Monatshefte für Chemie 117, 1157–1164 (1986)

Monatshefte für Chemie
Chemical Monthly

Note on Thermodynamic Instability of M_4C_3-Type Carbides of Gallium Group Metals

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(Received 17 June 1985. Revised 13 January 1986. Accepted 10 February 1986)

The paper deals with thermodynamic stability of hypothetical solid binary M_4C_3 carbides of gallium, indium and thallium. Heats of formation whose contribution to the stability of these compounds is dominant, were estimated by two independent methods: semiempirical theory of *Miedema* and empirical trends in the heats of formation of nitrides and carbides of Group III elements. Entropies were calculated with the use of the *Cantor* equation. The estimated values suggest that M_4C_3 carbides of gallium, indium and thallium are thermodynamically unstable with regard to their decomposition to elements.

(Keywords: Carbide; Gallium; Indium; Thallium; Thermodynamics; Stability)

Über die Instabilität von Galliumgruppenkarbiden des Typs M_4C_3

Es wird die thermodynamische Stabilität von hypothetischen Gallium-, Indium- und Thalliumkarbiden diskutiert. Zur Abschätzung von Bildungswärmen, deren Beitrag zur Stabilität dieser Verbindungen dominant ist, wurden zwei unabhängige Methoden verwendet: die semiempirische *Miedema*-Theorie und empirische Trends der Bildungswärmen bei den Nitriden und Karbiden der Elemente der III. Gruppe. Die Entropiewerte wurden mittels der *Cantor*-Gleichung berechnet. Aus den abgeschätzten Werten geht hervor, daß die Galliumgruppenkarbide bezüglich der Zersetzung in die Elemente thermodynamisch instabil sind.

Introduction

The realization of any compound is conditioned by its thermodynamic stability with respect to decomposition into single elements. A rough estimation of the course of reaction

$$M_4C_3 = 4\,M + 3\,C \qquad (1)$$

at a given temperature and pressure can be obtained with the use of expression

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{2}$$

since all the components participating in the reaction are in the condensed state and thus only a slight temperature dependence of heats of reaction and reaction entropies can be expected.

The estimation of standard heats of formation ΔH_f° and standard entropies S° of non-existing compounds is a complex problem and a number of approaches have been suggested. These methods are either based on the monotonic change of properties in a homologous set of compounds in a certain group of the periodical system, or they consider the property of a compound as a sum of atomic contributions.

The aim of this paper is to contribute towards clarifying the question of non-existence of binary M_4C_3 carbides of gallium, indium and thallium, mainly on the thermodynamic basis.

Results

Estimation of Heats of Formation

A number of methods have been described in literature for the estimation of heats of formation on the basis of component contributions. However, they can be used only for systems forming homogenous and relatively simple bonds such as ionic crystals or alloys of simple metals.

Miedema and co-workers [1] have suggested a simple semiempirical structureless model for binary systems which exhibits remarkable results in the estimation of heats of formation mainly for alloys of transition and non-transition metals, but also for carbides, nitrides, borides and silicides of transition metals [2, 3]. The model has not yet been used for carbides and nitrides of non-transition metals.

According to the model, the heat of formation for one mole of atoms in the $A_{x_A}B_{x_B}$ system is

$$H_f = \frac{2\, C_A C_B [1 + 8(C_A C_B)^2] (x_A V_A^{2/3} + x_B V_B^{2/3})}{(n_{ws}^A)^{-1/3} + (n_{ws}^B)^{-1/3}} \cdot$$

$$\cdot - P(\varphi_A - \varphi_B)^2 + Q(n_{ws}^A)^{1/3} - (n_{ws}^B)^{1/3\,2} \tag{3}$$

where

$$C_i = \frac{x_i V_i^{2/3}}{x_A V_A^{2/3} + x_B V_B^{2/3}}$$

is the molar surface fraction of component i, x_i, V_i and φ_i its molar fraction, molar volume and electronegativity, respectively, and n_{ws} is the surface density of electrons in *Wigner-Seitz* cells of pure components. To evaluate the adjustable parameters P and Q it is necessary to know the heats of formation of at least two analogical compounds. Since carbides of non-transition elements of Group III offer only this basic possibility, we have firstly verified the procedure with a series of nitrides of these elements for which the heats of formation are known [4]. With tabulated values [3] of V, φ and n_{ws} and experimental values [4]

$$h(\mathrm{BN}) = \frac{H_f^\circ(\mathrm{BN})}{R\,298} = -102, \quad h(\mathrm{AlN}) = -129$$

equation (3) yields:

$$h(\mathrm{GaN}) = -101, \quad h(\mathrm{InN}) = -29 \quad \text{and} \quad h(\mathrm{TlN}) = +12$$

The corresponding selected experimental values [4] are:

$$h(\mathrm{GaN}) = -81, \quad h(\mathrm{InN}) = -52 \quad \text{and} \quad h(\mathrm{TlN}) = -32$$

but their uncertainty rapidly increases with increasing atomic number of the metal and thus for TlN the selected value is merely a rough estimate.

Similarly for parameters P and Q evaluated from values [5] $h(B_4C) = -29$ and $h(Al_4C_3) = -84$ eq. (3) yields:

$$h(\mathrm{Ga_4C_3}) = +71, \quad h(\mathrm{In_4C_3}) = +368 \quad \text{and} \quad h(\mathrm{Tl_4C_3}) = +530.$$

The estimated values of the heats of formation of hypothetical carbides can be tested independently by comparing their systematic changes in the group. Such a change in a set of analogical compounds can be described, according to some authors, by the expression [6]

$$\frac{h}{n} = \log Z + \text{const.} \tag{4}$$

where n is the number of atoms in the formula and Z is the atomic number of metal.

It is obvious from Fig. 1 that with regard to the uncertainty of experimental data eq. (4) is satisfying for the Al-Ga-In-Tl sets of oxides (data [7]) and nitrides, regardless of their structural differences. Qualitative harmony with these trends is exhibited also by the course of experimental and estimated values of B_4C, Al_4C_3, Ga_4C_3, In_4C_3 and Tl_4C_3.

If eq. (4) satisfies two sets of compounds MX and MY, the following correlation may be expected:

$$\frac{h(MX)}{n} = a\frac{h(MY)}{m} + b \tag{5}$$

Fig. 2 shows these correlations for oxides and carbides of Al, Ga, In and Tl with nitrides as reference compounds. With the use of constants a, b

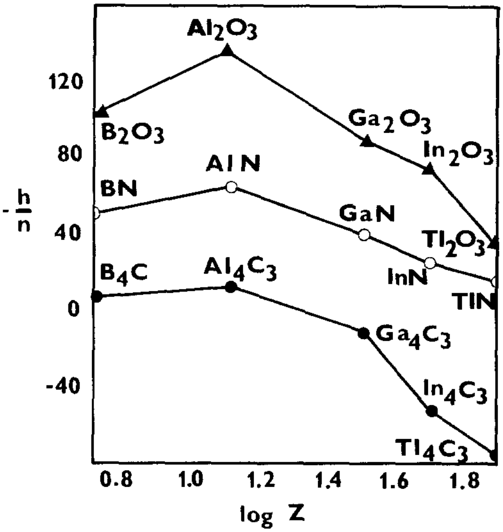

Fig. 1. Heats of formation of oxides, nitrides, and carbides of Group III non-transition elements

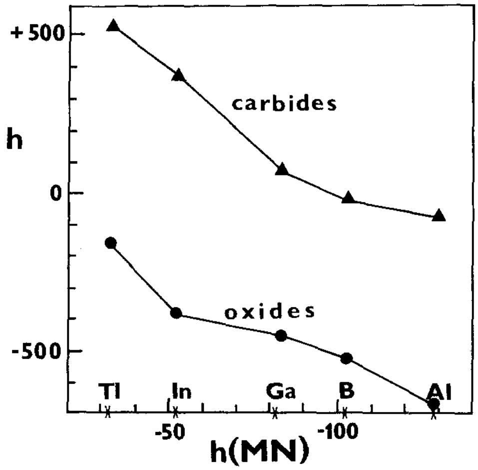

Fig. 2. Correlation between heats of formation of oxides, nitrides and carbides of Group III non-transition elements

evaluated from experimental values of carbides and nitrides of boron and aluminium, eq. (5) yields, after substituting the heats of formation of corresponding nitrides, the following estimates:

$$h(\mathrm{Ga_4C_3}) = -7, \quad h(\mathrm{In_4C_3}) = +40, \quad h(\mathrm{Tl_4C_3}) = +72.$$

The results based on the two completely independent estimations of the heats of formation of hypothetical carbides of the gallium group metals show identical conspicuous transition to positive values with increasing atomic number. The most probable values, i.e. the arithmetic means of the estimates, are given in Table 1.

Table 1. *Estimated heats of formation of hypothetical carbides*

Carbide	Ga_4C_3	In_4C_3	Tl_4C_3
$\frac{\Delta H_f^\circ}{\text{kJ/mol}}$	$+80(\pm 100)$	$+500(\pm 400)$	$+750(\pm 550)$

Estimation of Entropy

Kriplovich and *Paukov* [8] have tested a number of empirical expressions for the estimation of standard entropies of inorganic compounds. Weighing their results we have decided to use *Cantor*'s expression [9] which requires the value of entropy of only one reference compound. The reference compound used should be most closely related to the compound whose entropy is to be estimated, preferably it should be of the same bond type and number of atoms n in the formula. However, the use of *Cantor*'s equation for hypothetical compounds is hindered by unknown values of their molar volumes.

Nevertheless, for oxides and nitrides of Al, Ga, In and Tl, and for Al_4C_3 carbide we have found a very good correlation

$$\alpha r_A^3 + \beta r_B^3 = \mathit{const.}\, V \tag{6}$$

where r_i are covalent radii [10] and V are molar volumes of compounds A_α/B_β evaluated from crystallographic data [11, 4]. This correlation is illustrated in Fig. 3.

Substitution of expression (6) to the *Cantor*'s equation yields:

$$\frac{S_x^\circ}{R} = \frac{S_{ref}^\circ}{R} + 1.5(\alpha + \beta)\cdot \ln \frac{M_x\,(\alpha r_A^3 + \beta r_B^3)_x^{2/3}}{M_{ref}(\alpha r_A^3 + \beta r_B^3)_{ref}^{2/3}} \tag{7}$$

where S° and M are standard entropy and relative molecular mass, the subscripts x and ref correspond to the studied and reference compounds.

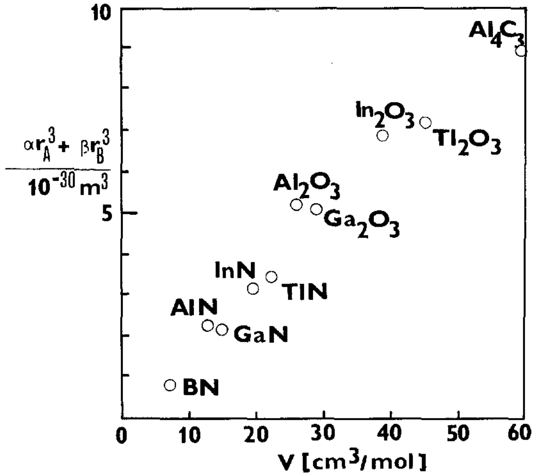

Fig. 3. Correlation between covalent radii and molar volumes of some $A_\alpha B_\beta$ compounds of Group III elements

Table 2 presents standard entropies of oxides, nitrides and carbides of Ga, In and Tl calculated with the use of *Cantor*'s original equation and the expression (7) with Al_2O_3, AlN and Al_4C_3 as reference compounds together with experimental values [4, 5, 7].

It is noteworthy that the substitution of another approximation to *Cantor*'s equation improves the agreement between the calculated and experimental values in all the given cases.

Table 2. *Calculated and experimental standard entropies of oxides, nitrides and carbides of metals of gallium group*

Compound	$\frac{S^\circ}{R}$ (*Cantor*'s eq.)	$\frac{S^\circ}{R}$ (eq. 7)	$\frac{S^\circ}{R}$ (exp.)
Al_2O_3	—	—	6.4
Ga_2O_3	11.6	10.9	10.2
In_2O_3	16.0	15.4	12.5
Tl_2O_3	20.4	19.3	19.1
AlN	—	—	2.42
GaN	4.7	4.5	4.4
InN	6.6	6.5	5.1
TlN	8.5	8.1	7.0
Al_4C_3	—	—	12.6
Ga_4C_3	—	20.8	—
In_4C_3	—	28.8	—
Tl_4C_3	—	33.9	—

Discussion

Using entropic data [5] for carbon, gallium, indium and thallium and estimated values presented in Tables 1 and 2, the following relations may be given for the decomposition of hypothetical carbides at constant temperature and pressure:

$$\frac{\Delta G^\circ(\mathrm{Ca_4C_3})}{\mathrm{J/mol}} = -80\,000 - T \cdot 7.9$$
$$\frac{\Delta G^\circ(\mathrm{In_4C_3})}{\mathrm{J/mol}} = -500\,000 - T \cdot 9.2 \qquad (8)$$
$$\frac{\Delta G^\circ(\mathrm{Tl_4C_3})}{\mathrm{J/mol}} = -750\,000 + T \cdot 7.9$$

It is thus evident that:

a) carbides of gallium, indium and thallium are thermodynamically unstable with respect to decomposition to elements

b) effects of entropy change during the decomposition reaction are small compared to those of enthalpy changes so that the carbides are unstable in a wide temperature range.

Thermodynamic instability does not mean that the compound cannot exist as for it may be stabilized kinetically. However, since carbides are prepared at higher temperatures, the kinetic hindrances cannot come into effect. Thus, it may be concluded that the main cause of the non-existence of M_4C_3-type carbides of the gallium group is the thermodynamic instability resulting from strongly endothermic heats of formation. According to the theory of *Miedema,* these positive values can be explained by the difference of electron densities at the interface of atomic cells of carbon and the gallium group metals. In ternary carbides of these metals the number of the destabilizing contacts decreases with the addition of a transition element. This explanation agrees with the reported fact that only in the ternary carbides gallium, indium and thallium can coexist with carbon in the solid state [12].

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