Miedema Calculator: A thermodynamic platform for predicting formation enthalpies of alloys within framework of Miedema's Theory

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ARTICLE INFO

ABSTRACT

The theoretical background and implementation of "Miedema Calculator", a thermodynamic platform for predicting formation enthalpies of various alloys within framework of Miedema's theory, is summarized and presented. Several user-friendly interfaces are designed for the following major functional modules, i.e. the formation enthalpies of binary intermetallic compounds based on the original Miedema's model and two more improved ones, the chemical, elastic and structural enthalpies of solid solutions, the formation enthalpies of amorphous alloys, the volume corrections upon alloying, and the formation enthalpies of ternary alloys based on various geometrical models. Various models and methods have been justified and implemented into the platform together with the unified model parameters and properties for each element as a basic database. A set of critical tests and evaluations have been performed on each module, providing its efficiency and validation for a fast screening of thermodynamic properties of various alloys.

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1. Introduction

The launching of "Materials Genome Initiative" strategic plan requires a fast and high-efficient discovery strategy in exploring new materials or novel properties of a known material, which strongly depends on the establishment of an accurate thermodynamic and kinetic database of materials [1–3], *e.g.* enthalpies in alloys, and is of vital importance to develop theories to provide physical insight into basic issues related to the thermodynamics and kinetics of various equilibrium and nonequilibrium alloy phases [4,5].

During the 1970s and 1980s, Miedema and his colleagues developed a semi-empirical theory that could predict formation enthalpies and other basic properties of various alloys [5–9]. It is based on a "macroscopic atom" model assuming that all atoms are regarded as a basic elemental block in their metallic states. The essence of the model lies in estimating quantitatively the enthalpy (energy) effects when bringing dissimilar elements into contact, which will change the electron density at the so-called Wigner–Seitz cell boundary, and would tend to shift their electron densities due to an electronegativity difference. Elimination of the discontinuities of electron densities requires inversely the extra energy which can be quantified by the electron density difference. Within macroscopic atom model, Miedema et al. provide an easy and physically sound idea to predict the mixing properties of various alloys including intermetallic compounds, solid solutions, amorphous alloy, *etc.* To be noted that CALPHAD (CALculation of PHAse Diagrams) method has been widely used to predict phase diagrams and thermodynamic properties based on the optimization and extrapolation of various experimental phase equilibrium data and/or thermodynamic properties. In the absence of experimental data however, Miedema's theory provides a unique supplement to CALPHAD method. We may refer to a comprehensive textbook [10] for more details of CALPHAD method.

In the meanwhile, extensive experimental studies have been performed to obtain the reliable thermodynamic properties of binary as well as ternary alloy systems. For instance, in the past decades, Kleppa et al. and Meschel et al. [11–22] measured hundreds of standard formation enthalpies of binary intermetallic compounds with the measuring error of around ± 5 kJ/mol. By comparing the experimental values with the calculated ones from original Miedema's model, it was found interestingly that over 90% of the calculated values are lower or more negative than the experimentally determined ones [23–25]. Such systematical deviation has brought a lot of interest and attention in materials community, and accordingly some modification schemes to Miedema's model have been proposed to improve its predictability. Among

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these studies, the atomic size difference (ASD) factor initiated by Zhang et al. [24,25] is generally believed to play an important role in improving the prediction precision, yet was not considered in the original Miedema's model. The introduction of ASD factor is based on the fact that a large deviation always appears in the binary systems featuring with large atomic size difference [24,25]. To account for it, a composition dependent ASD factor was firstly proposed [24], and consequently the systematic deviation could be significantly decreased. More recently, a parameterization scheme combined with comprehensive data mining has been used for deriving a composition independent ASD factor in order to solve such statistical deviation [26]. With the application of this new factor, one can achieve a high level of correlation with respect to available experimental data.

With the success of Miedema's model for binary alloys, a number of its extensions for multi-component alloy systems have also been proposed [27–32]. In general, the thermodynamic properties of multi-component alloys are estimated from those constituent binary ones, which generate both symmetric and asymmetric geometric models [33–41]. The typical symmetric models include the Kohler's model [34], Colinet's model [36] and Muggianu's model [37], whereas the Bonnier's model [33], Toop's model [35] and Hillert's model [39] belong to asymmetrical ones. It is clearly found that the symmetric models do not consider the effect of property difference of the three constituents, whereas the asymmetrical models do, yet the choice of asymmetric constituent is generally based on experience. To remedy this arbitrary characteristic, a general geometric model was proposed accordingly by Chou et al. [42–44], and later was simplified by Ouyang et al. [45,46] by replacing the integration computation required in Chou's model by the difference of dilute solution enthalpy of two constituents. To be noted that the thermodynamic properties can also be predicted via first principles or ab initio calculations in a higher precise, however, an empirical method may cost much less computational resources and provide a supplement in certain cases such as for statistical solid solutions and amorphous alloys that are much challenging for modern first principles calculations.

In this paper, we shall summarize the theoretical background of various models and methods and present the implementation of a simple thermodynamic platform for the formation enthalpy prediction of various alloys within the framework of Miedema's theory. Its major functional modules include the formation enthalpies of binary compounds, the chemical, elastic and structural enthalpies of statistical solid solutions, the formation enthalpies of amorphous alloys, the volume corrections in alloying, and the formation enthalpies of ternary alloys based on various geometrical models. In general, a consistent result is obtained through the present platform after lots of critical tests and evaluations. The paper is organized as follows: the detailed descriptions of various theoretical models and methods are outlined in Section 2, and then the algorithm for implementations are depicted in Section 3, various critical tests and evaluations are provided in Section 4 via comprehensive comparisons. A brief summary is finally given in Section 5.

2. Overview on theoretical models and methods

2.1. A general formulation of Miedema's theory

According to the Miedema's theory [5–8], the enthalpy (energy) effect takes place at the A–B interface when A and B forms an alloy, which can be evaluated by three critical parameters, i.e. the electronegativity difference $\Delta\phi$, which is defined as $\phi_A - \phi_B$, the electron-density discontinuity $\Delta n_{WS}^{1/3}$, which is defined as

$(n_{WS}^A)^{1/3} - (n_{WS}^B)^{1/3}$, and additional hybridization contribution parameter R for a combination of transition and non-transition metals. The electronegativity difference $\Delta\phi$ between two constituent metals is responsible for a negative contribution to the formation enthalpy, which can be expressed by the quadratic difference of work function of two constituent metals. The discontinuity of the electron density at the boundaries of the dissimilar Wigner–Seitz (WS) cells is defined as $\Delta n_{WS}^{1/3}$, which provides a positive contribution to the formation enthalpy. When alloying transition metals with non-transition metals, an additional term R is added owing to the filling of Brillouin zones of particular crystal structure. Accordingly, the interfacial enthalpy for solving one mole of metal A in an excess of metal B is expressed as [5,6]

$$\Delta\overline{H}_{A\ in\ B}^{inter} = V_A^{2/3} \Gamma_{AB}$$
$$= \frac{V_A^{2/3}}{(n_{WS}^{-1/3})_{av}} \left\{ -P(\Delta\phi)^2 + Q(\Delta n_{WS}^{1/3})^2 - R \right\}, \quad (1)$$

where $\Gamma_{AB} = \left\{ -P(\Delta\phi)^2 + Q(\Delta n_{WS}^{1/3})^2 - R \right\} / (n_{WS}^{-1/3})_{av}$ is a composition independent amplitude concerning the magnitude of the intrinsic chemical interaction for a binary alloy system. The $(n_{WS}^{-1/3})_{av} = \frac{1}{2}\left(\frac{1}{(n_{WS}^A)^{1/3} + (n_{WS}^B)^{1/3}} \right)$, and P, Q, and R are empirical constants. The ratio of Q/P is determined as $Q/P = 9.4\ eV^2/$(density units)$^{2/3}$, and three values for P were determined from available experimental thermodynamic data. In numerical calculation of formation enthalpy, P is adopted as $P = 14.2$, 10.7 and 12.35 for alloys of two transition metals, two non-transition metals and a transition metal with a non-transition metal, respectively [5,6]. In Ref. [7], the three P values are provided as $P = 14.1$, 10.6 and 12.3, respectively. As regards the determination of R, if the alloy consists of two transition metals or of two non-transition metals, $R = 0$, whereas if the alloy is consisted of one transition metal and non-transition metals, R can be obtained by multiplying two values, one (e.g. R_A) from the block of transition metals and the other (e.g. R_B) from the block of non-transition metals. Table 1 lists the classification of transition metal block and non-transition metal block for the choice of R_A or R_B for each element located at two different blocks [5,6]. Notice that as far as the value of P is concerned, alkaline-earth metals (Ca, Sr, Ba) are treated as non-transition metals [7].

In the calculation by Eq. (1), $V_A^{2/3}$ is supposed as the corrected volume of metal A in the alloy, and its value can be estimated by a simple approximate relationship suggested by Miedema et al. [5–7],

$$(V_A^{2/3})_{alloy} = (V_A^{2/3})_{pure} [1 + a f_B^A (\phi_A - \phi_B)] \quad (2)$$

where the constant a is experimentally determined as $a = 0.14$ for the alkaline metals, $a = 0.10$ for divalent metals, $a = 0.07$ for noble and trivalent metals, $a = 0.04$ for all other metals including divalent metals Ca, Sr and Ba [5–7]. Assuming the atomic concentrations c_A and c_B and molar volumes V_A and V_B for A–B alloy, the surface concentrations c_A^S and c_B^S are defined by $c_A^S = c_A V_A^{2/3}/(c_A V_A^{2/3} + c_B V_B^{2/3})$ and $c_B^S = c_B V_B^{2/3}/(c_A V_A^{2/3} + c_B V_B^{2/3})$, and accordingly $f_B^A = c_B^S \left[1 + \gamma \left(c_A^S c_B^S \right)^2 \right]$. In an infinite dilution, $f_B^A = 1$ for the calculation of the atomic volume of metal A solving in an excess of metal B [5–7,47], i.e. a composition independent volume correction by Eq. (2). In non-dilute solutions, $\gamma = 0$ [5,48] (or $\gamma = 4$ [49]) is used for a statistical solid solution without (or with) assumption of the existence of chemical short-range order (CSRO), $\gamma = 8$ for an intermetallic compound [5], and $\gamma = 0$ [5] (or $\gamma = 5$ [48], or $\gamma = 4$ [49]) for an amorphous alloy.

To provide a unified result, Table 2 provides the basic model parameters (ϕ, n_{WS} and V) [5,6] of each element in their metallic state as used in Miedema Calculator.

Table 1
Classification of transition metals and non-transition metals to define the values of R_i ($i =$ A or B) for the calculation of R/P of binary A–B systems [5].

Transition metal										Non-transition metal				
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Ca	Li	Be	B	C	N
0.7	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.3	0.4	0	0.4	1.9	2.1	2.3
Y	Zr	Nb	Mo	Tc	Ru	Ph	Pd	Ag	Sr	Na	Mg	Al	Si	P
0.7	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.15	0.4	0	0.4	1.9	2.1	2.3
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Ba	K	Zn	Ga	Ge	As
0.7	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.3	0.4	0	1.4	1.9	2.1	2.3
Th	U	Pu								Rb	Cd	In	Sn	Sb
0.7	1.0	1.0								0	1.4	1.9	2.1	2.3
										Cs	Hg	Ti	Pb	Bi
										0	1.4	1.9	2.1	2.3

Note that the value of parameter R (or in fact R/P in units V^2) for alloys of transition metals with polyvalent non-transition metals is obtained by multiplying two numbers for solid phase: one from the block of transition metals and the other from the block of non-transition metals. As far as the value of P is concerned, alkaline-earth metals (Ca, Sr, Ba) are non-transition metals [7].

2.2. Standard formation enthalpy of intermetallic compounds

The formation enthalpy of an intermetallic compound can be expressed by [5,6]

$$\Delta H_{AB}^{Mied} = c_A f_B^A \Delta \overline{H}_{A \, in \, B}^{inter} = c_A f_B^A V_A^{2/3} \, \Gamma_{AB}$$
$$= c_A^S c_B^S [1 + 8(c_A^S c_B^S)^2](c_A V_A^{2/3} + c_B V_B^{2/3}) \, \Gamma_{AB}, \quad (3)$$

where $f_B^A = c_B^S \left[1 + 8 \left(c_A^S c_B^S\right)^2\right]$, and the volume correction is done by Eq. (2).

In order to account for the statistical deviation of original Miedema's model from experiments, the ASD factor Sc was introduced because it would frequently lower the contact area between the two dissimilar WS cells and decrease the binding energy between the two dissimilar atoms, by the way of decreasing the package density of the crystalline lattice [24–26]. Accordingly, an improved version to Eq. (3) can be expressed in a general form [24–26]

$$\Delta H_{AB}^{form} = S_C \, \Delta H_{AB}^{Mied}. \quad (4)$$

When $S_C = 1$, the model becomes original Miedema's model. In the original improvement, the composition dependent ASD factor is given by $S_C = 1 - \frac{c_B^S \left| V_A^{2/3} - V_B^{2/3} \right|}{\left(c_A^S V_A^{2/3} + c_B^S V_B^{2/3}\right)^2}$ which depends on the choice of solute metal. To distinguish the solute and solvent elements in calculation, one may get two values of S_C by exchanging metal A and B and then take the larger one. More recently, another composition independent ASD factor is proposed as $S_C = \frac{\alpha \, V_A^{2/3} \, V_B^{2/3}}{\left(V_A^{2/3} + V_B^{2/3}\right)^2}$, in which α is an empirical parameter that is determined by a statistical data-driven regression for the intermetallic compounds consisting of transition, lanthanides and actinides metals which gives a value 3.2598 when $P = 14.2$ [26].

When a non-transition metal is a semiconductor in its reference state, an introduction of a positive transformation enthalpy ΔH^{trans} is used to account for the structural stability by transforming the semiconductor into a hypothetical metallic state [5]. The elements include H(100 kJ/mol), B(30 kJ/mol), C(180 kJ/mol), N(310 kJ/mol),

Si(34 kJ/mol), Ge(25 kJ/mol), and P(17 kJ/mol) [5], while ΔH^{trans} of the other elements are zero. So the total transformation enthalpy is calculated by

$$\Delta H_{AB}^{trans} = c_A \Delta H_A^{trans} + c_B \Delta H_B^{trans}. \quad (5)$$

And accordingly the total formation enthalpy of a binary compound is expressed as

$$\Delta H_{AB}^{form} = S_C \, \Delta H_{AB}^{Mied} + \Delta H_{AB}^{trans}. \quad (6)$$

2.3. Formation enthalpy of statistical solid solution

The concentrated statistical solid solution (SS) is an alloy when one component is randomly solved in the crystal structure of the other component, and its formation enthalpy can be calculated from [5,6]

$$\Delta H_{SS}^{form} = \Delta H_{SS}^{chem} + \Delta H_{SS}^{elast} + \Delta H_{SS}^{struct}. \quad (7)$$

The first term on the right side of Eq. (7) represents the chemical contribution which can be simply derived as [5,6]

$$\Delta H_{SS}^{chem} = c_A c_B (c_B^S \Delta \overline{H}_{A \, in \, B}^{inter} + c_A^S \Delta \overline{H}_{B \, in \, A}^{inter})$$
$$= c_A c_B \left(c_B^S V_A^{2/3} + c_A^S V_B^{2/3}\right) \, \Gamma_{AB}. \quad (8a)$$

In this equation, the volume correction is done by $(V_A^{2/3})_{alloy} = (V_A^{2/3})_{pure} [1 + a c_B^S(\phi_A - \phi_B)]$ i.e. $f_B^A = c_B^S$ in Eq. (2), and the chemical part can also be expressed by [48,49]

$$\Delta H_{SS}^{chem} = c_A f_B^A V_A^{2/3} \, \Gamma_{AB} = c_A^S c_B^S (c_A V_A^{2/3} + c_B V_B^{2/3}) \, \Gamma_{AB}. \quad (8b)$$

To admit the existence of CSRO in the statistical solid solution, Alonso et al. proposed to use $f_B^A = c_B^S \left[1 + \gamma \left(c_A^S c_B^S\right)^2\right]$ with $\gamma = 4$ [49] too.

The second term on the right side of Eq. (7) represents the elastic mismatch energy which arises from the different size between solute and solvent atoms. The corresponding elastic energy is estimated using the classical elasticity method by Eshelby and Friedel [50,51]. When a sphere of metal A with volume W_A is solved

Table 2
The values of the model parameters ϕ, n_{WS} and V [5,6].

Legend: each element cell lists the symbol, then ϕ (in volt), n_{WS} (in density units), V (in cm³).

Element	ϕ	n_{WS}	V
H	5.20	3.38	1.70
Li	2.85	0.94	13.00
Be	5.05	4.66	4.90
Na	2.70	0.55	23.78
Mg	3.45	1.60	14.00
Be	5.05	4.66	4.90
B	5.30	5.36	4.70
C	6.24	5.55	3.26
N	6.86	4.49	4.10
Mg	3.45	1.60	14.00
Al	4.20	2.70	10.00
Si	4.70	3.38	8.60
P	5.55	4.49	8.60
K	2.25	0.27	45.63
Ca	2.55	0.75	26.20
Sc	3.25	2.05	15.03
Ti	3.80	3.51	10.58
V	4.25	4.41	8.36
Cr	4.65	5.18	7.23
Mn	4.45	4.17	7.35
Fe	4.93	5.55	7.09
Co	5.10	5.36	6.70
Ni	5.20	5.36	6.60
Cu	4.45	3.18	7.12
Zn	4.10	2.30	9.17
Ga	4.10	2.25	11.82
Ge	4.55	2.57	9.87
As	4.80	3.00	11.85
Rb	2.10	0.22	56.07
Sr	2.40	0.59	33.93
Y	3.20	1.77	19.90
Zr	3.45	2.80	14.00
Nb	4.05	4.41	10.80
Mo	4.65	5.55	9.40
Tc	5.30	5.93	8.64
Ru	5.40	6.13	8.20
Rh	5.40	5.45	8.30
Pd	5.45	4.66	8.90
Ag	4.35	2.52	10.25
Cd	4.05	1.91	13.00
In	3.90	1.60	15.75
Sn	4.15	1.90	16.30
Sb	4.40	2.00	16.95
Cs	1.95	0.17	69.23
Ba	2.32	0.53	38.10
La	3.17	1.64	22.55
Hf	3.60	3.05	13.45
Ta	4.05	4.33	10.81
W	4.80	5.93	9.55
Re	5.20	6.33	8.85
Os	5.40	6.33	8.45
Ir	5.55	6.13	8.52
Pt	5.65	5.64	9.10
Au	5.15	3.87	10.20
Hg	4.20	1.91	14.08
Tl	3.90	1.40	17.23
Pb	4.10	1.52	18.28
Bi	4.15	1.56	19.32
Ce^{3+}	3.18	1.69	21.62
Pr	3.19	1.73	20.79
Nd	3.19	1.73	20.58
Pm	3.19	1.77	20.25
Sm	3.20	1.77	20.01
Eu^{3+}	3.20	1.77	19.97
Gd	3.20	1.77	19.90
Tb	3.21	1.82	19.32
Dy	3.21	1.82	19.00
Ho	3.22	1.82	18.76
Er	3.22	1.86	18.45
Tm	3.22	1.86	18.12
Yb^{3+}	3.22	1.86	17.97
Lu	3.22	1.91	17.77
Th	3.30	2.10	19.80
Pa			
U	3.90	3.44	13.15
Np			
Pu	3.80	2.99	12.06

in spherical site of metal B, the elastic energy can be expressed by bulk modulus K_A of solute A and the shear modulus G_B of the matrix B as

$$E^{elastic} = \frac{K_A \left(\Delta W_A \right)^2}{2 W_A} + \frac{2 G_B \left(\Delta W_B \right)^2}{3 W_B}, \tag{9}$$

where ΔW_A and ΔW_B are the volume changes of solute A and matrix B due to the internal stress. The pressure needs to be balanced such that it changes continuously across the interface between solute and matrix, leading to an expression for the elastic mismatch energy per mole of solute metal [5,6],

$$\Delta \overline{H}_{A\ in\ B}^{elast} = \frac{2 K_A G_B \left(W_A - W_B \right)^2}{3 K_A W_B + 4 G_B W_A}. \tag{10a}$$

Because the volume of the constituent atoms changes upon alloying, W_A will differ from $(V_A^{2/3})_{pure}$. The volume change for each component can be estimated by $W_A = V_A + \alpha \left(\phi_A - \phi_B \right) / n_{WS}^A$ and $W_B = V_B + \alpha \left(\phi_A - \phi_B \right) / n_{WS}^B$, in which $\alpha = 3 (V_A^{2/3})_{alloy} / 4 (n_{WS}^{-1/3})_{av}$. To be noted that Alonso et al. [47,49] adopted another simplified version of elastic mismatch energy by Eshelby [50,51],

$$\Delta \overline{H}_{A\ in\ B}^{elast} = \frac{2 K_A G_B \left(W_A - W_B \right)^2}{3 K_A W_B + 4 G_B W_B}. \tag{10b}$$

With Eq. (10) as input, the elastic mismatch part can be expressed as [5,6]

$$\Delta H_{SS}^{elast} = c_A\, c_B \left(c_B\, \Delta \overline{H}_{A\ in\ B}^{elast} + c_A\, \Delta \overline{H}_{B\ in\ A}^{elast} \right). \tag{11}$$

The third term on the right side of Eq. (7) represents the variation of lattice stability of the solid solution with atomic concentration. Assuming $E^{\sigma}(z)$ is the lattice stability of each crystal structure σ (= fcc, hcp or bcc), the structural part can be expressed as [47,52,53]

$$\Delta H_{SS}^{struct} = E^{\sigma}(\langle z \rangle) - E^{ref}(\langle z \rangle)$$
$$= E^{\sigma}(\langle z \rangle) - c_A E_A^{\sigma}(z_A) - c_B E_B^{\sigma}(z_B) \tag{12}$$

where $\langle z \rangle = c_A z_A + c_B z_B$, and the value $E^{\sigma}(\langle z \rangle)$ of the solution takes the most negative of the three energies $E_{hcp}^{\sigma}(\langle z \rangle)$, $E_{fcc}^{\sigma}(\langle z \rangle)$ and $E_{bcc}^{\sigma}(\langle z \rangle)$ as a function of the number of valence electrons [47,52,53]. The reference energy is a linear interpolation between the lattice stabilities of the two relevant metals in their equilibrium state, i.e. $E_A^{\sigma}(z_A)$ and $E_B^{\sigma}(z_B)$. In dilute solution, the structural contribution to the enthalpy in solving metal A in B (with crystal structure σ) is expressed by [47,52,53]

$$\Delta H_{A\ in\ B}^{struct} = E_B^{\sigma}(z_B) - E_A^{\sigma}(z_A) + (z_A - z_B) \left. \frac{dE^{\sigma}(z)}{dz} \right|_{z=z_B} \tag{13}$$

where the first two items come from the difference of structural energies of the two pure metals in their respective structures. The last one is the change of structural stability of the matrix B due to the change of average valence number by introducing solute A.

2.4. Formation enthalpies of amorphous alloys

The formation enthalpy of an amorphous alloy (AM) is generally higher than that of the intermetallic compound with the same composition. In contrast to the statistical solid solution there is no elastic mismatch item and structural item, and the total formation enthalpy is expressed as [5,6]

$$\Delta H_{AM}^{form} = \Delta H_{AM}^{chem} + \Delta H_{AM}^{topo}. \tag{14}$$

As a first approximation, Bakker assumes the chemical term of the amorphous state and of the statistical solid solution to be equal [5,6],

$$\Delta H_{AM}^{chem} = c_A c_B (c_B^S \Delta \overline{H}_{A\ in\ B}^{inter} + c_A^S \Delta \overline{H}_{B\ in\ A}^{inter})$$
$$= c_A c_B (c_B^S V_A^{2/3} + c_A^S V_B^{2/3}) \Gamma_{AB}. \qquad (15a)$$

In calculation of volume correction by Eq. (2), Bakker and Miedema et al. [5,6] suggests f_B^A to be equal to that in statistical solid solution as $f_B^A = c_B^S$, i.e. $(V_A^{2/3})_{alloy} = (V_A^{2/3})_{pure} [1 + a\, c_B^S(\phi_A - \phi_B)]$, while Weeber and Alonso et al. [48,49] proposed another equation for $f_B^A = c_B^S[1 + \gamma\ (c_A^S c_B^S)^2]$ to reflect the existence of CSRO with $\gamma = 5$ [48] or $\gamma = 4$ [49] for an amorphous alloy, and the chemical part can then be expressed by [48,49]

$$\Delta H_{AM}^{chem} = c_A^S c_B^S [1 + \gamma(c_A^S c_B^S)^2](c_A V_A^{2/3} + c_B V_B^{2/3}) \Gamma_{AB}. \qquad (15b)$$

The topological enthalpy accounts for the difference between the crystalline state and the amorphous state, which can be quantified by the heat of fusion with a magnitude of about $R\overline{T}_m$, where the gas constant $R = 8.3$ J/mol K and $\overline{T}_m$ is the average of the melting temperatures of two metals. The topological contribution can be estimated by [5,6]

$$\Delta H_{AM}^{topo} = \lambda\ (c_A T_{m,A} + c_B T_{m,B}) \qquad (16a)$$

where an average value of the constant $\lambda = 3.5$ is adopted. Similarly, Alonso et al. adopted the approximation based on the average heat of fusion of each component metal (H^{fus}) as [27,54]

$$\Delta H_{AM}^{topo} = c_A H_A^{fus} + c_B H_B^{fus}. \qquad (16b)$$

2.5. Volume corrections during alloying

Upon alloying, the volume of A atom will increase whereas the volume of B atom will decrease assuming that $\phi_A > \phi_B$ since the charge will transfer from B to A atom. In binary A–B alloy system, the change of volume per mole A on forming the $A_x B_{1-x}$ alloy can be expressed as [5]

$$\Delta V_{A_x B_{1-x}} = f_B^A \Delta \overline{V}_{A\ in\ B} \qquad (17)$$

where $\Delta \overline{V}_{A\ in\ B}$ is the volume effect per mole A if solute A is solved in an infinite B solution, and is given by [5]

$$\Delta \overline{V}_{A\ in\ B} = P_V V_A^{2/3} [\phi_A - \phi_B]\ \left(\frac{1}{n_{WS}^A} - \frac{1}{n_{WS}^B} \right) \Big/ (n_{WS}^{-1/3})_{av} \qquad (18)$$

where the empirical constant $P_V = 0.75$ is derived from experimentally observations. Upon reversal of A and B, the value of $\Delta \overline{V}_{A\ in\ B}$ is different from that of $\Delta \overline{V}_{B\ in\ A}$ since volume effect is proportional to $V^{2/3}$ of the solute metal. Assuming that $\alpha = 1.5\, V_A^{2/3}/(n_{WS}^{-1/3})_{av}$, the volume change of solute A when it is solved in an infinite B, is expressed by [6]

$$\Delta V_{A\ in\ B}^A (1\ mol\ A) = \alpha \frac{\phi_A - \phi_B}{n_{WS}^A}. \qquad (19)$$

Meanwhile the volume change of B by the electron transfer from B to A is expressed by [6]

$$\Delta V_{A\ in\ B}^B (1\ mol\ A) = -\alpha \frac{\phi_A - \phi_B}{n_{WS}^B}. \qquad (20)$$

In a non-dilute alloy, the charge will transfer in so far solute A are in contact with dissimilar B, so that the total volume change is expressed by [6]

$$\Delta V_{A\ in\ B}^{alloy} = f_B^A \alpha\ (\phi_A - \phi_B) \left(\frac{1}{n_{WS}^A} - \frac{1}{n_{WS}^B} \right) \qquad (21)$$

where $f_B^A = c_B^S$ is used for statistical solid solution, $f_B^A = c_B^S [1 + 8\ (c_A^S c_B^S)^2]$ for an intermetallic compound, and $f_B^A = c_B^S [1 + 5\ (c_A^S c_B^S)^2]$ [48,49] (or $f_B^A = c_B^S$ [5,6]) for an amorphous alloy, respectively.

Note that to make a self-consistent calculation for volume correction as suggested by Miedema et al. [9], one need first apply an estimated volume correction (e.g. by Eq. (2)), then derive c_A^S with the corrected volumes for $V_A^{2/3}$ and $V_B^{2/3}$ in between initial and final states, the final volume corrections is afterwards calculated [5].

2.6. Formation enthalpy of ternary alloy

Predicting thermodynamic property for a ternary alloy system from binary ones is one simplified way with high-efficiency. In the past decades, the core development of the geometrical methods can be related to such estimation. According to the method of selecting the binary composition, Hillert [39] has classified the related models into two categories: symmetrical and asymmetrical ones. For a complete summary, one may refer to the publications by Chou et al. [42,43,55], in which the thermodynamic properties of a ternary system are expressed as a combination of all binaries with an assigned probability as follows [42–44,55]:

$$\Delta G_{123}^E = W_{12}\Delta G_{12}^E + W_{23}\Delta G_{23}^E + W_{31}\Delta G_{31}^E \qquad (22a)$$

$$\text{or } \Delta H_{123} = W_{12}\Delta H_{12} + W_{23}\Delta H_{23} + W_{31}\Delta H_{31}, \qquad (22b)$$

where ΔG_{ijk}^E (ΔH_{ijk}) and ΔG_{ij}^E (ΔH_{ij}) represent the ternary and binary excess Gibbs free energies (enthalpies) of mixing, respectively, and W_{ij} is the weight probability for the binary ones, which can be calculated in terms of $W_{ij} = c_i c_j / X_i X_j$. If c_i and c_j are the ternary compositions, the capital X_i and X_j represent the compositions of the selected binary ones, i.e. $X_i = \frac{1+c_i-c_j}{2} - \delta_{ij}$ in which the term δ_{ij} can range from $\delta_{ij} = 1/2(c_i - c_j - 1)$ to $\delta_{ij} = 1/2(1 + c_i - c_j)$ and therefore there is infinite number of models accordingly [44,55].

In the present Miedema Calculator, several geometrical models are included, i.e., the Miedema's model [5], Toop's model [35], Bonnier's model [33], Hillert's model [39], Kohler's model [34], Muggianu's model [37], Colinet's model [36], Chou's model [42–44], and Ouyang's model [45,46]. Assuming a ternary ABC compound with a fraction c_A for component A, c_B for component B, c_C for component C, with $c_A + c_B + c_C = 1$, the formation enthalpy is expressed by

(1) Miedema's model [5]:

$$\Delta H_{ABC} = c_A f_B^A \Delta H_{AB}^{inter} \left(\frac{c_A}{c_A + c_B}, \frac{c_B}{c_A + c_B} \right)$$
$$+ c_A f_C^A \Delta H_{AC}^{inter} \left(\frac{c_A}{c_A + c_C}, \frac{c_C}{c_A + c_C} \right)$$
$$+ c_B f_C^B \Delta H_{BC}^{inter} \left(\frac{c_B}{c_B + c_C}, \frac{c_C}{c_B + c_C} \right) \qquad (23a)$$

or

$$\Delta H_{ABC} = (c_A + c_B) \frac{c_A V_A^{2/3} + c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3} + c_C V_C^{2/3}}$$
$$\times \Delta H_{AB} \left(\frac{c_A}{c_A + c_B}, \frac{c_B}{c_A + c_B} \right)$$
$$+ (c_A + c_C) \frac{c_A V_A^{2/3} + c_C V_C^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3} + c_C V_C^{2/3}}$$
$$\times \Delta H_{AC} \left(\frac{c_A}{c_A + c_C}, \frac{c_C}{c_A + c_C} \right)$$

$$+ (c_B + c_C) \frac{c_C V_C^{2/3} + c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3} + c_C V_C^{2/3}}$$

$$\times \Delta H_{BC} \left(\frac{c_B}{c_C + c_B}, \frac{c_C}{c_C + c_B} \right). \tag{23b}$$

(2) Toop's model [35]:

$$\Delta H_{ABC} = \frac{c_B}{1 - c_A} \Delta H_{AB} (c_A, 1 - c_A)$$
$$+ \frac{c_C}{1 - c_A} \Delta H_{AC} (c_A, 1 - c_A)$$
$$+ (c_B + c_C)^2 \Delta H_{BC} \left(\frac{c_B}{c_B + c_C}, \frac{c_C}{c_B + c_C} \right). \tag{24}$$

(3) Bonnier's model [33]:

$$\Delta H_{ABC} = \frac{c_B}{1 - c_A} \Delta H_{AB} (c_A, 1 - c_A)$$
$$+ \frac{c_C}{1 - c_A} \Delta H_{AC} (c_A, 1 - c_A)$$
$$+ (c_B + c_C) \Delta H_{BC} \left(\frac{c_B}{c_B + c_C}, \frac{c_C}{c_B + c_C} \right). \tag{25}$$

(4) Hillert's model [39]:

$$\Delta H_{ABC} = \frac{c_B}{1 - c_A} \Delta H_{AB} (c_A, 1 - c_A)$$
$$+ \frac{c_C}{1 - c_A} \Delta H_{AC} (c_A, 1 - c_A)$$
$$+ \frac{c_B c_C}{X_{BC} X_{CB}} \Delta H_{BC} (X_{BC}, X_{CB}), \tag{26}$$

where $X_{BC} = (1 + c_B - c_C)/2$ and $X_{CB} = (1 + c_C - c_B)/2$.

(5) Kohler's model [34]:

$$\Delta H_{ABC} = (c_A + c_B)^2 \Delta H_{AB} \left(\frac{c_A}{c_A + c_B}, \frac{c_B}{c_A + c_B} \right)$$
$$+ (c_B + c_C)^2 \Delta H_{BC} \left(\frac{c_B}{c_B + c_C}, \frac{c_C}{c_B + c_C} \right)$$
$$+ (c_C + c_A)^2 \Delta H_{CA} \left(\frac{c_C}{c_C + c_A}, \frac{c_A}{c_C + c_A} \right). \tag{27}$$

(6) Muggianu's model [37]:

$$\Delta H_{ABC} = \frac{c_A c_B}{X_{AB} X_{BA}} \Delta H_{AB} (X_{AB}, X_{BA}) + \frac{c_B c_C}{X_{BC} X_{CB}} \Delta H_{BC} (X_{BC}, X_{CB})$$
$$+ \frac{c_C c_A}{X_{CA} X_{AC}} \Delta H_{CA} (X_{CA}, X_{AC}), \tag{28}$$

where $X_{ij} = (1 + c_i - c_j)/2$.

(7) Colinet's model [36]:

$$\Delta H_{ABC} = \frac{1}{2} \left[\frac{c_B}{1 - c_A} \Delta H_{AB} (c_A, 1 - c_A) \right.$$
$$\left. + \frac{c_A}{1 - c_B} \Delta H_{AB} (1 - c_B, c_B) \right]$$
$$+ \frac{1}{2} \left[\frac{c_C}{1 - c_B} \Delta H_{BC} (c_B, 1 - c_B) \right.$$
$$\left. + \frac{c_B}{1 - c_C} \Delta H_{BC} (1 - c_C, c_C) \right]$$
$$+ \frac{1}{2} \left[\frac{c_A}{1 - c_C} \Delta H_{CA} (c_C, 1 - c_C) \right.$$
$$\left. + \frac{c_C}{1 - c_A} \Delta H_{CA} (1 - c_A, c_A) \right]. \tag{29}$$

(8) Chou's model [42–44]:

$$\Delta H_{ABC} = \frac{c_A c_B}{X_{AB} X_{BA}} \Delta H_{AB} (X_{AB}, X_{BA}) + \frac{c_A c_C}{X_{CA} X_{AC}} \Delta H_{CA} (X_{CA}, X_{AC})$$
$$+ \frac{c_B c_C}{X_{BC} X_{CB}} \Delta H_{BC} (X_{BC}, X_{CB}), \tag{30}$$

$$X_{AB} = c_A + c_C \xi_{AB}^C, \qquad X_{BA} = c_B + c_C (1 - \xi_{AB}^C), \tag{30a}$$

$$X_{CA} = c_C + c_B \xi_{AC}^B, \qquad X_{AC} = c_A + c_B (1 - \xi_{AC}^B), \tag{30b}$$

$$X_{BC} = c_B + c_A \xi_{BC}^A, \qquad X_{CB} = c_C + c_A (1 - \xi_{BC}^A), \tag{30c}$$

and

$$\xi_{ij}^k = \frac{\lambda_i}{\lambda_i + \lambda_j}, \quad \lambda_i = \int_0^1 (\Delta H_{ij} - \Delta H_{ik})^2 dc_i. \tag{30d}$$

(9) Ouyang's model [45,46]:

$$\Delta H_{ABC} = \frac{c_A c_B}{X_{AB} X_{BA}} \Delta H_{AB} (X_{AB}, X_{BA}) + \frac{c_A c_C}{X_{AC} X_{CA}} \Delta H_{AC} (X_{AC}, X_{CA})$$
$$+ \frac{c_B c_C}{X_{BC} X_{CB}} \Delta H_{BC} (X_{BC}, X_{CB}), \tag{31}$$

$$y_{AB} = c_A + c_C \frac{\lambda_A}{\lambda_A + \lambda_B},$$
$$y_{BA} = c_B + c_C \frac{\lambda_B}{\lambda_A + \lambda_B}, \tag{31a}$$

$$y_{AC} = c_A + c_B \frac{\lambda_A}{\lambda_A + \lambda_C},$$
$$y_{CA} = c_C + c_B \frac{\lambda_C}{\lambda_A + \lambda_C}, \tag{31b}$$

$$y_{BC} = c_B + c_A \frac{\lambda_B}{\lambda_B + \lambda_C},$$
$$y_{CB} = c_C + c_A \frac{\lambda_C}{\lambda_B + \lambda_C}, \tag{31c}$$

$$\lambda_A = \left[\Delta H_{C \text{ in } A}^{\text{inter}} - \Delta H_{B \text{ in } A}^{\text{inter}} \right]^2, \tag{31d}$$

$$\lambda_B = \left[\Delta H_{A \text{ in } B}^{\text{inter}} - \Delta H_{C \text{ in } B}^{\text{inter}} \right]^2, \tag{31e}$$

$$\lambda_C = \left[\Delta H_{B \text{ in } C}^{\text{inter}} - \Delta H_{A \text{ in } C}^{\text{inter}} \right]^2. \tag{31f}$$

For solid solutions, amorphous alloys or other types of alloys, one need only replace the formation enthalpies of binary compounds by the related binary ones.

3. Implementations

3.1. Algorithms

Most models and methods summarized in Section 2 have been implemented into Miedema Calculator that is written in C++ with different functional module interfaces. Miedema Calculator is compiled and runs on Windows with the screen resolution 1024 × 768 or higher. Fig. 1 depicts the flowchart of the algorithm for the implementation of Miedema Calculator, which includes two general databases that store the basic elemental properties and model parameters, and five major functional modules: (i) the formation enthalpies of binary intermetallic compounds; (ii) the formation enthalpies of ternary intermetallic compounds; (iii) the formation enthalpies of binary statistical solid solutions; (iv) the formation enthalpies of binary amorphous alloys; (v) the volume corrections of binary solid solutions and compounds upon alloying. A more detailed description for each module and an illustration is provided in supplementary materials (see Appendix A).
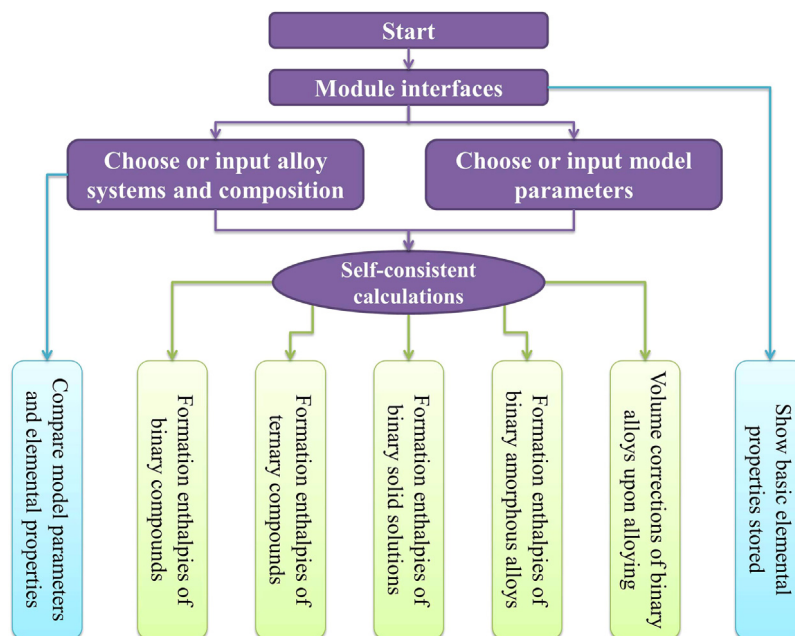
Fig. 1. Flowchart of the algorithm for the implementation of Miedema Calculator.

In the calculations of volume corrections by Eq. (2), and the calculations of chemical formation enthalpies for solid solutions and amorphous alloys, there are several different definitions of γ parameter for $f_B^A = c_B^S \left[1 + \gamma \left(c_A^S c_B^S \right)^2 \right]$. In Miedema Calculator, the choice of γ parameter follows the terminologies below: (a) for a statistical solid solution, $\gamma = 0$ [5] is termed as "Miedema's method", while $\gamma = 4$ [49] is used for "Alonso's method" to account for the existence of CSRO; (b) for an amorphous alloy, $\gamma = 0$ [5] is termed as "Miedema's method", while $\gamma = 4$ [49] and $\gamma = 5$ [48] is for "Alonso's method" and "Weeber's method", respectively.

Besides, in the calculations of elastic mismatch energy of a solid solution, Eq. (10a) is termed as "Miedema's method", while Eq. (10b) is for "Alonso's method" in Miedema Calculator, and in the calculations of the topological contribution of an amorphous alloy, Eq. (16a) is termed as "Miedema's method", while Eq. (16b) is for "Alonso's method" in Miedema Calculator.

3.2. Inputs and outputs

For each functional module, the minimum inputs are (i) the alloy system, (ii) the alloy composition, and (iii) the model parameters for each element as presented in Fig. 1. The major outputs from self-consistent calculations are the formation enthalpies for modules (i)–(iv), and the volume corrections for module (v). In addition, some critical model parameters and relevant intermediate results are also presented in module interface. To be noted that Miedema Calculator provides a special "input mode" by choosing the menu "Control"-> "Input mode" to make the model parameters editable in the region "Model parameters used". In such interactive mode, the self-consistent calculation is accordingly performed based on the model parameters that input/or is modified. It is suggested that the potential users read the supplementary materials in which we provide a brief tutorial for Miedema Calculator (see Appendix A).

3.3. Restrictions

The calculation of formation enthalpies for intermetallic compounds implemented in Miedema Calculator is generally valid for binary/ternary transition metal alloy systems and alloy systems consisted of at least one transition metal. However, it can also be applied for alloys with two/three non-transitional metals and polyvalence elements like N, B, C, etc., but it must be with caution according to Miedema's suggestion that only if one knows that an alloy is truly metallic can one give a reasonably accurate estimation [5]. For solid solutions and amorphous alloys, the applications of Miedema's method or Alonso's method are mostly restricted to the binary transition metal alloy systems so far. We may refer to the original publications by Miedema et al. and Alonso et al. [5,6,48,49] for more restrictions and guidance of applications of Miedema Calculator for statistical solid solutions and amorphous alloys. In case of ternary systems, most of the geometrical models mentioned in Section 2.5 are implemented in Miedema Calculator for intermetallic compounds, and other geometrical models may be included in the future.

4. Evaluations and discussions

The implementation to the above-mentioned methods will be critically evaluated by comparing the calculated values with the previously available ones in the following sections, including the formation enthalpies of various binary and ternary compounds, solid solutions, amorphous alloys and volume corrections.

4.1. Comparison of formation enthalpies of some binary compounds with previous values

We now first compare in Table 3 the calculated formation enthalpies of some Ti-based binary intermetallic compounds by the present Miedema Calculator based on original Miedema's model and the statistically improved one with those previously published ones [5]. Perfect agreement between them is obtained, providing a validation on the implementation of these models in Miedema Calculator. The capability of the statistically improved model can be identified from the comparison with experimental values [26], suggesting that the ASD factor plays an important role in affecting the calculation precise of the standard formation enthalpy. In case of binary hydrides of transition metals TmH (Tm = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, La, Hf, Ta, W, Re, Os, Ir, Pt, Th, U, Pu, Cu, Ag, Au), Table 4 compares

Table 3
The calculated formation enthalpies (ΔH) of Ti-based binary intermetallic compounds based on the original Miedema's model and the statistically improved one as implemented in Miedema Calculator and compared with the previous ones.

X	ΔH (kJ mol^{-1})						
	TiX$_3$	TiX$_2$	Ti$_2$X$_3$	TiX	Ti$_3$X$_2$	Ti$_2$X	Ti$_3$X
Sc	6.58[a]	8.65[a]	9.99[a]	11.11[a]	10.80[a]	9.77[a]	7.74[a]
	5.31[b]	6.98[b]	8.07[b]	8.97[b]	8.72[b]	7.89[b]	6.26[b]
	7[c]	9[c]	10[c]	11[c]	11[c]	10[c]	8[c]
V	−1.69[a]	−2.15[a]	−2.39[a]	−2.49[a]	−2.27[a]	−1.98[a]	−1.51[a]
	−1.37[b]	−1.75[b]	−1.94[b]	−2.02[b]	−1.84[b]	−1.60[b]	−1.23[b]
	−2[c]	−2[c]	−2[c]	−3[c]	−2[c]	−2[c]	−2[c]
Cr	−7.79[a]	−9.81[a]	−10.81[a]	−11.09[a]	−9.95[a]	−8.61[a]	−6.54[a]
	−6.28[b]	−7.91[b]	−8.72[b]	−8.94[b]	−8.03[b]	−6.94[b]	−5.27[b]
	−8[c]	−10[c]	−11[c]	−11[c]	−10[c]	−9[c]	−7[c]
Mn	−8.60[a]	−10.81[a]	−11.91[a]	−12.20[a]	−10.94[a]	−9.45[a]	−7.19[a]
	−6.93[b]	−8.72[b]	−9.60[b]	−9.84[b]	−8.82[b]	−7.62[b]	−5.79[b]
	−9[c]	−11[c]	−12[c]	−12[c]	−11[c]	−9[c]	−7[c]
Fe	−17.46[a]	−22.01[a]	−24.31[a]	−25.00[a]	−22.48[a]	−19.44[a]	−14.78[a]
	−14.08[b]	−17.76[b]	−19.62[b]	−20.17[b]	−18.13[b]	−15.67[b]	−11.91[b]
	−18[c]	−22[c]	−24[c]	−25[c]	−23[c]	−20[c]	−15[c]
Co	−29.91[a]	−37.57[a]	−41.35[a]	−42.28[a]	−37.83[a]	−32.62[a]	−24.75[a]
	−24.05[b]	−30.22[b]	−33.27[b]	−34.02[b]	−30.41[b]	−26.21[b]	−19.88[b]
	−30[c]	−38[c]	−41[c]	−42[c]	−38[c]	−33[c]	−25[c]
Ni	−36.53[a]	−45.88[a]	−50.48[a]	−51.61a	−46.14[a]	−39.78[a]	−30.17[a]
	−29.36[b]	−36.89[b]	−40.60[b]	−41.49[b]	−37.07[b]	−31.94[b]	−24.21[b]
	−37[c]	−46[c]	−51[c]	−52[c]	−46[c]	−40[c]	−30[c]
Y	12.35[a]	16.42[a]	19.30[a]	22.25[a]	22.58[a]	21.02[a]	17.15[a]
	9.69[b]	12.90[b]	15.17[b]	17.51[b]	17.78[b]	16.55[b]	13.51[b]
	12[c]	16[c]	19[c]	22[c]	23[c]	21[c]	17[c]
Zr	−0.20[a]	−0.26[a]	−0.30[a]	−0.33[a]	−0.32[a]	−0.29[a]	−0.23[a]
	−0.16[b]	−0.21[b]	−0.24[b]	−0.27[b]	−0.26[b]	−0.24[b]	−0.19[b]
	0[c]	0[c]	0[c]	0[c]	0[c]	0[c]	0[c]
Nb	1.88[a]	2.44[a]	2.77[a]	2.98[a]	2.81[a]	2.50[a]	1.94[a]
	1.53[b]	1.98[b]	2.25[b]	2.43[b]	2.29[b]	2.03[b]	1.58[b]
	2[c]	2[c]	3[c]	3[c]	3[c]	2[c]	2[c]
Mo	−3.41[a]	−4.40[a]	−4.97[a]	−5.30[a]	−4.95[a]	−4.37[a]	−3.38[a]
	−2.78[b]	−3.58[b]	−4.05[b]	−4.32[b]	−4.03[b]	−3.56[b]	−2.75[b]
	−4[c]	−5[c]	−5[c]	−5[c]	−5[c]	−4[c]	−3[c]
Tc	−37.26[a]	−47.96[a]	−54.17[a]	−57.86[a]	−53.94[a]	−47.53[a]	−36.66[a]
	−30.34[b]	−39.06[b]	−44.12[b]	−47.13[b]	−43.93[b]	−38.70[b]	−29.84[b]
	−37[c]	−48[c]	−54[c]	−58[c]	−54[c]	−48[c]	−37[c]
Ru	−42.27[a]	−54.25[a]	−61.06[a]	−64.84[a]	−60.06[a]	−52.73[a]	−40.54[a]
	−34.39[b]	−44.14[b]	−49.70[b]	−52.77[b]	−48.87[b]	−42.90[b]	−32.97[b]
	−42[c]	−54[c]	−61[c]	−65[c]	−60[c]	−53[c]	−41[c]
Rh	−50.67[a]	−65.09[a]	−73.34[a]	−78.02[a]	−72.41[a]	−63.64[a]	−48.97[a]
	−41.24[b]	−52.98[b]	−59.71[b]	−63.51[b]	−58.93[b]	−51.79[b]	−39.84[b]
	−51[c]	−65[c]	−73[c]	−78[c]	−72[c]	−64[c]	−49[c]
Pd	−61.46[a]	−79.39[a]	−90.04[a]	−96.90[a]	−90.99[a]	−80.50[a]	−62.29[a]
	−50.08[b]	−64.69[b]	−73.38[b]	−78.96[b]	−74.14[b]	−65.59[b]	−50.75[b]
	−62[c]	−79[c]	−90[c]	−97[c]	−91[c]	−80[c]	−62[c]
La	15.51[a]	20.69[a]	24.47[a]	28.60[a]	29.57[a]	27.89[a]	23.10[a]
	11.96[b]	15.97[b]	18.90[b]	22.13[b]	22.90[b]	21.61[b]	17.90[b]
	15[c]	21[c]	24[c]	28[c]	29[c]	28[c]	23[c]
Hf	0.13[a]	0.18[a]	0.20[a]	0.22[a]	0.22[a]	0.19[a]	0.15[a]
	0.11[b]	0.14[b]	0.16[b]	0.18[b]	0.17[b]	0.16[b]	0.12[b]
	0[c]	0[c]	0[c]	0[c]	0[c]	0[c]	0[c]
Ta	1.32[a]	1.71[a]	1.94[a]	2.10[a]	1.98[a]	1.76[a]	1.37[a]
	1.08[b]	1.40[b]	1.58[b]	1.71[b]	1.61[b]	1.43[b]	1.11[b]
	1[c]	2[c]	2[c]	2[c]	2[c]	2[c]	1[c]
W	−5.43[a]	−7.01[a]	−7.94[a]	−8.52[a]	−8.00[a]	−7.08[a]	−5.48[a]
	−4.42[b]	−5.71[b]	−6.47[b]	−6.95[b]	−6.52[b]	−5.77[b]	−4.47[b]
	−5[a]	−7[c]	−8[c]	−9[c]	−8[c]	−7[c]	−6[c]
Re	−24.26[a]	−31.25[a]	−35.33[a]	−37.80[a]	−35.30[a]	−31.15[a]	−24.05[a]
	−19.76[b]	−25.46[b]	−28.78[b]	−30.80[b]	−28.76[b]	−25.37[b]	−19.59[b]
	−24[c]	−31[c]	−35[c]	−38[c]	−35[c]	−31[c]	−24[c]
Os	−39.46[a]	−50.76[a]	−57.29[a]	−61.11[a]	−56.87[a]	−50.06[a]	−38.57[a]
	−32.13[b]	−41.33[b]	−46.65[b]	−49.76[b]	−46.31[b]	−40.75[b]	−31.39[b]
	−39[c]	−51[c]	−57[c]	−61[c]	−57[c]	−50[c]	−39[c]

Table 3 (continued)

X	ΔH (kJ mol^{-1})						
	TiX$_3$	TiX$_2$	Ti$_2$X$_3$	TiX	Ti$_3$X$_2$	Ti$_2$X	Ti$_3$X
Ir	−54.85[a]	−70.70[a]	−79.98[a]	−85.68[a]	−80.05[a]	−70.61[a]	−54.48[a]
	−44.67[b]	−57.59[b]	−65.15[b]	−69.79[b]	−65.20[b]	−57.51[b]	−44.36[b]
	−55[c]	−71[c]	−80[c]	−86[c]	−80[c]	−71[c]	−55[c]
Pt	−69.77[a]	−90.42[a]	−102.96[a]	−111.61[a]	−105.56[a]	−93.76[a]	−72.77[a]
	−56.86[b]	−73.69[b]	−83.91[b]	−90.95[b]	−86.03[b]	−76.41[b]	−59.31[b]
	−70[c]	−91[c]	−103[c]	−112[c]	−106[c]	−94[c]	−73[c]
Th	6.72[a]	8.93[a]	10.50[a]	12.11[a]	12.32[a]	11.48[a]	9.39[a]
	5.27[b]	7.01[b]	8.25[b]	9.53[b]	9.69[b]	9.03[b]	7.39[b]
	7[c]	9[c]	11[c]	12[c]	13[c]	12[c]	10[c]
U	−0.22[a]	−0.29[a]	−0.34[a]	−0.38[a]	−0.36[a]	−0.33[a]	−0.26[a]
	−0.18[b]	−0.24[b]	−0.27[b]	−0.30[b]	−0.29[b]	−0.27[b]	−0.21[b]
	0[c]	0[c]	0[c]	0[c]	0[c]	0[c]	0[c]
Pu	1.43[a]	1.87[a]	2.13[a]	2.33[a]	2.22[a]	1.99[a]	1.56[a]
	1.17[b]	1.52[b]	1.74[b]	1.89[b]	1.80[b]	1.61[b]	1.26[b]
	1[c]	2[c]	2[c]	2[c]	2[c]	2[c]	2[c]
Cu	−9.47[a]	−11.89[a]	−13.09[a]	−13.40[a]	−12.02[a]	−10.39[a]	−7.90[a]
	−7.62[b]	−9.58[b]	−10.55[b]	10.80[b]	−9.69[b]	−8.37[b]	−6.36[b]
	−9[c]	−12[c]	−13[c]	−13[c]	−12[c]	−10[c]	−8[c]
Ag	−1.50[a]	−1.95[a]	−2.21[a]	−2.39[a]	−2.25[a]	−2.00[a]	−1.56[a]
	−1.23[b]	−1.59[b]	−1.80[b]	−1.95[b]	1.84[b]	−1.63[b]	−1.27[b]
	−1[c]	−2[c]	−2[c]	−2[c]	−2[c]	−2[c]	−1[c]
Au	−43.37[a]	−56.51[a]	−64.80[a]	−71.29[a]	−68.67[a]	−61.74[a]	−48.48[a]
	−35.31[b]	−46.00[b]	−52.73[b]	−57.99[b]	−55.86[b]	−50.22[b]	−39.44[b]
	−43[c]	−57[c]	−65[c]	−71[c]	−69[c]	−62[c]	−48[c]

[a] This work, original Miedema's model.
[b] This work, modified model [26].
[c] Ref. [5].

Table 4
The comparison of the formations enthalpies (ΔH) of transition metal hybrids TmH (Tm = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, La, Hf, Ta, W, Re, Os, Ir, Pt, Th, U, Pu, Cu, Ag, Au) adopted from Table V-6.1 in Ref. [5] and the calculated ones by Miedema Calculator.

TmH	ΔH (kJ mol^{-1})	TmH	ΔH (kJ mol^{-1})	TmH	ΔH (kJ mol^{-1})	TmH	ΔH (kJ mol^{-1})
ScH	−38.81[a]	YH	−35.53[a]	LaH	−33.77[a]	ThH	−36.57[a]
	−56[b]		−52[b]		−50[b]		−53[b]
TiH	−38.64[a]	ZrH	−54.75[a]	HfH	−47.73[a]	UH	−33.74[a]
	−38[b]		−54[b]		−47[b]		−33[b]
VH	−18.46[a]	NbH	−27.07[a]	TaH	−27.23[a]	PuH	−36.09[a]
	−18[b]		−27[b]		−27[b]		−36[b]
CrH	−3.46[a]	MoH	−1.82[a]	WH	3.81[a]	CuH	26.55[a]
	−3[b]		−2[b]		4[b]		−10[b]
MnH	−12.06[a]	TcH	8.80[a]	ReH	11.42[a]	AgH	34.91[a]
	−12[b]		9[b]		12[b]		−9[b]
FeH	3.65[a]	RuH	10.42[a]	OsH	11.91[a]	AuH	35.25[a]
	4[b]		11[b]		12[b]		0[b]
CoH	4.45[a]	RhH	5.92[a]	IrH	10.09[a]		
	5[b]		6[b]		10[b]		
NiH	5.16[a]	PdH	2.27[a]	PtH	6.34[a]		
	5[b]		2[b]		7[b]		

[a] This work, original Miedema's model.
[b] Ref. [5].

the calculated formations enthalpies of transition metal hybrids TmH by the present Miedema Calculator and those adopted from Table V-6.1 in Ref. [5]. It is found surprisingly that there are some disagreements with the original publications [5] when the transition metal Tm is adopted as Sc, Y, La, Th, Cu, Ag, and Au. After checking different values of R parameter, we found that the previous values from Table V-6.1 in Ref. [5] are calculated by incorrectly using 1.0 for R parameter of these elements.

To give a further comparison of composition dependent formation enthalpies, Fig. 2 presents the comparison of the calcu-

lated values of ΔH_{AB} by the original Miedema's model and two improved models by ASD factors with the calculated data by ab initio high throughput data mining (HTDM) method for some selected Ag-binary systems, i.e., Ag–Au, Ag–Cd, Ag–Zr and Ag–Y [56]. It is generally seen from Fig. 2 that the predicted formation enthalpies from the improved model [25] are in reasonable agreement with the ab initio HTDM data [56]. However the original Miedema's model and statistically improved one do not provide desirable values for Ag–Zr as compared to HTDM ones because both models do not use the optimized parameters as suggested in Ref. [25].
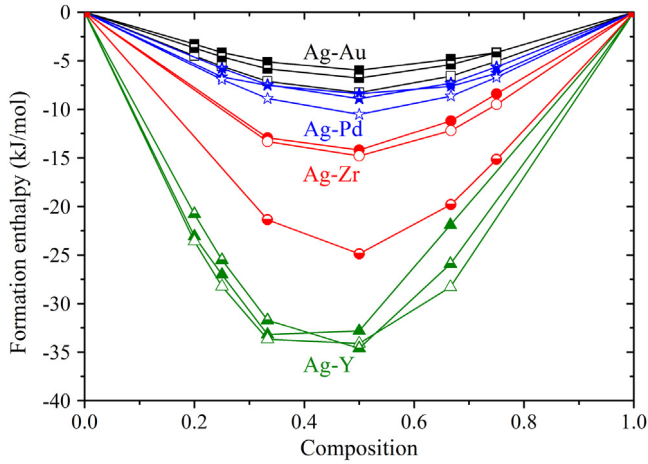
Fig. 2. Comparison of the calculated values (open symbol [25]) of ΔH_{AB} after parameter optimization, the calculated ones by statistical improved model (half-solid symbol [26]) of ΔH_{AB} without parameter optimization, with the calculated data (solid symbol) by the ab initio HTDM method for some selected Ag-binary systems [56].

but not sufficient, and therefore one may specially refine the model parameters for this system based on the reliable data known from experiments/or ab initio calculations. But it should be noted that the original physical meaning of the parameter must be preserved during the parameter refinement [25,26].

4.2. Comparison of formation enthalpies of ternary intermetallic compounds based on various geometrical models

In case of formation enthalpies of ternary compounds, we are using the Ouyang's geometrical model as an illustration. Table 5 lists the comparison of formation enthalpies of some ternary intermetallic compounds based on Ouyang's model, and Miedema's one [46,57], with the previously published values. It is seen that the calculated values are in agreement with the previous publications, providing a validation of the implementation of related geometrical ternary models in Miedema Calculator. It is additionally seen that the values calculated from different geometrical models do not show big difference, suggesting a strong dependence of formation enthalpies of ternary alloys on those of binary constituents.

4.3. Validations for interfacial enthalpies

Therefore, for a binary system with large deviation from experiments, *e.g.*, Ag–Zr system, a statistical improvement is necessary

In the calculations of volume correction upon alloying, two procedures are defined by Miedema et al. [5] and Bakker [6], which
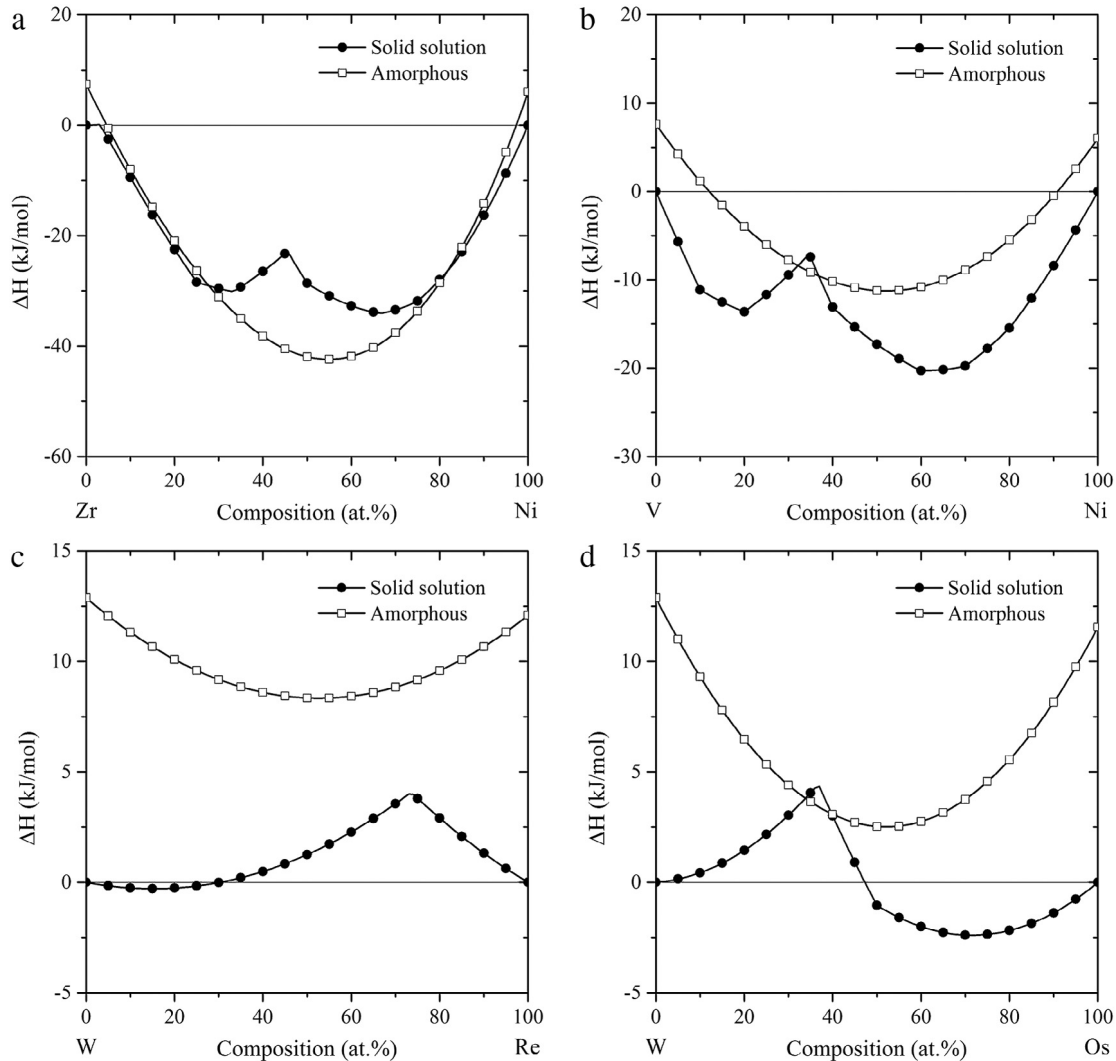

Fig. 3. The formation enthalpies of amorphous alloys and of the most stable statistical solid solutions vs. composition in (a) Zr–Ni, (b) V–Ni, (c) W–Re, and (d) W–Os systems. A comparison can be done with previous publications [6,53,58].

Table 5

The calculated formation enthalpies (ΔH) of some ternary intermetallic compounds based on Ouyang's model and Miedema's one as implemented in Miedema Calculator and compared with previous values published.

Phase	ΔH (kJ mol^{-1})	Phase	ΔH (kJ mol^{-1})
Al_3FeSi_2	−4.04[a]	Al_9FeNi	−16.09[a]
	1.34[b]		−17.17[b]
	−20.48[c]		−25.80[c]
	−4.2[c]		−17.0[c]
$Al_2Fe_3Si_4$	−12.91[a]	$Al_{10}Fe_3Ni$	−22.27[a]
	−9.32[b]		−24.27[b]
	−35.85[c]		−36.20[c]
	−9.0[c]		−23.6[c]
$Al_{71}Fe_{19}Si_{10}$	−13.01[a]	$AlNi_2Si$	−36.93[a]
	−10.79[b]		−37.49[b]
	−24.6[c]		−56.43[c]
	−9.4[c]		−38.1[c]
$Al_{31}Mn_6Ni_2$	−20.55[a]		
	−22.06[b]		
	−23.14[c]		
	−21.9[c]		

[a] This work, original Miedema's model.
[b] This work, Ouyang's model [45,46].
[c] Ref. [57] and references therein.

will generate different values of interfacial enthalpies. In original Miedema's model, the $(V_A^{2/3})_{alloy}$ in $\Delta\overline{H}_{A\ in\ B}^{inter}$ corresponds to the corrected volume by the charge transfer upon alloying based on Eq. (2), whereas, $(V_A^{2/3})_{pure}$ was used for calculation by Bakker [6] for simplification. So the users should notice the difference for the understanding of different values obtained from two procedures in some cases. The present Miedema Calculator follows the procedure of the original Miedema's model. The agreement can be clearly seen in Table 6 by comparing the calculated $\Delta\overline{H}_{A\ in\ B}^{inter}$ (kJ mol-1) and Γ_{AB} with those previous values [5] when A (Ti) is solved in other transition metals B which stands for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, La, Hf, Ta, W, Re, Os, Ir, Pt, Au (refer to Table V in Ref. [5] for more details).

4.4. Validations for formation enthalpies of solid solution and amorphous alloys

To demonstrate the capability of the present Miedema Calculator for the formation enthalpies of solid solutions and amorphous alloys, Fig. 3 shows the calculated phase stabilities between the amorphous alloy and the most stable crystalline solid solutions vs. composition in (a) Zr–Ni, (b) V–Ni, (c) W–Re, and (d) W–Os systems. By comparing with previous publications [6,53,58], it is seen that the present results are in good agreement with the previous ones. However, a slight lower value is obtained for solid solutions as compared to previous values, which can be attributed to the different values of the calculated $\Delta\overline{H}_{A\ in\ B}^{elast}$ from the previous ones [6]. Because the compiled database for elastic moduli of each element as originally used by Miedema et al. is not available, we cannot check the reason why their published values of $\Delta\overline{H}_{A\ in\ B}^{elast}$ in Ref. [5,59] is not reproduced exactly. After double check of our calculated values and compared with the published ones, we would attribute the difference to the following factors except for the uncertainty in incorrectness: (1) the model parameters used for shear and bulk moduli; (2) numerical precise; (3) whether the atomic volumes are corrected by the same procedure, etc. To be noted that the elastic moduli used in our Miedema Calculator comes from the compiled ones from Table A5 in Bakker's book [6,60].

4.5. Validations for volume correction calculation

As clarified in Section 2.4, the calculation of volume correction upon alloying is a self-consistent process [9]. With this as caution in reproducing the values of $\Delta\overline{V}_{A\ in\ B}$ published by Miedema et al. [5], we may refer to the agreement between the present calculated values and the previously published ones [5] in Table 7 by a comparison.

As clarified by Miedema et al. [5], a reverse of metal A and metal B $\Delta\overline{V}_{A\ in\ B}$ is different from $\Delta\overline{V}_{B\ in\ A}$ since the volume effect is proportional to $V^{2/3}$ of solute atoms. For example, for alloy rich in Zr and for alloys rich in the other constituent metals (e.g. Cr, Ir, Fe), the volume contraction differs: for Zr–Cr system, −1.269 versus −0.899, for Zr–Ir system, −2.589 versus −2.200 for

Table 6

The calculated $\Delta\overline{H}_{A\ in\ B}^{inter}$ (kJ mol^{-1}) and Λ_{AB} when A (Ti) is solved in other transition metals B (B = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, La, Hf, Ta, W, Re, Os, Ir, Pt, Th, U, Pu, Cu, Ag, Au).

B	$\Delta\overline{H}_{Ti\ in\ B}^{inter}$	Γ_{TiB}	B	$\Delta\overline{H}_{Ti\ in\ B}^{inter}$	Γ_{TiB}	B	$\Delta\overline{H}_{Ti\ in\ B}^{inter}$	Γ_{TiB}
Sc	27.31[a]	5.55[a]	Nb	7.82[a]	1.64[a]	Re	−100.87[a]	−22.17[a]
	28[b]	6[b]		8[b]	2[b]		−101[b]	−22[b]
Ti			Mo	−14.21[a]	−3.05[a]	Os	−164.14[a]	−36.39[a]
				−15[b]	−3[b]		−164[b]	−36[b]
V	−7.08[a]	−1.50[b]	Tc	−154.95[a]	−34.20[a]	Ir	−227.94[a]	−50.86[a]
	−7[b]	−2[b]		−155[b]	−34[b]		−228[b]	−51[b]
Cr	−32.73[a]	−7.03[a]	Ru	−175.96[a]	−39.01[a]	Pt	−289.44[a]	−64.86[a]
	−33[b]	−7[b]		−176[b]	−39[b]		−290[b]	−65[b]
Mn	−36.12[a]	−7.70[a]	Rh	−210.85[a]	−46.74[a]	Th	27.91[a]	5.68[a]
	−36[b]	−8[b]		−211[b]	−47[b]		28[b]	6[b]
Fe	−73.29[a]	−15.93[a]	Pd	−255.27[a]	−56.71[a]	U	−0.93[a]	−0.19[a]
	−74[b]	−16[b]		−256[b]	−57[b]		−1[b]	0[b]
Co	−125.73[a]	−27.52[a]	La	64.54[a]	13.06[a]	Pu	5.95[a]	1.24[a]
	−126[b]	−28[b]		64[b]	13[b]		6[b]	1[b]
Ni	−153.58[a]	−33.76[b]	Hf	0.56[a]	0.11[a]	Cu	−39.83[a]	−8.48[a]
	−154[b]	−34[b]		1[b]	0[b]		−40[b]	−9[b]
Y	51.34[a]	10.40[a]	Ta	5.50[a]	1.15[a]	Ag	−6.26[a]	−1.33[a]
	51[b]	10[b]		5[b]	1[b]		−6[b]	−1[b]
Zr	−0.83[a]	−0.17[a]	W	−22.57[a]	−4.88[a]	Au	−179.85[a]	−39.45[a]
	−1[b]	0[b]		−23[b]	−5[b]		−180[b]	−39[b]

[a] This work.
[b] Ref. [5].

Table 7

The calculated $\Delta \overline{V}_{A \, in \, B}$ (cm^3) when A (Ti) is solved in other transition metals B (B = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, La, Hf, Ta, W, Re, Os, Ir, Pt, Au).

B	$\Delta\overline{V}_{Ti \, in \, B}$	B	$\Delta\overline{V}_{Ti \, in \, B}$	B	$\Delta\overline{V}_{Ti \, in \, B}$
Sc	−0.571[a] −0.6[b]	Y	−0.838[a] −0.8[b]	La	−1.007[a] −1.0[b]
Ti		Zr	−0.136[a] −0.1[b]	Hf	−0.046[a] −0.0[b]
V	−0.147[a] −0.1[b]	Nb	−0.082[a] −0.1[b]	Ta	−0.076[a] −0.1[b]
Cr	−0.441[a] −0.4[b]	Mo	−0.508[a] −0.5[b]	W	−0.667[a] −0.7[b]
Mn	−0.161[a] −0.2[b]	Tc	−0.979[a] −1.0[b]	Re	−1.012[a] −1.0[b]
Fe	−0.668[a] −0.7[b]	Ru	−1.095[a] −1.1[b]	Os	−1.146[a] −1.1[b]
Co	−0.713[a] −0.7[b]	Rh	−0.895[a] −0.9[b]	Ir	−1.189[a] −1.2[b]
Ni	−0.764[a] −0.8[b]	Pd	−0.623[a] −0.6[b]	Pt	−1.092[a] −1.1[b]
Cu	0.101[a] 0.1[b]	Ag	0.312[a] 0.3[b]	Au	−0.189[a] −0.2[b]

[a] This work.
[b] Ref. [5].

Zr–Fe, respectively, all values in perfect agreement with previous values [5].

5. Conclusions

In summary, we presented here detailed descriptions of various thermodynamic models and methods within framework of Miedema's theory, and outlined the implementation of an integrated platform named "Miedema Calculator" for fast predicting the formation enthalpies of binary and ternary intermetallic compounds, statistical solid solutions and amorphous alloys, and the volume change upon alloying *etc.* The high efficiency and validations of the implementation of Miedema Calculator have demonstrated its reliability and promise as an effective tool in predicting the thermodynamic properties of unknown alloy systems. We expect the "Miedema Calculator" will find a wide range of applications with an increasingly improved capability. The relevant software is available for free from the authors or via https://sites. google.com/site/miedemacalc/ or http://miedemacalc.weebly. com/.

Acknowledgments

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.cpc.2016.08.013.

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