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DYNAMIC DIFFERENTIAL CALORIMETRY OF INTERMETALLIC COMPOUNDS

III. HEATS OF FORMATION, HEATS AND ENTROPIES OF FUSION OF $REIn_3$ AND $RETl_3$ COMPOUNDS

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ABSTRACT

Dynamic differential calorimetry has been employed to evaluate the heats of formation, heats and entropies of fusion of $REIn_3$ and $RETl_3$ compounds. The results obtained have been estimated to be corrected to within ±5–6%. The general trend, for both these series, is a decrease in the heat of formation from La to Lu which is correlated with the magnitude of the lanthanide contraction in these compounds. A simple correlation has been found between the heats of formation of REX_3 compounds and the ionic radii of the elements involved.

INTRODUCTION

This research follows previous work in which we described the use of the dynamic differential calorimetry (DDC) in the evaluation of the heats of formation, heats and entropies of fusion of the $RESn_3$[1] and $REPb_3$[2] compounds. This method is based on the direct measurement of the heat evolved during the reaction when the compound is formed from the elements, while the heats and hence the entropies of fusion can be measured as in the case of a pure element.

The theoretical treatment of this method has been given by Faktor and Hanks[3]; we have tested this theory in the temperature range of 200–1100°C and have applied the DDC method to the $REIn_3$ and $RETl_3$ compounds. These compounds have been chosen because Tl and In, like Sn and Pb, easily react with the RE's at a low temperature. The reaction is highly exothermic and the heat evolved is sufficient to melt the sample.

EXPERIMENTAL

The apparatus, standards and procedure to obtain the calibration curves, the sources of errors and the other operational details have been described elsewhere for $RESn_3$ phases[1]; no significant changes have been made when using this method for $REIn_3$ and $RETl_3$ compounds. $REIn_3$ and $RETl_3$ compounds, $AuCu_3$-type, are structurally well known. Their crystallographic properties can be found in current literature and some of them have recently been investigated while determining their heats of formation ($PrIn_3$: $\Delta H_f = -55.30$ kcal mol^{-1} (ref. 4); $NdIn_3$: $\Delta H_f = -55.84$ kcal mol^{-1} (ref. 5).

RE metals and partner elements used in this research were obtained from Koch-Light Laboratories, England, and had purities of 99.9 and 99.999%, respectively. Samples ranging from 0.75 to 2.50 g each were prepared from stoichiometric amounts of powders of the two metals (50 mesh) well mixed and pressed directly in the Mo containers. Manipulation of oxidizable substances such as light RE and Tl was carried out in a dry box filled with ultra-pure argon.

The reaction between RE and partner elements starts at low temperature, is very fast especially for the lighter RE and the thermal effect due to the melting of the partner element must be considered in the evaluation of the heat of formation of the corresponding compound. The other RE react at a higher temperature and the two-thermal effect, i.e., melting of the partner element and heat of reaction, are widely independent. Some examples of caracteristic thermograms have been reported in previous work[1,2]. To ensure reproducibility of the results, several samples for different heating rates were prepared and, at last, two "good" samples were considered in the evaluation of the heats of formation. After the reaction ended the samples were examined micrographically: only alloys which contained a single phase were considered and the subsequent X-ray examination showed only the presence of the REX_3 phase. The values of the lattice constants are in good agreement with literature values.

As the heats of formation are obtained at different temperatures, they should be reported, by means of the Kirchoff's relation at 298 K, corresponding to the reaction:

$$RE(s) + 3X(s) = REX_3(s) + \Delta H_f$$

The calculation would imply the knowledge of the heat capacities for RE, liquid and solid X element and for the compound but, if nothing whatever is known about the heat capacity of the compound, assuming the validity of the Neumann and Kopp's rule, ΔC_p may be considered to be zero for condensed reactions without affecting the results too much, especially when ΔT is small[6]. As in the case of $RESn_3$ and $REPb_3$ compounds the heats of formation were corrected only for the heat of fusion of X element and the values so obtained are reported in Table 1. The total error in their determination is evaluated to be of the order of 5–6%.

Heats and entropies of fusion were determined only for $RETl_3$ compounds, ($REIn_3$ phases having too high melting points) by preparing a new series of 1-g samples and sealing them by arc welding under argon atmosphere in Mo crucibles; this procedure is necessary to avoid losses of metals (Sm, Eu, Tm and Yb) at high temperatures via sublimation.

At the melting point of the alloys, which are in good agreement with the known values, the heats of fusion were determined by means of the calibration curves and hence the entropies of fusion were calculated; these values are reported in Table 2.

TABLE 1

HEATS OF FORMATION (kcal mol^{-1}) FOR $REIn_3$ AND $RETl_3$ COMPOUNDS AT 298 K

RE	*REIn*$_3$	*RETl*$_3$
La	−49.94	−43.27
Ce	−47.88	−42.97
Pr	−53.37	−43.77
Nd	−52.06	−39.82
Sm	−47.63	−37.91
Gd	−43.65	−35.22
Tb	−42.63	−34.08
Dy	−42.80	−32.60
Ho	−38.77	—
Er	−37.16	—
Tm	−34.92	—
Yb	−38.00	−35.37
Lu	−33.16	—

TABLE 2

HEATS AND ENTROPIES OF FUSION (kcal mol^{-1} and cal deg^{-1} mol^{-1}) FOR $RETl_3$ COMPOUNDS

T_m = melting point.

RETl$_3$	T_m (°C)	ΔH_m	ΔS_m
$LaTl_3$	1050	20.28	15.33
$CeTl_3$	1070	18.01	13.41
$PrTl_3$	1060	20.92	15.69
$NdTl_3$	1050	19.40	14.66
$SmTl_3$	850	17.44	15.53
$GdTl_3$	965	15.20	12.28
$TbTl_3$	950	12.54	10.25
$DyTl_3$	925	14.98	12.50
$YbTl_3$	585	9.71	11.32

DISCUSSION

Generally RE form with Sn, Pb, In and Tl series of isomorphous compounds, all crystallizing with the $AuCu_3$-type of structure, the only exception being: $EuIn_3$, $LuPb_3$, (Tb, Dy, Ho, Er, Tm, Lu)Sn_3. Compounds of Eu and Yb from magnetic measurements and lattice constant values are known to contain Eu^{2+} and Yb^{2+} and the values of the corresponding heats of formation agree with this assumption. In effect, if these rare earths were present in these phases in the trivalent state, their heats of formation, according to Gschneidner[7], should be about 23 and 9 kcal/g-at. greater (more positive), respectively, than the neighbouring trivalent RE compounds; the values of 23 and 9 kcal/g-at. being the energies required for the promotion of the extra

4f electron to a valence or outer electron level. This condition has never been verified for the compounds examined.

Examination of the data obtained and comparision with other "series", such as RECd[8] and REMg[9], lead to the conclusion that REX_3 are even more stable phases with increasing stability in the order Tl, Pb, In and Sn.

Recently Robinson and Bever[10] examined all thermodynamic data known for intermetallic compounds and showed that some indications concerning the type of bonding can be obtained simply by considering the magnitude of these data. The results obtained suggest for REX_3 compounds a chemical bond predominantly of the metallic type with ionic or covalent contributions, which are very small and increase in the series Tl, Pb, In and Sn.

The heats of formation for REX_3 compounds decrease from La to Lu and this behaviour, which is in agreement with the trend in the melting points, can be correlated with the lanthanide contraction in the compounds and compared with the contraction observed in the pure metals, as given by Gschneidner[11]. The unit cell volume of the REX_3 phases were divided by the atomic volume of the pure metal (RE) and these volume ratios were then divided by the volume ratio relative to the lanthanum compound giving a scale relative to lanthanum (1.000). The resulting values (Fig. 1) increase with RE atomic number, i.e., the lanthanide contraction in the compounds is less than in the pure metals and a decrease in the heats of formation can be expected in going from La to Lu. This result is evident for $REPb_3$[2], $RETl_3$, $REIn_3$ and at a lesser extent for $RESn_3$, due to the non-existence of some of these phases. This is also valid if we consider Ba, Eu and Yb as members of a "baride" family of divalent elements. Again, at least for isomorphous compounds, the volume ratio relative to barium and the heats of formation vs. atomic number should show the same trend for trivalent RE, as observed for $REPb_3$[2].

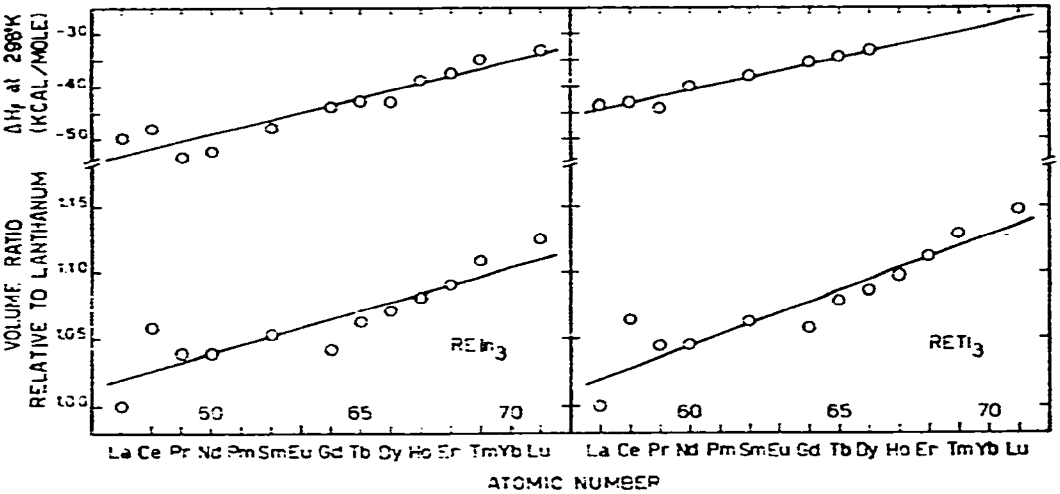

Fig. 1. Heat of formation and volume ratio for $REIn_3$ and $RETl_3$ compounds vs. atomic number.

According to recent work of Miedema[12], the heats of formation of binary alloys can be evaluated using a simple relation, which in case of REX_3 phases can be written as follows:

$$\Delta H = f(c)[-Pe(\Delta\phi^*)^2 + Q(\Delta n_{ws})^2 - R]$$

where

$f(c)$ = symmetrical function of the concentration;
$\Delta\phi^*$ = difference in the electronegativity parameter;
Δn_{ws} = difference in the electron density at the boundary of the Wigner–Seitz cells;
P, Q, R = experimental constants.

Although the relation does not take into account the particular type of structure adopted, it is possible to find a good agreement between observed and calculated values (Table 3). In these calculations the average values of ϕ^* and n_{ws} for RE were used but undoubtedly a better knowledge of these two functions, both for RE and partner elements, could lead to a higher degree of agreement with the experimental values.

TABLE 3
COMPARISON OF THE EXPERIMENTAL ΔH_f VALUES (kcal g-at.$^{-1}$) WITH THOSE CALCULATED FROM THE EQUATION OF MIEDEMA

	$\Delta H_{calc.}$	$\Delta H_{exp.}$
$LaSn_3$	−12.7	−15.1
$LaIn_3$	−11.0	−12.5
$LaPb_3$	−12.0	−12.3
$LaTl_3$	−12.7	−10.8

We have tried to correlate the heats of formation of these REX_3 compounds with a parameter which could take into account the dimensions of the elements involved, such as metallic, covalent or ionic radii. The best result is obtained when plotting the heats of formation of the REX_3 phases for a given rare earth, vs. the radii ratio $r(RE)/r(X)$ where $r(RE)$ is the ionic radius of the trivalent or divalent rare earth considered and $r(X)$ is the ionic radius of the X element corresponding to its higher valency state. The values of the ionic radii are taken from Ahrens[13]. In all cases (Fig. 2) a straight line is obtained, both for trivalent and divalent RE and also for those not reported in the figure. At a lesser extent a similar correlation seems to be valid using the covalent radii but not with the metallic radii.

The scatter in the value of $CeSn_3$ is not surprising as Ce in this compound has a valency higher than three[14], which causes a decrease in its ionic radius and is in better agreement with the straight line.

Even if the meaning of this correlation is not clear, it can be used to evaluate the heats of formation of the remaining isomorphous REX_3 phases. All the experimental

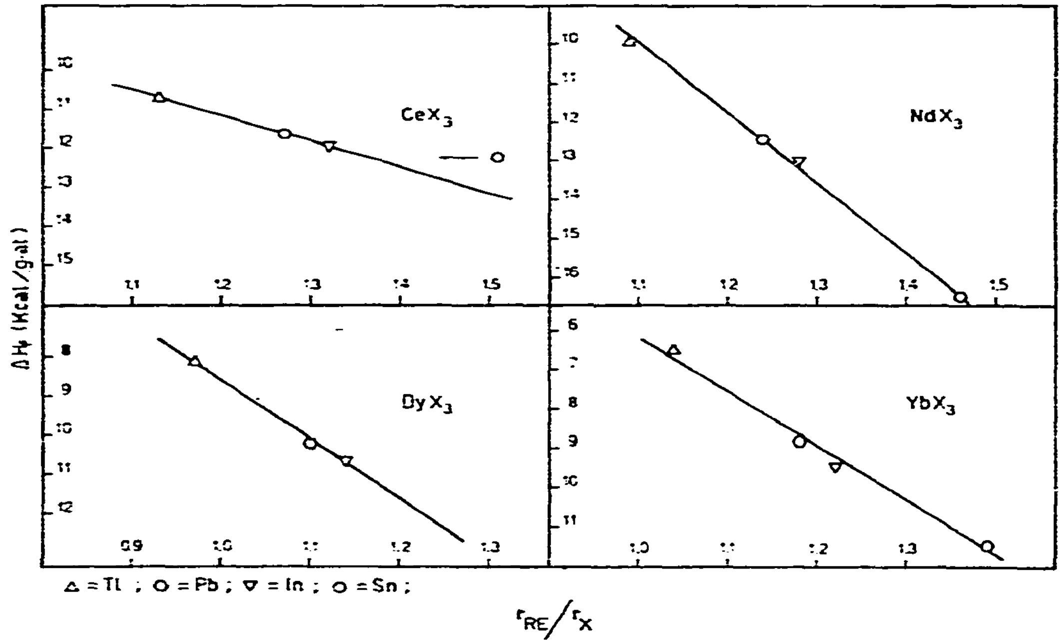

Fig. 2. Heats of formation vs. ionic radii ratio.

values were collected together and fitted to a straight line:

$$\Delta H_f = -11.10\, r(\mathrm{RE})/r(\mathrm{X}) + 2.27 \ (\pm 0.87 \text{ kcal/g-at.})$$

for trivalent RE and

$$\Delta H_f = -11.11\, r(\mathrm{RE})/r(\mathrm{X}) + 4.44 \ (\pm 0.40 \text{ kcal/g-at.})$$

for divalent RE.

As one can see, the coefficients of these two straight lines are slightly different from those reported previously[15], because for their determination we have also taken into account the values of the $\mathrm{REIn_3}$ phases which were not known[15], and probably could change again with the introduction of other values. Nevertheless the usefulness of such a correlation remains valid in the prediction of some ΔH_f values which, owing to experimental difficulties, can actually not be determined.

Such a correlation not only occurs for these $\mathrm{REX_3}$ phases but examining the literature data for the heats of formation of binary alloys we could find other "series" of compounds for which it also holds, such as: $\mathrm{Na_3}$(As, Sb, Bi); Sm(Zn, Cd, Hg); (Li, Na) (Sn, Pb, Tl); (Mg, Ca, Sr, Ba) (S, Se, Te); $\mathrm{Ga_2}$(S, Se, Te)$_3$; $\mathrm{Mg_2}$(Ge, Sn, Pb) and others.

Concluding, we can say that the DDC method can be employed with reasonable confidence when determining heats of formation and heats of fusion of intermetallic compounds. The method appears to prove itself competitive with other traditional techniques both for the total error (5–6%) which affects the results and for the speed and ease of operation. However, only highly exothermic and fast reactions, which lead to the complete formation of the desired compound, can be examined. The heats of formation of particular "series" of compounds can be correlated with the ionic radii ratios of the elements involved and such a correlation can be used in the prediction of some of these values whose experimental determination is actually impossible.

REFERENCES

1 A. Palenzona, *Thermochim. Acta*, 5 (1973) 473.
2 A. Palenzona and S. Cirafici, *Thermochim. Acta*, 6 (1973) 455.
3 M. M. Faktor and R. Hanks, *Trans. Faraday Soc.*, 63 (1967) 1122.
4 V. A. Degtyar, A. P. Bayanov, L. A. Vnuchkova and V. V. Serebrennikov, *Russ. J. Phys. Chem.*, 45 (1971) 1032.
5 V. A. Degtyar, A. P. Bayanov and V. V. Serebrennikov, *Tr. Tomsk. Gos. Univ.*, 204 (1971) 401.
6 O. Kubaschewski, E. L. Evans and C. B. Alcock, *Metallurgical Thermochemistry*, Pergamon Press, London, 1967.
7 K. A. Gschneidner, *J. Less-Common Metals*, 17 (1969) 13.
8 E. Veleckis, I. Johnson and H. Feder, *USAEC Report*, No. ANL-7175 (1966) 154.
9 J. R. Ogren, N. J. Magnani and J. F. Smith, *Trans. TMS-AIME*, 239 (1967) 766.
10 P. M. Robinson and M. B. Bever, in J. H. Westbrook (Ed.), *Intermetallic Compounds*, Wiley, New York, 1967, p. 38.
11 K. A. Gschneidner, *J. Less-Common Metals*, 17 (1969) 1.
12 A. R. Miedema, *J. Less-Common Metals*, 32 (1973) 117.
13 L. H. Ahrens, *Geochim. Cosmochim. Acta*, 2 (1952) 155.
14 J. R. Cooper, C. Rizzuto and G. L. Olcese, *J. Phys.* (*Paris*), *Colloq.*, *C1*, *Suppl. No. 2-3*, Tome 32, Fevrier–Mars 1971, C 1-1136.
15 A. Palenzona and S. Cirafici, paper presented at the *1974 A.C.S. Symposium on Analytical Calorimetry, April 5, Los Angeles, U.S.A.*