

Characterizing Atomic Interactions in Interstitial Non-Stoichiometric Compounds by Statistical Thermodynamics: Engineering Usage of Estimated Values of Statistical Thermodynamic Parameters

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Abstract

Statistical thermodynamics allows us to estimate atomistic interactions in interstitial non-stoichiometric compounds MX_x through analysis of experimentally determined pressure-temperature-composition (*PTC*) relationships for MX_x being in equilibrium with X_2 in gaseous state ($X = H, N, P$ or S) or for non-stoichiometric carbide MC_x being in equilibrium with excess C . In case of analysis for MC_x , chemical activity $a(C)$ of C in place of partial pressure $p(X_2)$ of X_2 gas must be known. On statistical modelling of crystal lattice structure for MX_x , an *a priori* assumption of constant nearest-neighbour $X-X$ interaction energy $E(X-X)$ within a homogeneity composition range at arbitrary temperature T was accepted to determine number θ of available interstitial sites for occupation by X atoms per M atom. Values of interaction parameters estimated as such appear rational and realistic noting consistency of the values for M 's in the same group in the Periodic Table of the Elements and compatibility with enthalpy values evaluated by conventional thermodynamic approach. Engineering insights gained for MX_x through analysis of atomistic interaction parameter values evaluated by the statistical thermodynamics are reviewed comprehensively in this paper. M might be substitutional alloy $A_{1-y}B_y$ composed of constituents, A and B , or MZ_z containing another interstitial constituent Z besides X . Insights acquired from this line of statistical thermodynamic analysis appear to be of pragmatic use for advanced alloy design as shall be demonstrated hereafter.

Keywords

Statistical Thermodynamics, Non-Stoichiometry, Interstitial Compound, Hydride, Nitride, Carbide, Phosphide, Sulfide

1. Introduction

Statistical thermodynamic analysis procedures were comprehensively summarized by Fowler and Guggenheim in a classical monograph published in 1949 [1]. Statistical thermodynamics is considered as a bridge connecting between invisible atomistic scale microscopic world and experimentally observable macroscopic state for interstitial non-stoichiometric compound MX_x possessing composition $x = [X]/[M]$ being in equilibrium with X_2 gas at partial pressure $p(X_2)$ at temperature T . By statistical thermodynamic analysis of equilibrium pressure-temperature-composition (*PTC*) relationships for MX_x , nearest-neighbour atomic interaction energy $E(i-j)$ between i and j atoms and atomic partition function f_i of constituent i in MX_x might be calculated ($i, j = M, X$).

Statistical thermodynamic parameters evaluated for extensive range of interstitial non-stoichiometric compounds including hydride, carbide, nitride, phosphide and sulfide were compiled in a monograph published by the author [2] that included calculation results reported by 2012 [3]-[46]. All these analyses [2]-[48] were made accepting an *a priori* assumption of constant interaction energy $E(X-X)$ between nearest-neighbour interstitial atoms X within a homogeneity composition range of MX_x lattice at arbitrary T . Parameter values estimated for M 's in the same group in the Periodic Table of the Elements for given X were comparable to each other. This evidence appeared to support validity of the *a priori* assumption of the constant $E(X-X)$ within a homogeneity composition range of MX_x at any T although there is no rigorous first-principle-based justification for this *a priori* assumption. Further, statistical thermodynamic parameter values for $E(X-M)$ and $E(X-X)$ evaluated as such yielded enthalpy values comparable to those determined by the conventional thermodynamics for Cr_2N [3] as well as for several hydrides [6] [18]. Hence, the atomic interaction parameter values evaluated as such by statistical thermodynamics must be considered realistic as well as rational.

Besides analysis for pure M , analysis was made also for substitutional alloy with $M = A_{1-y}B_y$ consisting of two alloying constituents, A and B [8] [9] [11] [12] [16] [17] [18] [19] [24] [29] [33] [35] [36] [37] [38] [40] [42] [44] [46] [47] as well as for ternary alloy MZ_xX_x containing another interstitial constituent Z besides X in which affinity of Z to M was stronger than that of X to M [13] [31] [32] [34].

In the early stage of this line of work to characterize nature of atomistic interaction in interstitial non-stoichiometric compound MX_x [2]-[47], attention was not paid explicitly on engineering significance of the parameter values evaluated by the statistical thermodynamic analysis. However, after the analysis was made

to evaluate interaction parameters for H absorption behaviours for Va-group metal-based alloy membranes [47], it occurred to the author that it might be of pragmatic convenience if the correlation was established between the estimated values of the interaction parameters by statistical thermodynamic analysis and the reported H permeation performance for the Va-group metal-based alloy membrane materials. This led the author to summarize somewhat speculative paper [48] soon after [47]. The background idea for this attempt of correlating the statistical thermodynamic parameter values evaluated for Va-group metal-based alloy membrane to the H permeation performance of the alloy membrane was to screen promising ones from candidate Va-group metal-based alloys so that the number of H permeation experiments could be minimized. H permeation experiment is time-consuming and the results are dependent on setting of $p(H_2)$ on the inlet side and that on the outlet side.

This special issue of *Journal of Modern Physics* bears title “Engineering Thermal Physics” with “statistical thermodynamics” being included as one of the possible fields of concern. Thus, the author decided to summarize this manuscript to review comprehensively the engineering significances of the interaction parameters estimated by statistical thermodynamics reported in the published works during the last four decades [2]-[48].

As the main purpose of this manuscript is to demonstrate potential usefulness of evaluated atomic interaction parameters for MX_x by statistical thermodynamics for advanced alloy design, *PTC* data sources used in the analyses are not cited as the *References*. Statistical thermodynamic analysis procedures for interstitial non-stoichiometric compound MX_x shall be reviewed in the next Chapter although they might be referred to elsewhere [2] [3] [6] [44] [47] [48] as the statistical thermodynamic analysis procedure, unlike mathematically well-defined conventional thermodynamic analysis procedure, is not yet widely accepted as a standard analysis tool among materials researchers.

Among literatures cited in *References* section of this paper, [22] [23] [25] and [28] were works in which results of statistical thermodynamic analysis were made use of for interpretation of the discussed matters rather than works of statistical thermodynamic analysis itself and [41] was a preparative work to convert the equilibrium data format reported for Fe-Cr-P system by the original authors of the experimental work to a format adequate for straightforward statistical thermodynamic analysis that was published eventually as [42].

2. Statistical Thermodynamic Analysis Procedure

2.1. Fundamental Equations

Generalized fundamental formulae proposed for this line of analysis of interstitial non-stoichiometric condensed phase MX_x are as follows.

$$A \equiv RT \ln \left\{ \left[\frac{(\theta - x)}{x} \right] \left[p(X_2) \right]^{1/2} \right\} = g(T) + \beta_x E (X - X) \quad (1)$$

$$K(T) = g(T) - \left[D(X_2) / 2 - RTC(T) \right] = Q - RT \ln Zf_x(T) \quad (2)$$

$$C(T) = -(1/2) \ln \left\{ \left[(4\pi m_x)^{3/2} / h^3 \right] \left[(T^{7/2} \Theta_r) (1 + \Theta_r / (3T)) \right] \left[\rho^2 \nu_0^* / 2 \right] \right\} \\ + \Theta_v / (4T) + (1/2) \ln [1 - \exp(\Theta_v / T)] \quad (3)$$

$$\ln f_x(T) = - \int_0^\infty g(\nu) \ln [1 - \exp\{-h\nu / (kT)\}] d\nu + \ln \rho \nu_0 \quad (4)$$

$$Q + \beta x E(X - X) = \partial E(MX_x) / \partial n_x \quad (5)$$

Symbols used in the above formulae are classified as follows:

<universal constants>

R : universal gas constant (=8.31451 J·mol⁻¹·K⁻¹),

h : Planck constant (=6.6260755 × 10⁻³⁴ J·s),

k : Boltzmann constant (=1.380658 × 10⁻²³ J·K⁻¹),

<materials constants>

m_x : mass of X atom,

ρ : nuclear spin weight,

Θ_r : characteristic temperature for rotation of X_2 ,

Θ_v : characteristic temperature for vibration of X_2 ,

ν_0^* : electronic state of normal state of X_2 molecule,

$D(X_2)$: dissociation energy of X_2 molecule per mole,

β : factor determined from crystal structure consideration,

θ_0 : geometrically available number of interstitial site per M in MX_x ,

ν_0 : statistical weight of tightly bound electrons around X in MX_x ,

ν : vibrational frequency of X atom in MX_x lattice,

$g(\nu)$: distribution function,

<experimentally measurable parameters>

$p(X_2)$: equilibrium pressure of ideal gas X_2 ,

T : absolute temperature (K),

x : composition (X/M atom ratio) in MX_x ,

n_x : number of X atoms in MX_x ,

n_M : number of M atoms in MX_x ,

<parameters to be evaluated>

Q : degree of stabilisation of X atom in MX_x lattice with reference to isolated X and M atoms in vacuum,

$E(i - j)$: interaction energy between i and j atoms in MX_x lattice,

$E(MX_x)$: lattice energy,

$f_x(T)$: partition function of X atom in MX_x ,

$f_M(T)$: partition function of M atom in MX_x ,

K & g : parameters determined by Equations (1) & (2), from the experimental PTC data for an assigned value of θ ,

<a factor to be assigned a priori>

θ : number of the interstitial sites per M atom available for occupation by X atoms in MX_x ,

<a resultant model parameter referring to extent of blocking of interstitial sites>

Z : extent of blocking of interstitial sites by X in MX_x ($= \theta_0 / \theta$); that is, when

one interstitial site in MX_x is occupied by an X atom, $(Z-1)$ neighbouring interstitial sites are blocked from occupation by other X atoms.

For example, in case that X atoms in MX_x occupy octahedral interstitial sites (O -sites) expression for Q in close packed lattices like fcc (face centred cubic) and hcp (hexagonal close packed) is simply,

$$Q(fcc/hcp) = 6E(X-M) \quad (6)$$

but that for bcc (body centred cubic) lattice is expressed as

$$Q(bcc) = 2E(X-M) + 4E(X-M)^{\theta} - E(X-X)^{\theta} \quad (7)$$

taking into account second nearest neighbour interactions, $E(X-M)^{\theta}$ and $E(X-X)^{\theta}$, besides nearest neighbour $X-M$ interaction $E(X-M)$ due to openness of the atom packing in the bcc crystal lattice [2] [8] [18].

On the other hand, geometrical factor β to $E(X-X)$ in Equation (1) might be non-integral number. For example, β is $4/3$ if X atoms are distributed over O -sites in bcc lattice [2] [8] [18].

Value of θ to fulfill the a priori assumption of constant $E(X-X)$ within a homogeneity range of MX_x at arbitrary T is usually close to the solubility limit of X in the MX_x . For example, in the statistical thermodynamic analysis of hypo-stoichiometric Cr_2N phase, θ was chosen to be 0.50 to fulfill the condition of constant $E(N-N)$ over the homogeneity composition range of Cr_2N [3]. When θ was chosen to be 1 ($=\theta_0$ for O -site occupation of N in the hcp lattice), $E(N-N)$ varied with x showing trend of increasing positive (repulsive) $E(N-N)$ with increasing x . If such variation of $E(X-X)$ takes place in MX_x , it is more natural to accept phase change to occur rather than to hold the same crystal lattice structure [2].

2.2. Analysis Procedure

At the onset of the analysis, isothermal A vs. x plots must be prepared from available isothermal PC relationship at arbitrary T using Equation (1) by varying θ . As understood from Equation (1), slope of isothermal A vs. x plot would become proportional to $E(X-X)$. To fulfill the a priori assumption of constant $E(X-X)$ within homogeneity composition range of MX_x at arbitrary T , θ yielding linear A vs. x relationship over entire homogeneity composition range of MX_x must be chosen for the subsequent calculations.

Then, from the intercept $g(T)$ calculated using Equation (1), $K(T)$ vs. T relationship must be drawn using Equation (2). Term Q on the right hand side in Equation (2) refers to extent of stabilization of atom X in the MX_x lattice due to formation of $X-M$ bonds in the MX_x lattice while the coefficient $R \ln[Zf_x(T)]$ to T refers to electronic contribution to entropy term in thermodynamic sense. In fact, partition function $f_x(T)$ of X atom in the MX_x lattice is a T -dependent function as represented by Equation (4) but, as the T range of statistical thermodynamic analysis for MX_x is typically no wider than 500 K, it has been a common practice to approximate $f_x(T)$ as a T -independent constant term [2]-[48].

For convenience of the readers, flow chart of the calculation procedure is presented below as **Figure 1**.

As represented by Equation (5), term $[Q + \beta x E(X-X)]$ refers to the net extent of stabilization of X atom in the MX_x lattice, $\partial E(MX_x)/\partial n_x$, taking into account the contribution of the $X-X$ interaction besides Q which represents contribution of the $X-M$ interaction alone where $E(MX_x)$ refers to lattice energy of compound MX_x calculated taking into account all nearest neighbour pairwise atomic interactions $E(i-j)$ for all combinations of i and j .

For pragmatic convenience of calculating $K(T)$ using Equation (2), $[D(X_2)/2 - RTC(T)]$ values for $X = H$ and N are presented in tabulated form in [2] and [37] at 100 K interval from 0 K up to 3000 K so that $[D(X_2)/2 - RTC(T)]$ value at arbitrary T is calculated readily by interpolation although values of $D(X_2)$ and $D(C)$ were taken from JANAF Thermochemical Tables [49] or NIST-JANAF Thermochemical Tables [50].

3. Some Insights Drawn from Statistical Thermodynamic Analysis Results for Interstitial Non-Stoichiometric Compounds

3.1. Stability of X in FeX_x Lattice

As might be understood from expressions for fundamental equations reviewed in 2.1., reference state of energy in the statistical thermodynamic analysis is each constituent atom in infinite separation in vacuum whereas the reference state of constituent in conventional thermodynamic analysis is the pure substance in standard state. That is, by conventional thermodynamic analysis, enthalpy of formation of MX_x from M and X_2 represents the difference in energy between the reaction product MX_x and the reactants, M and $(x/2)X_2$, rather than $E(X-M)$ evaluated by the statistical thermodynamic analysis. This makes straightforward comparison of extent of stabilization of different X atoms in a

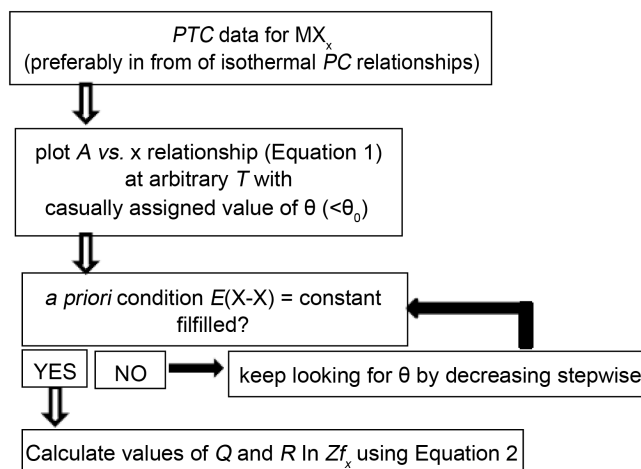


Figure 1. Flow chart of the statistical thermodynamic analysis procedure accepting a priori assumption of constant $E(X-X)$ within homogeneity composition range of MX_x at arbitrary temperature T .

given M lattice difficult through conventional thermodynamic analysis. In contrast, statistical thermodynamic analysis results allow us to compare straightforwardly the relative stability of different X 's in a given M as seen in **Table 1** for $M = \text{Fe}$ and $X = \text{H}, \text{C}, \text{N}, \text{P}$ and S [20].

The more stable the X in Fe lattice the more negative would become $Q(X)$ in FeX_x lattice. That is, according to **Table 1**, the stability of X in Fe lattice would decrease in the order of

$$C > N > P > S > H \quad (8)$$

implying that C is the most stable and H is the least stable in Fe lattice.

Further, it is notice in **Table 1** that, for given X , stability in Fe lattice would vary depending on the lattice structure of Fe

$$Q(C)^L < Q(C)^\gamma < Q(C)^\alpha (T < T_c) < Q(C)^\alpha (T_c < T) \quad (9)$$

$$Q(N)^\gamma < Q(N)^L < Q(N)^\alpha < Q(N)^\delta \quad (10)$$

$$Q(H)^\alpha < Q(H)^\gamma < Q(H)^\delta \quad (11)$$

implying that the most stable state of C in Fe is realized in molten state, that of N in γ phase and that of H in α phase.

In **Table 1**, θ value of some MX_x is not specified uniquely. This is due to inherent difficulty of determining exactly the value of θ for statistical thermodynamic

Table 1. Estimated values of Q in miscellaneous FeX_x (reproduced from Table 1 in [20]).

Compound	Range of T	θ	Q^b
	[K]		[kJ·mol ⁻¹]
$\alpha\text{-FeH}_x$ (<i>bcc</i>)	<1175	>0.01	-171
$\gamma\text{-FeH}_x$ (<i>fcc</i>)	1185 - 1590	(0.50) ^a	-138
$\delta\text{-FeH}_x$ (<i>bcc</i>)	1665 - 1715	(0.50) ^a	-100
$\alpha\text{-FeC}_x$ (<i>bcc</i>)	<1000	>0.10	-648
$\alpha\text{-FeC}_x$ (<i>bcc</i>)	1025 - 1150	>0.10	-613
$\gamma\text{-FeC}_x$ (<i>fcc</i>)	1175 - 1575	0.20	-679
FeC_x (molten)	1550 - 1775	1.00	-699
$\alpha\text{-FeN}_x$ (<i>bcc</i>)	<1115	>0.05	-420
$\gamma\text{-FeN}_x$ (<i>fcc</i>)	1250 - 1625	(0.50) ^a	-455
$\delta\text{-FeN}_x$ (<i>bcc</i>)	1675 - 1715	(0.50) ^a	-352
FeN_x (molten)	1850 - 2000	>0.10	-427
FeP_x (molten)	1475 - 1775	0.50	-347
FeS_x (molten)	1775 - 1875	1.00	-307

a. Value of θ used for convenience on calculating Q value for the very dilute interstitial solution. b. Q corresponds to partial molar enthalpy of solution $h(X)$ of X into Fe. Some $h(X)$ values reported by McLellan and co-workers (da Silva, J. R. G and McLellan, R. B. (1976) The Solubility of Hydrogen in Super-pure-ron Single Crystals. *J. Less Common Met.*, **50**, 1 - 5.; McLellan, R. B. and Farraro, R. J. Thermodynamics of the Iron-Nitrogen System. (1980) *Acta. Metall.*, **28**, 417-422.) were in good accord with the corresponding values of Q . $h(H)^\alpha = -177$ kJ·mol⁻¹; $Q(H)^\alpha = -171$ kJ·mol⁻¹; $h(C)^\alpha = -603$ kJ·mol⁻¹; $Q(C)^\alpha(T > T_c) = -613$ kJ·mol⁻¹; $Q(C)^\alpha(T < T_c) = -648$ kJ·mol⁻¹; $h(C)^\gamma = -650$ kJ·mol⁻¹; $Q(C)^\gamma = -699$ kJ·mol⁻¹; $h(N)^\alpha = -424$ kJ·mol⁻¹; $Q(N)^\alpha = -420$ kJ·mol⁻¹; $h(N)^\gamma = -460$ kJ·mol⁻¹; $Q(N)^\gamma = -455$ kJ·mol⁻¹, where T_c refers to Curie temperature 1043 K for Fe.

analysis in very dilute interstitial solution under certain circumstances as discussed in some detail in [15].

First cases of statistical thermodynamic analysis for very dilute interstitial solutions was made in [11] in which a priori condition of constant $E(X-X)$ was set to fulfill the condition

$$E(X-X) = 0 \quad (12)$$

noting the reality that, in the very dilute interstitial compound, there must be no neighbouring interstitial atom around any interstitial atom.

However, when solutions of H , C and N in α -Fe was investigated in terms of statistical thermodynamics, unambiguous specification of θ to fulfill condition (12) was difficult but, instead, when θ value was taken to be greater than certain threshold value, estimated value of Q converged to a constant level whereas, in the range of θ smaller than the threshold level, estimated value of Q showed steady variation with varying θ (cf. Figure 2 in [15]). On account of this situation, unique specification of θ was given up for some very dilute interstitial compounds and, as a compromising solution, θ value which must have been greater than the threshold level was used for the analysis because, by so doing, realistic value for Q was evaluated as discussed in [15] although value of the product Zf_x varied as a function of θ in the range of θ where Q value became constant with θ .

3.2. Atom Clustering in $Fe_{1-y}M_yX_x$ around X Atom

During the course of statistical thermodynamic analysis of PTC relationships reported for N solution in molten $Fe_{1-y}M_y$ in which affinity of M to N is stronger than that of Fe to N , it was concluded that certain types of atom clustering might develop around interstitial N atom [19] [24] [26]. This aspect shall be reviewed in the following.

As always in this line of statistical thermodynamic analysis, θ parameter values on analysis of molten $Fe_{1-y}Cr_yN_x$ for varying y were determined accepting an a priori assumption of constant $E(N-N)$ over homogeneity composition of $Fe_{1-y}Cr_yN_x$ as reproduced in Figure 2 and, by the statistical thermodynamic

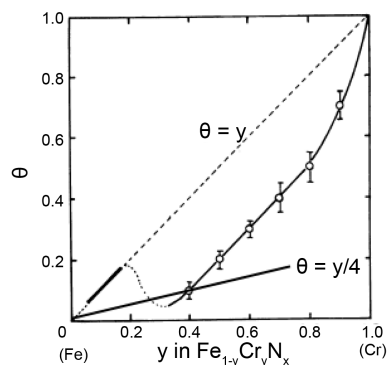


Figure 2. Relationship between θ and y in molten $Fe_{1-y}Cr_yN_x$ to fulfill the a priori condition of constant $E(N-N)$ over homogeneity composition range at arbitrary T (reproduced from Figure 3.57 in [2] or Figure 4 in [24]).

analysis done with the θ values determined as such, values of $R \ln Zf_N(Fe_{1-y}Cr_yN_x)$ (a) and $Q(Fe_{1-y}Cr_yN_x)$ (b) were obtained as a function of y as reproduced in **Figure 3**. In spite of somewhat peculiar variation pattern of θ with y (**Figure 2**), variation patterns of Q and $R \ln Zf_N$ with respect to y looked quite “regular” (**Figure 3**). In this analysis, molten $Fe_{1-y}Cr_yN_x$ at temperatures close to liquidus temperature above $Fe_{1-y}Cr_yN_x$ solid phase possessing *fcc* structure was assumed to hold *fcc* structure. In the range of low y not exceeding 0.2, θ varied following

$$\theta = y \quad (13)$$

For this range of $\theta (<0.2)$, the interpretation was quite simple. That is, N atom in an O site was assumed to become surrounded by one Cr atom and 5 Fe atoms (1 Cr/5 Fe cluster or Cr-N dipole) as depicted in **Figure 4(a)**. Q values determined

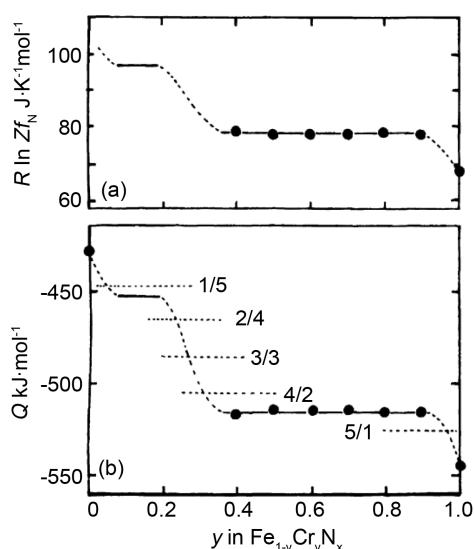


Figure 3. Estimated values of $R \ln Zf_N$ [$J \cdot K^{-1} \cdot mol^{-1}$] (a) and Q [$kJ \cdot mol^{-1}$] (b) for molten $Fe_{1-y}Cr_yN_x$ plotted as a function of y . In **Figure 2(b)**, positions of values of Q estimated from proportional sum of $E(N-Fe)^0 = -72$ [$kJ \cdot mol^{-1}$] and $E(N-Cr)^0 = -93$ [$kJ \cdot mol^{-1}$] at various satom ratios of Cr to Fe are given by horizontal dotted line (reproduced from Figure 3.58 in [2] or Figure 5 in [24]).

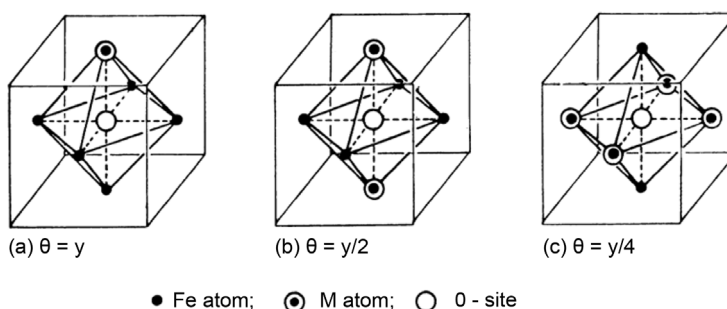


Figure 4. Possible atom clusters formed in *fcc* $Fe_{1-y}Cr_yN_x$ lattice in which affinity of M to N is stronger than that of Fe to N . (a) 1 M/5 Fe cluster (composed of one M atom and five Fe atoms around N); $\theta = y$, (b) 2 M/4 Fe cluster; $\theta = y/2$ and (c) 4 M/2 Fe cluster, $\theta = y/4$ (reproduced from Figure 3.59 in [2] or Figure 3 in [26]).

in the range of y smaller than 0.20 was constant with y being represented approximately by

$$Q(y < 0.2) \approx E(N-Cr)^0 + 5E(N-Fe)^0 \quad (14)$$

where $E(N-Cr)^0$ refers to $N-Cr$ interaction energy (≈ -93 [kJ·mol⁻¹]) in molten CrN_x and $E(N-Fe)^0$ N-Fe interaction (≈ -72 [kJ·mol⁻¹]) in molten FeN_x [2] [24].

On the other hand, it was felt difficult to appreciate rationally the variation pattern of θ with y in the range of y higher than 0.4 at first glance. However, as seen in **Figure 3**, Q values determined in the range of $0.4 \leq y < 1$ was constant with y being represented approximately by

$$Q(0.4 \leq y < 1) \approx 4E(N-Cr)^0 + 2E(N-Fe)^0 \quad (15)$$

implying formation of **4 Cr/2 Fe** cluster as depicted in **Figure 4(c)**.

Detected deviation of θ vs. y relationship from the one represented by

$$\theta = y/4 \quad (16)$$

in **Figure 2** was interpreted to be the consequence of Guinier-Preston zone type planar extension of **4 Cr/2 Fe** clusters as detected in **Figure 4(c)**.

To explain why θ vs. y relationship in range of y between 0.4 and 0.9 in **Figure 2** deviated from the relationship defined by Equation (16), model Guinier-Preston zone type planar extensions of **4 M/2 Fe** clusters for a fixed number 12 of M atoms leading to different values of θ are depicted in **Figure 5**. As seen in **Figure 5(b)** and **Figure 5(c)**, increased degree of planar extension would yield higher value of θ than the one anticipated from Equation (16) defined for the isolated **4 M/2 Fe** clusters depicted in **Figure 5(a)**.

It is intriguing to note that no evidence of existence of **2 M/4 Fe** cluster as depicted in **Figure 4(b)** was detected for $A_{1-y}B_yX_x$ type interstitial non-stoichiometric compounds analyzed so far.

3.3. Design Guideline for H Permeable Alloy Membrane

Yukawa and collaborators at Nagoya University [51] [52] [53] experimentally

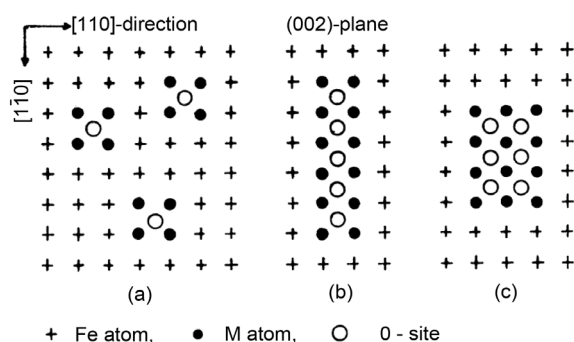


Figure 5. Some possible ways of planar extension of the **4 M/2 Fe** cluster depicted in **Figure 3(c)** over the (002) plane of fcc lattice leading to different values of θ with a fixed number of 12 M atoms. (a) isolated clusters, $\theta = y/4$, (b) planar extension leading to $\theta = (5/12)y$ and (c) planar extension leading to $\theta = (6/12)y = y/2$ (reproduced from Figure 3.60 in [2] or Figure 4 in [26]).

investigated H permeation behaviors as well as H absorption behaviors for Va-group metal-based alloy membranes. The author [44] [47] analyzed the reported PCT relationships by Yukawa and collaborators [49] [50] [51] and obtained values for parameters, Q and $R \ln Z_{f_H}^*$ as summarized in **Table 2**.

According to Yukawa and co-workers, Va-group metal-based alloys identified as favorable H permeation membrane includes $V_{0.95}Fe_{0.05}$ [49], $Nb_{0.95}Ru_{0.05}$ and $Nb_{0.95}W_{0.05}$ [50] as well as $Ta_{0.95}W_{0.05}$ [51]. Looking at values of θ and Q for these $A_{1-y}M_y$ type alloys containing Va-group metal (represented by A) in **Table 2**, it is noticed that θ was smaller and Q was more negative in this group of alloys than those in pure Va-group metal A except $Ta_{0.95}W_{0.05}$. Thus, it was proposed [48] to use the simultaneous fulfillment of conditions

$$\theta(A_{1-y}M_yH_x) < \theta(AH_x) \quad (17)$$

$$Q(A_{1-y}M_yH_x) < Q(AH_x) \quad (18)$$

for screening of H permeation alloy membrane from among the candidate alloys

Table 2. Available statistical thermodynamic interaction parameter for bcc $A_{1-y}M_yH_x$ that showed suppressed H solubility compared to that in bcc AH_x where A refers to Va-group metals (V, Nb or Ta) (reproduced from Table 1 in [48]).

$bcc A_{1-y}M_yH_x$	θ	Q^a	$R \ln Z_{f_H}^*$
		[kJ·mol ⁻¹]	[J·K ⁻¹ ·mol ⁻¹]
VH_x	0.55	-223.6	64.7
$V_{0.96}Cr_{0.04}H_x$	0.525	-220.0	26.9
$V_{0.916}Cr_{0.084}H_x$	0.475	-207.2	54.5
$V_{0.949}Mo_{0.051}H_x$	0.525	-207.3	37.5
$V_{0.95}Fe_{0.05}H_x$	0.45	-229.4	23.7
$V_{0.948}Co_{0.052}H_x$	0.45	-230.1	21.5
NbH_x	0.75	-229.5	61.7
$Nb_{0.95}Ru_{0.05}H_x$	0.55	-221.8	41.2
$Nb_{0.95}W_{0.05}H_x$	0.725	-243.1	14.1
$Nb_{0.90}Mo_{0.10}H_x$	0.45	-225.5	65.4
$Nb_{0.80}Mo_{0.20}H_x$	0.30	-228.2	61.3
$Nb_{0.70}Mo_{0.30}H_x$	0.20	-220.8	67.7
$Nb_{0.95}Al_{0.05}H_x$	0.60	-225.8	36.9
$Nb_{0.95}Cu_{0.05}H_x$	0.60	-223.5	41.2
$Nb_{0.95}Sn_{0.05}H_x$	0.60	-231.8	30.6
$Nb_{0.95}Ni_{0.05}H_x$	0.60	-219.2	45.0
$Nb_{0.95}Pd_{0.05}H_x$	0.60	-231.8	26.1
$Nb_{0.90}Pd_{0.10}H_x$	0.45	-213.9	45.5
TaH_x	0.55	-229.4	62.4
$Ta_{0.95}W_{0.05}H_x$	0.55	-228.6	32.1

a. Q values of θ for $A_{1-y}M_yH_x$ that were evaluated to be more negative than that for AH_x are displayed with **bold** letter.

based on Va-group metal.

On H permeation process, H_2 gas pressure $p(H_2)^{\text{in}}$ on the inlet side of the membrane is set higher than $p(H_2)^{\text{out}}$ on the outlet side. On the inlet side of the membrane, adsorbed H_2 gas over the membrane surface must be subjected to dissociation into adsorbed monatomic H atoms before being absorbed into $A_{1-y}M_y$ alloy lattice



Then, by concentration gradient along the membrane thickness, absorbed H in the $A_{1-y}M_y$ lattice is subjected to diffusion towards the outlet side of the membrane. On the reaction (20) to proceed at the inlet side of the membrane, condition (18) is certainly favourable to suck faster the H atoms into the $A_{1-y}M_x$ lattice from the inlet side surface.

Then, on release of the transported H atoms through the outlet side surface of the $A_{1-y}M_y$ membrane, successive inverse reactions, (19) and (20) in this order, must proceed to recombine the absorbed monatomic H atoms in the $A_{1-y}M_yX_x$ alloy lattice to be released in form of diatomic H_2 gas molecules. For this process of H_2 release to take place faster on the outlet side of the membrane surface, condition (17) is considered to be of convenience.

As such, simultaneous fulfillment of conditions, (17) and (18), was appreciated as rational for the alloy design guideline for Va-group metal-based H permeation membrane although this criterion did not seem to apply to $Ta_{0.95}W_{0.05}$ alloy.

Among Va-group metal-based alloys listed in **Table 2**, $V_{0.948}Co_{0.052}$, $Nb_{0.95}Sn_{0.05}$ and $Nb_{0.95}Pd_{0.05}$ fulfill the conditions, (17) and (18), simultaneously although the H permeation performance of these alloys remains unknown.

3.4. Constant- $a(C)$ Curves in $\gamma\text{-FeC}_x$ Phase

On account of pragmatic industrial importance of steel materials, intensive efforts have been invested on characterizing basic phase relationship for Fe-C binary system in equilibrium state. Taking advantage of abundance of equilibrium data for binary Fe-C system with high qualitative precision, statistical thermodynamic analysis for Fe-C system [20] was done choosing experimental data reported by Ban-ya *et al.* [54] in which chemical activity $a(C)$ of C in equilibrium with $\gamma\text{-FeC}_x$ was varied widely through control of $p(\text{CO})/p(\text{CO}_2)$ ratio instead of using C in solid state.

In common experimental equilibrium study of metal carbide, excess graphite (reference state of C) is arranged to co-exist in the synthesized carbide MC_x . Under such condition, $a(C)$ is fixed to be 1 and, as such, influence of $a(C)$ on x in MC_x cannot be evaluated.

From the statistical thermodynamic analysis, values of θ and Q listed for $\gamma\text{-FeC}_x$ in **Table 1** were calculated and constant- $a(C)$ curves as reproduced in **Figure 6** were drawn [20]. This presentation of **Figure 6** might be of no practical industrial importance but must be of fundamental significance towards profound

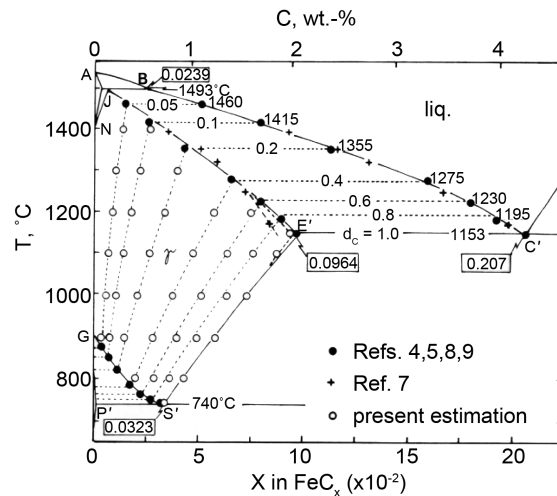


Figure 6. Binary Fe-C equilibrium phase diagram compiled by Hansen and Anderko <7> with the estimated constant- $a(C)$ curves and some available experimental results <4>, <5>, <8>, <9> (reproduced from Figure 1 in [20]). <4> Ban-ya, S, Elliott, J. F. and Chipman, J. (1969) Activity of Carbon in Fe-C Alloys at 1150°C. *Trans. Metall. Soc. AIME*, **245**, 1199 - 1206; <5> Ban-ya, S., Elliott, J. F. and Chipman, J. (1970) Thermodynamics of Austenitic Fe-C Alloys, *Metall. Trans.*, **1**, 1313 - 1320; <7> Hansen, M. and Anderko, K. (1958) Constitution of Binary Alloys, 2nd Ed., McGraw-Hill, New York, Tronto and London; <8> Chipman, J. (1970) Thermodynamics of Liquid Fe-C Solutions, *Metall. Trans.*, **1**, 2163 - 2168; <9> Chipman, J. (1972) Thermodynamics and Phase Diagram of the Fe-C System. *Metall. Trans.*, **3**, 55-64.

understanding for inherent nature of interstitial non-stoichiometric compounds like $\gamma\text{-FeC}_x$.

4. Conclusions

A few example cases of estimating properties of interstitial non-stoichiometric compounds with potential industrial applications on the basis of atomic interaction parameters evaluated by statistical thermodynamic analysis were demonstrated in this review article. Looking at the variation pattern of θ parameter value referring to number of available interstitial sites per metal atom M (M might be pure M , $A_{1-y}B_y$ type substitutional alloy or AZ_z type compound containing another interstitial constituent Z besides interstitial constituent X) with respect to change of y or z , significant insight in atom clustering tendency in the condensed phase might be gained. There are several other materials properties predictable by referring to statistical thermodynamic analysis results including interstitial site occupation information for intermetallic alloys. Interested readers are advised to refer to original papers by the author [8] [12] [18] to look into further details.

The reviewed standardized statistical thermodynamic analysis procedure accepting an *a priori* assumption of constant $E(X-X)$ in MX_x within homogeneity composition range at arbitrary T was proved applicable to interstitial compound holding metallic characteristics but this analysis procedure is not applicable to non-stoichiometric compounds with ionic bonding characteristics

like non-stoichiometric oxide.

Compared with standardized conventional thermodynamic analysis procedure to determine enthalpy, entropy and a few types of free energies through well-established mathematical procedure, statistical thermodynamic analysis is quite tedious demanding reliable *PCT* data set at least at three different *T* levels over certain range of $p(X_2)$ and additional necessity for composing realistic statistical model. This is certainly a drawback of statistical thermodynamic analysis compared with conventional thermodynamics but this feature of statistical thermodynamic approach might be considered as a merit in some sense as the evaluated interaction parameters possess unambiguous physical significance provided that the statistical model used for the analysis is a valid one.

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