edge sharing of the basic (4:1) units was only needed. Mixed cases were to except. Lebreton and Hobbs (83Leb) introduced the three ways of clustering : *edge sharing along  $\langle 100 \rangle$  (Type I)*, *corner sharing along  $\langle 110 \rangle$  (Type II)*, and *corner sharing along  $\langle 111 \rangle$  (Type III)*. Mixed ways are to be envisaged. Clusters based on composition alone are possible exceptions (ex. the cluster (10:3)). Labidi and Monty (See (91Lab) p. 100-101) resumed differently the situation with the *types 1 (face shared) aligned in the direction  $\langle 100 \rangle$* , *2 (edge shared) aligned in the direction  $\langle 110 \rangle$* , and *3 (corner shared) aligned in the direction  $\langle 111 \rangle$* . Worrall and Coley (See (R-13Wor) p. 24-26) classified the clusters available in the literature in three types defined as *a type 1 (corner shared as in magnetite)*, *a type 2 (edge shared sharing one octahedral vacancy)*, and *a type 3 (edge shared sharing two octahedral vacancies)*.

### III. Structural approaches. Models of short and long range orders

#### 1- Roth model: the cluster (2:1)

Having regard to experimental uncertainties inherent to X-ray diffraction on polycrystalline materials, it was necessary to use neutron diffraction experiments to correctly determine the site occupancies relative to iron atoms in octahedral and tetrahedral sites of the NaCl-like lattice. The first results relative to quenched wüstite were obtained using neutron diffraction by W.L Roth (60Rot) who determined the octahedral and tetrahedral site occupancies of vacancies and  $\text{Fe}^{3+}$  cations, respectively represented by  $z+t$  and  $t$ . The first characterization of the ratio  $R = (z+t)/t$  was found close to  $R=2$  for samples quenched from high temperature. The neutron diffraction patterns obtained at 290 K and 4.2 K suggested the presence of defects constituted of two cation vacancies associated with one interstitial cation in tetrahedral site. The average magnetic moment per cation site was found to be much smaller than expected.

#### 2 - The Manenc's observations of phases P, P', P''

Using X-ray diffraction analyses on quenched wüstites, the first structural determinations were performed by Manenc *et al.* (63-68Man) (See p. 15-16 ). This work was extensively recalled in section II-3 above. The main feature of this key work resided in the description of three types of

wüstites P, P' and P'' observed in quenched samples.

### 3- The historical Koch and Cohen (13:4) cluster

In 1969, a study by X-ray diffraction was published by Koch and Cohen (69Koc) on a single crystal of  $\text{Fe}_{0.902}\text{O}$  ( $z=0.098$ ) obtained after quenching from 1000 °C, and corresponding to the P' phase of Manenc. The authors proposed a new commensurate defect structure based on (13:4) large clusters (Figure III-1) distributed in the fcc lattice (cell parameter a) with a repetition distance

(3a,3a,3a) noted 3X. For the first time, a detailed crystallographic determination proposed a cluster corresponding to the corner sharing type <110> agglomeration of four basic (4:1) clusters.

To perform their structural refinements, the authors fixed this model of cluster assuming that the resulting superstructure should be a 3X one (clusters being arranged only with regular distances of three cell parameters), in agreement with the known composition  $z=0.098$ , despite the fact that the additional superstructure peak corresponded to a superstructure 2.6X with which they are not compatible.

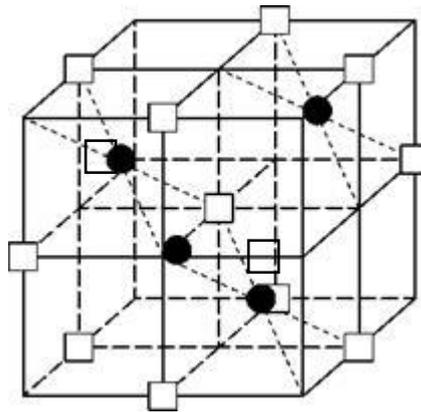


Fig. III-1 - The (13:4) cluster by Koch and Cohen associated with wüstite  $\text{Fe}_{0.902}\text{O}$ .

4- Using *in situ* neutron diffraction, Cheetham *et al.* (71Che) showed that the ratio  $R = (z+t)/t$  ranged between 3 and 4, with a mean value of 3.2, which was compatible with a specific (13:4) cluster ( $R = 3.25$ ). Using neutron diffraction coupled with magnetic scattering, Battle and Cheetham (79Bat) determined ratios  $R = 2.78, 2.82, 3.01$  and concluded that a cluster (8:3) could be consistent with their observations. They coupled neutron diffraction experiments to Mössbauer effect analyses (See Fig. 4 p. 343) and studied the antiferromagnetic coupling of iron cations in octahedral and tetrahedral sites of the FeO lattice. For the first time, these authors showed that atomic clustering could be characterized from the study of magnetic properties of clusters in a lattice.

5- The numerous results obtained by Radler *et al.* (90Ra) from neutron diffraction patterns on

polycrystalline samples under equilibrium give rise to values of  $R > 3$  corresponding to mixtures of clusters (4:1), (7:2) type <110>, (10:3) above 1185 K, and  $R < 3$  to clusters larger than (10:3) at 1173 K.

6- Schweika *et al.* (92- 95Sch) found a ratio of vacancies to interstitials  $R = 4.0 (\pm 0.5)$  yielded under *in situ* conditions from a single crystal by neutron diffuse scattering, for a sample with  $z = 0.08$ , at  $T=1150$  °C. Their analysis of the diffuse scattering patterns led them to conclude that 30% of the vacancies were free, while a further 15% of the defects are bound in isolated (4:1) defect clusters. In a Discussion (92Sch), the authors state that their results invalidate the drawn predominance of large clusters at elevated  $z$ . The (13:4) cluster as an example cannot fit the diffuse scattering that they characterize near the origin.

**7- Welberry and Christy** (95- 97- 14Wel) present a detailed study of the X-ray diffuse scattering of a single crystal with composition  $z=0.057$ , obtained after quenching from a temperature which is not indicated. Their sample correspond to the Manenc's P phase (*See* (68Man) and (77And)), or the W1 domain proposed by Vallet *et al.* (64- 79- 89Val). The X-ray analysis coupled with a « paracrystalline » modeling gave information on defect distribution, defect cluster size, number of interstitials and lattice strain. The authors described (statistically) a specific crystal constituted of ordered zones of clusters randomly distributed in a fcc lattice.

**8- Saines *et al.*** (13Sai) study by neutron diffraction a polycrystalline sample of wüstite  $Fe_{0.902}O$  quenched from 900 °C from the domain of W'. Their proposed nuclear and magnetic clusters are defined when using an elaborate Reverse Monte Carlo modeling. The nuclear structure is described by islands of V4T units connected along the  $\langle 110 \rangle$  directions « *into a Koch-Cohen arrangement* ». The magnetic structure in the bulk between the clusters is described as a *non-collinear variant* of the antiferromagnetic structure along the [111] axis as previously envisaged (79Bat). Free vacancies are near the clusters.

This structural approach might be compared with the *paracrystalline* description of the defect distribution by Welberry *et al.* (95Wel) (14Wel).

### 9- Gavarrí-Carel-Weigel' works

In 1979, using *in situ* neutron diffraction experiments, Gavarrí *et al.* (79Gav) develop an

analysis of the structural evolution in CO/CO<sub>2</sub> atmospheres at high temperature. A systematic determination of the ratio of the vacancy rate ( $z+t$ ) divided by the interstitial rate  $t$ ,  $R = (z+t)/t$ , was carried out. Quasi-constant values of R close to  $2.4 \pm 0.4$ , at two equilibrium temperatures (985 and 1075 °C) and compositions  $z$  ranging between 0.058 and 0.120, were determined, with standard errors induced by the uncertainties on the separation between Bragg peaks and a complex diffuse scattering.

Figure III-2 displays the R values obtained by different authors. In the case of *in situ* studies the major part of them are included between 2.4 and 3.5. The authors (79Gav) observed two types of signals: (i) Bragg peaks from which this ratio R was determined, (ii) additional scattering corresponding to superstructure peaks, thermal and static diffuse scattering associated with defect clustering, disorder and static distortions. The intensities  $I_A(T, z)$  of this additional scattering increased linearly with composition  $z$  and decreased with temperature. The ratios  $I_A/I_{220}$  where  $I_{220}$  is the intensity of (220) Bragg peak vary as follows:

- $I_A/I_{220}$  (985 °C) =  $0.19 + 4.05(z-0.062)$
- $I_A/I_{220}$  (1075 °C) =  $0.15 + 4.25(z-0.058)$

In other terms, these linear variations coupled with a small variation of the superstructure  $k$  parameter argue in favor of a quasi invariance of the cluster size with clusters agglomerated in domains, the extension of these domains increasing with  $z$ .

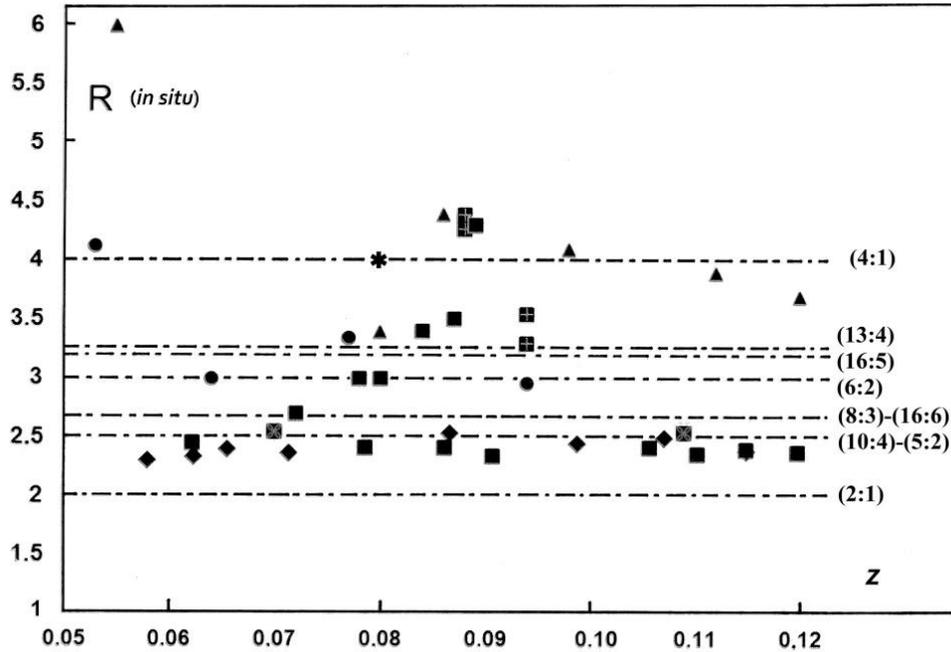


Fig. III-2 -  $R=(z+t)/t$  values vs  $z$ , determined under equilibrium, from the literature:

- : at 800°C and ■: at 925, 1050, 1125, 1180°C Cheetham *et al.* (71Che);
- ◆: at 1075°C and ■: at 985°C Gavarri *et al.* (79Gav); ■: at 900°C Gartstein *et al.* (86Gar);
- ▲: at 1050°C and ■: at 850-1100°C Radler *et al.* (90Rad); \*: at 1150°C Schweika *et al.* (95Sch)

The position of the centroid of this scattering allowed determining an average superstructure corresponding to an irregular spacing of clusters quasi constant with  $z$  or  $T$ . The average distance between clusters was evaluated to  $2.7a_0$ ,  $a_0$  being the cell parameter of ideal wüstite for a fixed temperature.

In their later work on quenched samples of magnesio- and calciowüstites by neutron diffraction, using Rietveld refinements, Carel and Gavarri (90Car) determined  $R$  values close to 2.5 for pure wüstites or for magnesio-wüstites  $Fe_{(1-z-y)}Mg_yO$ . In the case of calciowüstites  $Fe_{(1-z-y)}Ca_yO$ , as the composition  $y$  increases, the ratio  $R$  increased strongly with  $R > 4$  and the superstructure vanished. In these conditions, the cluster sizes were strongly modified, and a majority of free vacancies probably appeared. These studies clearly showed that the formation of clusters was stabilized in the case of Mg doping, and destabilized in the case of Ca doping, giving rise to free vacancies coexisting with residual clusters. It should be noted that the diffuse scattering due to

long-range order was similar in diffraction patterns of quenched and *in situ* samples. In other terms, only a little difference between the nature of defects and their organization in the FCC lattice, at high and room temperatures, might exist.

In Table III-1 below, the  $R$ -values corresponding to the quenched pure and substituted wüstites resulting from these studies are reported.

Figure III-3 shows an example of a neutron diffraction pattern obtained from a quenched polycrystalline calciowüstite ( $z = 0.065$ ;  $y = 0.030$ ). In addition to Bragg peaks, the complex signal due to the superstructure and the structural disorder can be observed. For this sample  $R = 3.3 (\pm 0.5)$ .

The values of the ratio  $R = (z+t)/t$  obtained from the literature on quenched pure and Ca or Mg substituted wüstites are displayed in Fig. III-4. The utmost value  $R = 8.2$  was obtained for a calcium-rich calciowüstite ( $y = 0.05$ ).

It should be noted that **Gleiter and Goodenough** (R-85Gle) suggested that the ratio  $R = 2.4 \pm 0.4$  found by Gavarri *et al.* for all values of  $x$  «... seems to be indicative of a single structural

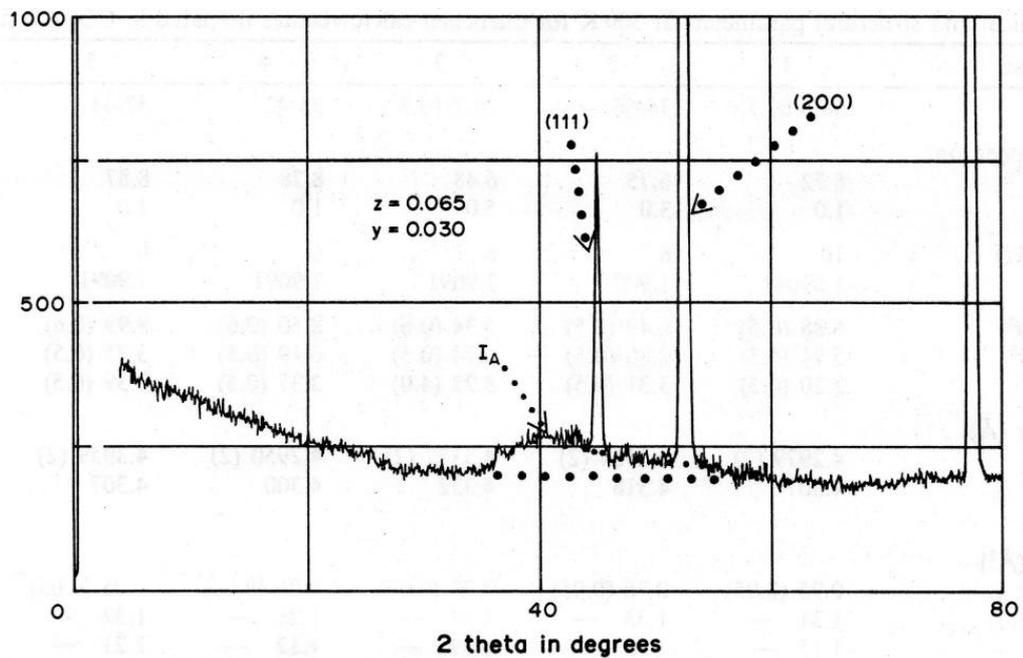
principle. This result does not establish the structural binding block uniquely, but it does seem to eliminate several alternatives such as the Koch-

Cohen cluster and the isolated 4:1 unit » (See (R-85Gle) p. 51-54).

**Table III-1: R = (z+t)/t values from quenched substituted wüstites (90Car).**

$\text{Fe}_{1-z-y}\text{Mg}_y\text{O}$	Fraction y (Mg)	$R = (z+t)/t$
$z=0.065$	0.075	2.53(0.5)
$z=0.085$	0.030	2.88(0.6)
$\text{Fe}_{1-z-y}\text{Ca}_y\text{O}$	Fraction y (Ca)	$R = (z+t)/t$
$z=0.0688$	0.010	2.20(0.5)
$z=0.0649$ (*)	0.030 (*)	3.31(0.5)
$z=0.0534$	0.050	8.22(4.0)
$z=0.085$	0.010	2.37(0.5)
$z=0.0899$	0.030	3.39(0.5)

(\*) See Figure III-3



Carel and Gavarri (90Car)

**Figure III-3 - Neutron diffraction pattern ( $\lambda = 1.9 \text{ \AA}$ ) of a quenched polycrystalline calciowüstite  $\text{Fe}_{1-z-y}\text{Ca}_y\text{O}$  ( $z = 0.065$ ,  $y = 0.03$ ), in room conditions. Presence of a large diffuse scattering ( $I_A$ ) due to the superstructure ( $k$  close to 2.7), and (110) small peak ( $36^\circ 2\theta$ ) due to vacancies and interstitial  $\text{Fe}^{3+}$  in the lattice. The intensity of  $I_A$  decreases with the calcium fraction  $y$ . Cell parameter  $a(25^\circ \text{C}) = 4.3164 \text{ \AA}$ .  $R(z = 0.065, y = 0.03) = (z+t)/t = 3.3$ .**

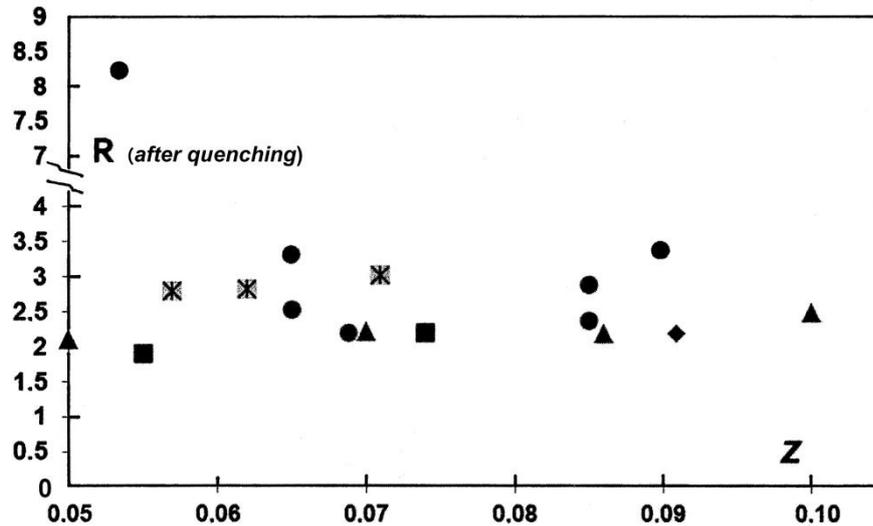


Fig. III-4 - R values vs z from literature determined after quenching.

WMg and WCa, ● = Carel and Gavarri (90Car).

Pure Fe<sub>1-z</sub>O: ■ = Roth (60Rot); ▲ = Smuts (66Smu); ◆ = Gavarri *et al.* (79Gav);

✱ = Battle and Cheetham (79Bat).

### 10- Transmission Electron Microscopy analyses

In the past, various microstructural analyses using electron diffraction and HREM images were performed. See particularly the analyses of Andersson and Sletnes (77And) (See II 4: p. 18). The images obtained by Iijima (74Iij) for a sample Fe<sub>0.92</sub>O (provided by Prof. Cohen) are often referenced.

### The hypothetical cluster (10:4) <110> type with ZnS-blende configuration

When re-interpreting the images obtained from electron microscopy experiments by Ishiguro and Nagakura (85Ish), Gavarri *et al.* (88Gav2) then Nihoul *et al.* (91Nih), showed that the possible cluster (10:4) corresponding to the ideal ratio R = 2.5 might be compatible with all experimental data (at least for quenched wüstites). This cluster was formed of a « FeO » cubic cell surrounded by an envelope of Fe<sup>3+</sup> cations with total 3D dimension (2a x 2a x 2a).

Figure III-5 depicts this cluster. The authors (88Gav2) and (91Nih) showed that image simulations from this model of cluster could be in good agreement with the high-resolution images obtained by Ishiguro & Nagakura (85Ish), in the

case of crystals quenched from 1000 °C, and with a composition z = 0.10.

In a previous publication (81Gav), Gavarri *et al.* proposed a specific order of (10:4) clusters. The formation of local ordered domains of them could be at the origin of all observations including the mean ratio R close to 2.5, and a quasi-invariant superstructure. The authors proposed a progressive ordering of clusters as z increased: for low z values, repetition distances 3a linkable to the P variety by Manenc, or W1, were observed, for intermediate z values, repetition distances 3a and 2.55a (monoclinic associations) linkable to P' or W2, would appear, and finally ordered superstructures (2.55a x 2.55a x 2.55a) would be formed in local zones linkable to W3 or P". Specific well-ordered superstructures could be based on a 3D superstructure with (5a x 5a x 5a) cell parameters, which could be associated with the limiting existence on the boundary W/Fe<sub>3</sub>O<sub>4</sub>. Finally, the distinction between «varieties of wüstite» or the pseudo-phases could be due to both modifications of long-range order of clusters and coexistence of different clusters including free vacancies.

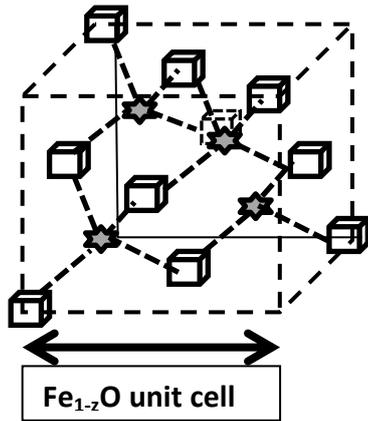


Fig. III-5: The cluster (10:4) ZnS blende type.

- ★ = Fe<sup>3+</sup> in tetrahedral site
- = Iron vacancy in octahedral site

To correctly define an isolated cluster, it is necessary to take into account its envelope of Fe<sup>2+</sup> and Fe<sup>3+</sup> cations in octahedral sites. The charge of this cluster can be firstly postulated by assuming the individual charges of vacancies and iron charges.

In Figure III-6 below, we illustrate the possible arrangement of these ZnS blende defect clusters (10:4), in the FCC lattice. The minimum distance between two clusters would be  $[(2.5a)^2 + (0.5a)^2]^{1/2} = 2.55a$ , with possible distances of  $3a$ . This model is based on a cluster core (10:4) with a double envelope of octahedral iron cations. If we assume that a cluster (m:n) would have a global charge  $Q =$

$3n-mq$  ( $m$  vacancies with formal charges  $q$  ( $=2,1,0$ ) and  $n$  interstitials Fe<sub>i</sub><sup>+++</sup> with charges  $+3$ ), the (10:4) cluster would have a charge of  $Q = -8, +2$  or  $+12$  for  $q = 2, 1$  or  $0$ , respectively. The electroneutrality would be ensured by envelopes with charges  $-Q$ . Using this type of defect structure, a model of ordered (10:4) clusters was proposed (88Gav2 and 91Nih), thus allowing simulating HREM images in two directions  $[001]$  and  $[101]$  of the crystal. These hypothetical distributions of clusters (Fig. III-7) agreed well with the HREM images by Ishiguro and Nagakura (85Ish).

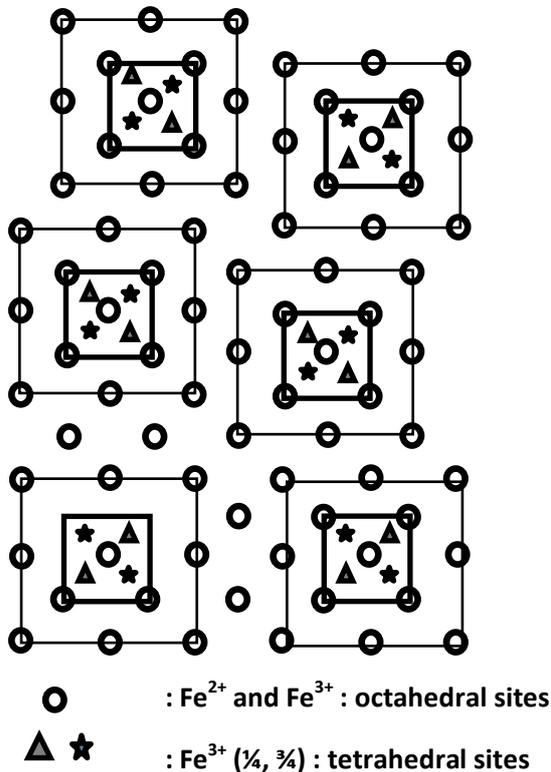
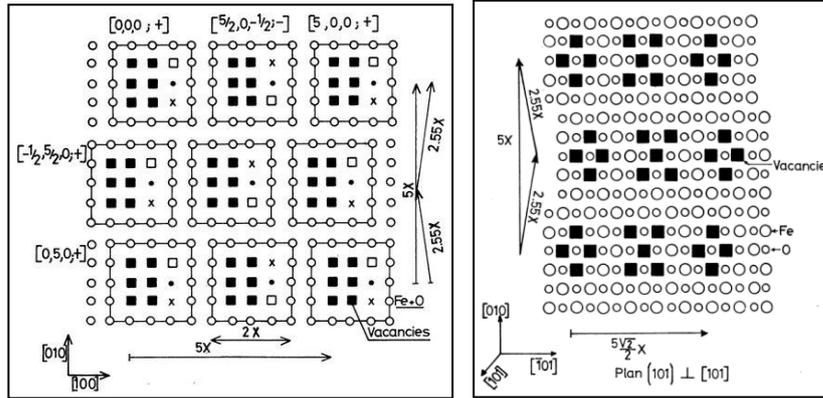


Figure III-6 - Various orderings of (10:4) clusters in the FCC lattice of wüstite. The basic cluster can be the (13:4), (10:4) or other possibility with 4 interstitial sites occupied by cations Fe<sup>3+</sup>. Disorder can develop by statistical displacement in one, two or three directions.  $2.55a$  could be the smaller inter-cluster distance ( $a$  = cell parameter of the “FeO” lattice).



**Fig. III-7 - Model of local ordering of (10:4) clusters by (88Gav-b) and (91Nih). This model allows reproducing the experimental HREM images from Ishiguro and Nagakura (85Ish).**

#### IV- The hypothesis of a mix system of clusters and/or cluster zones

##### 1- Mix system of defect clusters

Having regard to the publications by Gavarri and Carel (79- 81Gav<sub>1,2</sub>), a new specific relationship can be established taking into account ordered zones of clusters and zones in which free vacancies could be distributed. A mix system of different clusters  $(m:n)_1$  and  $(m:n)_2$  could exist with additional free vacancies. As a first approach, the authors consider a lattice based on N cells of  $Fe_{1-z}O$ , with a proportion  $V(z)$  of zones without defect. If  $N_i$  is the number of cells where clusters  $(m:n)_i$  are formed,  $m_i$  and  $n_i$  the characteristics of a specific cluster,  $k_i$  the distance between two clusters, the relation between cluster sizes and long-range order in the case of the FCC lattice of wüstite can be expressed as follows

$$1-V(z) = 4z \cdot \sum_i \left\{ \pi_i (k_i)^3 / (m_i - n_i) \right\} \text{ with } \pi_i = N_i/N \quad (IV-1)$$

For a unique cluster with continuous order (high z values) it results

$$(m-n) / (k)^3 = 4z \rightarrow (m-n) = 4zk^3 \quad (IV-2)$$

Considering the experimental k values available in the literature, ranging between 2.5 and 3, this parameter k is characteristic of zones in which clusters are partly ordered: this means that, for low values of z, zones without clusters exist and that they can be occupied by isolated defects (free vacancies).

In this case, an alternative simplified approach could be proposed. If we assume that ordered zones are progressively formed in the lattice as z increases, and that free vacancies (with local fraction  $z_{free}$ ) coexist out of these cluster zones, we can express a simple relation between the z value and the effective  $z_{cluster}$  fraction of vacancies in cluster zones, using repartition coefficients  $\alpha_1$  for cluster zones and  $\alpha_2$  for free vacancies zones

$$z = \alpha_1 \cdot z_{cluster} + \alpha_2 \cdot z_{free} \quad \text{with } \alpha_1 + \alpha_2 = 1 \quad (IV-3)$$

For a fixed equilibrium temperature, the phase diagram allows determining the compositions  $z_{min}$  and  $z_{max}$  corresponding to the existence of wüstite. We can easily show that the coefficients  $\alpha_1$  and  $\alpha_2$  are expressed as follows

$$\alpha_1(T) = (z - z_{min}) / (z_{cluster} - z_{min}) \quad \text{and} \\ \alpha_2(T) = 1 - \alpha_1(T) \quad (IV-4)$$

The coefficient  $\alpha_1(T)$  is equal to zero for  $z = z_{min}$  (no cluster zone) and equal to  $(z_{max} - z_{min}) / (z_{cluster} - z_{min})$  for  $z = z_{max}$ . The concentration  $z_{cluster}$  can be considered as being close to  $z_{cluster} = z \cdot (k_1)^3 / (m_1 - n_1)$ . This simplified approach could explain a large part of the experimental observations of the literature.

For low z values, only few cluster zones would be formed, coexisting with free vacancies distributed between these zones. The major part of the crystal lattice should be dominated by disordered point defects, with conduction by holes.

For intermediate  $z$  values, the cluster zones could join themselves together, forming percolation paths of ordered zones. A mix conduction should be expected. For high  $z$  values, the lattice should be fully covered by ordered clusters, with probably small modifications of the arrangement of clusters (variable  $k$  values from 3 to 2.5). The conduction should be conditioned by neutral vacancies and electrons in conduction band.

In this description, we could clearly recognize the W1 disordered phase of p type conduction, the intermediate phase W2 as a mixture of cluster zones and free vacancy zones with mix conduction, W3 an ordered phase with conduction of n type by electrons in the conduction band.

## 2- Variation of parameter $k$

A large set of structural data can be found in the studies by **Bauer *et al.*** Part I (R-80Bau) and Part II (80Bau). These authors developed a series of studies by X-ray diffraction on powders of quenched wüstites and observed linear variations of the cell parameter as a function of composition  $z$ , and of the position of superstructure peaks. They characterized these latter by the parameter  $\delta = 1/k$ , where  $k$  designates the superstructure parameter used above, varying between 0.37 to 0.39, that is to say that the corresponding  $k$  value varied between 2.7 and 2.56. This variation observed in quenched samples was in good agreement with the model presented just above where the minimum  $k$  value would be 2.55. In this study, the authors considered that their data did not permit to observe any phase transition. However, they suggested that wüstite could be described by an incommensurate lattice of clusters with the presence of different clusters based on the cluster (4:1).

## 3- Statistical analysis of diffuse scattering and new cluster

In 1982, **Gartstein and Mason** (Gart82) showed that p conduction was observed in wüstite and that electrical conduction was based on hopping mechanism between near clusters. In 1986, Gartstein *et al.* published then a crystallographic analysis of a  $\text{Fe}_{1-z}\text{O}$  ( $z=0.07$ ) single crystal, using X-ray diffraction at 1173 K (Gart86). They

developed a detailed analysis of diffuse scattering and Bragg peaks, and concluded to the existence of asymmetric new clusters (5:2) constituted of 5 vacancies and 2 interstitials corresponding to the ideal ratio  $R = 2.5$  in agreement with the values found by (79Gav). Gartstein *et al.* proposed an ordering of these clusters with an average repetition distance of  $2.5a$ , which is not far from the hypothetical value  $2.55a$  proposed earlier (88Gav $\mathbf{1,2}$ , 91Nih).

**4- Summary.** As a conclusion of this section, it should be remarked that there would be a competition between the concept of a mix system of disordered clusters with various forms, and the concept of zones with identical disordered clusters, coexisting with zones of free point defects. The concept of incommensurability, applied to specific compositions  $z$ , was also proposed as a mathematical approach of disorder. Finally, the proposition of the irregular cluster (5:2), resulting from the analysis of diffuse scattering by the authors (Gart86), seemed to confirm the quasi-constant value  $R = (z+t)/t = 2.4 \pm 0.4$  proposed presently.

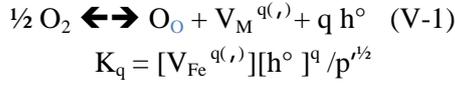
## V - Defect clustering and equilibrium equations

In this section, the well-known classical models of defect equilibria in the case of the cation deficient non-stoichiometric oxide  $\text{Fe}_{1-z}\text{O}$  are recalled. In addition, new specific possible models applicable to wüstite (*See particularly* (R-81Sor)) are also proposed. A series of equilibrium equations with increasing complexity are presented, in relation with the historical evolution of concepts concerning point defects in oxides.

In non-stoichiometric monoxide  $\text{Fe}_{1-z}\text{O}$ , in which only  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations (also noted  $\text{Fe}_{\text{Fe}}$  and  $\text{Fe}_{\text{Fe}}^{\circ}$ , in Kröger and Vink notations) could coexist, three possible charge states of cation vacancies can be stabilized, doubly charged vacancies  $\text{V}_{\text{Fe}}''$ , simply charged vacancies  $\text{V}_{\text{Fe}}'$  and neutral vacancies  $\text{V}_{\text{Fe}}^{\times}$  (noted  $\text{V}_{\text{Fe}}$ ). Singly charged iron vacancies  $\text{V}_{\text{Fe}}'$  were previously proposed in place of doubly charged iron vacancies  $\text{V}_{\text{Fe}}''$  by Kofstad and Hed (68Kof) (*See* section II §11 p.21). Oxygen

vacancies will not be taken into account because their number can be neglected in comparison with the one of iron vacancies.

Three hypothetical equilibria previously presented in section II (in which the activity of oxygen  $O_O$  in the solid is taken equal to 1) are recalled below, with  $q=0, 1$  or  $2$  and  $p'=p(O_2)$

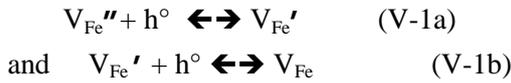


Considering the relationship  $-q \cdot [V_M^{q(\prime)}] + [h^\circ] = 0$  (electroneutrality condition) with  $[V_{Fe}^{q(\prime)}] = z$ , we can derive the general expression in which  $s=2(q+1)$

$$\rightarrow \log z = 1/s. \text{ / } 1/s \log (K/C)^2 \quad (\text{with } C = (q)^{2q})$$

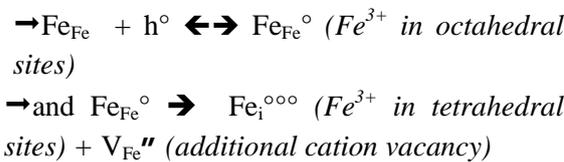
Three hypothetical values of  $s$  can be derived for  $q = 2, 1, 0$  :  $s = 6, 4, 2$  successively.

The modifications of the nature of vacancies can be described in terms of two equilibriums involving holes  $h^\circ$  in the valence band



In other terms, three domains corresponding to these three types of vacancies might exist in all systems presenting significant cation non-stoichiometry.

In the case of  $Fe_{1-z}O$ , as two valences ( $Fe^{2+}$  and  $Fe^{3+}$ ) exist, additional reactions occur:



As a first step, assuming that the sole point defects might be iron vacancies associated with  $Fe^{3+}$  ( $Fe_{Fe}^\circ$ ) coexisting with  $Fe^{2+}$  ( $Fe_{Fe}$ ) in  $Fe_{1-z}O$ , the general relationship between composition  $z$  and oxygen partial pressure  $p'$  might be as follows



with the equilibrium constant:

$$K_q = [Fe_{Fe}^\circ]^q \cdot [V^{q(\prime)}] / ([Fe_{Fe}]^q \cdot p'^{1/2})$$

In this expression  $[Fe_{Fe}] = 1-3z$ ,  $[Fe_{Fe}^\circ] = 2z$ . The activity of  $O_O$  is taken equal to 1.

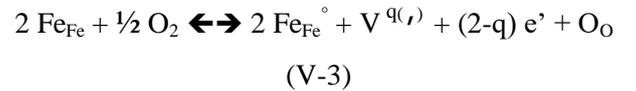
As all molar fractions are related to the composition  $z$ , we can derive the relationship:

$$K_{IV-2} = [Fe_{Fe}^\circ]^q \cdot [V^{q(\prime)}] / ([Fe_{Fe}]^q \cdot p'^{1/2})$$

$$= 2^q \cdot z^{(q+1)} / (1-3z)^q \cdot p'^{1/2}$$

If this simple model was correct, in a reduced composition range, the term  $(1-3z)$  would vary slowly with  $z$ , which means that the activity of  $Fe_{Fe}$  could be considered as being constant. In this assumption,  $z$  would be roughly proportional to  $(p')^{1/s}$ , with  $s = 2(q+1)$ , integer characteristic of the nature of defects. For  $q = 2$  (doubly charged vacancies) we obtain  $s \approx 6$ . For  $q = 1$  (singly charged vacancies)  $s \approx 4$ . For neutral vacancies,  $s \approx 2$ .

If electrons were present in the system, and keeping the same approximations as above

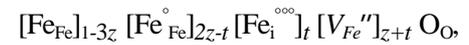


the equilibrium constant would be

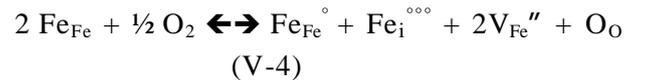
$$K_{IV-3}(q) = [Fe_{Fe}^\circ]^2 \cdot [V^{q(\prime)}] \cdot [e']^{(2-q)} / ([Fe_{Fe}]^2 \cdot p'^{1/2})$$

For  $q=0$  (neutral  $V$ ),  $z$  would be roughly proportional to  $(p')^{1/10}$ , so  $s = 10$ ; for  $q=1$  (simply charged vacancies) we would obtain  $s = 8$ ; for  $q=2$ ,  $s = 6$ .

In the case of  $Fe^{3+}$  cations partly located in tetrahedral sites, using the chemical formula



the equation would be:



giving rise to the equilibrium constant (with all appropriate approximations):

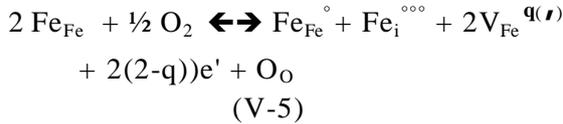
$$K_{IV-4} = [Fe_{Fe}^\circ] [Fe_i^{\circ\circ\circ}] [V_{Fe}']^2 / p'^{1/2} =$$

$$(2z-t)(t)(z+t)^2 / ([Fe_{Fe}]^2 \cdot p'^{1/2})$$

Having regard to the X-ray and neutron diffraction experiments from various authors (see section on structures), the ratio  $R = (z+t)/t$  was found to be

comprised between the values 2 and 4. In other terms, if we assume that  $t = z / (R-1)$  is roughly proportional to  $z$  ( $R$  quasi constant), and the term  $[Fe_{Fe}]^2$  slowly variable, we can note that  $z$  would be roughly related to  $p'^{1/8}$  giving a value  $s=8$ .

If we take into account the existence of free electrons associated with the modification of vacancy charges (noted  $q(r)$  or  $-q$ ), we can express additional equilibriums

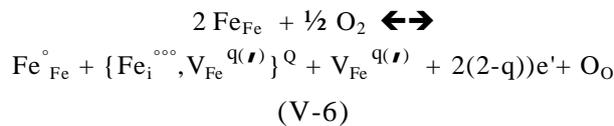


$K_{IV-5} =$

$$[Fe_{Fe}^{\circ}][Fe_i^{\circ\circ\circ}][V_{Fe}^{q(r)}]^2[e']^{2(2-q)} / ([Fe_{Fe}]^2 \cdot p'^{1/2})$$

For  $q=2, 1, 0 \rightarrow s=8, 12, 16$

Now, we introduce the notion of clusters of defects, in a simplified description to avoid excessive complications. In the case of clusters sharing envelopes (for high  $z$  values) the notion of isolated cluster cannot be kept in the strict sense of the term. As a first step, the charge of a cluster (noted  $Q$ , positive or negative) will be calculated from the individual charges of  $Fe^{3+}$  in tetrahedral sites and of octahedral iron vacancies. From this hypothesis, we can express the formation of simplified clusters



$$Q = 3 - q$$

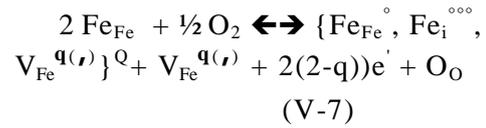
$$K_{IV-6} = [Fe_{Fe}^{\circ}] \cdot [\{Fe_i^{\circ\circ\circ}, V_{Fe}^{q(r)}\}] \cdot [V_{Fe}^{q(r)}] \cdot [e']^{2(2-q)} / ([Fe_{Fe}]^2 \cdot p'^{1/2})$$

In this equilibrium, we introduce simplified clusters  $\{Fe_i^{\circ\circ\circ}, V_{Fe}^{q(r)}\}^Q$  with hypothetical electrical charges  $Q=3-q$  ( $q=0,1,2$ ), coexisting with free  $Fe^{3+}$  (or  $Fe_{Fe}^{\circ}$ ) in octahedral sites. As  $z$  increases, it is reasonable to consider that all fractions of species  $[Fe_{Fe}^{\circ}]$ ,  $[Fe_i^{\circ\circ\circ}]$ ,  $[V_{Fe}^{q(r)}]$ ,  $[V_{Fe}^{q(r)}]$  and  $[e']$  are proportional to  $z$  and the equilibrium constant can be expressed considering a specific term  $C$  depending of activity coefficients as follows:

$$K_{IV-6} = C [z^3 \cdot z^{2(2-q)}] / [(1-3z)^2 \cdot p'^{1/2}]$$

If we consider composition domains in which the activity coefficients of  $Fe_{Fe}$  vary slowly as a function of  $z$ , the term  $C$  can be considered as being constant. For intermediate and high  $z$  values, the function  $z^{(7-2q)} / (1-3z)^2$  can be approximated by an average function  $z^X$  with  $3 < X < 4$  for  $q=2$ ,  $4 < X < 5$  for  $q=1$  and  $6 < X < 7$  for  $q=0$ . So, it results that the values of  $s$  will be close to  $6 < s < 8$  (low  $z$  values and  $q=2$ ),  $9 < s < 10$  (intermediate  $z$  values and  $q=1$ ) and  $11 < s < 12$  (high  $z$  values  $q=0$ ).

In a supplementary step, a cluster can be formed from point defects  $Fe_{Fe}^{\circ}$ ,  $Fe_i^{\circ\circ\circ}$ ,  $V_{Fe}^{q(r)}$  with  $Fe_{Fe}^{\circ}$  in the envelope of the basic cluster. So it results:



$$Q = 4 - q$$

$$K_{IV-7} = [\{Fe_{Fe}^{\circ}, Fe_i^{\circ\circ\circ}, V_{Fe}^{q(r)}\}] [V_{Fe}^{q(r)}] [e']^{2(2-q)} / [Fe_{Fe}]^2 \cdot p'^{1/2}$$

In this equilibrium, we consider clusters  $\{Fe_{Fe}^{\circ}, Fe_i^{\circ\circ\circ}, V_{Fe}^{q(r)}\}$  with their  $Fe^{3+}$  envelopes. As  $z$  increases, it is reasonable to consider that all fractions of species  $[\{Fe_{Fe}^{\circ}, Fe_i^{\circ\circ\circ}, V_{Fe}^{q(r)}\}]$ ,  $[V_{Fe}^{q(r)}]$  and  $[e']$  are proportional to  $z$  and the equilibrium constant can be expressed considering a specific term  $C$  depending of activity coefficients as follows:

$$K_{IV-7} = C [z^2 \cdot z^{2(2-q)}] / [(1-3z)^2 \cdot p'^{1/2}]$$

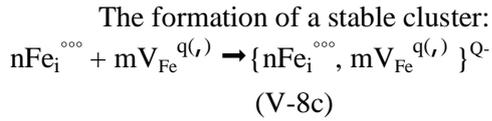
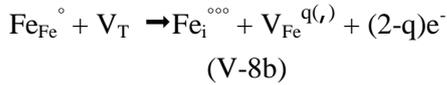
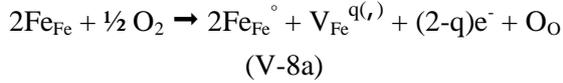
If we consider composition domains in which the activity coefficients vary slowly as a function of  $z$ , the term  $C$  can be considered as being constant. For intermediate and high  $z$  values, the function  $z^{(6-2q)} / (1-3z)^2$  can be approximated by the function  $z^X$  with  $X < 2, 4$  or  $6$  respectively for  $q=2,1,0$  (see equation IV.6 above). So, it results that the values of  $s$  will be lower than (but close to)  $s=4$  (low  $z$  values and  $q=2$ ),  $s=8$  (intermediate  $z$  values and  $q=1$ ) and  $s=12$  (high  $z$  values  $q=0$ ).

At this stage, we should note that, in the case of the example given in section II, these calculated  $s$  values are not far from the values observed in the literature. We gather in Table V-1a,b below, the hypothetical equations (1a) and the possible values

of coefficient  $s$  characteristic of various possible equilibria (1b).

### Complex clusters

In the following section, we introduce complex  $(m:n)^Q$  clusters with variable formal charges  $Q$  and we consider successive reactions in which vacant tetrahedral sites  $V_T$  are introduced:



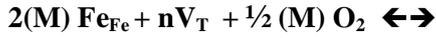
with  $Q = 3n - qm$  (positive or negative charge). The formal charge  $Q$  of a cluster will be assumed to result from individual charges of vacancies with invariant charges of interstitials  $Fe^{3+}$  ( $Fe_i^{\circ\circ\circ}$  in tetrahedral sites). As a first approximation, we fix the charge of interstitials to simplify the calculations: however, the  $Fe^{3+}$  interstitials can be modified into  $Fe^{2+}$  interstitial cations due to electron jumping, and, as a result, a more complete model should take into account various possible  $Q$  values of cluster charges due to the modification of interstitial charges.

**Table V-1a,b: Characteristic exponents  $s$  associated with different elemental models of defect equilibria, expressed in the form:  $\log z \approx (1/s)I'$**

1a : Defects and hypothetical equilibrium equations	
Eq. (V-2)	$q Fe_{Fe} + \frac{1}{2} O_2 \leftrightarrow q Fe_{Fe}^{\circ} + V^{q(r)} + O_O$
Eq. (V-3)	$2 Fe_{Fe} + \frac{1}{2} O_2 \leftrightarrow 2 Fe_{Fe}^{\circ} + V^{q(r)} + (2-q) e^- + O_O$
Eq. (V-5)	$2 Fe_{Fe} + \frac{1}{2} O_2 \leftrightarrow Fe_{Fe}^{\circ} + Fe_i^{\circ\circ\circ} + 2 V_{Fe}^{q(r)} + 2(2-q)e^- + O_O$
Eq. (V-6)	$2 Fe_{Fe} + \frac{1}{2} O_2 \leftrightarrow Fe_{Fe}^{\circ} + \{ Fe_i^{\circ\circ\circ}, V_{Fe}^{q(r)} \} + V_{Fe}^{q(r)} + 2(2-q)e^- + O_O$
Eq. (V-7)	$2 Fe_{Fe} + \frac{1}{2} O_2 \leftrightarrow \{ Fe_{Fe}^{\circ}, Fe_i^{\circ\circ\circ}, V_{Fe}^{q(r)} \} + V_{Fe}^{q(r)} + 2(2-q)e^- + O_O$

1.b: Calculations of $s$ according to $\log z \approx (1/s)I'$					
The fractions of defects are assumed to be proportional to $z (Fe_{I-z}O)$					
Charges $q$ $V^{q-}$	Exponent $s$ Eq. (V-2)	Exponent $s$ Eq. (V-3)	Exponent $s$ Eq. (V-5)	Exponent $s$ Eq. (V-6)	Exponent $s$ Eq. (V-7)
2	6	6	8	6	4
1	4	8	12	10	8
0	2	10	16	14	12
<b>Experimental agreement</b>	Bad	Good	Bad	Unrealistic	Acceptable

Following a more general hypothesis implying a cluster (m:n), and adding the presence of free sites  $V_T$  (tetrahedral vacant sites), a complex equation (V-9) could be expressed as follows:



$$\{mV_{Fe}^{q(r)}, nFe_i^{\circ\circ}\}^Q + (2M-n).Fe^{\circ} + (M-m+n).V_{Fe}^{q(r)} + (M+n)(2-q).e^- + (M).O_O \quad (V-9)$$

with the hypothesis:  $Q = 3n - qm$  (positive or negative).

In this equation, the integer  $M \geq m$  is arbitrarily introduced to take into account the possible presence of additional free species  $Fe_{Fe}^{\circ}$  and  $V_{Fe}^{q(r)}$ , associated with free electrons in the conduction band. We have considered the tetrahedral sites as being initially the vacant sites  $V_T$  susceptible to receive an  $Fe_i^{\circ\circ}$  cation. As the major part of these sites (8 sites for 4 FeO units in a FCC cell) is vacant, their activity can be considered as being quasi-constant, and could not play any significant role in the calculation of equilibrium constants. The resulting equilibrium constant is as follows, with the reduced notation  $CL = \{mV_{Fe}^{q(r)}, nFe_i^{\circ\circ}\}^Q$

$$K(T) = \frac{[CL].[Fe_{Fe}^{\circ}]^{(2M-n)}.[V_{Fe}^{q(r)}]^{(M-m+n)}.[e^-]^{(M+n)(2-q)}}{([Fe_{Fe}]^{2M}.[V_T]^n.(p')^{M/2})}$$

Applying the same approximations as in previous equilibrium equations, the equilibrium constant can be expressed as follows with the additional hypothesis  $M=m$ :

$$K(T) = \frac{z.z^{(2M-n)}.z^{(M-m+n)}.z^{(M+n)(2-q)}}{(1-3z)^{2M}.(p')^{M/2}} \quad ((1-3z)^{2M}.(p')^{M/2})$$

$$\approx z^{(2m+1+(2-q)(m+n))} / (1-3z)^{2m}.(p')^{m/2}$$

In this expression, no activity coefficient is taken into consideration. This means that in a restricted range of composition  $z$ , no significant modification of interactions between point defects or clusters would occur.

To illustrate the possible values of the  $s$  parameter corresponding to the three hypothetical  $q$  values,

we have simulated  $l'$  as a function of  $\log z$  using the expressions of  $K(T)$  developed above, and determining the slopes of the curves ( $l'$  vs  $\log z$ ). We have chosen two specific clusters to determine the various coefficients  $s$  depending on the charges  $q$  of vacancies. It results that:

- For a cluster **(4:1)**, the three coefficients  $s$  could be equal to 5.7, 8.2 and 10.7 for  $q=2, 1$  and 0 respectively.
- For a cluster **(10:4)**, the three coefficients  $s$  could be equal to 5.4, 8.2 and 11 for  $q=2, 1$  and 0 respectively.

It should be remarked that, whatever the cluster (4:1) or (10:4), coefficients  $s$  resulting from the calculations are quite similar for a given  $q$  value. However, having regard to approximations of the model and experimental uncertainties, these simulated values (from  $s = 5$  to 11) are congruent with the experimental  $s$  values obtained in the literature and ranging between 4 and 10. In other terms, the existence of pseudo-phases could be reasonably associated with the variation of the electrical charges ( $q$ -) of vacancies, more generally with the variations of the electrical charge  $Q$  of the clusters. These modifications of electrical charges could be strongly correlated with the increasing density of these charges. Two neighboring vacancies  $V''$  with same negative charges would give rise to two singly charged  $V'$  or neutral  $V$  vacancies, which would decrease the coulombian repulsions, and would require additional free electrons in the conduction band.

Now, using all the preceding values of  $s$  resulting from diversified models, it is possible to bear a first justification of the various modifications observed by the authors including Vallet *et al.* (64-79-89Val), Geiger *et al.* (66Gei), Fender and Riley (69Fen), Takayama and Kimizuka (80Tak), Worrall and Coley (10- R-13Wor).

Particularly, let us keep in mind the three values  $s(W1) = 4.6$ ,  $s(W2) = 6.2$ ,  $s(W3) = 9.2$ , extracted from the data by Vallet *et al.*, as well as the three other values  $s(W1) = 4.8$ ,  $s(W2) = 6$ ,  $s(W3) = 9$  extracted from the data by Takayama and

Kimizuka (80Tak). Several equilibria might be in agreement with these experimental values of  $s$ . Among the possible solutions of Table IV-1 it should seem reasonable to consider the equilibria (V-3) and (V-7) in relative agreement with experiments, with  $q$  values varying from 2 to 0. However, the general equation (V-9) based on clusters ( $m:n$ ) seems to be in better agreement with thermodynamic and structural data of the literature, *i.e.* with the three observed  $s$  values  $\approx 5, 6, 9$  corresponding with the three activation energies - 2.20, -2.52, -2.67 eV (*cf.* II-2, § 1), and with  $q$  values varying from 2 to 0 as  $z$  increases. In other terms, for low  $z$  values, the existence of doubly charged iron vacancies  $V_{Fe}''$  would be associated with a major population of holes, which would correspond to a  $p$  mode of conduction. For high  $z$  values, the existence of singly charged or neutral vacancies would be associated with a conduction of  $n$  mode. For intermediate  $z$  values, an intermediate state would exist with a mix of holes in valence band and electrons in conduction band, following a variable rate from  $z_{1/2}$  to  $z_{2/3}$ .

These observations could be supported by the  $p$ - $n$  transition early described in the literature (*See* (62Tan), Fig. II-10). These approaches supply with a full interpretation of the existence of various defect configurations corresponding to pseudo-phases in the whole wüstite phase diagram. The W1, W2 and W3 « varieties » could be thus justified from the preceding last equation V-9.

For low values of  $z$ , the neutron diffraction data show that the clusters would be assembled in limited ordered zones. For high values of  $z$ , the ordered cluster zones would percolate (*See* HREM images,  $z=0.08$  by (74Iij)), and the change in vacancy charge as  $z$  increases would be accompanied by formation of free electrons in the conduction band. As temperature  $T$  increases, the size of the cluster zones would decrease and their number would increase, correlatively the population of free defects would increase. The W1 pseudo-phase could be associated with a small number of clusters assembled in cluster zones, and a large population of free defects with numerous free  $V_{Fe}''$  vacancies. In this domain, holes would be the major electronic charge carriers. The W3

pseudo-phase would be constituted of large clusters zones covering the whole lattice at the limit with magnetite. The neutralization of vacancies (or decreasing  $q$  charges) would be associated with a large number of electrons occupying the conduction band. Because the pseudo-phase W2 seems to be characterized by a combination of two thermodynamic behaviors corresponding to the phases W1 and W3, a progressive evolution should be observed at the percolation scale. It should exist an intermediate structural configuration corresponding to the formation of percolation paths between cluster zones, and the mix of conduction modes involving holes and electrons.

## VI - Percolation approach

A primitive *composite picture* of possible evolution of the defect structure needing only two clusters and distinct populations through the subdomains was proposed by (82Gav). Nearly at the same time, such a simple model of the defect structure was similarly modeled in terms of the so-called theoretical Cluster Component Method (R-77Men) at the first step of applying it by Men and Carel (83Men). Three components noted ①, ② and ③ were formed from structural blocks. Their distribution was figured qualitatively, and reproduced above in Fig. II-11.

In Figure VI-1 a schematic representation of the distributions of clusters inside cluster zones (CLZ) and cluster zones in the lattice is drawn in likely percolation processes. Black squares represent cluster zones (CLZ), the size of which is conditioned by the equilibrium temperature. White squares represent zones with only disordered point defects (free vacancies, individual interstitials  $Fe^{3+}$  ...).

- In the W1 domain, CLZ's are isolated and immersed in a defect lattice. The transition line W1/W2 would correspond to a specific  $z$  threshold value (for fixed  $T$ ) where there would be a starting percolation state.
- The W2 domain would be constituted of large black zones and white zones, with percolative paths through the lattice for both types of zones. The W2/W3 transition

line should be reached when the residual white zones would be no more percolative.

- The W3 state should be reached when black zones would envelop white zones up to a limit state where all lattice should be covered by a continuum of clusters, *i.e.* at the boundary W3/Fe3O4.

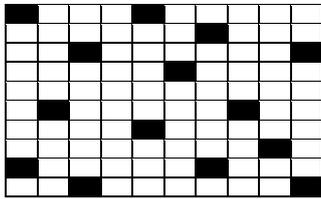
The effect of temperature would be to modify the sizes of clusters zones and to modify the limits of compositions of each boundary. As temperature increases, the cluster zones would be destabilized and the sizes of these zones would decrease.

Because of the complexity of this system, it is obvious that no unique specific model could represent the various evolutions. Nevertheless, this shows that the phase modifications W1, W2, W3

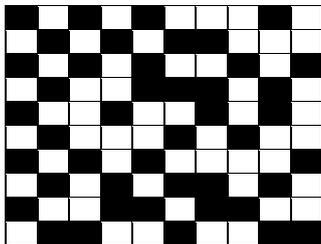
may be justified at least from changes in electrical charges of point defects thus of clusters, strongly correlated with composition  $z$ , and degree of ordering of them.

This scheme would imply rather continuous transformations from  $W_i$  to  $W_{(i+1)}$  at the level of the slight deviations from the main diffraction process. However, the discontinuities observed on the partial molar properties (Fig. II-6 and -7) at the compositions  $x_{i/j}$  on the boundaries of subdomains, would correspond to abrupt differences in internal energy and configurational entropy due to the change of cluster type (or charge), and to the change in long-range order of clusters.

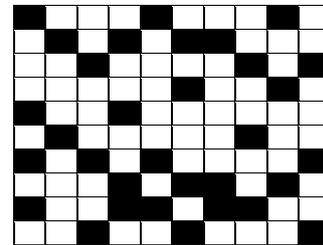
#### Low $z$ values: W1 pseudo phase



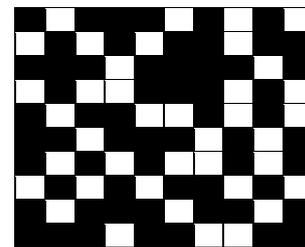
Intermediate  $z$  values  
on the boundary W2/W3  
(no percolation for white zones)



#### Percolation for limit $z$ value on the boundary W1/W2



#### W3 pseudo-phase



#### Limit of existence of W3

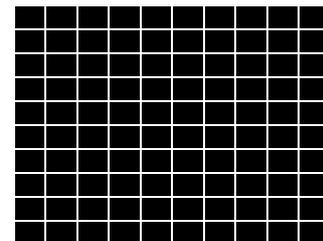
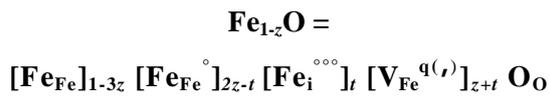


Figure VI-1: schematic representation of the pseudo phases W1, W2, W3.  
A similar point of view was previously proposed in the literature (R-97Gle).

## VII - CONCLUSIONS.

**Point defects.** Up to now, the subdivision of the equilibrium phase diagram of wüstite appears as being highly complex, with the existence of domains with different thermodynamic behaviors and high order transitions (at least of second order). The general chemical formula is based on the presence of iron vacancies noted  $V_{Fe}^{q(r)}$  where  $q^{(r)}$  designates the effective charge with  $q = 0$  to  $2$ , associated with  $Fe^{3+}$  distributed on octahedral sites (fraction:  $2z-t$ ) and tetrahedral sites (fraction:  $t$ ) of the basic FCC lattice of NaCl type:



The electroneutrality would be ensured by holes in the valence band and/or electrons in the conduction band.

**Clusters.** Works of different origins clearly demonstrated the existence of clusters of defects constituted of iron vacancies coupled with cations  $Fe^{3+}$  in tetrahedral interstitial sites, and mixture of  $Fe^{2+}/Fe^{3+}$  cations in octahedral sites of the basic FCC lattice. These clusters would coexist with free vacancies. However, up to date, the exact form of clusters noted (m:n) (m vacancies  $V^{q(r)}$  linked to n interstitials  $Fe_i^{\circ\circ}$ ) is far from being definitively determined.

The ratio  $R = (z+t)/t$  was obtained mainly from neutron diffraction experiments in the range 2 to 4 depending on authors. Several of them observed quasi constant R values in the range 2 to 3, while other authors observed a variable or constant value in the range 2.8 to 4. It should be remarked that if the wüstite lattice was occupied only by the sole (m:n) isolated cluster, the ratio R should be equal to  $(z+t)/t = m/n$ .

**The pseudo-phases.** Inside the initial phase diagram, the existence of distinct areas corresponding to the pseudo phases W1, W2, W3 is supported by some experimental evidences from different authors. It is necessary to recall that the term “boundary” designates a threshold of percolation at the exact separation between two

thermodynamic behaviors, corresponding to progressive evolutions of short and long range orderings (Fig. IV-I).

A supplementary first order transition  $W \rightleftharpoons W'$  was directly linked to the first order transition  $\alpha Fe \rightleftharpoons \gamma Fe$  at 912 °C. Up to now, the lack of systematic studies close to the isotherm at 912 °C limits the correct definition of this part of the Fe-O phase diagram, despite some advanced thermodynamic studies (81See) (86Sjö), the interpretation of which needs to be developed.

**Changes in cluster form.** Having regard to the existence of clusters (m:n) and the variation of the ratio R observed by certain authors, a first description of the pseudo-phases W1, W2, W3 was proposed in terms of structure modifications of these clusters, with an increasing cluster size as z increased. However, many contradictions must be noted. The historical (13:4) cluster resulting from X-ray diffraction analyses on a crystal seems to be in contradiction with the composition of the studied wüstite and the 3X superstructure chosen to perform calculations. The (10:4) ZnS-blende cluster could agree with neutron diffraction experiments at equilibrium and in quenched samples, and with electron microscopy images for some compositions z of quenched samples. The (12:4) <110> specific cluster proposed by Lebreton & Hobbs could also agree with a superstructure of P” type (5a x 5a x 10a) for a high composition z.

The existence of separated ordered cluster zones should agree with the quasi-constant k parameter. It should be noted that significant modifications in cluster form (e.g. (13:4) or (10:4) transformed into (4:1)) as z or T varies were never demonstrated for the whole phase diagram. In addition, in studies of samples at equilibrium or after a quenching process, all observations of superstructure Bragg peaks or diffuse scattering due to disorder show that the k values (k close to 2.6-2.7) vary slowly with z, thus characterizing a quasi-constant repetition distance between clusters. If clusters (m:n) changed strongly in their forms, the repetition distance k.a would also change strongly, which is not the case.

**New possible description of pseudo-phases.**

Probably the W1 pseudo-phase (low  $z$  values and high  $T$  values) would be characterized by free vacancies coexisting with a weak proportion of small zones of clusters.

The W3 pseudo-phase at high  $z$  values and low  $T$  values would correspond to clusters covering the whole lattice with a minimum distance of  $2.55a$  between clusters corresponding to a  $5X$  superstructure resulting from a zigzag ordering of clusters. .

The W2 pseudo-phase was identified as a solution of W1 and W3 of opposite energetic evolutions above its critical temperature of  $300\text{ }^{\circ}\text{C}$ . That would induce zones of ordered clusters and zones of free vacancies, with a progressive built up from boundary  $z_{12}$  to boundary  $z_{2/3}$  of junctions between cluster zones which could percolate.

The p to n transition would be associated with a starting of this percolation. This could be located in the W2 domain, but not only, and probably connected with a change in electrical charges of vacancies and clusters.

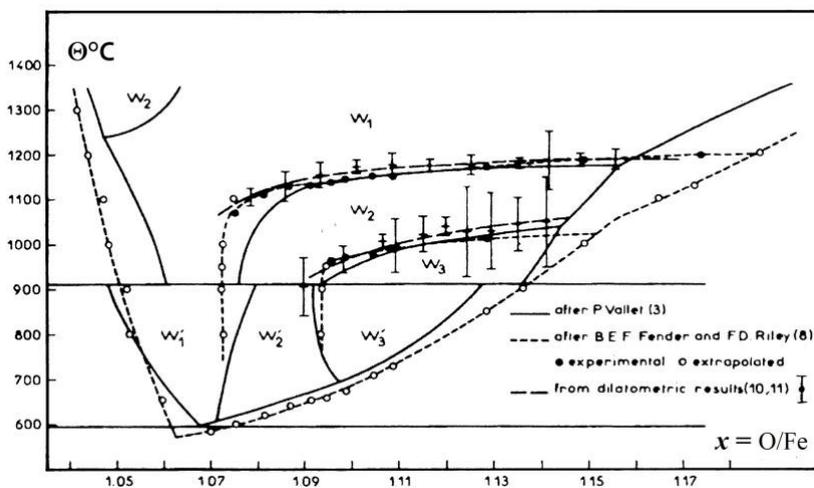
Finally, an additional feature would explain the observed electrical modifications. As  $z$  increases,

due to interactions between charges, the electrical charges of vacancies ( $V^{q(i)} = V'', V'$  or  $V$ ) and clusters would change with  $q$  varying from  $q=2$  (low  $z$ ) to  $q=0$  (high  $z$ ). This modification of charges  $q$  would be associated with an increasing number of electrons in the conduction band.

**The transition close to  $911\text{ }^{\circ}\text{C}$ .** Up to day, the three varieties W'1, W'2 and W'3 associated to  $\alpha\text{-Fe}$  below  $912\text{ }^{\circ}\text{C}$  were never directly characterized on a structural point of view. Because of tiny energetic differences, their defect structure might be close to the one of the W1, W2, W3 pseudo-phases, as this was proposed by Worrall and Coley in their kinetic analyses, and in a systematic sorting of a large pattern of clusters from the literature (10Wor) (R-13Wor). Nevertheless, these authors have provided new indisputable elements highlighting such pseudo-phases within the wüstite equilibrium diagram.

# Annex 1

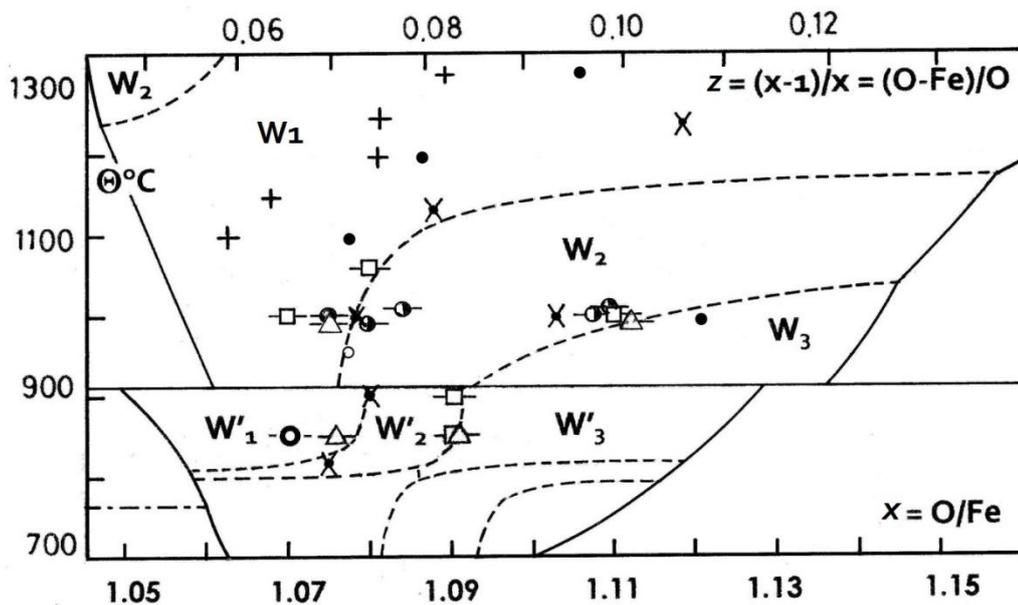
## 1 - Plot of the two first versions of the $\Theta(x)$ phase diagram with three subdomains



by Carel and Gavarri (76Car)

Fig. A1-1-Comparative plot of experimental phase diagram versions by Vallet and Raccah (64Val), and Fender and Riley (69Fen).

## 2 - Several sets from the literature of transitions located in diagram $\Theta$



**Fig. 1-2-Transitional effects located in the diagram [ $^{\circ}\text{C}$ , x]**

a- G.H. Geiger, R.L. Levin, J.B. Wagner jr, Studies on the Defect Structure of Wüstite using Electrical Conductivity and Thermoelectric Measurements, *J. Phys. Chem. Solids* **27** (1966) 947-956, p.955 Table 4: “unexpected changes in the slopes of  $\log \sigma$  vs  $\log p\text{O}_2$ ”  
 $\Rightarrow \square$

b- I. Bransky and A. Z. Hed, Thermogravimetric Determination of the Composition-oxygen Partial Pressure Diagram of Wustite ( $\text{Fe}_{1-y}\text{O}$ ), *J. Amer. Ceram. Soc.- Discuss. and Notes* **51** (1968) 231-32 ; breaking points at 1000, 1100, 1200, 1300°C re-calculated for correlations of  $\log p(\text{O}_2)$  vs z  
 $\Rightarrow \bullet$

c- E. Riecke and K. Bohnenkamp, Über die Kinetik der Oxydation und Reduktion von Wüstit innerhalb seines Existenzgebietes, *Archiv Eisenhüttenwes.* N°9 (1969) 717-725, p.722 Fig 7; reaction rate vs 100y ( $\text{Fe}_{1-y}\text{O}$ ) at 1000°C,  $p\text{H}_2\text{O}/p\text{H}_2$ , re-analyzed curves (I), (III) oxidation, curve (II) reduction [(I):+10°shift, (III): -10°shift in the figure], changes in the slope of quasilinear successive segments  
 $\Rightarrow \odot$

d- E. Takayama and N. Kimizuka (80Tak), Thermogravimetric method in the temperature range 1100°-1300°C  
 $\Rightarrow +$

e- J. Molenda, A. Stokłosa, W. Znamirowski, Transport Properties of Ferrous Oxide  $\text{Fe}_{1-y}\text{O}$  at High Temperature, *phys. stat. sol. (b)* **142** (1987) 517 ; Fig 2 p.519: experimental  $\log(\sigma)$  vs  $\log p\text{O}_2$  (818-1307°C), successive segments defined from Raccach-Vallet’s isotherms to model the curvature; Fig.4: isothermal  $\sigma(y)$ , resulting intersections in successive linear segments of  $\sigma(y)$   
 $\Rightarrow \times$

f- E. J. Worrall and K. S. Coley, Kinetics of the Reaction of  $\text{CO}_2/\text{CO}$  Gas Mixtures with Iron Oxide, *Metallurgical and Materials Transactions B* **41** (2010) 813-823; another interpretation of Fig. 9 at 850°C gives rise to an additional point close to  $x = 1.078$  as a second order type transition, identified for  $\text{W}^1 \leftrightarrow \text{W}^2$ . Another transition for  $x = 1.090$  appears as a discontinuity at the location of  $\text{W}^2 \leftrightarrow \text{W}^3$   
 $\Rightarrow \triangle$

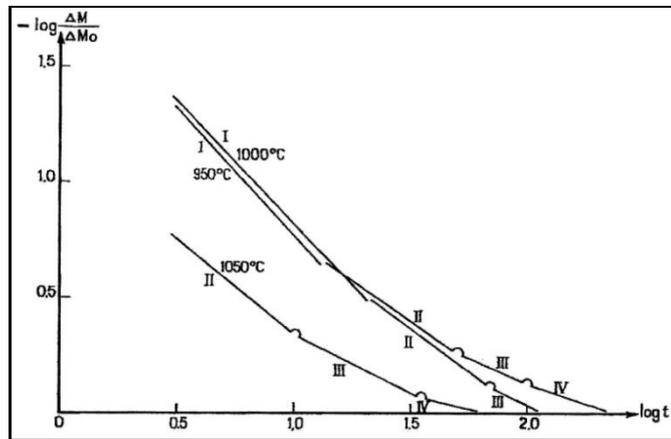
**Point  $\omega$**  located close to  $x = 1.070$  approximate the common intersection of the three lines for re-interpreting the kinetics at 850 °C (See Annex 2)  $\Rightarrow \odot$

**Annex 2**

**1 - Separate diffusion sequences in the thermogravimetric study of the reduction in  $\text{H}_2/\text{H}_2\text{O}$  gas mixtures**

The first experimental confirmation of the three  $\text{W}_i$  out of Vallet’s team was published by (66Gei). At the same time the work of Landler and Komarek (66Lan) was available. A numerical analyse made be revealed three

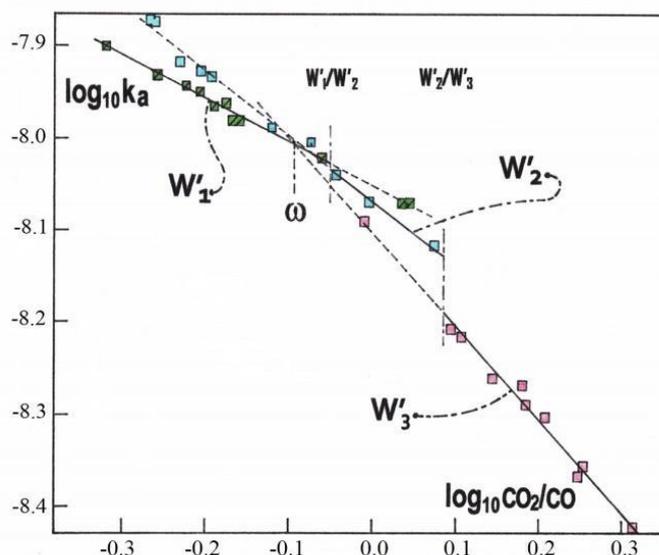
diffusion sequences distributed rather randomly across the analysed domain. It was thus published (67Car). The following Fig. 2-1 was drawn as a summarized result of the determinations.



by Carel (67Car)

**Fig. 2-1 - Typical runs of reduction under  $\text{H}_2\text{O}/\text{H}_2$  identified by (66Lan).**

## 2 - Re-analysis of kinetic data related to the isotherm at 850°C by (10Wor)



**Fig. 2-2-Intersection  $W'1/W'2$  for  $\log \text{CO}_2/\text{CO} = -0.05052 \Rightarrow x=1.0776$ , expected 1.0779;  
 $W'2/W'3$  for  $\log \text{CO}_2/\text{CO} = -0.08468 \Rightarrow x=1.0903$ , expected 1.0901;  
 point  $\omega$ :  $x = 1.0698$  where the three variations are convergent.**

In Fig. 9 p. 821 by Worrall and Coley (10Wor), it is possible to separate three linear variations of  $\log k_a = -m \cdot \log(\text{CO}_2/\text{CO}) + \log k_0$  display in Fig.2-2, rather than only two variations. The L. S. coefficients  $m = 0.48 \pm 0.03$  ( $W'1?$ ),  $0.71 \pm 0.05$  ( $W'2?$ ),  $1.03 \pm 0.09$  ( $W'3?$ ) have been calculated. They are statistically identical to those of equations [36], [37], [38] at 1268 K by ((10Wor) p. 820). A discontinuity is observed at the location of the transition  $W'2 \leftrightarrow W'3$  forecasted at equilibrium by (89Val). It should correspond to a sharp process (nuclear or electronic change in cluster

structure, change in percolation mode, germination of a surstructure ( $2.5a_0 \times 3$ ).

**Point  $\omega$**  approximates the common graphical intersection of the three variations where the continuity for transitions  $W'j \leftrightarrow W'j+1$  seems to be carried out. Coordinates of point  $\omega$  are found to be  $\log k_a = -8.00558$  and  $\log p_{\text{CO}_2}/p_{\text{CO}} = -0.9180$ , i.e.  $l'(\omega, 1093\text{K}) = -17.38387$ ;  $\log p(\omega, 1093\text{K}) = -12.12992$ . The corresponding composition would be  $x = 1.069_8$  ( $\cong 1.070$  at point C (86Val)). Such a convergence has been also observed  $\forall T$  for  $\Delta \bar{H}_Q(W_i)$  (cf § II.2 the converging point  $\Omega$  in Fig. II-5).

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