Statistical Thermodynamics as a Tool for Evaluating Atom Clustering around Interstitial Atom

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In statistical thermodynamic analysis for condensed phase (either liquid or solid), atomistic (or microscopic) information of the condensed phase is derived from experimentally determined macroscopic equilibrium P-T-C (pressure-temperature-composition) relationships. This analysis procedure is especially adequate for non-stoichiometric compound containing at least one interstitial constituent. Atomistic information derived by statistical thermodynamics includes clustering pattern of metal atoms around an interstitial atom as well as pair-wise interaction among constituent atoms. Desired calculation in the statistical thermodynamic analysis is not very demanding and thence, compared with some other branches of computational materials science and engineering research, statistical thermodynamics requires only modest computational capacity of currently available advanced high-performance PC (personal computer). In this article, I would like to review aspects of atom clustering evaluation by statistical thermodynamics as also potentiality of statistical thermodynamics for predicting optimal material manufacturing condition.

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1. Introduction

Statistical thermodynamic analysis undertaken with a simplifying a priori assumption of constant $E(X-X)$ (interaction energy between neighbouring interstitial atoms $X$ in $MX_r$) within a given homogeneity composition range at any given temperature $T$ yielded rational set of parameters for variety of non-stoichiometric interstitial compounds $MX_r$. Thus, the employed a priori assumption of constant $E(X-X)$ within the same phase at respective $T$ was concluded to be acceptable on the empirical basis although it is not possible to theoretically justify validity of this a priori assumption from the first principle. Metal atoms $M$ in the non-stoichiometric interstitial phase $MX_r$ might be a single metal species or substitutional alloy lattice consisting of two or more metallic elements. In the latter type of ternary system $(M_1)_{1-y}(M_II)_yX_r$ containing two metallic elements, $M_1$ and $M_{II}$, certain preferential metal atom arrangement (atom cluster) might develop around interstitial atom $X$ depending on balance between $M_1X$ interaction and $M_{II}X$ interaction in the condensed phase $(M_1)_{1-y}(M_{II})_yX_r$.

In this paper, calculation procedure of statistical thermodynamics taking the simplifying a priori assumption of constant $E(X-X)$ over the homogeneity range at each $T$ is presented with focus placed on the aspects of atom clustering.

2. Fundamental Formulae

2.1 $MX_r$ in equilibrium with ideal diatomic $X_2$ gas

In statistical thermodynamics, partition function $PF$ for condensed phase (either solid or liquid) under consideration is first composed taking into account nearest neighbour atomic interactions. Then, from partial derivation of $PF$ with respect to number $n_i$ of constituent element $i$ in the condensed phase, chemical potential $\mu(i)^c$ of constituent $i$ in the condensed phase is derived. Thereafter, $\mu(i)^c$ is put equal to $\mu(i)^g$ in the gas phase.

The expression for $\mu(X)^g$ of ideal diatomic gas $X_2$ is readily available in the classical textbook authored by Fowler and Guggenheim.\(^{35}\) The detailed derivation process of $\mu(X)^g$ for the condensed phase $MX_r$ might be referred to elsewhere.\(^{1,4,6,9}\) Then, we get following set of fundamental formulae for the statistical thermodynamic analysis.

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

(1)

$$K = g - [D(X_2)/2 - RTC(T)] = Q - RT \ln f_X(T)$$

(2)

$$C(T) = -(1/2) \ln[(4\pi R_X)^{3/2}/h^3]$$

$$\times [(T^{7/2}/\Theta_v)(1 + \Theta_v/3T)][\mu^2 v_0^2/2]$$

$$- \Theta_v/4T + (1/2) \ln[1 - \exp(-\Theta_v/T)]$$

(3)

$$\ln f_X(T) = - \int_0^\infty g(v) \ln[1 - \exp(-hv/kT)]dv + \ln \rho v_0$$

(4)

$$Q + \beta x E(X-X) = \partial E/\partial n_X$$

(5)

Symbols

$R$: universal gas constant
$h$: Planck constant
$p(X_2)$: equilibrium pressure of ideal gas $X_2$
$\Theta_v$: characteristic temperature for rotation of $X_2$
$m_X$: mass of $X$ atom
$g(v)$: distribution function
$v_0^*$: electronic state of normal state of $X_2$ molecule
$\theta$: lattice energy
$T$: absolute temperature (K)
$k$: Boltzmann constant
$D(X_2)$: dissociation energy of $X_2$ molecule per mole
$\Theta_v$: characteristic temperature for vibration of $X_2$
$\rho$: nuclear spin weight
$v$: vibrational frequency of $X$ atom in $MX_r$, lattice
\( v_0 \): statistical weight of tightly bound electrons around X in MX\(_x\)

\( n_X \): number of X atoms in MX\(_x\)

\( Q \): degree of stabilisation of X atom in MX\(_x\) lattice with reference to isolated X atom in vacuum

\( E(i - j) \): interaction energy between i and j atoms in MX\(_x\) lattice

\( f_i(T) \): partition function of constituent i in the condensed phase at T

\( K \& g \): parameters determined by eqs. (1) \& (2) from the experimental P-T-C (pressure-temperature-composition) data

\( \beta \): factor determined from crystal structure consideration

\( \theta \): number of the interstitial sites per M atom available for occupation by X atoms in MX\(_x\)

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Table 1: Values of \( D(X_2) \), RTC(T) and \( [D(X_2) - RTC(T)] \) for H\(_2\), N\(_2\) and O\(_2\) and D(C) for C (graphite) (in kcal/mole) together with plots of \( [D(X_2) - RTC(T)] \) for H\(_2\), N\(_2\) and O\(_2\) and D(C) for C (graphite) as a function of T.

* Values of dissociation energy D are taken from JANAF Thermochemical Tables and converted with rate 1 cal = 4.184 J.

\( C(T) \) for H\(_2\) is calculated taking nuclear spin weight \( \rho = 2 \) for H (\( \rho = 3 \) for D).

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<th>T (K)</th>
<th>H(_2) D/2</th>
<th>N(_2) RTC(T)</th>
<th>O(_2) RTC(T)</th>
<th>C (graphite) D(C)</th>
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\( \Theta_0(H) = 6, 100 \text{ K} \)

\( \Theta_0(N) = 3, 340 \text{ K} \)

\( \Theta_0(O) = 2, 230 \text{ K} \)

\( \Theta_0(H) = 85.4 \text{ K} \)

\( \Theta_0(N) = 2.86 \text{ K} \)

\( \Theta_0(O) = 2.07 \text{ K} \)
2.2 MC₆ in equilibrium with carbon with activity a(C)
For non-stoichiometric carbide MC₆ in equilibrium with free carbon with activity a(C), fundamental formula is given by

\[ RT \ln[a(C) (\theta - x)/x] = Q + D(C) - RT \ln f_C(T) + \beta x E(C - C) \]  

(6)
in place of eq. (1) for MX₇, being in equilibrium with ideal diatomic gas X₂.

For convenience of calculation, values of \([D(X₂) - RT(C)]\) for H₂, N₂, and O₂ and D(C) for C (graphite) as a function of T are listed in Table 1 together with their plots at the bottom of the table.

3. Analysis Procedure

First, we must determine value for \(\theta\) parameter to fulfill the a priori condition of constant \(E(X-X)\) (or \(E(X-X) = 0\) for very dilute interstitial solution) over a composition range at each T. Then, we prepare plots of A vs. x isotherms using eq. (1) (or eq. (6) for X = C). From the determined values of g at different T, K vs. T plot is prepared (eq. (2)). Slope of this plot gives R ln f(X(T) value and the intercept at \(T = 0\) gives Q value (\(Q = 6E(X-M)\) for O-site occupation in fcc

Table 2. List of reported statistical thermodynamic analysis results for (M₄, M₅)X₇ type compounds and MZ, X₇ type compounds.

<table>
<thead>
<tr>
<th>System</th>
<th>Remarks</th>
<th>Ref.</th>
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<td>(M₄, M₅)X₇</td>
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<tr>
<td>X=H</td>
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<td>Nbₓ₋ₓ,MₓHₓ</td>
<td>M=Mo</td>
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<td>M=Al,Cu,Sn,Ni,Pd</td>
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<tr>
<td></td>
<td>M=Ti</td>
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<tr>
<td>MCoₓHₓ</td>
<td>M= Dy, Er</td>
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<tr>
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<td>M=Er, Tm</td>
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<td>CuₙCa type structure</td>
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<tr>
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<td>M=Mo, Re, Ru; very dilute N solution</td>
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<tr>
<td>Feₓ₋ₓ,MₓNₓ</td>
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<td></td>
<td>M=Ti (molten)</td>
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<tr>
<td></td>
<td>M=Mn (molten)</td>
<td>17,27</td>
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<td></td>
<td>M=Al (molten)</td>
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<tr>
<td>Feₓ₋ₓ,CrₓNₓ</td>
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<td></td>
<td>0.4 &lt; y &lt; 0.9 (molten)</td>
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<tr>
<td>X=C</td>
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<tr>
<td>Coₓ₋ₓ,NₓCₓ</td>
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<tr>
<td>MZ,X₇</td>
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<tr>
<td>ThZₓHₓ</td>
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<tr>
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<td>FeZₓNₓ</td>
<td>Z=C, Si (molten); low z</td>
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<td></td>
<td>Z=C, Si (molten); high z</td>
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<td>FeCₓXₓ</td>
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<td>X=S (molten)</td>
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4. Analysis Examples

Representative analysis results are reviewed in the following. Sources of P-T-C data used for the analyses are not given in the following text as they were cited in the respective original reports. Range of ternary compounds analysed in the past by the statistical thermodynamics are listed in Table 2.

4.1 (M₄, M₅)Nₓ systems

4.1.1 Molten Fe₁₋ₓ,CrₓNₓ systems

Molten Fe₁₋ₓ,CrₓNₓ is considered as very dilute solution of N into Fe₁₋ₓ,Crₓ lattice with fcc configuration. Thus, determination of \(\theta\) values for the analysis was made to yield constant A term in eq. (1) over homogeneity range x (i.e., \(E(X-X) = 0\)) at each T. This situation is depicted in Fig. 1. For example, \(\theta = 0.3\) was taken for molten Fe₀.₄Cr₀.₆Nₓ because this choice of \(\theta\) value yielded the constant A against x while choice of \(\theta = 0.4\) yielded positive slope and choice of \(\theta = 0.2\) negative slope as seen in Fig. 1.

Figure 2 plots the thus-determined values of \(\theta\) against y in molten Fe₁₋ₓ,CrₓNₓ. Using \(\theta\) values determined as such, analysis was done and variation patterns for R ln f(X) and Q with composition y in molten Fe₁₋ₓ,CrₓNₓ as depicted in Fig. 3 were derived.

Figure 3 seemed to suggest that cluster as depicted in Fig. 4(a) developed in molten Fe₁₋ₓ,CrₓNₓ in the range of y smaller than 0.2 while the cluster as depicted in Fig. 4(c) in the range of y between 0.4 and 0.9. Reason for this interpretation is as follows. In either the low range of y (0-0.2) or the high range of y (0.4-0.9), values of parameters, Q and R ln f(X), held constant over the range of y (Fig. 3) in spite of varying \(\theta\) with y (Fig. 2). Noting that Q refers to the degree of stabilisation of N atom in the Fe₁₋ₓ,Crₓ lattice, constancy of Q would mean that the surrounding of N atom occupying the O-site in the Fe₁₋ₓ,Crₓ lattice does not change within the
Fig. 2  Determined values of $\theta$ vs. $y$ in molten Fe$_{1-x}$Cr$_y$N$_x$.\(^{22}\)

Fig. 3  Values of $R \ln f_N$ [J/(K mol)] (a) and $Q$ [kJ/mol] (b) in molten Fe$_{1-x}$Cr$_y$N$_x$ as a function of $y$; horizontal dotted lines in (b) show positions of values of $Q$ estimated from simple arithmetic sum of $E$(N-Fe) = $-71.2$ kJ/mol and $E$(N-Cr) = $-90.1$ kJ/mol at various ratios of Cr to Fe.\(^{37,22,27}\)

Fig. 4  Possible atom clusters formed in fcc Fe$_{1-x}$M$_x$N$_x$ lattice.\(^{25}\) (a) 1 M/5 Fe cluster (cluster composed of one M atom and five Fe atoms); $\theta = y$. (b) 2 M/4 Fe cluster; $\theta = y/2$. (c) 4 M/2 Fe cluster; $\theta = y/4$.

Fig. 5  Some possible ways of planar extension of the cluster depicted in Fig. 5(c) over the (002)-plane leading to different values of $\theta$; situations with a fixed number of 12 M atoms.\(^{26}\) (a) Isolated clusters; $\theta = y/4$. (b) Planar extension leading to $\theta = (5/12)y$. (c) Planar extension leading to $\theta = (6/12)y (= y/2)$.

On the other hand, $f_N$ represents the electronic state of the N in O-site and thence the constancy of $R \ln f_N$ over the respective $y$ ranges also ensures that the surrounding of N atom occupying the O-site in the Fe$_{1-x}$Cr$_y$ lattice does not change.

Anyway, there was one aspect to be clarified. That was, why the $\theta$ value for Fe$_{1-x}$Cr$_y$N$_x$ in the range of $0.4 < y < 0.9$ deviated from $\theta = y/4$ line anticipated from the cluster model as depicted by Fig. 4(c). To provide answer to this question, planar extension of 4 M/2 Fe type cluster was considered (Fig. 5). As might be understood from Fig. 5, increased degree of planar extension would yield higher $\theta$ value than the one anticipated from $\theta = y/4$ defined for the isolated 4 M/2 Fe clusters.

The 1 M/5 Fe type cluster (Fig. 4(a)) was defined as M-X dipole by Tagashira and co-workers\(^{37-42}\) and its presence in Fe alloy lattice was discussed with reference to electric resistance variation of the specimen as well as to preferential recrystallisation texture evolution.

On the other hand, the 4 M/2 Fe type cluster (Fig. 4(c)) was reported to develop in the nitried Fe-Ti alloy in planar extended form like G-P (Guinier-Preston) zone by Rickerby \textit{et al.}\(^{43-45}\) and its presence was visualised by TEM (transmission electron microscope) observation.
4.1.2 Molten Fe_{1-x}Ti_yN_x

Range of y for the analysed P-T-C data for molten Fe_{1-x}Ti_yN_x was no more than 3 x 10^{-3} but, in spite of very low range of y, the analysis indicated the formation of 4 Ti/2 Fe type cluster rather than 1 Ti/5 Fe type cluster around the dissolved N unlike the situation for the molten Fe_{1-x}Cr_yN_x for which the formed cluster up to y = 0.2 was 1 Cr/5 Fe type. Trend of forming 4 Ti/2 Fe type cluster in such very dilute range of Ti was concluded to be ascribable to strong affinity of N to Ti (E(N-Ti) = -129.1 kJ/mol)\(^{26,27}\) compared with the N-Cr or N-Fe interaction (E(N-Cr) = -90.1 kJ/mol and E(N-Fe) = -72.1 kJ/mol)\(^{17,22,27}\).

4.1.3 Molten Fe_{1-x}Mn_yN_x and Fe_{1-x}V_yN_x

For these systems (E(N-Mn) = -81.0 kJ/mol; E(N-V) = -99.1 kJ/mol)\(^{27}\), only 1 Mn/5 Fe type clustering was found through analysis of the available P-T-C data up to now. But this might be merely due to the fact that the data available were limited to y no more than 0.1 for Fe_{1-x}Mn_yN_x and y no more than 0.2 for Fe_{1-x}V_yN_x and we cannot rule out the possibility of developing 4 Mn/2 Fe type cluster for these systems in the higher range of y, especially for Fe_{1-x}V_yN_x.

4.1.4 Molten Fe_{1-x}Al_yN_x

In contrast to the above discussed systems, increased y in this system led to decrease in N solubility. Analysis results indicated that Q value in Fe_{1-x}Al_yN_x tended to become less negative with the increasing y while R ln f_N value held practically constant with y at a level comparable to the one for FeN_x. Thence, it was concluded that the observed rise in Q (de-stabilisation of N) with increased y in Fe_{1-x}Al_yN_x was ascribable to the increased lattice strain as the consequence of alloying with Al. There is no cluster formation in this alloy system. On the contrary, O-sites around Al atom might be blocked from occupation by N atoms.

4.2 LnM_nH_{(n+1)x} systems (Ln: lanthanide, n: integer)

These systems were analysed using a fundamental formula

\[
A = RT \ln \left( \frac{\theta - x}{(x - \theta')} \right) \left[ \frac{p(H_2)}{P} \right]^{1/2}
\]

\[
= g + \beta x E(X - X)
\]

(7)
in place of eq. (1). The additional parameter \(\theta'\) enters in the analysis in the following way. On careful examination of P-T-C relationships of LnM_nH_{(n+1)x}, it was noticed that the lower composition limit \(x_0\) was quite close to either 1/(n+1) or \(n/(n+1)\). This observation suggested the possibility that, in these intermetallic compounds, there is a strong preference for occupation of certain types of sites among \(\theta n_m\) available sites (n_m: total number of metal atoms). More specifically, \(\theta' n_m\) sites among \(\theta n_m\) sites are occupied preferentially by H atoms first and then the remaining \((\theta - \theta') n_m \) hydrogen atoms distribute themselves randomly over \((\theta - \theta') n_m\) interstices. Accepting this supposition, the number W of configuration of H atoms in LnM_nH_{(n+1)x} is represented by

\[
W = (\theta n_m - \theta' n_m)! / [((\theta n_m - \theta' n_m)! / ((\theta n_m - n_H)!)]
\]

(8)

Consequently, the expression as given by eq. (7) must be used for the analysis of LnM_nH_{(n+1)x} type phase.

Fig. 6 Effect of the choices of \(\theta\) and \(\theta'\) on \(RT \ln \left( \frac{\theta - x}{(x - \theta')} \right) \left[ \frac{p(H_2)}{P} \right]^{1/2}\) vs. \(x\) for ErFe_2H_{3x} at 353 K.\(^{16}\) (a) \(RT \ln \left( \frac{(1-x)}{(x - \theta')} \right) \left[ \frac{p(H_2)}{P} \right]^{1/2}\) vs. \(x\) with \(\theta' = 0.60\) (○), 0.575 (+) and 0.55 (●). (b) \(RT \ln \left( \frac{\theta - x}{(x - 0.575)} \right) \left[ \frac{p(H_2)}{P} \right]^{1/2}\) vs. \(x\) with \(\theta = 1.15\) (○) and 0.95 (●).
Table 3. Chosen parameters, θ and θ', and estimated parameters, Q and R ln f_{H}, for LnM_{x}H_{y+1}X_{4}.6,10,16

<table>
<thead>
<tr>
<th>LnM_{x}H_{y+1}X_{4}</th>
<th>Range of x</th>
<th>θ</th>
<th>θ'</th>
<th>Q (kJ/mol)</th>
<th>R ln f_{H} (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErFe_{2}H_{3}</td>
<td>0.5–1</td>
<td>0.975</td>
<td>0.575</td>
<td>−219.1</td>
<td>−19.1</td>
</tr>
<tr>
<td>TmFe_{2}H_{3}</td>
<td>0.5–1</td>
<td>1.0</td>
<td>0.65</td>
<td>−217.0</td>
<td>−29.5</td>
</tr>
<tr>
<td>DyCo_{3}H_{4}</td>
<td>0.25–0.5</td>
<td>0.475</td>
<td>0.25</td>
<td>−215.2</td>
<td>22.3</td>
</tr>
<tr>
<td>ErCo_{3}H_{4}</td>
<td>0.25–0.5</td>
<td>0.475</td>
<td>0.275</td>
<td>−212.8</td>
<td>16.6</td>
</tr>
<tr>
<td>DyCo_{3}H_{4}</td>
<td>0.75–1.1</td>
<td>1.05</td>
<td>0.725</td>
<td>−230.4</td>
<td>−70.2</td>
</tr>
<tr>
<td>ErCo_{3}H_{4}</td>
<td>0.75–1.1</td>
<td>1.05</td>
<td>0.775</td>
<td>−266.5</td>
<td>−174.4</td>
</tr>
</tbody>
</table>

4.2.1 LnFe_{2}H_{3} (Ln=Er, Tm)10,16
A determination of the set of parameters, θ and θ', might be made as depicted in Fig. 6. Figure 6(a) indicates the effect of variation in θ’ on the A vs. x plots. Taking into account the upper composition limit of H in the compound, the value of θ was temporarily fixed at 1.0. From Fig. 6(a), θ’ was decided to be taken as 0.575. Then, the plots shown in Fig. 6(b) were prepared for determination of θ against θ’ = 0.575. Finally, a combination of θ = 0.975 and θ’ = 0.575 was adopted for the analysis of ErFe_{2}H_{3} (0.5 < x < 1) as presented in Table 3. The sets of values of θ and θ’ for the other systems listed in Table 3 were determined in the similar fashion.

4.2.2 LnCo_{3}H_{4} (Ln=Dy, Er)6,10,16

(1) Range of x between 0.25 and 0.506,10,16
This system was analysed using a model in which nM/4 sites are preferentially occupied (θ’ ≈ 0.25). In fact, this ratio correlates well to atom ratio of Ln to LnCo_{3}. Thus, the interstices around Ln was concluded to be preferentially occupied by H atoms in LnCo_{3}H_{4} over x ranging between 0.25 and 0.50.

(2) Range of x between 0.75 and 1.110,16
For the analysis of LnCo_{3}H_{4} over x range between 0.75 and 1.1, θ’ close to 3/4 was chosen implying that preferential site of occupation of H atoms in this composition range was Co rather than Ln.

It is noticed in Table 3 that R ln f_{H} values for LnCo_{3}H_{4} (0.25 < x < 0.5) were positive while those for LnCo_{3}H_{4} (0.75 < x < 1.1) negative suggesting that the sites preferentially occupied by H atoms are different in these different concentration ranges. For LnFe_{2}H_{3} (0.5 < x < 1), R ln f_{H} values were negative (Table 3) and θ’ values chosen were more close to 2/3 rather than 1/3 and thence, in LnFe_{2}H_{3}, as well as in LnCo_{3}H_{4} (0.75 < x < 1.1), the sites preferentially occupied by H atoms were speculated to be M (=Fe or Co) rather than Ln (=Er, Dy or Tm).

4.3 MZ_{x}X_{y} systems11,14,15,29,30
In ternary alloy system MZ_{x}X_{y} composed of one metal constituent M and two interstitial species, Z and X, configuration of interstitial atoms would vary depending on the interaction between Z and X. For example, experimental evidence for hcp ThC_{2}H_{4} showed that x tended to become higher with increasing z and this system was analysed on the basis of trapped H atoms in T-sites around O-site occupied by C atom.11 On the other hand, molten FeZ_{x}P_{y} (Z=B, C) was analyzed using a model with preliminary random occupation of O-sites by Z atoms and the random occupation of the rest of O-sites by P atoms and with negligible Z-P interaction.14

5. Concluding Remark
During the course of analysis of extensive range of non-stoichiometric compounds containing at least one interstitial constituent by statistical thermodynamics under the simplifying a priori assumption of constant E(X−X) within the same phase at any given T,13−34 capability of this line of approach to elucidate atom clustering besides pair-wise interaction intensity became evident. This aspect was reviewed in this manuscript.

As pointed out earlier in the text, calculation is not very demanding for this analysis and thence it might be not very relevant to classify this line of work in the category of computational materials science and engineering research. It only requires iterative calculations using experimentally determined P−T−C relationships towards determination of the θ value fulfilling the a priori assumption of constant E(X−X) over homogeneity range at respective T. But, once the θ value is determined, the rest is straightforward routine calculation. For the works done during eighties, the calculations were made using programmable calculator (TI 58 of Texas Instruments) although the calculations done in nineties were made using PC. Anyway, fast automated calculation by means of PC is definitely favourable to the old-fashioned manual calculation.

As values of the interaction parameters E(X−M) for extensive range of X−M combinations are now became available13−34 together with certain atom clustering information in ternary alloy systems (Tables 2 and 3), prediction of P−T−C relationships for which the experimental data are not available yet might be made on the basis of statistical thermodynamic modeling and, for this, use of PC must be very effective.

It would be also very important to look into compatibility of the statistical thermodynamic analysis results (both the atom clustering information and the pair-wise interaction intensity among constituent atoms) with the results obtained from the first principle calculation such as DV-Xa method46−50 which appeared to be developed to such advanced stage that even optimisation for practical refractory alloy composition might be made.

Besides, there are some aspects left unsolved in the past work in this line. For example,

(1) Whether the 2 M/4 Fe type cluster (Fig. 4(b)) exist in any Fe_{1−x}M_{x}X_{4} compound ?
This type of cluster was never encountered in the analysis of Fe-base alloy systems added with M whose affinity to X is stronger than the affinity between Fe and X till now but there is no reason why this type of clustering should not develop.

(2) What would be the atom clustering in the intermediate range of y between 0.2 and 0.4 for molten Fe_{1−x}Cr_{x}Ni_{y} (Fig. 3) ?
This question relates to the above doubt (1). Cluster of the type 2 Cr/4 Fe would develop in this intermediate transition regime or mixture of clusters, 1 Cr/5 Fe and 4 Cr/2 Fe type, would represent the situation in this regime is the question.

(3) What types of planar extension of 4 Cr/2 Fe clusters (Fig. 5) are developed in the range of y between 0.4 and 0.9 in the molten Fe_{1−x}Cr_{x}Ni_{z} alloy to yield the θ vs. y relationship
as reproduced in Fig. 2?

Towards elucidation of the above doubts, some computer simulation would be of help but it is outside the scope and capacity of the present author and thus some contribution from computational materials scientists is hoped for.

REFERENCES