Note

Stability of Interstitial Elements in Metal Lattice Evaluated by Statistical Thermodynamics

1. Introduction

It is known that statistical thermodynamics is a bridge spanning between microscopic (atomistic) materials parameters (*e.g.*, magnitude of interaction energy E_{i-j} between component atoms, i and j , and mode of atomic clustering in MX_x) and macroscopic (phenomenological) materials behaviors (*e.g.*, equilibrium P-T-C (pressure-temperature-composition) relationship). Nonetheless, probably due to apparent mathematical complexity of formulation, statistical thermodynamics does not seem to be widely employed among materials scientists compared with traditional thermodynamics. However, in actuality, we can reduce statistical thermodynamic formulae to a set of simplifying equations which are readily applicable to analysis of experimental P-T-C data for interstitial solution of X (non-metal) in M (metal), MX_x .¹⁻¹⁹⁾

One of merits of statistical thermodynamic approach is its feasibility to derive E_{X-M} value which is directly referring to $X-M$ bond strength in MX_x with common reference state of energy zero taken at each component atom at rest being in infinite separation in vacuum. Thence, the relative stability of the interstitial elements X in the same metal M might be easily compared.

Comparison of this nature is not feasible by thermodynamic means, since reference states for different interstitial elements are usually not identical. For example, as depicted in Fig. 1, $\Delta H_f(MX_x)$ refers to the difference in energy between the condensed phase MX_x and their reference states, namely 1 mol of pure condensed phase of M and $x/2$ mol of X_2 gas (in case that the stable state of element X is diatomic X_2 gas). Thus, comparison between ΔH_f values for different elements X would not provide any useful information on relative stability of concerned interstitial elements in one metal, while such comparison might be of help to judge the stability of a specific interstitial element X in different metals.

In this report, some distinguishable features of statistical thermodynamic analysis from those of traditional thermodynamics are presented by summarizing integrally the results obtained by now.¹⁻¹⁹⁾

2. Fundamental Statistical Thermodynamic Equations

Statistical thermodynamic equilibrium condition

for interstitial solution MX_x might be summarized into following set of generalized equations¹⁻¹⁹⁾:

$$A \equiv RT \ln \{[(\theta-x)/x] \cdot a_x\} = K - \mu_x^0 + \beta x E_{X-X} \quad \dots\dots\dots(1)$$

$$K = Q - RT \ln f_x \quad \dots\dots\dots(2)$$

$$\partial E / \partial n_x = Q + \beta x E_{X-X} \quad \dots\dots\dots(3)$$

- where, a_x : the activity of the element X
 E : the lattice energy of MX_x
 f_x : the atomic partition function of element X in MX_x
 n_x : the number of component atoms X in MX_x
 Q : the extent of stabilization of X atom through formation of $X-M$ bonds in MX_x with reference to isolated X atom
 R : the universal gas constant
 T : the absolute temperature
 β : a factor determined by crystal structure consideration (*e.g.*, $\beta=12$ for interstitial solution with NaCl type structure)
 θ : the number of interstitial sites available for occupation by X atoms per M atom in MX_x
 μ_x^0 : the standard chemical potential of X with reference state being taken as mono-atomic X at rest in vacuum.

Expressions of the parameters, a_x and μ_x^0 , vary depending on the stable form of the element X as summarized in Table 1.

In this line of analysis, *a priori* assumption of constant E_{X-X} within a phase at a given T was taken and value of θ was chosen to satisfy this assumption. Validity of this assumption appeared to be supported by following features of estimate results^{5,8,9,14)}; values of θ are close to solubility limit of X in MX_x ; Q -values for the element X in the metals in the same group in the periodic table are comparable to one another (*cf.*,

- $E(MX_x)$: The lattice energy of the interstitial solution MX_x
 $D(M)$: The sublimation energy of pure M per mol
 $D(X_2)$: The dissociation energy of X_2 gas per mol
 $\Delta H_f(MX_x)$: The thermodynamic heat of formation of MX_x

Fig. 1. Energetic relations among the states of matters.

Table 1. Expressions of a_X and μ_X^0 for different interstitial elements.

Stable form of X	a_X	μ_X^0	Example	Ref.
Ideal diatomic gas X_2	$\sqrt{p(X_2)}$	$-(1/2D)(X_2) - (1/2)RT \ln \{[(4\pi m_X)^{3/2}(kT)^{5/2}/h^3] \cdot (T/\Theta_r) \cdot [1 + (\Theta_r/3T)] \cdot (\rho^2/2)] + (1/4)R\Theta_v + (1/2)RT \ln [1 - \exp(-\Theta_v/T)]\}$	H_2, N_2, P_2	1)-6), 8)-12), 14), 15), 17)-19)
Ideal monoatomic gas X	$p(X)$	$-RT \ln \{[(2\pi m_X)^{3/2}(kT)^{5/2}/h^3]\}$	S	13)
Pure condensed X	a_X	$-D(X)$	C	7), 11), 16)

$p(X_2), p(X)$: Equilibrium pressure of X_2 gas and that of X gas, respectively,

h : Planck's constant,

k : Boltzmann's constant,

m_X : Mass of X atom,

Θ_r : Characteristic temperature of rotation of X_2 molecule,

Θ_v : Characteristic temperature of vibration of X_2 molecule,

ρ : Nuclear spin weight of X atom

Fig. 2. Graphic presentation of Q -values for primary H-solutions in II~V-group metals estimated by statistical thermodynamics.

Fig. 2).

3. Analysis Results for FeX_x ($X=H, C, N, P, S$)

The results obtained from the analyses along this line for several interstitial solutions FeX_x might be summarized as shown in Fig. 3 (see also Table 1 in Ref. 16)).

This figure appears to indicate clearly that the stability of the interstitial elements in Fe-lattice increases as the following order:

$$H < S < P < N < C \quad \dots\dots\dots(4)$$

Or, more specifically, it might be argued as follows:

- (A) When compared for interstitial elements of 4th to 6th groups in the periodic table, there appears to be a trend that stability of the element in Fe-lattice decreases as group number increased.
- (B) Through comparison for N and P, it might be said that stability of the element in Fe-lattice tends to decrease as periodic number increased within the group.

It is accepted that the atomic radii of these interstitial elements increases as the following order:

$$H < N < C < P < S \quad \dots\dots\dots(5)$$

Provided that the elastic strain energy term is the decisive factor for the stability of these elements in Fe-lattice, H must be the most stable and S the least stable. However, as shown in Eq. (4), statistical thermodynamic evaluation suggests that C is the most stable in Fe-lattice and H the least stable. Therefore, it is evident that the decisive factor for the stability of these interstitial elements in Fe-lattice must

Fig. 3. Graphical presentation of Q -values for miscellaneous interstitial elements in Fe-lattice.^{11-13,16,18)}

be the nature of electronic (chemical) interaction between X atom and Fe atom in FeX_x rather than the elastic strain energy term.

When comparison is made among the Q -values for different FeN_x phases, following features might be pointed out:

- (C) N atom in fcc γ - FeN_x phase appears to be the most stable (Note that H in α - FeH_x seems to be more stable than H in γ - FeH_x).
- (D) N atom in high temperature bcc phase (δ -phase) is less stable than that in low temperature bcc phase (α -phase).
- (E) Stability of N atom in molten FeN_x is higher than that in bcc phases but lower than that in fcc phase (Note that C in molten FeC_x seems to be more stable than C in γ - FeC_x).

These features do not appear to be incompatible with available experimental solubility data (*e.g.*, Table 1 and Fig. 2 in Ref. 20) for N-solubility: Fig. 1 and Table 2 in Ref. 21) for H-solubility).

During the course of analysis of α - FeC_x ,¹⁶⁾ it was noticed that Q -value might be affected to an appreciable extent by the magnetic transition occurring at around Curie temperature ($T_C \sim 1000$ K); *i.e.*, $Q_C^a(T < 1000$ K) = -648 kJ/mol and $Q_C^a(1025$ K $< T < 1150$ K) = -613 kJ/mol. The observed trend of more negative Q_C^a at T lower than T_C than that at T higher than T_C appears to be in qualitative accord with earlier available analysis result (*e.g.*, Ref. 22)). However, no such effect was discernible for α - FeH_x and for α - FeN_x . Thus, further detailed examinations are desired to clarify this point.

4. Analysis of Ternary MZ_zX_x Phase with Two Interstitial Constituents

In the earlier works, P solubility in ternary molten FeZ_zP_x ($Z=B, C$)¹²⁾ and S solubility in molten FeZ_zS_x ($Z=C, P$)¹³⁾ were briefly discussed. In these studies, it was concluded that θ available for occupation of X atoms in FeZ_zX_x ($X=P, S$) might be expressed as follows:

$$\theta(FeZ_zX_x) = \theta(FeX_x) - sz \quad \dots\dots\dots(6)$$

where, s : a constant determined for combinations of elements, X and Z (e.g., $s=0.4$ for $Z=B$ and $s=1.25$ for $Z=C$ in molten FeZ_zP_x ¹²⁾ and $s=4$ for $Z=C$ and $s=2.75$ for $Z=P$ in molten FeZ_zS_x ¹³⁾).

Eq. (6) suggests that solubility limit θ of element X in molten FeZ_zX_x tends to decrease from that in FeX_x , $\theta(FeX_x)$, as z increased. Validity of Eq. (6) was also appreciated as the evidence of negligible E_{X-Z} in these molten FeZ_zX_x phases discussed there.^{12,13)}

With reference to the stability hierarchy of interstitial elements in Fe-lattice given as Eq. (4), it might be noticed that it is essential to take more stable interstitial element in Fe-lattice as Z and less stable one as X in deriving relation like Eq. (6). For example, in analyzing FeC_zP_x , it would be realistic to consider FeC_zP_x as the solution of P in FeC_z possessing a fixed composition z , as was done in Ref. 12). However, it would not be practical, on the contrary, to consider FeC_zP_x as the solution of C in FeP_x possessing a fixed composition x , since the stability of C in Fe-lattice is higher than that of P and, hence, by forced addition of C to FeP_x to form FeC_zP_x , P might be expelled from Fe-lattice and the composition x might be shifted easily from its initial value.

Stability hierarchy of interstitial elements as given by Eq. (4) might be of pragmatic use for planning purification processes of metals.

As such, statistical thermodynamics appears to be a useful analysis tool for ternary MZ_zX_x with two interstitial components as well as for binary MX_x , leading to unambiguous definition for solubility limit through parameter θ and for stability of interstitial element through parameter Q calculated on the basis of chosen θ -value.

Re-constructed $\log p(P_2)$ vs. x relations for FeC_zP_x ¹²⁾ and re-constructed $\log [p(H_2S)/p(H_2)]$ vs. x relations for FeC_zS_x ¹³⁾ on the basis of estimated statistical thermodynamic parameters appeared to reproduce experimental P-T-C relations reasonably well.

5. Concluding Remark

Feasibility of direct comparison of relative stability among different interstitial elements in a metal lattice in terms of parameter Q is one of attractive merits of statistical thermodynamics. Direct comparison of this nature is not feasible with thermodynamic parameters,

while thermodynamics is a useful tool for comparing relative stability of certain interstitial element among several metal lattices and for analyzing substitutional solutions and stoichiometric compounds.

When ternary phase MZ_zX_x with two interstitial constituents, X and Z , is under consideration and Z is known to be more stable than X in M -lattice, it appears to be rational to consider MZ_zX_x as the solution of X in MZ_z rather than the other way round.

In spite of the term *statistical*, discussion on the basis of statistical thermodynamics proved to be useful for clarifying ordering phenomena of interstitial elements in MX_x .^{17,23)} In addition, careful analysis of variation of statistical thermodynamic parameter for $Fe_{1-y}M_yN_x$ with respect to y ^{15,18,19)} led straightforwardly to the model with definite clustering of metal atoms $Fe_{6-n}M_n$ ($n=1$ or 4 for $M=V, Cr$ depending on y ^{15,18)} and $n=4$ for $M=Ti$ ¹⁹⁾) surrounding an N atom on O-site. Such aspect of atomic clustering in alloys cannot be derived easily with traditional thermodynamic approach.

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