JOURNAL OF MATERIALS SCIENCE 21 (1986) 2147–2152

Comparative study of solubilities of hydrogen, nitrogen and carbon in α-iron

N. SHOHOJI
Laboratório Nacional de Engenharia e Tecnologia Industrial, Departamento de Tecnologia dos Materiais, 1699 Lisboa Codex, Portugal

Solubility data of hydrogen, nitrogen and carbon in α-iron are analysed on the basis of statistical thermodynamics. Present analysis appears to yield realistic values for the enthalpy term of the solutions of these interstitial elements into α-Fe, while the entropy terms remain ambiguous. During the course of this analysis a parameter θ_X, which refers to the solubility limit of the specific interstitial element X (X = hydrogen, nitrogen or carbon), is also estimated; $\theta_H < \theta_N < \theta_C$. This order of θ_X values appears to be in accord with the observation that, under normal conditions, the solubility of carbon is the highest and that of hydrogen the lowest in α-Fe, while the atomic size increases with the order hydrogen < nitrogen < carbon.

1. Introduction

α-iron possesses a b c c (body centred cubic) lattice and dissolves only small amounts of hydrogen (H), nitrogen (N) and carbon (C) to form interstitial solid solutions. When we express these interstitial solid solutions by the form FeX_x (X = H, N, C) the value of x is no more than 0.001 for temperatures (T) below 1000 K. Due to the low rates of x the experimental determination of solubilities of H, N and C in α-Fe is rather difficult and the available experimental solubility data have not always been in good agreement.

McLellan *et al.* [1, 2] have made experimental efforts to determine the reliable values of x in FeX_x for X = H and N using super-pure iron under normal pressure (1 atm) of super-pure X_2 gases. Their results are summarized in Fig. 1.

Before then Hillert and Jarl [3] had tried to rationalize the existing experimental solubility data for FeN_x and proposed the following empirical equation for the solubility x_N^α of N in α-Fe (Equation 6 in [3])

$$x_N^\alpha = 1.44 \times 10^{-7}(p_{N_2})^{1/2} \times \exp\left(1.30 \ln T - \frac{2575}{T}\right) \quad (1)$$

where the equilibrium nitrogen pressure p_{N_2} is given in atm and T in K. A solubility curve based on this equation is drawn in Fig. 1, which shows reasonable agreement with the experimental values reported by McLellan and Farraro [2]. Thus, both the experimental values reported by McLellan and Farraro [2] and the empirical Equation 1 proposed by Hillert and Jarl [3] for N solutions in α-Fe may be granted as reasonably reliable.

Then, the experimental values of solubility x_H^α of H in α-Fe reported by da Silva and McLellan [1] may be as reliable as x_N^α values reported by McLellan and Farraro [2]. The empirical equation proposed by Smith (p. 29 in [4])

$$x_H^\alpha(\text{Smith}) = 2.85 \times 10^{-3}(p_{H_2})^{1/2} \times \exp\left(-\frac{3454}{T}\right) \quad (2)$$

however, does not appear to fit these experimental results very well. Instead, the analogous equation to Equation 1

$$x_H^\alpha = 6.0 \times 10^{-8}(p_{H_2})^{1/2} \times \exp\left(1.30 \ln T - \frac{1750}{T}\right) \quad (3)$$

appears to be approximating the experimental data better than Smith's (Equation 2), as shown in Fig. 1. The first term, (1.30 ln T), in the exponential of Equation 3 was taken to be the same as that in Equation 1. It appears that this term is somehow related to the degree of freedom of the diatomic gas molecule (translational and rotational motions) [5].

Concerning the solubility of C in α-Fe, the experimental values are available for α-FeC_x in equilibrium with cementite (p. 399 in [6]). They are plotted in Fig. 1. They fall into the following relationship [6]

$$x_C^\alpha(\text{cementite}) = 0.12 \exp\left(-\frac{4890}{T}\right) \quad (4)$$

However, it appears that no experimental solubility is available for α-FeC_x in equilibrium with graphite, while Darken and Gurry (p. 401 in [6]) summarized the thermodynamically estimated values based on the experimental solubility limit x_C^α(cementite) in α-FeC_x in equilibrium with Fe_3C. They are also plotted in Fig. 1 and fit the following equation

$$x_C^\alpha(\text{graphite}) = 3.05 \exp\left(-\frac{8250}{T}\right) \quad (5)$$

0022–2461/86 $03.00 + .12

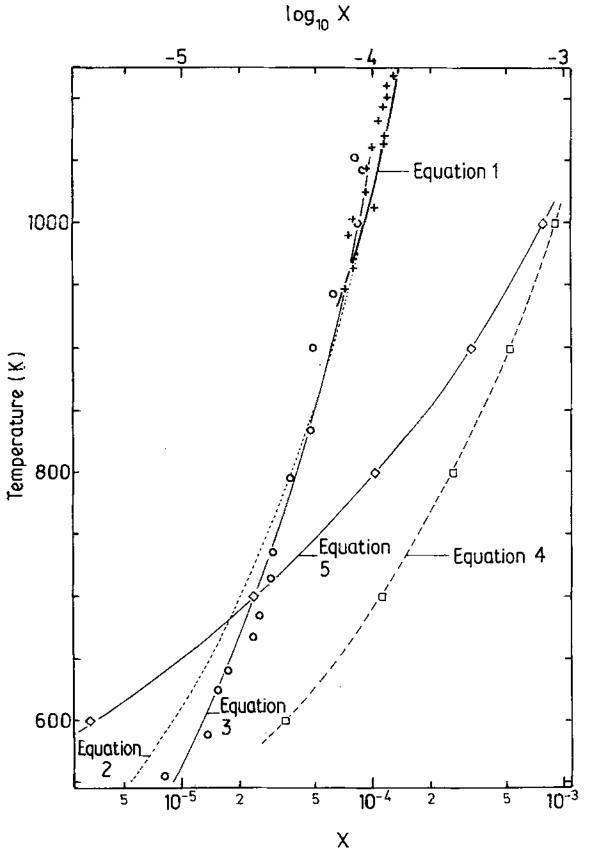

Figure 1 Solubilities of H, N and C in α-Fe. (○) x_H^α under $p_{H_2} = 1$ atm [1]; (+) x_N^α under $p_{N_2} = 1$ atm [2]; (◇) x_C^α(graphite) [6]; and (□) x_C^α(cementite) [6].

It is obvious that all these α-FeX_x under consideration are classified as very dilute interstitial solid solutions, in which no nearest-neighbour (n–n) solute–solute (X–X) interaction is in operation. Application of statistical thermodynamics to such very dilute interstitial solid solutions on the basis of the assumption

$$E_{X\text{-}X} = 0 \qquad (6)$$

has been discussed in an earlier work [7].

In the present work the solutions of H, N and C in α-Fe are analysed comparatively on the basis of statistical thermodynamics. One of the significant features noticeable from the plots in Fig. 1 is that, in spite of its larger atomic radii, solubility of C in α-Fe is higher than that of H and N, when compared at the same temperature under normal conditions. It is shown how this feature is reflected by the statistical thermodynamic parameters.

2. Statistical thermodynamic analysis

Since the detailed procedures for analysis might be referred to in the series of works [7–13], they are not given in the following text. Nomenclature and essential equations used for the present analysis are summarized in an Appendix at the end of the text. Nuclear spin weight ϱ for N and C is taken to be unity, but that for H to be 2. α-FeN_x will be examined first.

2.1. α-FeN_x

For the statistical thermodynamic analysis of the very dilute interstitial solid solutions on the basis of the Equation 6 the first step is to find the proper value of the parameter θ which yields x-independent values of $A = RT \ln \{[(\theta - x)/x] p_{X_2}^{1/2}\}$ for a given T [7]. It would not be difficult to do so, when the experimental equilibrium pressure–temperature–composition (P–T–C) relationships are available for a range of p_{X_2}, as have been determined previously [7]. Unfortunately, the experimental solubility data for α-FeN_x reported by McLellan and Farraro [2] are limited to a fixed value of $p_{N_2} = 1$ atm. Under these circumstances, the determination of a θ value based on the experimental P–T–C relationships is not feasible.

TABLE I $RT \ln \left[\dfrac{\theta - x}{x} p_{N_2}^{1/2} \text{(atm)}\right]$ against p_{N_2} for α-FeN_x at 1000 K based on Equation 1

p_{N_2} (atm)	$RT \ln \left(\dfrac{\theta - x}{x} p_{N_2}^{1/2}\right)$ (kJ mol^{-1})				
	θ				
	0.001	0.005	0.01	0.05	0.10
10	17.40	33.04	39.04	52.61	58.40
1	19.36	33.36	39.20	52.64	58.41
0.1	19.89	33.46	39.25	52.65	58.41
0.01	20.04	33.48	39.25	52.64	58.40

One possible way to overcome this difficulty may be to rely on the empirical Equation 1. For example, we take $T = 1000$ K and estimate the x-values for $p_{N_2} = 10$, 1, 0.1 and 0.01 atm. Then, we are able to obtain A against x relationships for various values of θ. The results of this examination are summarized in Table I, in which p_{N_2} values are listed, instead of x values. These results show that the variation of A against p_{N_2} (i.e. against x) at a given T tends to become less significant with increasing θ. For example, with $\theta \geqslant 0.05$ the values of A are almost constant irrespective of p_{N_2}, whereas with $\theta = 0.001$ A decreases with increasing p_{N_2}. However, it does not seem to be very clear whether we should take 0.05 as the θ value satisfying Equation 6 or $\theta = 0.01$ or even 0.005. This ambiguity in determining the proper θ value needs to be avoided somehow in order to derive the well-defined parameters.

In the following we are going to see how the choice of θ affects the estimated parameters, Q_N and $R \ln (Zf_N)$ (cf. Equations A2 to A4 in the Appendix as well as [7, 8, 10]). The factor Z might be appreciated as the index of the range of blocking of the interstices from occupation by the solute atoms around an occupied interstitial site [7, 14]. For example, the combination of $\theta^d = 0.05$ and $Z \simeq 30$ was estimated for the very dilute range of H solution in bcc titanium, while $\theta = 1.25$ was assigned for the moderate concentration of H in the same bcc titanium (superscript "d" refers to the very dilute solute concentration range). It appears that Z is roughly equal to θ/θ^d.

Experimental data reported by McLellan and Farraro [2] at $p_{N_2} = 1$ atm are analysed with various values of θ and the results are plotted in Fig. 2. As you might notice in this figure, the value of Q_N tends to converge to the constant value of ~ -420 kJ mol^{-1} as θ increases. This observation might suggest that there is some proper choice of the combination of θ^0 and Z^0,

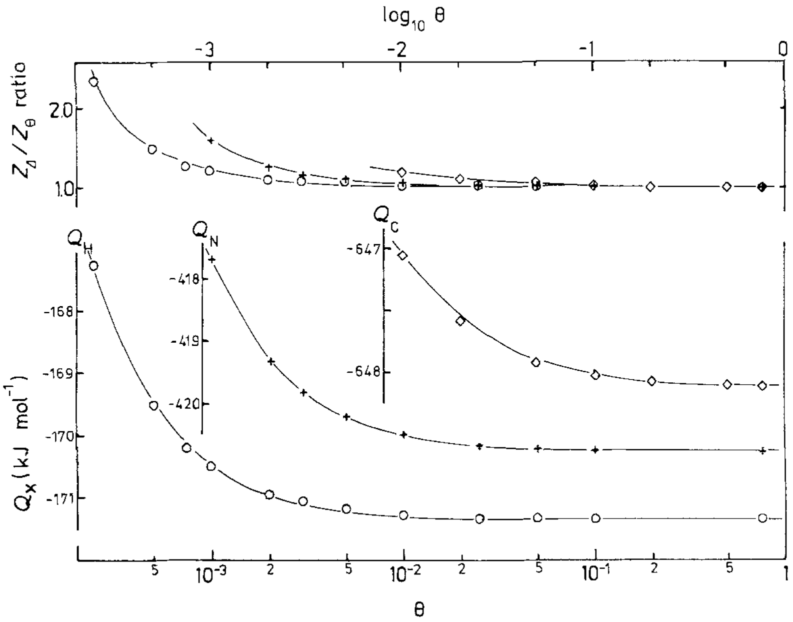

Figure 2 Z_Δ/Z_θ ratio and Q_X value as a function of θ. (○) H; (+) N; and (◇) C.

which might lead to the realistic distribution model of the interstitial atoms, and that if we construct our analysis on the basis of θ^+ ($>\theta^0$) a realistic Q value may still be obtained, while the choice of θ^- ($<\theta^0$) may result in the erroneous estimation of Q. The meaning of this implication may be appreciated as follows.

According to this opinion, ($Z^0 - 1$) relevant interstices around the occupied interstitial site are supposed to be blocked from the occupation by the other interstitial atom. This blockage may be due to the strain in the host metal lattice induced by the interstitial atom and to the limitation stemming from electronic structure [10, 11]. The value of θ^0 should satisfy the Equation 6.

Consider the situation, in which we choose θ^+ ($>\theta^0$) for the analysis. A corresponding value of Z^+ may be $\sim Z^0\theta^0/\theta^+$ ($<Z^0$). The pattern of the *statistical* (random) distribution of n_N atoms over $\theta^+ n_{Fe}$ available *sites* (or strictly speaking, $\theta^+ n_{Fe}$ groups of imaginary extended unit cell each containing Z^+ relevant interstices) may not be very far from that of n_N atoms over $\theta^0 n_{Fe}$ *sites*, considering that the "mesh" Z^+ of the chosen unit cell is finer than the realistic "mesh" Z^0 and that these types of distribution may be classified as *normal* or *Gaussian* (since we assume X–X interaction is negligible).

On the other hand, if we employ θ^- ($<\theta^0$) for the analysis the situation may not be the same. The choice of θ^- may mean $Z^- > Z^0$; the "mesh" Z^- is coarser than the realistic Z^0. This might lead to overlooking some of the realistic *statistical* distributions, hence, resulting in an improper model.

If the choice of θ^+ still yields an acceptable statistical model, f_N as well as Q_N may hold approximately the same value irrespective of the chosen value of θ^+ [7]. Plots of Z_Δ/Z_θ ratios summarized in Fig. 2 are prepared in order to examine this point. When we take a large enough value of θ for the reference (i.e. $\theta_{ref} \gg \theta^0$; e.g. $\theta_{ref} = 1.5$ is employed for the construction of Fig. 2), the corresponding Z_{ref} might be taken as unity [7, 8, 10, 14]. Thus, the value of Z may be estimated from the following comparison

$$\Delta = R\ln(Zf) - R\ln f_{ref} = R\ln(Zf/f_{ref}) \qquad (7)$$

Provided that f is approximately equal to f_{ref} [7], $\exp(\Delta/R)$ would yield the estimation of Z ($\equiv Z_\Delta$). Z_Δ estimated in this way is expected to be equal to the ratio of θ_{ref}/θ ($\equiv Z_\theta$), if θ is in the range $\theta_{ref} \geqslant \theta \geqslant \theta^0$. Fig. 2 shows that the Z_Δ/Z_θ ratio tends to deviate from unity when θ becomes too small, which appears to occur parallel to the deviation of the Q_N value from the converged value of ~ -420 kJ mol^{-1}. These results appear to suggest that the proper θ^0 value for α-FeN$_x$ may exist somewhere between 0.01 and 0.05, although exact specification of θ^0 value is still difficult only using this information.

Consideration given above may imply that the simple choice of θ_0 (total number of relevant crystallographically available interstices per M would lead to the realistic estimation of Q values for the very dilute interstitial solid solutions. This opinion may appear to be ironical, considering that the proper choice of θ value was essential for the similar analysis of the interstitial solid solutions of the moderate solute concentration range [8–13]. It was shown that the choice of larger θ value than the proper value θ^0 would result in the unrealistic variation of $E_{X\text{-}X}$ with the composition x of MX$_x$ within the same phase at a given temperature for the moderate solute concentration range. This rigid limitation of the choice of θ value may be attributable to the existence of finite X–X interaction, which tends to uniquely determine the mutual geometrical configuration of the interstitial atoms within the grain of the crystal.

On the other hand, in the very dilute solute concentration range, the X–X interaction is negligible and, hence, the realistic model of *statistical* distribution of solute atoms may be well represented as long as the "mesh" Z is taken to be finer than Z^0. It must be noted, however, that one serious handicap of the analysis of the very dilute interstitial solid solutions based on θ_0, instead of assigning a proper value of θ^0, would be the unresolved ambiguity in the $R\ln(Zf)$

term, which relates to the entropy in the thermodynamic terms.

2.2. α-FeH$_x$

By comparing the solubility data obtained using the super-pure single crystal iron equilibrated with super-pure H_2 gas with earlier experimental results obtained by miscellaneous authors for irons having different grades of impurity and grain sizes, da Silva and McLellan [1] came to the conclusion that the solubility x of α-FeH$_x$ is not markedly affected by the purity grade of the iron and that x is rather insensitive to the presence of grain boundaries. Based on the x values under $p_{H_2} = 1$ atm reported by da Silva and McLellan [1] the plots of Q_H and the Z_Δ/Z_θ ratio as a function of θ are obtained (Fig. 2). The value of Q_H converges to $\sim -171\,\mathrm{kJ\,mol^{-1}}$ for $\theta > 0.01$. The deviation of the Z_Δ/Z_θ ratio from unity appears to occur in parallel with the deviation of Q_H from $\sim -171\,\mathrm{kJ\,mol^{-1}}$ as the θ value decreases. Judging from Fig. 2, the proper value of θ for α-FeH$_x$ may lie somewhere between 0.002 and 0.01; i.e. $\theta_H < \theta_N$. This observation appears to suggest that the parameter θ is a reasonable figure representing well the solubility limit of a specific interstitial element into the metal lattice, considering that the solubility of N is higher than that of H in α-Fe under the same conditions of temperature and p_{X_2} (X = H, N) (cf. Fig. 1). On the other hand, this observation may suggest the invalidity of the simple rigid sphere model of the atoms for α-FeX$_x$, considering that $r_H < r_N$, where r_X refers to the atomic radii of the interstitial element X in the metal lattice (cf. Table II). If the rigid sphere model were valid, the strain energy term in α-Fe lattice arising from the occupation by N atoms is larger than that by H atoms, and eventually leads to $Z^0_N > Z^0_H$ and $\theta^0_N < \theta^0_H$. This point will be considered in some detail later in the discussion.

2.3. α-FeC$_x$

The plots in Fig. 2 for α-FeC$_x$ in equilibrium with graphite are obtained on the basis of Equation A5. The carbon activity a_C of graphite holds unity at any temperature, since graphite provides the standard state of carbon. In this system, therefore, it is in principle not feasible to determine a θ value by the same method as commonly employed in metal–gas systems (i.e. through the linearity of A against x plots at a given temperature) [7–12]. The control of a_C as an experimental variable is not so easy as the control of a_X of the gaseous elements through p_{X_2} [13].

As Fig. 2 shows, Q_C tends to deviate from the converged value of $\sim -648\,\mathrm{kJ\,mol^{-1}}$ with decreasing value of θ, which appears to occur parallel with the deviation of the Z_Δ/Z_θ ratio from unity, as was the case for X = H and N. Judging from Fig. 2, θ^0_C may lie somewhere between 0.05 and 0.2; i.e. $\theta^0_C > \theta^0_N > \theta^0_H$ in accordance with the order of the solubilities of these interstitial elements in α-Fe under normal conditions.

TABLE II Available values for the atomic radii of the interstitial elements

Element	Atomic radii (nm)	
	[15]	[16]
Hydrogen	0.046	0.037
Boron	0.097	0.078
Carbon	0.077	0.077
Nitrogen	0.071	0.055
Oxygen	0.060	0.060

3. Discussion

The reliability of available x–T relationships for α-FeX$_x$ (X = H, N, C) was briefly examined and the analysis was made on the basis of statistical thermodynamics. It appeared that for those very dilute interstitial solid solutions the analysis based on the θ_0 value, instead of the proper value of θ^0 which might be chosen so that Equation 6 might be fulfilled, would still yield the satisfactory value of Q. It might be due to this fact that the partial molar enthalpy $\bar{H}_u$ for hydrogen solution ($= -176.9\,\mathrm{kJ\,mol^{-1}}$) [2] and that for nitrogen solution ($= -423.7\,\mathrm{kJ\,mol^{-1}}$) [1] in α-Fe estimated by McLellan *et al.* with $\theta = 6$ (i.e. equal to θ_0 of tetrahedral-site (T-site) occupation) are in reasonable agreement with the values of the corresponding parameters, Q_H ($\simeq -171\,\mathrm{kJ\,mol^{-1}}$) and Q_N ($\simeq -420\,\mathrm{kJ\,mol^{-1}}$), estimated in the present study. The values of atomic partition function f_X, however, would remain ambiguous unless the values of the parameters, Z and θ, are specified by some means.

Present analysis led to $\theta^0_H < \theta^0_N < \theta^0_C$, although these θ^0_X values were not specified uniquely. This order is in accord with the order of the solubility limits of these interstitial elements in α-Fe under normal conditions. In this respect this result appears to reaffirm that θ is a physically meaningful parameter referring to the number of available interstices per metal atom for a specific interstitial element.

On the other hand, if we consider the commonly accepted values of r_X as summarized in Table II ($r_H < r_N < r_C$), the expected order of θ^0_X on the basis of a rigid sphere model would be $\theta^0_H > \theta^0_N > \theta^0_C$, which is in a reverse order from the observed. However, a question remains how seriously can we rely on these r_X values. You readily notice in Table II that, except for X = C and O, the values for r_X for the same element X taken by different authors [15, 16] do not agree with each other. In addition, Jack [17] reported that "anomalous" effective atomic sizes were observed in ternary Fe–C–N systems; i.e. r_N appeared to be larger than r_C in the fcc Fe lattice. According to his estimation based on X-ray diffraction results, $r_N = 0.0683$ nm and $r_C = 0.0675$ nm in ζ carbonitrides of Fe and $r_N = 0.0677$ nm and $r_C = 0.0663$ nm in ε carbonitrides of Fe. Jack [18] concluded that although these interstitial atoms are probably not fully ionized they do contribute some free electrons to the metal lattice. His suggestion concerning the direction of electron transfer (i.e. interstitial atom to metal lattice) would not be supported wholly, judging from the results of recent analyses [8, 11, 19–23] which suggest electron transfer from metal lattice to the interstitial atom. However, these considerations [8, 11, 17–23] as a whole appear to imply strongly that re-consideration would be necessary for the concept of the "size" of interstitial elements in the metal lattice.

Anyway, if $r_C < r_N$ were valid in the bcc α-Fe lattice, as were the cases for the fcc carbonitrides of Fe [17], the observation $\theta^0_N < \theta^0_C$ would appear to be acceptable. However, the consideration along this line on the basis of size effect would fail to explain the smaller θ^0_H than θ^0_N and θ^0_C, since there is no way to expect r_H being larger than r_N and r_C.

In the earlier reports [10, 11] it was pointed out, through the comparisons of solubility limits of H in miscellaneous metal lattices, that the nature of electronic interaction between metal atom and the interstitial atom, rather than the ambiguous concept of "size" of the interstitial elements, may be a decisive factor for the solubility limit of interstitial elements. For example, we may take the parameter Q_X as the one representing the electronic interaction between metal atom and the interstitial atom. The observed order $Q_H > Q_N > Q_C$ (Fig. 2) suggests that C is the most stable in the α-Fe lattice and H the least stable among these three interstitial elements. This order of Q_X does not appear to be in contradiction with the result $\theta^0_H < \theta^0_N < \theta^0_C$.

Another possible explanation for the observed order of θ^0_X may be made in terms of the feasibility of diffusion of these interstitial atoms in the α-Fe lattice. The rate of diffusion of N and that of C in α-Fe are comparable and much slower than that of H, when compared at the same temperature (e.g. p. 68 in [24]). This larger mobility of H may manifest itself as a large value of Z^0_H and, thus, might lead to a smaller θ^0_H value relative to θ^0_N and θ^0_C, as observed.

A brief consideration will be given in the following concerning the site occupation of these interstitial elements in the bcc α-Fe lattice. It appears to be commonly accepted (e.g. [24]) that N and C occupy octahedral-sites (O-sites), whereas the O-site is smaller than the T-site in the bcc structure. On the other hand, H atoms are supposed to occupy T-sites rather than O-sites. According to recent theoretical considerations [25, 26] the H atom in the Va-group metals (vanadium, niobium, tantalum) having the bcc structure may be thought of as being distributed over four T-sites around an O-site (4T-model). This situation might be appreciated as being equivalent to O-site occupation at least in statistical thermodynamic terms [7, 9–12]. Thus, if the 4T-model also applies to H in α-Fe, an expression for Q_X for X = H, N and C may have a common form as given by Equation A1.

In relation to the discussion given above for site occupation problems, the necessity may be realized for the consideration of the anisotropic nature of the valence electron distribution in bcc lattice. Fig. 3 depicts schematically the cross-section of the close-packed {1 1 0} plane of the bcc lattice. In the bcc structure the rigid spheres touch one another along the ⟨1 1 1⟩ directions, which suggests that the valence electron distribution may be enhanced along the ⟨1 1 1⟩ directions and that the extension of the valence electron clouds towards the ⟨1 0 0⟩ and ⟨1 1 0⟩ directions may be suppressed. Then, the electron-deficit zones might be depicted as the shaded rhombic areas in Fig. 3. This void is apparently larger than either the O-site or T-site of the rigid sphere model. Although this is merely a very crude model and further sophistication will be necessary, the fundamental idea that the strong directional preference may exist in the distribution of the valence electron clouds in the crystalline solids does not appear to be very unrealistic. The consideration for this directional preference of the valence electron distribution might be of special importance in the bcc structure, which is, unlike the fcc and hcp (hexagonal close packed) structures, not the closed packed structure. It must also be noted that the centre of this void coincides with the centre of the O-site. This enlarged void model may lead to diminishing strain energy contribution for all the interstitial atoms under consideration and might help understanding the observations that N and C appear to occupy O-sites rather than T-sites in α-Fe.

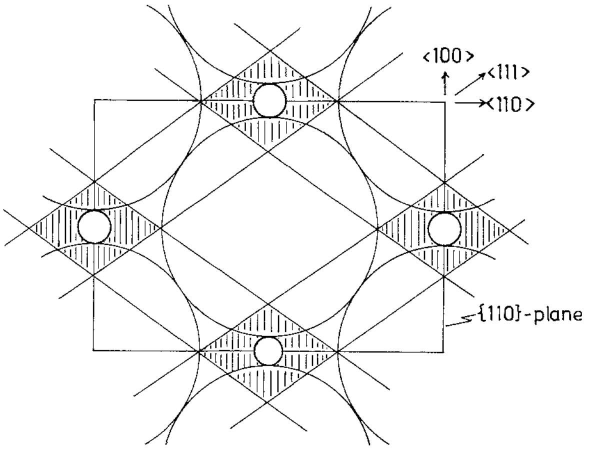

Figure 3 Cross-section of the close-packed {1 1 0} plane of the bcc structure. (Larger circle) rigid sphere host metal atom (bcc); (smaller circle) rigid sphere O-site; and (shaded zone) extended interstitial void.

Further studies based on the electronic band calculations as well as on the elastic theory of the crystal lattice would be necessary to fully clarify these problems, which are, however, beyond the scope of statistical thermodynamics.

4. Conclusions

The following conclusions may be derived from the present consideration.

1. Solubility of diatomic gas X_2 in α-Fe may be expressed as

$$x^{\alpha}_X = a(p_{X_2})^{1/2} \exp(c \ln T - b/T) \qquad (8)$$

where a and b are constants whose values depend on the species X but the value of c appears to be roughly equal to 1.30 irrespective of X.

2. Solubility limit of C in α-FeC$_x$ may be given as

$$x^{\alpha}_C = a \exp(-b/T) \qquad (9)$$

When α-FeC$_x$ is in equilibrium with graphite, $a = 3.05$ and $b = 8250$ (cf. Equation 5).

3. Unambiguous determination of the θ^0_X values satisfying the condition of $E_{X\text{-}X} = 0$ was difficult for α-FeX$_x$ under consideration. However, by constructing the plots as shown in Fig. 2, the values of Q_X were

determined as follows:

$$Q_{\mathrm{H}} = -171\,\mathrm{kJ\,mol^{-1}} \quad (10)$$

$$Q_{\mathrm{N}} = -420\,\mathrm{kJ\,mol^{-1}} \quad (11)$$

$$Q_{\mathrm{C}} = -648\,\mathrm{kJ\,mol^{-1}} \quad (12)$$

without specifying the value of θ_{X}^0 uniquely.

4. Values of $R \ln f_{\mathrm{X}}$ remain ambiguous, since neither the values of Z_{X}^0 nor θ_{X}^0 were uniquely specified.

5. Judging from the observation that $\theta_{\mathrm{H}}^0 < \theta_{\mathrm{N}}^0 < \theta_{\mathrm{C}}^0$ (cf. Fig. 2), simplifying rigid sphere model of the atoms may not provide a realistic model for α-FeX_x under consideration.

Appendix

Nomenclature

R	gas constant.
h	Planck constant.
k	Boltzmann constant.
m_{X}	mass of the X atom.
p_{X_2}	equilibrium X_2 pressure in atm.
D_{X_2}	dissociation energy of X_2 molecule per mol.
$\mathrm{D_C}$	dissociation energy per mol of carbon (graphite).
θ_{r} and θ_{v}	characteristic temperatures of rotation and vibration of the X_2 molecule.
f_{X}	atomic partition function of X in α-FeX_x.
E_{ij}	interaction energy between component atoms i and j in α-FeX_x (i, j = Fe, X).
n_i	number of component atoms i in α-FeX_x.
E	lattice energy of α-FeX_x.
θ	number of available interstitial sites for occupation by X per Fe in α-FeX_x.
θ_0	total number of crystallographically possible interstitial sites per Fe in α-FeX_x, e.g. $\theta_0 = 3$ for O-site and $\theta_0 = 6$ for T-site.
β	a factor relating to crystal structure.
O-site	octahedral interstices.
T-site	tetrahedral interstices.

Expression for Q_{X} in α-FeX_x

$$\begin{aligned} Q_{\mathrm{X}} &= \frac{\partial E}{\partial n_{\mathrm{X}}} - \beta x E_{\mathrm{X\text{-}X}} \\ &= 2E^{(\mathrm{I})}_{\mathrm{X\text{-}Fe}} + 4E^{(\mathrm{II})}_{\mathrm{X\text{-}Fe}} - E^{(\mathrm{II})}_{\mathrm{Fe\text{-}Fe}} \qquad (\mathrm{A1}) \end{aligned}$$

where the superscripts, (I) and (II), refer to the 1st and 2nd n–n's, respectively. Note also that in deriving Equation A1 X atoms are supposed to be distributed over O-sites.

Relations for α-FeX_x (X = H, N)

$$\begin{aligned} K_{\mathrm{X}} &= RT \ln \left(\frac{\theta - x}{x} p_{X_2}^{1/2} \right) + \mu_{\mathrm{X}}^0 \\ &= Q_{\mathrm{X}} - RT \ln (Zf_{\mathrm{X}}) + \beta x E_{\mathrm{X\text{-}X}} \\ &\simeq Q_{\mathrm{X}} - RT \ln (Zf_{\mathrm{X}}), \quad (\text{for } x \ll 1) \qquad (\mathrm{A2}) \end{aligned}$$

$$\mu_{\mathrm{X}}^0 = -\tfrac{1}{2} D_{\mathrm{X}_2} + RT\,C(T) \qquad (\mathrm{A3})$$

$$\begin{aligned} C(T) = &-\tfrac{1}{2} \ln \left[\frac{(4\pi m_{\mathrm{X}})^{3/2} k^{5/2}}{h^3} \frac{T^{7/2}}{\theta_{\mathrm{r}}} \left(1 + \frac{\theta_{\mathrm{r}}}{3T} \right) \frac{\varrho^2}{2} \right] \\ &+ \frac{\theta_{\mathrm{v}}}{4T} + \tfrac{1}{2} \ln \left[1 - \exp \left(- \frac{\theta_{\mathrm{v}}}{T} \right) \right] \qquad (\mathrm{A4}) \end{aligned}$$

Relation for α-FeC_x in equilibrium with graphite

$$\begin{aligned} K_{\mathrm{C}}^0 &= RT \ln \left(\frac{\theta - x}{x} \right) - D_{\mathrm{C}} \\ &= Q_{\mathrm{C}} - RT \ln (Zf_{\mathrm{C}}) + \beta x E_{\mathrm{C\text{-}C}} \\ &\simeq Q_{\mathrm{C}} - RT \ln (Zf_{\mathrm{C}}), \quad (\text{for } x \leqslant 1) \qquad (\mathrm{A5}) \end{aligned}$$

References

1. J. R. G. DA SILVA and R. B. McLELLAN, *J. Less-Common Met.* **50** (1976) 1.
2. R. B. McLELLAN and R. J. FARRARO, *Acta Metall.* **28** (1980) 417.
3. M. HILLERT and M. JARL, *Metall. Trans.* **6A** (1975) 553.
4. D. P. SMITH, in "Hydrogen in Metals" (The University of Chicago Press, Chicago, 1948).
5. R. H. FOWLER and E. A. GUGGENHEIM, in "Statistical Thermodynamics" (Cambridge University Press, Cambridge, 1949).
6. L. S. DARKEN and R. W. GURRY, in "Physical Chemistry of Metals" (McGraw-Hill, New York, 1953).
7. N. SHOHOJI, *Z. Metallkde* **76** (1985) 192.
8. N. SHOHOJI, M. KATSURA and T. SANO, *J. Less-Common Met.* **38** (1974) 59.
9. N. SHOHOJI, *ibid.* **90** (1983) L27.
10. *Idem, ibid.* **102** (1984) 53.
11. *Idem, ibid.* **114** (1986) 249.
12. *Idem, Mater. Lett.* **3** (1985) 206.
13. *Idem, Mater. Chem. Phys.* **13** (1985) 567.
14. R. SPEISER and W. SPRETNAK, *Trans. Amer. Soc. Met.* **47** (1955) 493.
15. C. S. BARRETT and T. B. MASSALSKI, in "Structure of Metals", 3rd Edn. (McGraw-Hill, New York, 1966).
16. E. A. MOELWYN-HUGHES, in "Physical Chemistry" (Pergamon Press, New York, 1961).
17. K. H. JACK, *Proc. R. Soc.* **A195** (1948) 41.
18. *Idem, Acta Crystallogr.* **5** (1952) 404.
19. M. KATSURA and T. SANO, *J. Nucl. Sci. Technol.* **4** (1967) 283.
20. *Idem, Technol. Rep. Osaka Univ.* **20** (1970) 451.
21. A. C. SWITENDICK, *J. Less-Common Met.* **74** (1980) 199.
22. T. HORI, H. ADACHI and S. IMOTO, *Trans. Jpn. Inst. Met.* **18** (1977) 31.
23. L. P. MOKHRACHEVA, V. A. TSKHAI and P. V. GELD, *Phys. Status Solidi (b)* **84** (1977) 465.
24. D. A. PORTER and K. E. EASTERLING, in "Phase Transformations in Metals and Alloys" (Van Nostrand Reinhold, New York, 1981).
25. H. SUGIMOTO and Y. FUKAI, *Trans. Jpn. Inst. Met., Suppl.* **21** (1980) 41.
26. H. SUGIMOTO and Y. FUKAI, *Phys. Rev.* **B22** (1980) 670.

Received 12 April
and accepted 10 September 1985