Entropy Terms in Statistical Thermodynamic Analysis Formula for Non-stoichiometric Interstitial Compounds

Nobumitsu Shohoji

LEN - Laboratório de Energia, LNEG - Laboratório Nacional de Energia e Geologia I.P., Lisboa, Portugal

Abstract A series of statistical thermodynamic analyses were made since 1974 for different types of non-stoichiometric interstitial compounds MXx under simplifying *a priori* assumption of constant interaction energy E(X-X) between nearest neighbour interstitial atoms X within a homogeneity composition range of MX_x at arbitrary temperature T [K]. Mode of distribution of X atoms in interstitial sites in MX_x lattice is represented by number θ of available interstitial sites for occupation by X atoms per M atom and the value of θ is determined to fulfil the *a priori* assumption. Mode of atomic configuration would yield major contribution to entropy term ΔS that appears in conventional thermodynamic expression of Gibbs free energy of formation, ΔG, in form of $T\Delta S$. In the statistical thermodynamic formulation, contribution of tightly bound electron appearing in form of $RT \ln f_X$ where f_X refers to atomic partition function of X atom in the MX_x lattice and R the universal gas constant. Judging from this mathematical form of the term, $R \ln f_X$ is considered to represent entropic contribution from tightly bound electron to X atom in MX_x lattice. In the published series of works on statistical thermodynamic analysis for non-stoichiometric interstitial compounds, calculated values for $R \ln f_X$ were reported but they were not reviewed with serious attention because $R \ln f_X$ was considered merely as a secondary factor compared to principal factor E(X-M) referring to interaction energy between X and M in MX_x lattice that represents enthalpy ΔH in conventional thermodynamic term. In this review article, consideration is given exclusively to the factor $R \ln f_X$ evaluated in statistical thermodynamic approach to non-stoichiometric interstitial compounds.

Keywords Entropy terms, Statistical thermodynamics, Interstitial compound, Non-stoichiometry

1. Introduction

Statistical thermodynamics is a unique analysis tool to span a bridge between **the experimentally measurable macroscopic thermodynamic state parameters** such as temperature T, equilibrium partial pressure $p(X_2)$ of X_2 gas and composition x in non-stoichiometric interstitial compound MX_x consisting of metal M and interstitial element X and **the non-measurable atomistic interaction energy parameters** $E(i\text{-}j)$ $(i, j = M$ or $X)$. Condensed phase MX_x subjected to statistical thermodynamic analysis might be in either solid or molten state.

Basic principles of statistical thermodynamics as well as practical analysis procedures are summarized in a classical text book authored by Fowler and Guggenheim [1].

In a monograph published in 2013 entitled "Statistical Thermodynamic Approach to Interstitial Non-stoichiometric Compounds (Hydride, Carbide, Nitride, Phosphide and

Sulphide)" [2], results of statistical thermodynamic analysis acquired on the basis of the simplifying *a priori* assumption of constant E(X-X) within a homogeneity composition range of MX_x at arbitrary T were compiled [3-46] while a few more publications in this line of work arose thereafter [47-49]. In those publications, values for dissociation energy of X_2 gas molecules, $D(X_2)$ [kJ·mol^{-1}], characteristic temperature for rotation of X_2 molecule, Θ_r [K], and characteristic temperature for vibration of X_2 molecule, Θ_v [K], were taken from JANAF Thermochemical Tables [50] in the earlier works [3-43] or from its successor NIST-JANAF Thermochemical Tables [51] for the more recent calculations [44-49].

Metal constituent M in non-stoichiometric interstitial compound MX_x might be a single metal but might be binary substitutional alloy to be represented by $A_{1-y}B_y$ or even multi-component alloy with number of metallic constituents being greater than 2. For such alloys represented by $A_{1-y}B_y$, statistical thermodynamic analysis results demonstrated that, depending on difference in affinity of X atom to constituent A and to constituent B, atom cluster might develop in the alloy lattice of $A_{1-y}B_yX_x$ [9, 11, 16-19, 23, 25, 29, 33, 35-38, 40, 44, 46-49]. Statistical thermodynamic analysis was also made for alloy systems represented by MZ_zX_x in which Z is interstitial constituent whose affinity to M is stronger than

that of X to M and composition z might be pre-determined arbitrarily before measuring equilibrium pressure - temperature - composition (*PTC*) relationships between MZ_zX_x and X_2 gas [13, 31, 32, 34].

Literature information for *PTC* data source used in the cited statistical thermodynamic analysis works is not given in the text below as the *PTC* data sources used for the calculations were cited in References section in each publication.

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 [2, 3, 11, 12, 18, 20, 23, 25, 36, 37, 49].

$$A \equiv RT \ln \{[(\theta - x)/x] \cdot [p(X_2)]^{1/2}\}$$
$$= g(T) + \beta x E(\text{X-X}), \tag{1}$$

$$K(T) = g(T) - [D(X_2)/2 - RTC(T)]$$
$$= Q - RT \ln Zf_X(T), \tag{2}$$

$$C(T) = -(1/2) \ln \{[(4\pi m_X)^{3/2}k^{5/2}/h^3] \cdot$$
$$[(T^{7/2}/\Theta_r) \langle 1 + \Theta_r/(3T)\rangle \langle \rho^2\upsilon_0^*/2\rangle] + \Theta_v/(4T) +$$
$$(1/2) \ln [1 - \exp(-\Theta_v/T)], \tag{3}$$

$$\ln f_X(T) = -\int_0^\infty g(\nu) \ln [1 - \exp(-h\nu/(kT)]d\nu + \ln \rho\upsilon_0, \tag{4}$$

$$Q + \beta x E(\text{X-X}) = \partial E(\text{MX}_x)/\partial n_X. \tag{5}$$

Symbols used in the above formulae are listed in the **APPENDIX** according to the classification of quality of the parameters.

In right hand side of Eq. (2), term Z is included explicitly in the second term, $RT \ln Zf_X(T)$. However, in the earlier publications on statistical thermodynamic analysis for non-stoichiometric interstitial alloy systems, explicit inclusion or not of this term was practised rather casually, except for analysis of very dilute interstitial alloy systems [11]. In reality, $Z = 1$ is valid for many MX_x systems with x being close to 1. However, during the course of writing a monograph [2], it came to the author's mind that it is better to include the term Z in Eq. (2) explicitly. In fact, in the very first publication [3] in this line of work done for Cr sub-nitride, Cr_2N, formulation was made with $Z = 2$ for $\theta = 0.50$ ($Z \cdot \theta = \theta_0 = 1$ for octahedral sites (O-sites) occupation in hexagonal close-packed (*hcp*) lattice).

2.2. Partition Function

Procedure to derive fundamental equation (1) is reviewed briefly in the following.

Starting point of statistical thermodynamic analysis for non-stoichiometric interstitial alloy MX_x is the compilation of partition function $PF(MX_x)$ for the condensed phase MX_x

and $PF(X_2)$ for ideal gas X_2 at partial pressure $p(X_2)$ being in equilibrium with MX_x at arbitrary T.

Formula for $PF(X_2)$ at partial pressure $p(X_2)$ and at temperature T is readily available in a classical text book authored by Fowler and Guggenheim [1]. On the other hand, $PF(MX_x)$ has to be composed taking into account lattice structure of M and mode of distribution of X atoms over interstitial sites. Generalized formula for $PF(MX_x)$ is represented by

$$PF(MX_x) = W(MX_x) f_M(T)^{nM} f_X(T)^{nX} \cdot$$
$$\exp[-E(MX_x)/(RT)], \tag{6}$$

where $W(MX_x)$ refers to number of configurations of constituent atoms in MX_x lattice and $E(MX_x)$ lattice energy of MX_x.

Expression for $W(MX_x)$ is

$$W(MX_x) = Z^{nX} \cdot (\theta \cdot n_M)!/[n_X! \cdot (\theta \cdot n_M - n_X)!]. \tag{7}$$

In most of MX_x compounds with non-ionic (metallic) characteristics (X = H, C, N, P or S; but not O), proportion of vacancies in M lattice is empirically acknowledged to be negligibly small even at elevated temperatures close to melting point. On the other hand, X atoms occupy interstitial sites (either octahedral interstitial sites (O-sites) or tetrahedral interstitial sites (T-sites)) according to mode of atomic distribution defined by the parameter θ.

The term $W(MX_x)$, along with f_M and f_X, relates to entropy in conventional thermodynamic formulation as reviewed in some detail in [3].

By partial differentiation of $PF(MX_x)$ with respect to number n_i of constituent i (i = M or X), chemical potential $\mu_i(MX_x)$ in MX_x is evaluated

$$\mu_i(MX_x) = -RT \cdot \{\partial[\ln PF(MX_x)]/\partial n_i\}. \tag{8}$$

As it is common to evaluate *PTC* relationship through isothermal experiment done for MX_x being in equilibrium with X_2 gas at partial pressure $p(X_2)$, statistical thermodynamic analysis is made for i = X rather than for i = M using equilibrium relationship

$$\mu_X(MX_x) = \mu_X(X_2). \tag{9}$$

Expression for $\mu_X(X_2)$ is readily drawn from the classical text book of Fowler and Guggenheim [1] and, as such, fundamental formula (1) is derived for statistical thermodynamic analysis of MX_x in equilibrium with X_2 gas.

2.3. 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 Eq. (1) by varying θ. As understood from Eq. (1), slope of isothermal A vs. x plot would become proportional to E(X-X). To fulfil the *a priori* assumption of constant E(X-X) within a homogeneity composition range of MX_x at arbitrary T, θ yielding linear A vs. x relationship over the entire homogeneity composition range of MX_x must be chosen for the subsequent calculations.

Then, from the intercept $g(T)$ calculated using Eq. (1),

$K(T)$ vs. T relationship must be drawn using Eq. (2). Term Q on the right hand side in Eq. (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 factor as represented by Eq. (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 factor [2-49].

For convenience of the readers, flow chart of the iterative determination procedure for a value of the parameter θ is presented as Fig. 1.
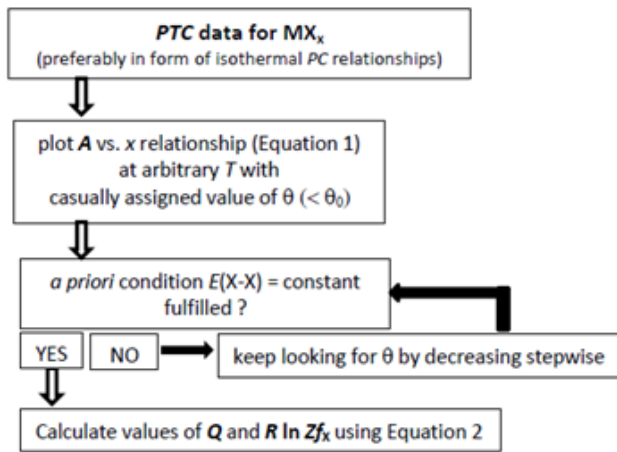

Figure 1. Flow chart of the statistical thermodynamic analysis procedure accepting the a priori assumption of constant E(X-X) within a homogeneity composition range of MX_x at arbitrary T. (Reproduced from Fig. 1 in [49])

As represented by Eq. (5), term $[Q + \beta xE(X\text{-}X)]$ refers to the net extent of stabilization of X atom in the MX_x lattice taking into account additionally the contribution $\beta xE(X\text{-}X)$ from the X-X interaction besides Q which represents contribution of the X-M interaction. In Eq. (5), $E(MX_x)$ refers to lattice energy of compound MX_x calculated taking into account all nearest neighbour pair-wise atomic interactions $E(i\text{-}j)$ for all combinations of i and j.

For pragmatic convenience of calculating $K(T)$ using Eq. (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.

3. Values of the Term R ln $Zf_X(T)$ in MX_x Lattice Evaluated by Statistical Thermodynamics

Some representative calculation results for the term R ln $Zf_X(T)$ in MX_x reported in the past publications are reviewed hereafter classifying M into different categories.

3.1. Estimated R ln $Zf_X(T)$ Values under Approximation of Constant f_X with T

In the standard statistical thermodynamic analysis carried out by the author, T-dependence of atomic partition function of $f_X(T)$ was not taken into account and $f_X(T)$ was assumed to hold T-independent constant value. For some MH_x systems in which values of vibration frequency ν are available, attempts were made to evaluate R ln $f_X(T)$ as a function of T. The tentative calculation resuls for R ln $f_X(T)$ values as a function of T are reviewed later in the text in 3.2.

3.1.1. Primary Solid Solutions MH_x

Values of R ln Zf_H and other parameters evaluated for primary solid solutions MH_x are summarized in Table 1.

Table 1. Values of R ln Zf_H and other parameters evaluated for primary solid solutions MH_x

MH_x	R ln Zf_H [J·K^{-1}·mol^{-1}]	Q [kJ·mol^{-1}]	θ	Ref.
ScH$_x$ (hcp)	72.1	-252	1.0	8
BaH$_x$ (hcp)	76.0	-249	1.5	8
TiH$_x$ (bcc)	33.2	-254	1.25	11
ZrH$_x$ (bcc)	33.6	-265	1.25	11
VH$_x$ (bcc)	64.7	-224	0.55	8
NbH$_x$ (bcc)	61.8	-230	0.75	8
TaH$_x$ (bcc)	62.4	-229	0.55	8
GdH$_x$ (hcp)	49.4	-259	1.0	7
TbH$_x$ (hcp)	43.8	-267	1.0	7
DyH$_x$ (hcp)	45.6	-266	1.0	7
LuH$_x$ (hcp)	39.7	-276	1.0	7

hcp: hexagonal close-packed crystal lattice.
bcc: body centered cubic crystal lattice.

It is intriguing to note that R ln Zf_H values as well as Q values in MH_x for metals in the same group in the Periodic Table of the Elements are comparable to each other even when θ values chosen to fulfil the *a priori* assumption for constant E(H-H) within the given phase at arbitrary T were not the same; e.g. θ = 1.0 for ScH$_x$ and θ = 1.5 for BaH$_x$ (IIa-group metals) and θ = 0.55 for VHx and TaHx while θ = 0.75 for NbH$_x$ (Va-group metals).

Table 2. Expression for Q for representative crystal lattice structures. (Reproduced from Table 1 in [18])

Crystal structure of MX_x	Expression for Q *		
	O-site occupation		T-site occupation
bcc	$2E$(X-M)$^{(I)}$ + $4E$(X-M)$^{(II)}$ - E(M-M)$^{(II)}$		$4E$(X-M)$^{(I)}$
fcc or hcp	$6E$(X-M)		$4E$(X-M)

fcc: face centered cubic crystal lattice.   * Super-scripts, (I) and (II), to E(X-M) and E(M-M) for bcc structure refer to first- and second-nearest neighbours, respectively.

Similarity in the values for R ln Zf_H and Q, respectively, for MH_x of metals belonging to the same group in the Periodic Table appeared realistic supporting indirectly the

validity of the proposed statistical thermodynamic analysis procedure.

As presented in Table 2, expression for Q varies depending on whether the X atoms in MX_x lattice are distributed over O-sites or T-sites as well as on whether the crystal lattice structure is close-packed (*fcc* or *hcp*) or open (*bcc*). It must be noted that, in relatively open *bcc* lattice, contribution from second-nearest neighbour would enter into the expression for interaction energy term Q.

3.1.2. Hyper-stoichiometric Di-hydrides $MH_{2+\delta}$ of Lanthanides and Actinide

Analyses for hyper-stoichiometric di-hydrides $MH_{2+\delta}$ of lanthanides (La, Ce, Pr, Nd, Sm) and actinides (Np, Pu, Am) with *fcc* lattice structure were made under assumption that H atoms up to H/M = 2.0 occupy the T-sites and H atoms exceeding H/M = 2.0 occupy randomly the O-sites [6]. Accepting this model, $PF(MH_{2+\delta})$ is represented by (in the original paper [6], the hyper-stoichiometric phase is represented by MH_{2+x} instead of $MH_{2+\delta}$)

$$PF(MH_{2+\delta}) = \{n_M!/[(n_H-2n_M)!(3n_M-n_H)!]\} \cdot$$
$$f_M{}^{nM} (f_H{}^O)^{nH-2nM} (f_H{}^T)^{2nM} \exp[-E(MH_{2+\delta})/(RT)], \quad (10)$$

where $f_H{}^O$ refers to atomic partition function of H atoms distributed over O-sites, $f_H{}^T$ that of H atoms distributed over T-sites and $E(MH_{2+\delta})$ lattice energy of $MH_{2+\delta}$.

Using this expression for $PF(MH_{2+\delta})$, expression for chemical potential $\mu_H(MH_{2+\delta})$ of H in $MH_{2+\delta}$ crystal lattice is represented by

$$\mu_H(MH_{2+\delta})=RT \ln [\delta/(1 - \delta)] - RT \ln f_H{}^O + 6E(H\text{-}M)^O +$$
$$8E(H\text{-}H)^{O\text{-}T} + 12\delta E(H\text{-}H)^{O\text{-}O}, \quad (11)$$

where $E(H\text{-}M)^O$ refers to interaction energy between the H atom in O-site and the M atom, $E(H\text{-}H)^{O\text{-}T}$ interaction energy between the H atom in O-site and the H atom in T-site and $E(H\text{-}H)^{O\text{-}O}$ interaction energy between the nearest neighbour H atoms in O-sites.

Table 3. Values of $R \ln f_H{}^O$ and other parameters evaluated for hyper-stoichiometric $MH_{2+\delta}$. (Reproduced from Table 1 in [6])

$MH_{2+\delta}$ (fcc)	$R \ln Zf_H{}^O$ [J·K^{-1}·mol^{-1}]	Q_1 [kJ·mol^{-1}]	Q_2 [kJ·mol^{-1}]	D(M) [kJ·mol^{-1}]
LaH$_{2+\delta}$	45.4	-249.5	-1028	431
CeH$_{2+\delta}$	69.1	-236.7	-1021	423
PrH$_{2+\delta}$	59.1	-241.9	-993	360
NdH$_{2+\delta}$	57.0	-242.6	-919	326
SmH$_{2+\delta}$	54.3	-239.4	-----	-----
NpH$_{2+\delta}$	45.9	-255.1	-965	469
PuH$_{2+\delta}$	43.3	-256.9	-----	-----
AmH$_{2+\delta}$	53.5	-244.8	-842	276

$Q_1 = 6E(H\text{-}M)^O + 8E(H\text{-}H)^{O\text{-}T}$
$Q_2 = 6E(M\text{-}M) + 8E(H\text{-}M)^T + 6E(H\text{-}H)^{T\text{-}T}$
$D(M) \approx -6E(M\text{-}M)^0$
$E(M\text{-}M)$: nearest neighbour M-M interaction energy in $MH_{2+\delta}$.
$E(H\text{-}M)^T$: interaction energy between H atom in T-site and M atom.
$E(H\text{-}H)^{T\text{-}T}$: interaction energy between nearest neighbour H atoms in T-sites.
D_M: dissociation energy of pure metal M.
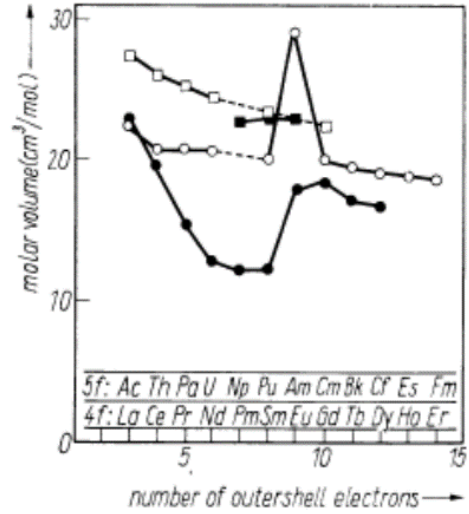$E(M\text{-}M)^0$: nearest neighbour M-M interaction energy in pure metal M.

Figure 2. Molar volume of some lanthanides (4*f*-group elements), actinides (5*f*-group elements) and their hydrides; M [52]: (○) 4f, (•) 5f. $MH_{2.0}$ [53]: (□) 4f, (■) 5f. (Reproduced from Fig. 5 in [6])

In Table 3, values of Q_2 estimated from consideration for $\mu_M(MH_{2+\delta})$ are listed besides Q_1 evaluated from consideration for $\mu_H(MH_{2+\delta})$. Unlike similarities in values of $R \ln Zf_H{}^O$ and Q_1 among lanthanides (4*f*-group elements) and among actinides (5*f*-group elements), values of Q_2 vary appreciably among lanthanides and among actinides. This aspect with Q_2 was appreciated in terms of considerable extent of variation of molar volume of M [52] and $MH_{2.0}$ [53] of 4*f*- and 5*f*-elements with respect to number m of the outer-shell *f*-electrons as represented in Fig. 2 and resultant variations of dissociation energy D(M) of these *f*-group metals with respect to number of the outer-shell *f*-electrons as listed in Table 3 [6].

3.1.3. Suppressed H Solubility for Va-group Alloys $A_{1-y}M_yH_x$ (A = V, Nb or Ta) by Alloying with Substitutional Metallic Constituent M (= Al, Co, Cr, Cu, Fe, Mo, Ni, Pd, Sn, Ru or W)

Statistical thermodynamic evaluations for parameters, θ, Q and $R \ln Zf_H$, were made for $A_{1-y}B_yH_x$ alloys of Va-group metals (A = V, Nb or Ta) through alloying with substitutional metallic constituents M (= Al, Co, Cr, Cu, Fe, Mo, Ni, Pd, Sn, Ru or W). The evaluation results are listed in Table 4 [49]. Graphical presentation of values for $R \ln Zf_H$ and Q for $Nb_{1-y}M_yH_x$ alloys with suppressed H absorption from that in Nb through alloying with M (= Pd, Sn, Al, Cu, Ni or Mo) are reproduced in Fig. 3 [9].

It is evident in Table 4 that value of θ for *bcc* $A_{1-y}M_yH_x$ in which solubility of H is suppressed from that in AH_x became smaller than that for AH_x. However, it is noticed in Table 4 that, for some $A_{1-y}M_yH_x$ in which H solubility was suppressed from that in AH_x, $Q(A_{1-y}M_yH_x)$ became more negative than $Q(AH_x)$ meaning H in such $A_{1-y}M_yH_x$ lattice was more stable with regard to interaction energy between H atom and metal atoms in $A_{1-y}M_y$ lattice than H in AH_x in spite of the suppressed extent of H solubility; e.g. $V_{0.95}Fe_{0.05}H_x$, $V_{0.948}Co_{0.052}H_x$, $Nb_{0.95}W_{0.05}H_x$, $Nb_{0.95}Sn_{0.05}H_x$ and

$Nb_{0.95}Pd_{0.05}H_x$ in Table 4 for which the Q values are presented in bold letters. It is intriguing to notice in Table 4 that R ln Zf_H values for these alloys with suppressed H solubility are relatively small compared with those for the other alloys with suppressed H solubility listed in this table.
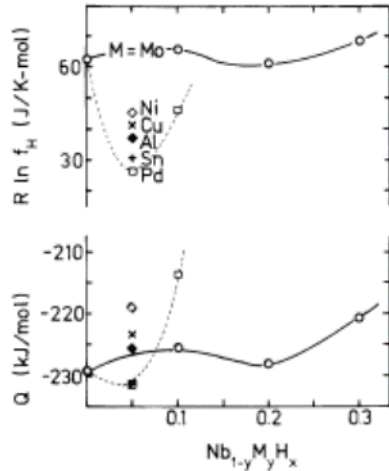

Figure 3. Values of R ln Zf_H and Q plotted as a function of y in bcc $Nb_{1-y}M_yHx$ (M = Pd, Sn, Al, Cu, Ni or Mo). (Reproduced from Fig. 4 in [9])

Table 4. Available statistical thermodynamic interaction parameter values 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 2 in [49])

bcc $A_{1-y}M_yH_x$	θ	Q [kJ·mol^{-1}]	R ln Zf_H [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
$Nb_{0.90}Mo_{010}H_x$	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

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

In Table 4, unique situation is encountered for $Ta_{0.95}W_{0.05}H_x$ in which H solubility was suppressed compared for TaH_x but $\theta(Ta_{0.95}W_{0.05}H_x)$ was 0.55 holding

equal to $\theta(TaHx)$ and $Q(Ta_{0.95}W_{0.05}H_x)$ was comparable to $Q(TaH_x)$ while R ln $f_H(Ta_{0.95}W_{0.05}H_x) < R$ ln $f_H(TaH_x)$. ^{74}W is neighbouring element to ^{73}Ta in the Periodic Table of the Elements and the outer-shell electron structure of ^{74}W, $5d^46s^2$, is quite similar to that of ^{73}Ta, $5d^36s^2$, and this fact might have led to similar values for θ and Q between TaH_x and $Ta_{0.95}W_{0.05}H_x$, while electronic surrounding around H atom was modulated somewhat from TaH_x to $Ta_{0.95}W_{0.05}H_x$ to lead to appreciable change in R ln f_H from TaH_x (62.4 [J·K^{-1}·mol^{-1}]) to $Ta_{0.95}W_{0.05}H_x$ (32.1 [J·K^{-1}·mol^{-1}]).

Values of Q and R ln Zf_H evaluated for $Nb_{0.95}M_{0.05}H_x$ (M = Pd, Sn, Al, Cu or Ni) are plotted in Fig. 3 (in the original publication [9], R ln Zf_H axis was indicated as R ln f_H as seen above). It is seen in Fig. 3 that, at a fixed $y = 0.05$ for $Nb_{1-y}M_yH_x$, R ln $Zf_H(Nb_{0.95}M_{0.05}H_x)$ as well as $Q(Nb_{0.95}M_{0.05}H_x)$ and $\theta(Nb_{0.95}M_{0.05}H_x)$ (see Table 4) varied appreciably depending on the alloying constituent M reflecting difference in extent of modulation of electronic structure in the $Nb_{0.95}M_{0.05}$ metal sub-lattice depending on the electronic structure around the alloyed M to Nb.

It is seen in Table 4 that $\theta(Nb_{1-y}Mo_yH_x)$ decreased monotonically with increasing y from 0.75 at $y = 0$, through 0.45 at $y = 0.10$ and 0.30 at $y = 0.20$, to 0.20 at $y = 0.3$. Nevertheless, variation patterns for R ln $Zf_H(Nb_{1-y}Mo_yH_x)$ and for $Q(Nb_{1-y}Mo_yH_x)$ are not at all monotonical with respect to variation of y (Fig. 3). The same is true for $Nb_{1-y}Pd_yH_x$; θ decreased monotonically with increasing y from 0.75 at $y = 0$ through 0.60 at $y = 0.05$ to 0.45 at $y = 0.10$ (Table 4) but patterns of variations of R ln $Zf_H(Nb_{1-y}Pd_yH_x)$ and Q ($Nb_{1-y}Pd_yH_x$) were not at all monotonical with respect to variation of y (Fig. 3).
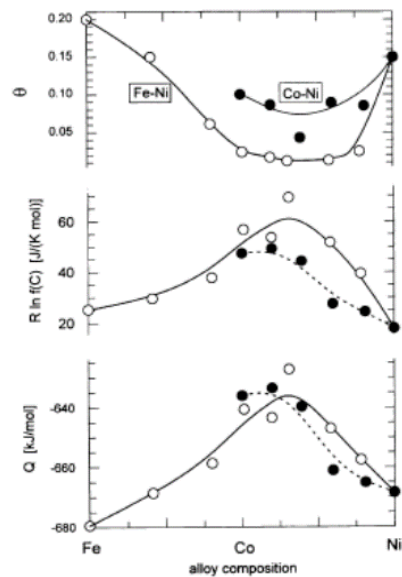
Figure 4. Estimated values of θ, R ln Zf_C and Q for *fcc* $Fe_{1-y}Ni_yC_x$ and for *fcc* $Co_{1-y}Ni_yC_x$ plotted as a function of alloy composition (mean number m of 3d electrons was 6 for Fe, 7 for Co and 8 for Ni). (Reproduced from Fig. 2 in [35])

Estimated values of θ, Q and R ln Zf_C for *fcc* $Fe_{1-y}Ni_yH_x$ and for *fcc* $Co_{1-y}Ni_yH_x$ are plotted in Fig. 4 [35]. Composition axis of this plot corresponds to number of outer-shell $3d$

electrons; mean number m of $3d$ electrons being 6 for Fe, 7 for Co and 8 for Ni. Analysis for these alloys were done considering they were very dilute solutions of C in $A_{1-y}B_y$ alloy lattice by taking an a priori assumption of

$$E(\text{C-C}) = 0, \qquad (12)$$

within the given phase at arbitrary T.

As seen in Fig. 4, variation patterns of θ for fcc Fe$_{1-y}$Ni$_y$H$_x$ and for fcc Co$_{1-y}$Ni$_y$H$_x$ with respect to m is not monotonical but it appears that, for both iron-group alloys, θ value took minimum at around $m \approx 7.25$ and, correspondingly, peak values for $R \ln Zf_C$ and Q emerged at around $m \approx 7.25$.

3.1.4. Influences of Concentration Range x and Isotope Effect of Solute Element X in MX$_x$ (M = Ti or Zr; X = H or D) on $R \ln Zf_X$

Very dilute solution ranges of H and D (deuterium) in IVa-group metals, Ti and Zr, were analyzed under *a priori* assumption of

$$E(\text{X-X}) = 0, \qquad (13)$$

at arbitrary T where X refers to H or D [11].

Analysis results are summarized in Table 5 in which results of analysis for MXx in the moderate concentration range are also listed.

Table 5. Values of Q and $R \ln Zf_X$ for the very dilute ($x < 0.015$) and the modest ($0.1 < x < 0.8$) solute concentration ranges in MX$_x$ (M = Ti or Zr; X = H or D). (Reproduced from Table 1 in [11])

MX$_x$	very dilute solute range		moderate solute range		
	Q^d [kJ·mol^{-1}]	$R \ln Zf_X{}^d$ [J·K^{-1}·mol^{-1}]	Q [kJ·mol^{-1}]	$R \ln Zf_X$ [J·K^{-1}·mol^{-1}]	Z
TiH$_x$	-255.3 ± 1.4	60.5 ± 1.2	-253.5 ± 1.7	33.2 ± 1.4	≈ 27
TiD$_x$	-265.7 ± 1.2	78.8 ± 1.1	-265.2 ± 1.8	50.4 ± 1.5	≈ 30
ZrH$_x$	-249.9 ± 1.2	71.0 ± 1.0	-259.3 ± 2.2	33.6 ± 1.9	≈ 89
ZrD$_x$	-273.4 ± 2.1	77.4 ± 1.8	-257.6 ± 3.7	61.6 ± 3.1	≈ 7

Q^d: $Q(\text{MX}_x)$ in the very dilute range of x,
$f_X{}^d$: f_X in the very dilute range of x.

On undertaking statistical thermodynamic analysis for MD$_x$ being in equilibrium with D$_2$ gas, $C(T)$ for D$_2$ gas had to be calculated using Eq.(3). On this calculation, common approximations were employed for estimating values of $\Theta_r(\text{D}_2)$ and $\Theta_v(\text{D}_2)$, respectively, from available values of $\Theta_r(\text{H}_2)$ and $\Theta_v(\text{H}_2)$

$$\Theta_r(\text{D}_2) \approx \Theta_r(\text{H}_2)/2, \qquad (14)$$

$$\Theta_v(\text{D}_2) \approx \Theta_v(\text{H}_2)/2^{1/2}. \qquad (15)$$

Values $D(\text{D}_2)$ of dissociation energy of D$_2$ gas as a function of T were not available in JANAF Thermochemical Tables [50]. Hence, following approximation was used on the basis of the difference between $D(\text{D}_2)$ at 0 K and $D(\text{H}_2)$ at 0 K listed in [54] to estimate $D(\text{D}_2)$ at arbitrary T

$$D(\text{D}_2) \approx D(\text{H}_2) + 7.5 \, [\text{kJ·mol}^{-1}]. \qquad (16)$$

Further, ρ was taken to be 2 for H and 3 for D. On the basis of these approximations, analysis results summarized in Table 5 were obtained.

In [11], brief review was made on isotope effect of H and D in Ti lattice for atomic partition function expressed by Eq.(4). The essence of the review is summarized in the following.

Accepting the expression for $\ln f_X(T)$ represented by Eq.(4), difference between $\ln f_D$ and $\ln f_H$ is given by

$\ln f_D - \ln f_H = \ln [f_D(T)/f_H(T)] =$

$\int_0^\infty \ln\{1-\exp[-h\nu_H/(kT)]\}d\nu_H - \int_0^\infty \ln\{1-\exp[-h\nu_D/(kT)]\}d\nu_D$

$+ \ln\{3\nu_0(\text{D})/[2\nu_0(\text{H})]\}. \qquad (17)$

Experimental data available on vibrational mode of H in M lattice were scarce [6, 8, 18, 55-57]; $\nu_H = 550$ cm^{-1} for H at O-sites in fcc Pd and $\nu_H(1) = 970$ cm^{-1} (singlet) and $\nu_H(2) = 1400$ cm^{-1} (doublet) for H at T-sites in bcc V, Nb or Ta.

Thus, in the earlier works [6, 8, 18], very crude tentative approximations were made to assume that the vibration frequency ν_H in the metallic lattice was 750 cm^{-1} and that the multiplicity at this ν_H was triple. Results of approximate calculations accepting this very crude vibrational mode for H in MH$_x$ lattices are summarized in Table 6 as reviewed later in 3.2.

Accepting this crude model, Eq. (17) is reduced to

$\ln (f_D/f_H) = 3 \ln\{[1 - \exp[-h\nu_H/(kT)]/[1 - \exp[-h\nu_D/(kT)]\}$

$+ \ln\{3\nu_0(\text{D})/[2\nu_0(\text{H})]\}, \qquad (18)$

where ν_D might be estimated by approximating harmonic oscillator accepting $\nu_H = 750$ cm^{-1}

$$\nu_D = \nu_H/2^{1/2} \approx 530 \, \text{cm}^{-1}. \qquad (19)$$

Accepting this value for ν_D, value of the ratio $\nu_0(\text{D})/\nu_0(\text{H})$ was calculated to be 2.9 at $T = 1200$ K implying that the statistical weight $\nu_0(\text{D})$ of D atom in TiD$_x$ is different from $\nu_0(\text{H})$ of H atom in TiD$_x$ which seemed realistic (isotope effect). It is also noticed in Table 3 that $Q(\text{TiD}_x)$ and $Q(\text{TiH}_x)$ in both the very dilute and the moderate solution concentrations were different from each other by the same degree of about 10 [kJ·mol^{-1}] from each other in either the very dilute and the modest solution concentration range (isotope effect).

Looking at Table 5, it is noticed that difference between $R \ln Zf_D{}^d$ (= 78.8 [J·K^{-1}·mol^{-1}]) and $R \ln Zf_H{}^d$ (= 60.5 [J·K^{-1}·mol^{-1}]) in the very dilute solution range and the difference between $R \ln f_D$ (= 50.4 [J·K^{-1}·mol^{-1}]) and $R \ln f_H$ (= 33.2 [J·K^{-1}·mol^{-1}]) in the moderate solute concentration range were approximately the same being around 18 [J·K^{-1}·mol^{-1}]. It is also noticed that Z estimated for the very dilute TiH$_x$ was 27 which was comparable to $Z = 30$ estimated for the very dilute TiD$_x$.

As such, parameter values estimated for TiH$_x$ and TiD$_x$ in both the very dilute and the moderate solution concentration ranges look generally consistent among themselves. In contrast, such consistency among the estimated parameters for ZrH$_x$ and ZrD$_x$ were not found in Table 5. Although the lacking inconsistency among the estimated statistical

thermodynamic parameter values for ZrH_x and that for ZrD_x might be genuine origin and might be interpreted rationally but we cannot rule out the possibility that the results for ZrH_x and for ZrD_x were affected by inherent presence of Hf (hafnium) impurity in industrially pure Zr.

3.2. Attempts to Estimate $R \ln Zf_X(T)$ Values Taking into Account T-dependence of $f_X(T)$

As represented by Eq. (4), expression for $\ln f_X(T)$ is a function of T

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

As pointed out above, there are scarce information on ν values for atoms X in non-stoichiometric interstitial solid solution MX_x. Anyway, using a few available information for values of ν_H [55-57], very crude estimation was attempted to evaluate $R \ln Zf_H(T)$ values as a function of T by taking $\nu_H = 750$ cm^{-1} assuming the multiplicity of this vibrational mode of H being 3. The estimation results are summarized in Table 6.

Table 6. Estimated values for $R \ln Zf_H(T)$ taking into account T-dependence of $f_H(T)$ for some MHx compared with estimated values for $R \ln Zf_H$ according to standard statistical thermodynamic analysis procedure

MH_x	$R \ln Zf_H(T)$ [J·K^{-1}·mol^{-1}]	$R \ln Zf_H$ [J·K^{-1}·mol^{-1}]	Ref.
$LaH_{2+\delta}$	38.1 (450℃) - 35.2 (250℃)	45.4	6
$CeH_{2+\sigma}$	50.7 (600℃) - 46.4 (300℃)	69.1	6
$PrH_{2+\delta}$	51.9 (450℃) - 49.0 (250℃)	59.1	6
$NdH_{2+\delta}$	49.5 (450℃) - 46.6 (250℃)	57.0	6
$SmH_{2+\delta}$	46.9 (450℃) - 44.0 (250℃)	54.3	6
$NpH_{2+\delta}$	37.1 (550℃) - 34.2 (350℃)	45.9	6
$PuH_{2+\delta}$	35.4 (500℃) - 32.5 (300℃)	43.3	6
$AmH_{2+\delta}$	45.3 (600℃) - 41.0 (300℃)	53.5	6
VH_x	61.6 (554.0℃) - 59.5 (245.6℃)	64.7	8
NbH_x	57.1 (671.0℃) - 54.6 (352.5℃)	61.8	8

In Table 6, it is noticed that $R \ln Zf_H(T)$ range for any MH_x system were lower than $R \ln Zf_H$ value estimated from standard statistical thermodynamic analysis procedure under implicit assumption of T-independence of f_H. There is, for the moment, no rational explanation for this.

4. Concluding Remarks

Characteristic features of entropy terms appearing in statistical thermodynamic analysis formula for non-stoichiometric interstitial compound MX_x are reviewed.

On undertaking the statistical thermodynamic analysis for MX_x, essential first step is to compose plausible partition function $PF(MX_x)$ to MX_x by taking realistic distribution model for interstitial non-metallic constituent X in MX_x lattice. For this criterion to be fulfilled, it was proposed in the first publication [3] of this series of work to choose the number θ of available interstitial sites per M atom that appears in fundamental formula Eq. (1) in a way to yield

constant $E(X-X)$ at arbitrary T over entire homogeneity composition range of MX_x. The system analyzed in [3] was hypo-stoichiometric nitride of chromium, $CrN_{0.50-\delta}$, and θ to fulfil the *a priori* assumption of constant $E(N-N)$ was determined to be 0.5 and the analysis results looked realistic holding rational compatibility with the available thermodynamic parameter values for Cr_2N phase.

This choice of θ parameter value for analysis of $CrN_{0.50-\delta}$ would mean that available sites for N atom occupation in hcp $CrN_{0.50-\delta}$ lattice were O-sites and occupation of one O-site by N atom would block occupation by a neighbouring O-site by another N atom (i.e., $Z = 2$).

Geometrically available number θ_0 of available interstitial sites per M atom in close-packed MX_x lattice (*fcc* or *hcp*) would be 1 if the O-sites are occupied or 2 if T-sites are occupied

$$\theta_0(fcc/hcp; O) = 1, \quad (20)$$

$$\theta_0(fcc/hcp; T) = 2. \quad (21)$$

On the other hand, that for rather open bcc lattice might be represented by

$$\theta_0(bcc; O) = 3, \quad (22)$$

$$\theta_0(bcc; T) = 6. \quad (23)$$

Deviation of θ from θ_0 might be quite significant for some MX_x as experienced for analysis of primary solid solution MH_x with bcc lattice structure for Va-group transition metals (M = V, Nb, Ta) [5]; $\theta = 0.55$ was chosen for V and Ta (that is $Z \approx 5$) while $\theta = 0.75$ was chosen (that is, $Z = 4$) for M = Nb while $\theta_0(bcc; O) = 3$.

Without accepting the proposed a priori assumption of constant $E(X-X)$ at arbitrary T within a given phase, conclusions drawn from statistical thermodynamic analysis would become with great arbitrariness and meaningless. For example, when $\theta = \theta_0(hcp; O) = 1$ (that is, random distribution of N atoms over geometrically available O-sites in *hcp* lattice of $CrN_{0.50-\delta}$) is accepted for analysis of $CrN_{0.50-\delta}$, variation of $E(N-N)$ with composition of x at arbitrary T is derived showing trend of increasing repulsive nearest neighbour N-N interaction with increasing x. Such situation is not realistic because if $E(N-N)$ interaction changed with composition x, phase change should be induced at certain threshold x.

As such, choice of realistic θ representing configurational entropy term of MX_x is the essential first step of initiating statistical thermodynamic analysis for MX_x.

Then, as the consequence of the statistical thermodynamic analysis carried out on the basis of this simplifying a priori assumption, apparently realistic conclusion was drawn for value of the term $R \ln Zf_H$ for MH_x of Va-group metals in spite of different θ values assigned for M = V and Ta and for M = Nb (cf. Table 1) that fell at around 63.5 ± 2 [J·K^{-1}·mol^{-1}]. As also seen in Table 1, Q values evaluated for these MH_x were also comparable to each other being around -227 ± 3 [kJ·mol^{-1}].

Discussion on contribution of electronic term $R \ln Zf_X$ of tightly bound electrons in MX_x lattice remains still rather

primitive and imperfect. It is hoped that this aspect is exploited further being assisted by compiled data on vibrational frequency ν of interstitial constituent X in MX_x lattice.

As reviewed in this paper, entropy terms in multi-component alloys including non-stoichiometric interstitial alloys are consisted of contribution from tightly bound electrons besides contribution from configuration of constituent atoms over crystal lattice points.

Unlike enthalpy term, entropy term is not straightforwardly measurable by experiment for alloys. For example, in spite of strategic importance of entropy term in characterizing fashionable high-entropy alloys, report appears to be scarce on values of entropy terms in published works on high-entropy alloys.

The concept of high-entropy alloy was born in 2004 by Cantor et al. [58] being defined originally as "equi-atomic multi-component alloy". After being christened with distinctive name "high-entropy alloys" [59], research on this category of alloys became highly fashionable. Nevertheless, in available works published on high-entropy alloys [60], explicit quantitative evaluation for entropy term did not seem to be made very seriously. This is somewhat peculiar and surprising.

High-entropy alloys are classified in substitutional alloys and thence the analysis procedure used in this work for interstitial alloy systems cannot be applied straightforwardly. However, if effort is invested to evaluate somehow contribution from electronic terms as well as from atomic configuration term, rate of progress in high-entropy alloy might be raised.

ACKNOWLEDGEMENTS

Appendix / Symbols

<universal constants>

R: universal gas constant (= 8.31451 [J·mol^{-1}·K^{-1}]),

h: Planck constant (= $6.6260755 \times 10^{-34}$ [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,

υ_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,

υ_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 macroscopic parameters>

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

T: absolute temperature [K],

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

n_X: number of X atoms in MX_x lattice,

n_M: number of M atoms in MX_x lattice,

<atomistic 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,

$E(i\text{-}j)$: 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 lattice,

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

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 lattice,

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

Z: extent of blocking of interstitial sites by X in MX_x lattice (= θ_0/θ); 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.

REFERENCES

[1] R. H. Fowler and E. A. Guggenheim: Statistical Thermodynamics. Cambridge University Press, Cambridge, UK, 1949.

[2] N. Shohoji: Statistical Thermodynamic Approach to

Interstitial Non-stoichiometric Compounds (Hydride, Carbide, Nitride, Phosphide and Sulphide). Lambert Academic Publishing, Saarbrücken, Germany, 2013. ISBN: 978-3-659- 45506- 3.

[3]   N. Shohoji, M. Katsura and T. Sano: Statistical model for the non-stoichiometric Cr_2N phase. *J. Less-Common Met.* 38 (1974) 59-74, DOI: 10.1061/0022-5088(74)90203-3.

[4]   N. Shohoji: Comments on "Hysteresis in metal hydride". *J. Less-Common Met.* 90 (1983) L5-L6, DOI: 10.1061/0022-5088(83)910129-7.

[5]   N. Shohoji: On the construction of a statistical model for primary solid solutions of hydrogen in the group Va transition metals (vanadium, niobium and tantalum). *J. Less-Common Met.* 90 (1983) L27-L29. DOI: 10.1061/0022-5088(74)90082-6.

[6]   N. Shohoji: Statistical thermodynamic approach to some hyperstoichiometric dihydrides of lanthanides (La, Ce, Pr, Nd, Sm) and actinides (Np, Pu, Am). *Physica Status Solidi (B)* 118 (1983) 811-822. DOI: 10.1002/pssb.2221180238.

[7]   N. Shohoji: Statistical thermodynamics of hydrogen solution in some lanthanides. *Physica Status Solidi (B)* 119 (1983) K87-K90. DOI: 10.1002/pssb.222190169.

[8]   N. Shohoji: Statistical thermodynamics of metal-hydrogen systems. *J. Less-Common Met.* 102 (1984) 53-65. DOI: 10.1016/0022-5088(84)90388-6.

[9]   N. Shohoji: Statistical model for the hydrogen solutions in *bcc* $Nb_{1-y}M_y$ alloys (M = Al, Cu, Sn, Ni, Pd). *Mater. Lett.* 3 (1985) 206-208. DOI: 10.1016/0167-577X(85)90056-4.

[10] N. Shohoji: Statistical thermodynamics of carbon solutions in metals. *Mater. Chem. Phys.* 13 (1985) 567-575. DOI: 10.1016/0254-0584(85)90006-9.

[11] N. Shohoji: Statistical thermodynamics of the very dilute interstitial solid solutions. *Z. Metallkde.* 76 (1985) 192-197.

[12] N. Shohoji: The application of statistical thermodynamics to interstitial solid solutions. *J. Less-Common Met.* 114 (1985) 249-256. DOI: 10.1016/0022-5088(85)90443-6.

[13] N. Shohoji: Statistical thermodynamic study of the ternary compounds ThX_yH_x (X = C, N; $y < 1$, $x < 2$). *J. Nucl. Mater.* 127 (1985) 88-96. DOI: 10.1016/0022-3115(85)90064-2.

[14] N. Shohoji: Interaction between hydrogen atoms in metals. *J. Mater. Sci. Lett.* 5 (1986) 522-524.
DOI: 10.1007/BF01728678.

[15] N. Shohoji: Comparative study of solubilities of hydrogen, nitrogen and carbon in α-iron. *J. Mater. Sci.* 21 (1986) 2147-2152. DOI: 10.1007/BF00547962.

[16] N. Shohoji: Statistical thermodynamic analysis of phosphorus solubility in molten iron. *Trans. Iron Steel Inst. Jpn* 26 (1986) 194-197. DOI: 10.2355/isijinternational1986.26.194.

[17] N. Shohoji: Statistical thermodynamics of sulphur solution in molten iron. *Trans. Iron Steel Inst. Jpn* 26 (1986) 547-550, DOI: 10.2355/isijinternational1986.26.547.

[18] N. Shohoji: Statistical thermodynamic aspects of hydrogen in metals. *Surface Coatings Technol.* 28 (1986) 365-382, DOI: 10.1026/0257-8972(86)90093-9.

[19] N. Shohoji: Statistical model for nitrogen solution in molten

iron and molten iron alloys. *Mater. Sci. Technol.* 3 (1987) 43-48. DOI: 10.1179/mst.1987.3.1.43.

[20] Shohoji, N. Carbon solubilities in iron at elevated temperatures analysed by statistical thermodynamics. *Mater. Sci. Technol.* 3 (1987) 404-410,
DOI: 10.1179/mst.1987.3.6.404.

[21] N. Shohoji and T. Marcelo: Tetragonality in crystal lattice of zirconium dihydride, *J. Mater. Sci. Lett.* 6 (1987) 1251-1253. DOI: 10.1007/BF01794578.

[22] N. Shohoji: Estimation of carbon-metal interaction in the carbides of d-transition metals. *Mater. Chem. Phys.* 17 (1987) 391-398. DOI: 10.1016/0254-0584(87)90089-7.

[23] N. Shohoji: Statistical model for molten $Fe_{1-y}Cr_yN_x$ ($0.4 \leq y \leq 0.9$). *Mater. Sci. Technol.* 4 (1988) 867-870. DOI: 10.1179/ mst.1988.4.10.867.

[24] N. Shohoji and J. Botas: Glass-forming ability of multicomponent alloys viewed from statistical thermodynamic standpoint. *J. Mater. Sci. Lett.* 7 (1988) 903-905. DOI: 10.1007.BF00720724.

[25] N. Shohoji: Clustering of atoms in molten $Fe_{1-y}Ti_yN_x$. *Mater. Chem. Phys.* 24 (1989) 163-173. DOI: 10.1016/0254-0584(89)90055-2.

[26] N. Shohoji: Unique features of hydrogen in palladium metal lattice: hints for discussing the possible occurrence of cold nuclear fusion. *J. Mater. Sci. Lett.* 9 (1990) 231-232. DOI: 10.1017/BF00727727.

[27] N. Shohoji: Stability of interstitial elements in metal lattice evaluated by statistical thermodynamics. *ISIJ Internat. (Successor to Trans. Iron Steel Inst. Jpn)* 30 (1990) 472-474. DOI: 10.2355/isijinternational.30.472.

[28] N. Shohoji and M. Katsura: Statistical thermodynamic appreciation of metal nitrides at elevated temperatures. *J. Nucl. Mater.* 170 (1990) 109-112.
DOI: 10.1016/0022-3115(90) 90333-1.

[29] N. Shohoji: Nitrogen solution in molten $Fe_{1-y}M_y$ (M = Al, Mn) analyzed using statistical thermodynamics. *Mater. Sci. Technol.* 7 (1991) 213-217, DOI: 10.1179/mst.1991.7.3.213.

[30] M. C. Monteiro Dias and N. Shohoji: Stability of hydrogen and nitrogen in VIa-group metals (Cr, Mo, W) and iron-group metals (Fe, Co, Ni) evaluated by statistical thermodynamics. *J. Mater. Sci.* 27 (1992) 5154-5158,
DOI: 10.1007/BF02403809.

[31] N. Shohoji: Statistical model for nitrogen solution in molten iron containing another interstitial constituent (carbon or silicon). *Mater. Chem. Phys.* 32 (1992) 153-159. DOI: 10.1016/ 0254-0584(92)90271-9.

[32] M. C. Monteiro Dias and N. Shohoji: Atomic configuration in hexagonal-close-packed TiC_zH_x phase estimated by statistical thermodynamics. *Mater. Chem. Phys.* 39 (1995) 193-199. DOI: 10.1016/0254-0584(94)01429-K.

[33] N. Shohoji: Statistical thermodynamic approach to carbon solubility in face centred cubic Fe1-yNiy alloy lattice. *Mater. Sci. Technol.* 12 (1996) 373-377.
DOI: 10.1179/026708396790165867.

[34] M. C. Monteiro Dias and N Shohoji: A theory of suppressed nitrogen solubility in Fe-Z-N ternary alloy systems in the

relatively high range of concentration of Z (Z = Si or C). *Mater. Chem. Phys.* 50 (1997) 275-279, DOI: 10.1016/S0254-0584(97)01944-5.

[35] N. Shohoji: Carbon solubility in face centred cubic $Co_{1-y}Ni_y$ alloy lattice analysed by statistical thermodynamics. *Mater. Chem. Phys.* 51 (1997) 265-268. DOI: 10.1016/S0254-0584(97)80316-1.

[36] N. Shohoji: Atomic clustering in non-stoichiometric interstitial alloy systems evaluated by statistical thermodynamics -example cases of analysis of short-range ordering for molten $Fe_{1-y}M_yN_x$ (M = Cr, Ti, V, Mn, Al). Advances in Materials Engineering and Technology, Special Publication of *Internat. J. Mater. Product Technol.*, SPM1, 2001, Inderscience Enterprises Ltd. Geneva, Switzerland, Vol. 1, pp.41-48.

[37] N. Shohoji: Statistical thermodynamics as a tool for evaluating atom clustering around interstitial atom. *Mater. Trans.* 42 (2001) 2225-2231. DOI: 10.2320/matertrans.42.2225.

[38] N. Shohoji and M. C. Monteiro Dias: Statistical thermodynamic approach to austenitic $Fe_{1-y}Nb_yN_x$ system. *Mater. Sci. Technol.* 19 (2003) 429-434. DOI: 10.1179/026708303225009319.

[39] N. Shohoji: Interaction energy parameters in hypo-stoichiometric mono-carbides, TiC_x and NbC_x, evaluated by statistical thermodynamics. *Mater. Sci. Technol.* 19 (2003) 1469-1472. DOI: 10.1179/026708303225006033.

[40] N. Shohoji: M-C dipole formation in *fcc* (face centred cubic) $Fe_{1-y}M_yC_x$ solid solution (M = Ti, Nb). *Mater. Sci. Technol.* 20 (2004) 301-306. DOI: 10.1179/026708304225012297.

[41] N. Shohoji and M. C. Monteiro Dias: Empirical expression of phosphorus solubility in molten $Fe_{1-y}Cr_y$ expressed as functions of temperature and phosphorus activity. *ISIJ Internat.* 45 (2005) 1226-1231. DOI: 10.2355/isijinternational.45. 1226.

[42] N. Shohoji and S. Figueiredo Marques: Statistical thermodynamic approach to molten Fe-Cr-P. *Internat. J. Mater. Research (Successor to Z. Metallkde.)* 99 (2008) 245-250. DOI: 10.3139/146.101630.

[43] N. Shohoji: Hydrogen absorption in epitaxial *bcc* V (001) thin film analysed by statistical thermodynamics. *Thin Solid Films* 518 (2010) 7167-7173. DOI: 10.1016/j.tsf.2010.06.052.

[44] N. Shohoji: Suppressed hydrogen solubility in body centred cubic Va-group metals (Nb and Ta) by alloying with W or Ru analysed on the basis of statistical thermodynamics. *Internat. J. Mater. Eng. Technol.* 7 (2012) 33-54.

[45] N. Shohoji: Statistical thermodynamic analysis for hydrogen absorption behaviour in a four monolayers (4 ML) thick *bcc* vanadium (110) superlattice being in contact with molybdenum layer. *Mater. Trans.* 53 (2012) 1273-1277. DOI: 10.2320/matertrans.M2012071.

[46] N. Shohoji: Statistical thermodynamic analysis for isothermal hydrogenation performances of $Mg_{2-y}Pr_yNi_4$ intermetallics (*y* = 0.6, 0.8, 1.0). *Internat. J. Mater. Chem.* 2 (2012) 90-100. DOI: 10.5923/j.ijmc.20120203.02.

[47] N. Shohoji: Suppressed hydrogen (H) solubility in body centred cubic vanadium (V) by alloying with molybdenum

(Mo), chromium (Cr), Iron (Fe) or cobalt (Co) appreciated in terms of statistical thermodynamics. *Mater. Trans.* 57 (2016) 321-328. DOI: 10.2320/matertrans.M2015415.

[48] N. Shohoji: Proposing design guideline for hydrogen permeation membrane alloy based on Va-group metals (V, Nb and Ta) taking into account interaction energy parameter evaluated by statistical thermodynamics. *Internat. J. Mater. Eng. Technol.* 15 (2016) 75-92. DOI: 10.17654/MT015010075.

[49] N. Shohoji: Characterizing atomic interactions in interstitial non-stoichiometric compounds by statistical thermodynamics: engineering usage of estimated values of statistical thermodynamic parameters. *J. Modern Phys.* 8 (2017) 365-381. DOI: 10.4236/jmp.2017.83025.

[50] D. R. Stull, H. Prophet and G. C. Sinke G.C. (Ed.): JANAF Thermochemical Tables; Joint Army, Navy and Air Force, Dow Chemicals Co., Midland, MI, USA, 1965.

[51] M. W. Chase Jr.: NIST-JANAF Thermochemical Tables, 4th Edition; J. Phys. Chem. Ref. Data, Monograph No. 9, Amer. Chem. Soc. and Amer. Inst. Phys., 1998.

[52] S. Imoto: Electronic structure of actinide metals and semi-metallics. *J. Atom. Energy Soc. Jpn.* 20 (1978) 694-702. DOI: 10.3327/jaesj.20.694.

[53] C. E. Messer and M. K. Park: Dissociation pressures and related thermodynamic functions and hydrogen solution parameters in the systems PrH_2-PrH_3, NdH_2-NdH_3, and SmH_2-SmH_3. General considerations for the related lanthanide and actinide hydride systems. *J. Less-Common Met.* 26 (1972) 235-246, DOI: 10.1016/0022-5088(72)90043-4.

[54] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, (Ed.): Selected Values of Chemical Thermodynamic Properties, N.B.S. Circular 500 - Part I, USA, 1961.

[55] J. J. Rush and H. E. Flotow: Vibration spectra of vanadium hydride in three crystal phases by inelastic neutron scattering. *J. Chem. Phys.* 48 (1968) 3795-3804. DOI: 10.1063/1.1669686.

[56] N. A. Chernoplekov, M. G. Zemlyanov, V. A. Somenkov and A. A. Chertkov:. Study of the dynamics of group V transition-metal hydrides by means of inelastic neutron scattering. *Sov. Phys. - Solid State* 11 (1970) 2343-2349.

[57] R. Yamada, N. Watanabe, K. Sato, H. Asano and M. Hirabayashi: Localized modes in tantalum hydrides studied by neutron inelastic scattering. *J. Phys. Soc. Jpn* 41 (1976) 85-90. DOI: 10.1143/JPSJ.41.85.

[58] B. Cantor, I. T. H. Chang, P. Knight and A. J. B. Vincent: Microstructural development in equiatomic multicomponent alloys. *Mater. Sci. Eng. A* 375-377 (2004) 213-218. DOI: 10.1016/j.mesa.2003.10.257.

[59] J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsau and S. Y. Chang: Nanostructured high-entropy alloy with multiple principal elements: novel design concepts and outcomes. *Adv. Eng. Mater.* 6 (2004) 299-303. DOI: 10.1002/adem.200300567.

[60] S.-L. Wei, H. Feng and C. C. Tasan: Metastability in high-entropy alloys: a review. *J. Mater. Res.* 33 (2018) 2924-2937. DOI: 10.1557/jmr.2018.306.