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Note

The heat of formation of the $YbAl_2$ compound

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The interest in the $YbAl_2$ compound is mainly due to its singular magnetic, electronic and crystallographic properties which have been studied extensively by several authors[1-4]. The expansion coefficient evaluated from X-ray diffraction experiments in the temperature range $-180 \div 600$°C shows an anomalous behavior if compared with those of other isostructural compounds such as $CaAl_2$ and $LuAl_2$. The magnetic susceptibility, in the same temperature range, does not follow the Curie-Weiss law and shows values intermediate between those corresponding to divalent or trivalent ytterbium compounds. On the assumption that $YbAl_2$ contains Yb^{II} and Yb^{III} ions in quantities depending on temperature, the results mentioned above can be explained[5], but, with a more realistic model[6], for each ytterbium ion transitions or fluctuations may occur between the two valence states depending on temperature, giving rise to interesting properties.

The available data on the thermodynamic properties of $YbAl_2$ are however scarce: Kulifeev et al.[7] in a work concerning the production of pure Yb by aluminothermic reduction of Yb_2O_3, derived the following expression for the Gibbs free energy of formation of $YbAl_2$ valid in the temperature range 500 to 600°C:

$$\Delta G_f^0 = -17473.16 \div 9405\,T \text{ cal mol}^{-1}$$

from which

$$\Delta H_f^0 = -17.5 \text{ kcal mol}^{-1}$$

We have, therefore, undertaken a research in order to determine some of these properties and here we report the results of two independent determinations of the standard heat of formation for $YbAl_2$.

EXPERIMENTAL AND RESULTS

DDC method

The dynamic differential calorimetric method previously described[8] is based on the direct measurement of the heat evolved in the reaction of compound formation from the elements. The mixture of the two reacting metals, closed in a Ta crucible, is heated at a constant rate, together with a reference substance, until reaction occurs. The heat evolved is then evaluated by using a calibration curve obtained from elements with known heat of fusion.

The method has been employed for the measurements of heats of formation, heats of fusion, and heats of transformation of a wide number of intermetallic compounds of the rare earths, Y, Th, and U[9, 10], and proved to have a good reliability. Ytterbium reacts easily with aluminum at its melting point according to the reaction:

$$\mathrm{Yb(s)} + 2\mathrm{Al(l)} = \mathrm{YbAl_2(s)} + \Delta H_f^0\ (T = 660\,^\circ\mathrm{C}) \qquad (1)$$

Several samples have been prepared, examined micrographically and by X-ray, disregarding those not perfectly homogeneous and single phase. The mean value obtained from these experiments was: ΔH_f^0 (660°C) = −24.0 kcal mol^{-1}. By use of known thermodynamic data for the elements[11] and of the heat capacity of $YbAl_2$, recently determined in our laboratories[12] as: $C_p(YbAl_2) = 17.40 + 1.40 \times 10^{-2}\, t(^\circ C)$ in the temperature interval 0–150°C and 20.16 cal deg^{-1} mol^{-1} in the temperature interval 150–800°C, the standard heat of formation for $YbAl_2$ was found to be: ΔH_f^0 (25°C) = −18.2 kcal mol^{-1}.

Effusion method

The experimental technique used to determine the vapour pressure of Yb(g) over the $YbAl_2$(s) intermetallic phase and, accordingly, to derive the thermodynamic functions for its formation, was the Knudsen effusion-weight loss method. The rate of the mass loss of the sample effusing from a classical Knudsen cell was recorded with a Setaram Ugyne-Eyraud model B60 vacuum microbalance. Details of the experimental apparatus and method employed have been reported elsewhere[13, 14]. In the present case, the Knudsen cell was made of tantalum and had an effusion hole 1 mm in diameter drilled in a tantalum foil 0.05 mm thick. The vapour pressure measurements on the $YbAl_2$ sample prepared as described in the previous section were made in the temperature interval 847°–1023°C assuming the following incongruent vaporization reaction:

$$\mathrm{YbAl_2(s)} = \mathrm{Yb(g)} + 2\mathrm{Al(l)} \qquad (2)$$

The vapour pressure data (a set of ten points) were fitted to the least-squares equation:

$$\log P(\mathrm{atm}) = (5.49 \pm 0.15) - (12792 \pm 174)/T \qquad (3)$$

where the errors associated to the constants are standard deviations. From the slope and intercept of eqn (3), the enthalpy and entropy of sublimation of Yb(g) from the compound at the average temperature of 935°C were found to be: 58.54 ± 1.74 kcal mol^{-1} and 25.1 ± 1.5 cal deg^{-1} mol^{-1}, respectively. These values were combined with the data relative to the vaporization of pure ytterbium[11] to yield the enthalpy and entropy of formation of $YbAl_2$ at 935°C: ΔH_f^0 (935°C) = −26.72 ± 0.17 kcal mol^{-1}, ΔS_f^0 (935°C) = −3.3 ± 1.5 cal deg^{-1} mol^{-1}.

By use of the heat capacity of $YbAl_2(s)$ and the enthalpic functions relative to Yb(g), Yb(l), Al(l)[11], the standard heat of formation for $YbAl_2(s)$ was found to be: ΔH_f^0 (25°C) = -18.5 kcal mol^{-1}.

DISCUSSION

As one can see, the results of the two independent measurements are in very good agreement and lead to a mean value of -18.4 ± 0.5 kcal mol^{-1} for the standard heat of formation of $YbAl_2$ while the value of Kulifeev et al.[7] seems to be too small.

If compared with other isostructural MAl_2 phases, where M = Ca, rare earths, Y and U, the value for $YbAl_2$ resembles that of U (-22.4 kcal mol^{-1}) more than that of a rare earth (La: -36.0; Ce: -39.0 kcal mol^{-1}). This fact could be due to the decrease in the heats of formation with the increase in the atomic number, generally observed in most isostructural series of rare earth compounds and, in part, to the energy required for the interconfigurational fluctuations valence of the Yb ions.

A more useful comparison would result with the neighbouring RAl_2 compounds, $TmAl_2$ and $LuAl_2$, with regard to the heat of formation and heat capacity, but, due to experimental difficulties, most of these data are not available and their acquisition will be the object of further investigations.

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