THERMODYNAMICAL CALCULATION OF FORMATION ENTHALPIES FOR ALKALINE METAL ALLOYS[①]

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ABSTRACT   Miedima's theory has been applied to calculate systematically the mixing enthalpies of liquid binary alkaline metal alloys and the formation enthalpies of solid binary alkaline metal alloys. The calculated values for the liquid alloys are in good agreement with the experimental values available and those of the first-principle or *ab initio* calculations. For solid alloys, the present results are in reasonable agreement with those of the first-principle pseudopotential theory calculations.

Key words: Miedema theory alkaline metal alloy mixing enthalpy formation enthalpy

1 INTRODUCTION

A lot of theoretical calculation schemes for the formation enthalpies of alloys have been developed, which can be divided roughly into two classes. One is the so called first principle or *ab initio* calculation scheme, including the augmented spherical wave method (ASM)[1], the perturbation method[2], the cluster method[3], the density functional theory method[4], the pseudopotential approach[5] and the theory of energy bands[6]. The calculation procedures of these schemes are rather complex, and the different simplified approximations should be introduced for the different calculation problems, so that the calculation procedures have no universality and the accuracies of them are not high, though their physical bases are reliable and only the atomic numbers of the constituents of an alloy are needed for the input parameters. Another class of calculation scheme is the so called empirical or semiempirical scheme, including the empirical method of the energy bands[7], the pair potential method[8], the embedded-atom method model[9,10] and the Miedema thermodynamical theory[11,12]. From several input parameters and from comparing the calculation results and the experimental data to revise these input parameters, these schemes predicted the heats of formation for a numbers of alloy systems. To compare the former calculation schemes, the calculation procedures of these schemes are rather simple but universal, the accuracies of these calculations are relatively high, and the heats of formation for a number of alloy systems can be calculated, but the shortcomings of them are generally of no deeply physical bases.

The alkaline metals have only one electron out of their nuclei as for the simplest atomic structure in the cubic system, for which the theoretical treatment is rather simple, so that Wigner and Seitz[13] studied the properties of the metal sodium with the quantum mechanics method early in the thirties. Later on, Harrison first calculated successfully the energy difference of structures for the alkaline metals[14]. Hafner calculated the mixing enthalpies of the equiatomic liquid binary alloys for the alkaline metals[15] following the same calculation scheme of Harrison. Singh[16] calculated the mixing enthalpies of liquid NaK, NaCs and KRb alloy systems with the

pseudopotential theory. Iniguez and Alonso calculated the heat of formation of disordered alkaline metal-alkaline metal solid alloys with the density functional-pseudopotential approach[17]. All of these works made the research for the heat of formation of alkaline metal alloys advanced, but the study still was not systematically, also the agreement between the calculations and the experimental data should be improved. Miedema and Coworkers[11] calculated the heat of formation of almost binary metal alloys with the Miedema theory, but those for the alkaline metal alloys were calculated very few. The mixing and formation enthalpies for the binary alkaline metal alloys, therefore, have been calculated systematically with the Miedema theory in this paper.

2 MIEDEMA THEORY

Miedema and Coworkers[18] developed an empirical theory as so called Miedema theory later to calculate the thermodynamical properties of metal alloys in the seventies, which has been applied to a lot of respects, such as solid solution[19], the formation of amorphous alloys[20], the surface energy of alloys[21], the formatoin energy of vacancy[22] and the calculation of phase diagrams[23], especially the calculations of the formation enthalpy of the binary transition metal alloys[11,12], to which the formation enthalpies of all binary alloys based on the two or one transition metals have been calculated and the agreement between the calculated and experimental data was good so that the theory was successful.

The key for the Miedema theory is its macroscopic atom picture, which is an extension for the Wigner-Seitz model. The basic assumptions of the Miedema theory are that an alloy or intermetallic compound is thought to be built up of atomic cells of two metals and alloying effect resulting from the contact interactions which take place at the interface between dissimilar atoms. When two blocks of different metals are brought in contact, the charge redistribution will not be limited to the inside of each block, but there will be not charge transfer, governed by the difference in contact potential between the two metals. Charge will flow to places of lower potential energy, until the resulting dipole layer compensates the potential difference. Visualized on an atomic scale, this charge transfer corresponds to a negative, ionic contribution to the enthalpy of formation. On the other hand, when dissimilar cells are brought into contact in the alloy, there will be discontinuities in the electron density. Elimination of such discontinuities requires energy, in fact, electrons have to be transferred to higher energy levels. Hence a positive contribution to interfacial energies can be expected and thus to the enthalpies of formation. The enthalpy of formation of binary alloys come from the sum of the two mentioned energies.

After analysing systematically, Miedema *et al* obtained the key expression for the enthalpy of formation of binary alloys as follows:

$$\Delta H = \frac{V_A^{2/3}}{(n_{WS}^A)^{-1/3} + (n_{WS}^B)^{-1/3}}$$
$$\times [- P(\Delta\Phi^*)^2 + Q(\Delta n_{WS}^{1/3}) - R] \qquad (1)$$

$\Delta\Phi^* = \Phi_A^* - \Phi_B^*$, the difference in potential, $\triangle n_{ws}$ the difference in electron density, n_{ws} the electron density at the boundary of the Wigner-Seitz cell for the pure element in the metallic state, A and B the two metals in an alloy, $V^{2/3}$ the contact-surface area, and P, Q, R constants. For the binary alloys consist of two alkaline metals,

$$P = 10.6 \qquad (2)$$
$$Q/P = 9.4 \qquad (3)$$

R comes from an addition energy contribution for the alloys of transition metals with non-transition metals. Because of study on the alloys of one valence alkaline metals in present case, therefore

$$R = 0 \qquad (4)$$

so equation (1) becomes

$$\Delta H = \frac{V_A^{2/3}}{(n_{WS}^A)^{-1/3} + (n_{WS}^B)^{-1/3}}$$
$$\times [- P(\Delta\Phi^*)^2 + Q(\Delta n_{WS}^{1/3})^2] \quad (5)$$

The concentration dependence should be

considered. If x_A is the atomic concentration of metal A, the degree to which an atomic cell of metal A is in contact with dissimilar atomic cell (B) on average f_B^A is:

$$f_B^A = 1 - C_A \quad (6)$$

for a statistically ordered alloy in the liquid phase, and is:

$$f_B^A = (1 - C_A)\{1 + 8[C_A$$
$$\times (1 - C_A)]\} \quad (7)$$

for ordered alloys, where C_A is the surface concentration of metal A

$$C_A^s = x_A V_A^{2/3}/[x_A V_A^{2/3}$$
$$+ (1 - x_A)V_B^{2/3}] \quad (8)$$

where V_A and V_B are the molar volumes of metal A and B, respectively.

The volume of a metal in an alloy will be changed, Miedema used the following simple approximate relationship:

$$(V_A^{2/3})_{\text{alloy}} = (V^{2/3})_{\text{pure}A}$$
$$\times [1 + a \cdot f_B^A$$
$$\times (\Phi_A^* - \Phi_B^*)] \quad (9)$$

where a is a constant, which is derived from experimental volume contractions in compounds. $a = 0.14$ for the alkaline metals.

In summary, the enthalpy of formation $\triangle H^{\text{for}}$ can be obtained for arbitary concentrations from

$$\Delta H^{\text{for}} = x_A f_B^A \Delta H \quad (10)$$

It should be noted that, since f_B^A is a function of $V_A^{2/3}$, the calculation of ($V_A^{2/3}$)$_{\text{alloy}}$ in principle requires an iteration procedure, but as pointed out by Miedema only two steps can lead to a sufficient accuracy. When calculating the mixing enthalpy, equation (6) for f_B^A is used, and when calculating the enthalpy of formation for solid alloys, equation (7) for f_B^A is used. The parameters of the alkaline metals are listed in Table 1.

3　RESULTS AND DISCUSSION

3.1　*Mixing Enthalpy for Liquid Alloys*

According to the calculation procedure mentioned in the above section, the calculated results are obtained. Fig. 1 shows the mixing enthalpy as a function of the composition (dash

Table 1　Model parameters for calculating the enthalpy of formation for the alkaline metals

Symbol	Φ^*	$n_{ws}^{1/3}$	$V^{2/3}$	a
Li	2.85	0.98	5.33	0.14
Na	2.70	0.82	8.27	0.14
K	2.25	0.65	12.77	0.14
Rb	2.10	0.60	14.65	0.14
Cs	1.95	0.55	16.86	0.14

curve) in 10 binary liquid alloys. The experimental data available, the calculation by Singh[16] with the pseudopotential theory for the K-Na, K-Rb and Na-Cs alloy systems, are shown in the figure too. For Na-Rb, K-Cs and Rb-Cs alloy systems, the experimental data available are included. As for the four alloy systems related to metal Li, the calculations by Hafner and Jank[24] and the experimental data for Li-Na alloy system are presented, but for the other three alloy systems only the present results are included because of no any experimental data or theoretical results found in the literature.

From the calculation results, it can be seen that there are some general features for the mixing enthalpy of the alkaline liquid alloys. One is all of the mixing enthalpy are positive. Another is the mixing enthalpy increases as increasing the distance between the locations in the period table for the two components in alloys. The third is the asymmetry for the mixing enthalpy as a function of the composition also increases as increasing the departure between the location in the period table for two constituents in alloys, and the asymmetry is partial to the side of the smaller radius of atom.

It can be seen from Fig. 1 that the calculations for all other alloy systems except Rb-Cs system are in good agreement with the experimental data and those calculated by the first principle. For Rb-Cs system, the calculated results are in contrary to the experimental data, but the magnitudes for both two values are rather small, and the difference of them can be understood by conditions in experiment and the selection of imput parame-

ters in the calculation.

Table 2 shows the calculated results for the mixing enthalpy of equiatomic liquid alloys, the experimental data available and those calculated by the first principle. It can be found from the table that the agreement between the present calculations and the experi-

Table 2 Mixing enthalpy for liquid equiatom alloys(eV/atom)

	$\triangle H$ (present work)	$\triangle H^{[25]}$	$\triangle H^{[17]}$
RbCs	0.000 3	−0.001 3	0.0026
KRb	0.000 2	0.001 3	0.0052
KCs	0.001 0	0.001 2	0.0092
NaK	0.014 2	0.007 2	0.0204
NaRb	0.019 8	0.012 6	
NaCs	0.025 8	0.009 5	0.0812
LiNa	0.036 1	0.034 0[24]	0.0529, 0.0381[24]
LiK	0.114 9		
LiRb	0.138 2		
LiCs	0.160 7		

mental data is better than that between the calculations by Hafner with the first principle and the experimental data. Though the agreement of calculations for NaK and KRb systems by pseuopotential approach with experimental data is better than that for the present-calculations, but for NaCs systems, our results are more close to the data. For RbCs system, both calculations by the present authors and by Hafner are positive, which is in contrary to the experimental data, but the magnitudes for the present results are more close to the data. For Li-Na system our results are in good agreement with the experimental data and theoretical results.

Many works sought to explain the alloying formation of metals. The famous and successful theory is the Hume-Rothery empirical theory[26], which concludes that the main factors affecting the formation of alloys based on simple metals are the size fator, eletronegativity and relative valency effect. For the alkaline metals, there is only one electron in the outer shell, therefore only the size factor and electronegativity should be considered. Generally speaking, the electronegativity for the alkaline metals are closed though decreases slightly as increasing the atomic number, so the effect of electronagativity is also not important.

That is to say the mixing enthalpy is mainly affected by the size factor. In order to understand the effect of the size factor, Fig. 2 shows the mixing enthalpy as a function of the
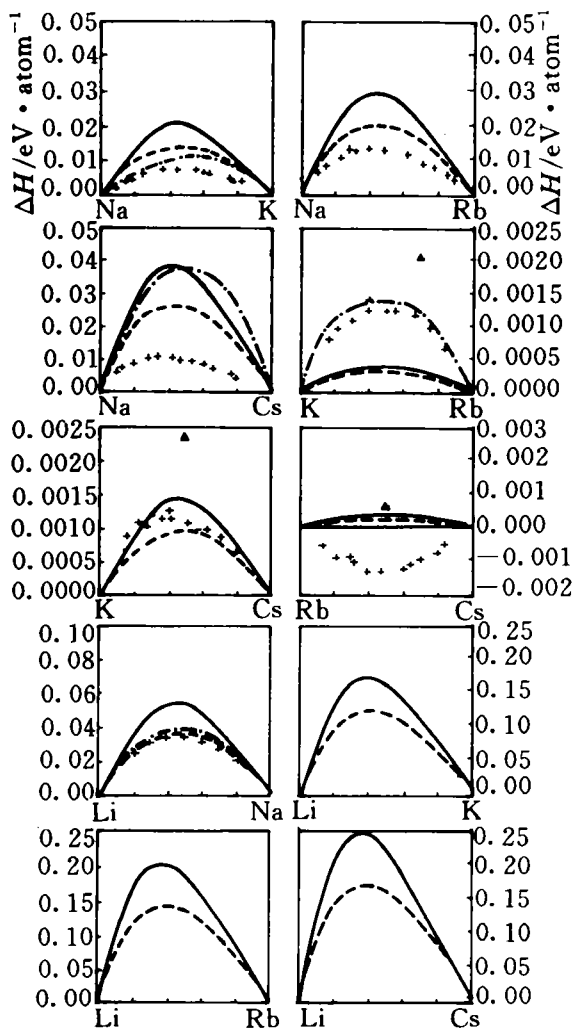

Fig. 1 Mixing enthelpy and formation enthalpy as a function of the composition in binary alkaline metal alloys

······the present calculations for the mixing enthalpy of liquid alloys. ——the present calculations for the formation enthalpy of solid alloys. − the calculations for the mixing enthalpy of liquid alloys by Singh[16] and Hafner *et al*[21]. + the experimental data for the mixing enthalpy of liquid alloys. ▲ the experimental data for the formation enthalpy of solid alloys

size factor, where the atomic radius is represented by half of the empirical interatomic distance of elements. We can see from the Figure that all of the points are located on or closed to three lines, one is relevent to the alloys containing Cs as a constituent, another to those containing Li as a constituent, the third to other alloys. It belongs to the group of alloys of Li for the alloy of Li with Cs. As for the end elements of the alkaline metal group, Li has the smallest atomic radius and the largest electronegativity, and in contrary Cs has the largest atomic radius and the smallest electronegativity. Fig. 2 therefore just presents the features of the two elements during forming alloys, also shows that the size factor has very important effect but the effect of electronegativity cannot be ignored when the alkaline metals form alloys.

3.2　Formation Heat for Solid Alloys
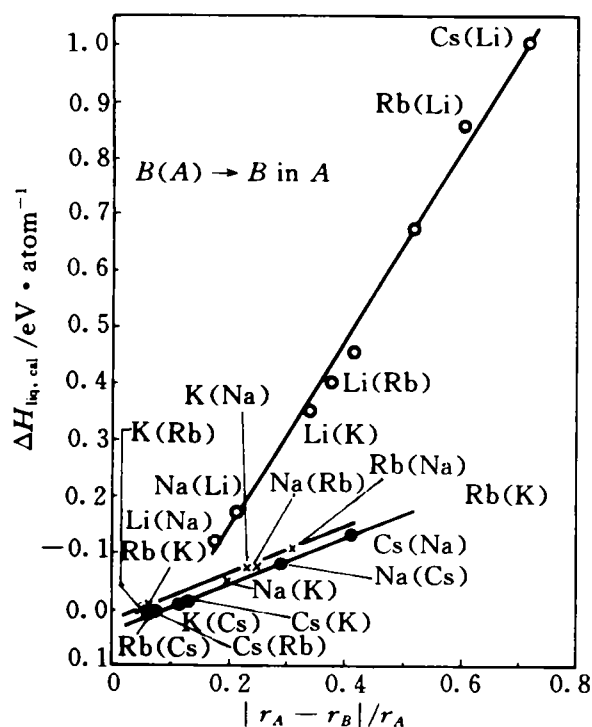
The present calculations for the heat of

formation of solid alloys are shown by the solid curve in Fig. 1. If combining them into one figure, the results is shown in Fig. 3. It can be found from the two Figures that all of the heat of formation for the solid slloys are the same as those for liquid alloys, i. e. are positive but the magnitudes for the former are larger than those of the later. The heat of formation increases as the departure between the locations of elements in the period table increases. The curve for the heat of formation versus the composition of alloys also is not symmetry, but partly to the side of the element having smaller atomic radius.

Fig. 3 is similiar to the results calculated by Iniguez and Alonso[12] with the density functional-pseudopotential approach, i. e. Fig. 1 in Ref. [17]. But there are two points are different. One is the order of increasing for $\triangle H$, ours is KRb, RbCs, KCs, NaK, NaRb, NaCs, LiNa, LiK, LiRb, and LiCs,
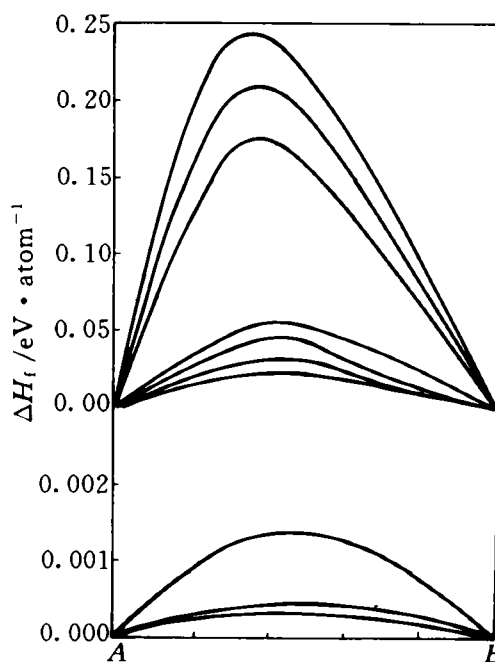

Fig. 2　Mixing enthalpy for the
equiatomic alloy versus size factor

Fig. 3　Heat of formation versus composition
in AB alloys. The curve correspond (in
order of increasing $\triangle H$) to the alloys
KRb, RbCs, KCs, Nak, NaRb, NaCs,
LiNa, LiK, LiRb and LiCs.

and theirs is KRb, RbCs, KCs, KCs, NaLi, Nak, NaRb, NaCs, LiK, LiRb and LiCs. It seems that our results are reliable and the results for LiNa calculated by Inquez and Alonso by considering the order increasing of the size factor for these alloys and the phase diagrams of them — the series of solid solution for RbCs, KRb and KCs, the eutetic for NaLi, NaRb and NaCs, the complex type for LiNa, and not mixing in liquid phase for LiK. Another is that their calculations are general larger than ours, two to three times for the Li based alloys, five to eight times for the Na based alloys, and 15 to 20 times for the other three alloys. But the calculations by Hafner and Sommer[28] using an orthogonalized-plane-wave based first-principles pseudopotential method are closed to the present calculations for the heat of formation of equiatomic solid alloys, as shown in Table 3. The estimated values for three solid alloys in Table 3[25] also are closed to our calculations. Fig. 4 shows the calculations and results calculated by Hafner *et al*[29] and Iniguez *et al*[17] for the heat of formation of solid K-Rb alloys. One can see from the Figure that the results by Iniguez *et al* are much larger than those by the present authors and by Hafner *et al*. Yokokava *et al*[25] estimated the heat of formation of 0. 002 eV/atom, for $K_{0.33}Rb_{0.67}$ extrapolated from liquid
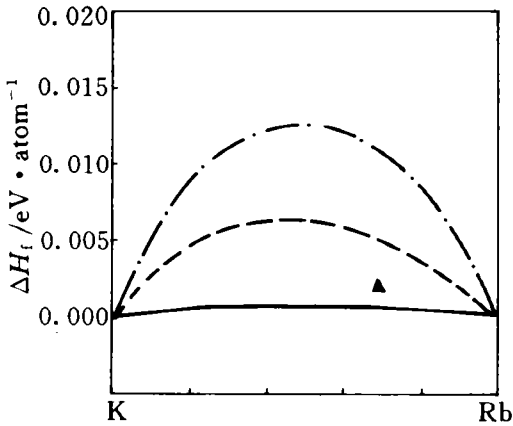

Fig. 4   **Heat of formation for the K-Rb alloy system**
— - the presnt calculations
······calculations by Hafner *et al*[29]
— —calculations by Iniguez *et al*[17]
▲extrapolated from liquid alloy data

alloy which is larger than the present value of 0. 000 3 eV/atom, but is much smaller than those by Hafner *et al* and by Iniguez *et al*. Therefore we can conclude that the present calculations are in more good agreement with the data.

In order to explain the calculations further, we plot the heat of formation for e-quiatomic solid alloys versus the size factor, as drawn in Fig. 5. The present results show that the heats of formation represent good linearity according to the order of LiNa-LiK-LiRb-LiCs, NaK-NaRb-NaCs and KRb-KCs, respectively, which shows that the size factor plays a very important role in deciding the heat of formation of the alkaline metal based alloys. The calculations by Iniguez and Alonso[17] and Hafner[28] using microscopic quantum theory are also included in the figure. They all are similar to the present results except the linearity for the results by Iniguez and Alonso is worse than that for ours. It should be noted that the order of magnitude for the three groups in the present calculations are 10^{-1}, 10^{-2}, and 10^{-3} eV, respectively. The agreement with experimental data leaves to be approved because of no such data for the rest of the alloys right now.

Table 3   Heat of formation for equiatomic solid alloys (eV/atom)

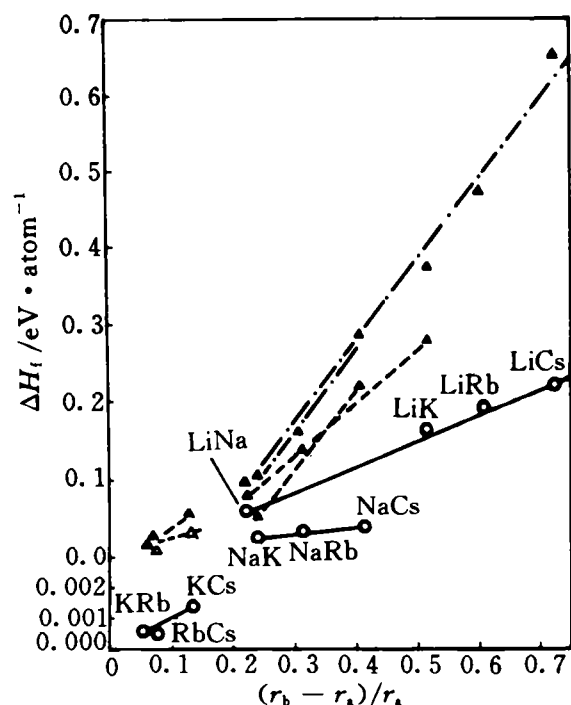| AB	$(r_a - r_b)/r_a$ (%)	ΔH_f (Present results)	$\Delta H_f^{[17]}$	$\Delta H_f^{[28]}$	ΔH_{fexp}^*
RbCs	7. 4	0. 000 4	0. 02	0. 005	0. 000 5
KRb	5. 6	0. 000 4	0. 007 7	0. 006 3	
$K_{0.3}Rb_{0.7}$	5. 6	0. 000 3	0. 006 7		
KCs	13. 4	0. 001 4	0. 005 3	0. 029	0. 001 9
NaK	24. 2	0. 021 0	0. 10	0. 048	0. 007
NaRb	31. 2	0. 029	0. 16	0. 013	
NaCs	40. 9	0. 037	0. 28	0. 215	
LiNa	22. 4	0. 053	0. 094	0. 074	
LiK	51. 9	0. 160	0. 37	0. 274	
LiRb	60. 5	0. 19	0. 47		
LiCs	72. 4	0. 215	0. 65		

* Extrapolated from liquid alloy data.

Fig. 5　Heat of formation for equiatomic solid alloys versus size factor

◯— the present results;

△—the calculation by Hafner[28];

▲—the calculatons by Iniguez and Alonso[17]

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