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# Determination of the standard enthalpies of formation of $Pd_2Ga$ and PdGa by high-temperature direct synthesis calorimetry

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**Abstract**

The standard enthalpies of formation of PdGa and $Pd_2Ga$ have been determined by high-temperature direct synthesis calorimetry at (1473 ± 2) K. The following values of $\Delta_fH^0$ in kJ (mol of atoms)$^{-1}$ are reported: PdGa (−71.6 ± 2.3); $Pd_2Ga$ (−64.4 ± 2.0). The results are compared with reported calorimetric data and with predicted values from the semi-empirical model of Miedema et al. © 1997 Elsevier Science B.V.

*Keywords:* Calorimetry; Enthalpy of formation; Palladium–Gallium alloys; Thermodynamics

## 1. Introduction

During recent years, we have conducted in this laboratory systematic studies of the thermochemistry of transition metal and rare-earth (RE) carbides, silicides, germanides and borides by high-temperature calorimetric methods [1]. These investigations began with the work of Topor and Kleppa on some characteristic borides and silicides of Group III metals [2–4] and, subsequently, by Jung and Kleppa on the corresponding germanides [5]. In addition, the present authors also studied the thermochemistry of 3*d*, 4*d* and 5*d* aluminides [6–8]. During the past three years, this study was extended to the enthalpies of formation of Group III carbides [9] and, most recently, to the carbides, silicides, germanides, stannides and borides of the lanthanide elements [9–13].

In our systematic studies of the RE metals with Group IVB and IIIB elements, we noted the special position of Ga in the periodic table. As a neighbor of Al, one might expect its compounds to exhibit thermochemical behavior similar to the transition metal and rare-earth aluminides. We noted in previous communications that the enthalpies of formation of the compounds of the lanthanide elements with IVB elements exhibit a roughly parabolic relationship when plotted against the IVB elements [10–13]. In these correlations, the germanides always have the most exothermic enthalpy of formation. We also demonstrated that a similar relationship exists for the compounds of the lanthanide elements with the IIIB elements [10–13]. In these correlations, the gallides are in the same position as the germanides. Hence, they might be expected to have the most exothermic enthalpies of formation. However, for most of the rare-earth gallide systems, we found no enthalpy of formation data in the published literature. We also

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searched the literature for thermochemical information on transition metal gallides, and again found that relatively few systems have been studied. The gallides of Fe, Co, Ni, Pd and Pt have been studied by Vogelbein et al., Predel et al. and by Martosudirjo and Pratt, all by tin and lead solution calorimetry [14–17]. The enthalpies of formation of $Mo_3Ga$, PtGa and some phases in the Pd–Ga system were measured by direct synthesis calorimetry by Han et al. [18], Anres et al. [19], El Allam et al. [20] and Pratt et al. [21], respectively. The published literature also offers thermodynamic information on some transition-metal and lanthanide gallides derived from EMF measurements [22–30]. The heat conductivity of $V_3Ga$ was studied in some detail, since it exhibits superconducting properties along with $Nb_3Al$, $Nb_3Ge$ and $Nb_3Sn$ [31]. These compounds belong to a class of superconductors which possess relatively high superconducting temperatures and, hence, are potential candidates for technological applications.

Since the enthalpies of formation provide valuable information on the thermochemical stability and bonding character of the compounds, a systematic study of transition-metal and lanthanide gallides is of significant interest. For this reason, we decided to expand our study of the alloys of the transition and lanthanide metals with the group IIIB elements in the periodic table to include the gallides.

In the present paper, we report our first measurements of the standard heat of formation of two transition metal gallides, $Pd_2Ga$ and PdGa, by high-temperature direct synthesis calorimetry. We selected the Pd–Ga system, which has been studied by several investigators, to make sure that our new technique is fully compatible with measurements by other methods before embarking on larger scale systematic work.

The phase diagram and the structures of several compounds in the Pd–Ga system are well documented [32]. Although Massalski et al. do not include the phase $Pd_3Ga$ in the most recent phase diagram available [32], the published literature offers a value for the heat of formation of an alloy of this composition obtained by tin and lead solution calorimetry [14]. We also found heats of formation for both $Pd_2Ga$ and PdGa by high-temperature direct synthesis calorimetry [20,21]. The heats of formation by solution calorimetry apply at 1000 K [14], while the values obtained by direct synthesis calorimetry are referred to 1410 K [20] and 320 K [21], respectively. The reference state of gallium is the solid metal in the determinations by Vogelbein et al. [14] and Pratt [21], but liquid gallium in the measurements by El Allam et al. [20]. The reference state of the metal and the adopted temperature by Pratt [21] is fairly similar to that used in our work. We will compare our results with the earlier data and also with the predictions based on the semi-empirical model of Miedema et al. [33].

## 2. Experimental and materials

The experiments were carried out at (1473 ± 2) K in a single unit differential microcalorimeter which has been described in an earlier communication from this laboratory [34]. All the experiments were performed under a protective atmosphere of argon gas, which was purified by passing it over titanium chips at 900°C. A boron nitride crucible was used to contain the samples.

Pd was purchased from Johnson Matthey/Aesar, Ward Hill, MA, while the Ga metal was obtained some years ago from Alcoa. The Ga metal was reported to be 99.99% pure, while the purity of Pd was 99.95%. The particle size of Pd was 200 mesh. Gallium melts at 29°C. Since its melting point is so close to room temperature, we anticipated some problems with the preparation of the alloy samples. We kept the Ga sample in the refrigerator until it was ready to be powdered. We crushed it as well as possible in an agate mortar, while keeping it colder than room temperature, which was ~25°C. In this way, we were able to prepare small chips rather than a true powder. In the preparation of the pellets the pressure applied in the press proved to be critical. Since this process generates some heat, the pressure was kept very low. If not, the Ga metal squeezes out of the sample. Fortunately, this problem can be checked by monitoring the weight of the pressed pellet compared to the weight of the unpressed mixture.

The two components were carefully mixed in the appropriate molar ratio, pressed into 4 mm pellets and dropped into the calorimeter from room temperature. In a subsequent set of experiments, the reaction products were dropped into the calorimeter from room temperature to measure their heat contents. Between the two sets of experiments the samples were kept in the refrigerator in a closed container.

Calibration of the calorimeter was achieved by dropping weighed 4 mm diameter pellets prepared from 2 mm OD high-purity copper wire from room temperature into the calorimeter at (1473 ± 2) K. We believe that by using copper pellets of similar size and geometry to the sample pellets, rather than wire segments, we may improve our experimental precision. The enthalpy of pure copper at 1473 K, 46.465 kJ (mol of atoms)$^{-1}$, was obtained from Hultgren et al. [35]. The calibrations were reproducible to within ±1.2%.

The reacted samples were examined by X-ray powder diffraction to assess their structures and to ascertain the absence of unreacted metals. The results of these analyses were conclusive. Hence, we did not feel the need to check the samples further by X-ray microprobe analysis.

## 3. Results and discussion

The phase diagram of the Pd–Ga system shows several congruently melting compounds, namely $Pd_2Ga$, which melts at 1265°C, PdGa which melts at 1045°C and $Pd_5Ga_4$ for which the melting point is not listed [32]. The structures of several compounds in the Pd–Ga system are found in the ASTM powder diffraction file. However, the structures of the congruently melting compounds $Pd_2Ga$ and PdGa are not included. We therefore generated the X-ray diffraction patterns of these compounds from the available unit cell parameters and the atomic coordinates [36]. We prepared both of these compounds in the calorimeter. The X-ray diffraction patterns of both $Pd_2Ga$ and PdGa showed excellent agreements with the computer generated patterns. We found no unreacted metals or any other phases. The most intense lines in the generated patterns are presented in Table 1.

The standard enthalpies of formation of the palladium gallides, determined in this study, were obtained as the difference between the results of two sets of measurements. In the first set, the following reaction takes place in the calorimeter:

$$\mathrm{Pd(s,\ 298\,K)} + m\mathrm{Ga(s,\ 298\,K)} = \mathrm{PdGa}_m\mathrm{(s\,or\,l,\ 1473\,K)} \quad (1)$$

where $m$ is the molar ratio in the considered compounds.

The reacted pellets were re-used in a subsequent set of measurements to determine their heat contents:

$$\mathrm{PdGa_m(s,\ 298\,K)} = \mathrm{PdGa_m(s\,or\,l,\ 1473\,K)} \quad (2)$$

The standard enthalpy of formation is given by

$$\Delta_f H^0 = \Delta H(1) - \Delta H(2) \quad (3)$$

where $\Delta H(1)$ and $\Delta H(2)$ are the enthalpy changes per mol of atoms in the compound associated with Eq. (1) and Eq. (2).

The experimental results are summarized in Table 2. The second column shows the melting point of the phase. The heat effects associated with Eq. (1) and Eq. (2) are given in kJ (mol of atoms)$^{-1}$ as the

Table 1
Structural information for PdGa and $Pd_2Ga$, based on unit cell parameters and atomic coordinates given by Pearson [36]

| Compound | Structure type; space group no. | Generated X-ray diffraction pattern; most prominent lines | | |
|---|---|---|---|---|
| | | d | 2Θ | Intensity |
| PdGa | FeSi; 198 | 2.8665 | 31.18 | 16.3 |
| | | 2.2204 | 40.60 | 100.0 |
| | | 2.0269 | 44.67 | 54.0 |
| | | 1.3269 | 70.97 | 24.0 |
| $Pd_2Ga$ | $Co_2Si$; 62 | 2.5063 | 35.80 | 28.3 |
| | | 2.2756 | 39.57 | 59.2 |
| | | 2.2469 | 40.10 | 31.5 |
| | | 2.1929 | 41.13 | 100.0 |
| | | 2.1848 | 41.29 | 79.7 |

Table 2
Standard enthalpies of formation of $Pd_2Ga$ and PdGa. Data in kJ (mol of atoms)$^{-1}$

| Compound | M.P. (°C) | $\Delta H(1)$ [a] | $\Delta H(2)$ [a] | $\Delta_f H^0$ |
|---|---|---|---|---|
| PdGa | 1045 | −20.5 ± 1.2(5) | 51.1 ± 2.0(5) | −71.6 ± 2.3 |
| $Pd_2Ga$ | 1265 | −29.7 ± 1.7(3) | 34.7 ± 1.1(3) | −64.4 ± 2.0 |

[a] Numbers in parentheses indicate numbers of experiments averaged.

Table 3
Comparison of the measured standard enthalpies of formation with some experimental data in the literature and with predicted values from the semi-empirical model of Miedema et al. [33]. Data in kJ (mol of atoms)$^{-1}$

| Compound | $\Delta_f H^0$ (exptl); this study Pd(s), Ga(s) | $\Delta_f H^0$ (exptl); literature | Method | $T$/K; ref. state | $\Delta_f H^0$ (pred.) |
|---|---|---|---|---|---|
| PdGa | −71.6 ± 2.3 | −71.7 ± 5 | Calor. [20] | 1322 K; Ga(l) | −79 |
| | | −72.19 ± 0.3 | Calor. [21] | 320 K; Ga(s) | |
| $Pd_2Ga$ | −64.4 ± 2.0 | −77.9 ± 5 | Calor. [20] | 1410 K; Ga(l) | −66 |
| $Pd_3Ga$ | — | −59.1 ± 1.7 | Solution<br>Calor. [14] | 1000 K; Ga(s)<br>Pb solvent | −51 |
| | | −59.2 ± 1.3 | Calor. [14] | 1000 K; Ga(s) Sn solvent | |

averages of 3–5 measurements with the appropriate standard deviations. The last column shows the standard enthalpies of formation of $Pd_2Ga$ and PdGa. The standard deviations given in the last column include a small contribution from the uncertainties in the calibrations. The samples were kept for 5–10 min on a solid brass block maintained at ~23°C prior to dropping them into the calorimeter.

In Table 3, we compare the standard enthalpies of formation reported in the present study with experimental values from the published literature and with the predicted values from the semi-empirical model of Miedema et al. [33]. Table 2 shows that our value for the enthalpy of formation of PdGa agrees very well with the value obtained by Pratt et al. [21], where the temperature and reference state of Ga are similar to ours. The heat of fusion of Ga at the melting point is 5.6 kJ (mol of atoms)$^{-1}$ [35]. If we make the usual assumption that the heat of fusion of the pure metal does not vary with temperature, we can adjust the heat of formation of PdGa reported by El Allam et al. [20] for the contribution of the heat of fusion. That will make the value 2.8 kJ (mol of atoms)$^{-1}$ less exothermic, i.e. −68.9 kJ (mol of atoms)$^{-1}$ for Ga(s), at 1322 K. The agreement with our value at 298 K is still quite good. However, our value for the enthalpy of formation of $Pd_2Ga$ does not agree with the value reported by El Allam et al. [20]. This value was measured at 1410 K and the reference state of Ga is liquid. For the molar composition $Pd_2Ga$, the contribution of the heat of fusion is 1.9 kJ (mol of atoms)$^{-1}$. This makes the heat of formation for $Pd_2Ga$ of El Allam et al. [20] −76.0±5 kJ (mol of atoms)$^{-1}$ for the reference state Ga(s) at 1410 K. Even with this adjustment the difference from our value is very considerable. If we compare our new value for $Pd_2Ga$ with the value for $Pd_3Ga$ of Vogelbein et al. [14], we find reasonable agreement, consistent with the small difference in the mole fractions. The observed enthalpy differences suggest that the enthalpy of formation has a simple $X(1-X)$ dependence on composition. In fact, all the heat of formation values listed in Table 2 correlate roughly with the $X(1-X)$ relationship except for the value for $Pd_2Ga$ reported by El Allam et al. [20].

Our experimental measurements agree well with the values predicted by the semi-empirical model of Miedema et al. [33].

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## References

[1] O.J. Kleppa, J. Phase Equilibria, 15 (1994) 240.
[2] L. Topor and O.J. Kleppa, J. Chem. Thermodyn., 16 (1984) 993.
[3] L. Topor and O.J. Kleppa, Met. Trans. B, 20 (1989) 879.
[4] L. Topor and O.J. Kleppa, J. Less Common Metals, 167 (1990) 91.
[5] W.G. Jung and O.J. Kleppa, J. Less Common Metals, 169 (1991) 85.
[6] S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds, 191 (1993) 111.
[7] S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds, 197 (1993) 75.
[8] S.V. Meschel and O.J. Kleppa, Metallic alloys: Experimental and theoretical perspectives, J.S. Faulkner and R.G. Jordan (Eds.), Kluwer Academic Publ., The Netherlands (1994) p. 103–12.
[9] S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds, 205 (1994) 165.
[10] S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds, 221 (1995) 37.
[11] S.V. Meschel and O.J. Kleppa, J. Alloy and Compounds, 224 (1995) 345.
[12] S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds, 233 (1996) 272.
[13] S.V. Meschel and O.J. Kleppa, J. Alloys and Compounds, 234 (1996) 137.
[14] W. Vogelbein, M. Ellner and B. Predel, Thermochim. Acta, 44 (1981) 141.
[15] B. Predel, W. Vogelbein and U. Schallner, Thermochim. Acta, 12 (1975) 367.
[16] B. Predel and W. Vogelbein, Thermochim. Acta, 13 (1975) 133.
[17] S. Martosudirjo and J.N. Pratt, Thermochim. Acta, 17 (1976) 183.
[18] Q. Han, R. Schmidt-Fetzer, A. Belgacem-Bouzida, J. Charles, M. Notin and J. Hertz, J. Chim. Phys., 90 (1993) 445.
[19] P. Anres, M. Gaune-Escard and J.P. Bros, J. Alloys and Compounds, 234 (1996) 264.
[20] D. El Allam, M. Gaune-Escard, J.P. Bros and E. Hayer, Metall. Trans., 23B (1992) 39.
[21] J.N. Pratt, A.W. Bryant and D.T. Underhill, Final Technical Report, U.S. Army Res. Contract, DAJA 37-70-C-0632 (1971).
[22] V.N. Eremenko, G.M. Lukashenko and V.R. Sidorko, Sov. Phys. Dokl., 29 (1984) 509.
[23] I. Katayama, N. Kemori and Z. Kozuka, Trans. Jpn. Inst. Met., 16 (1975) 423.
[24] L.V. Goncharuk and G.M. Lukashenko, Russ. Metall., #, 1 (1981) 57.
[25] L.A. Vnuchkova, A.P. Bayanov and V.V. Serebrennikov, Russ. J. Phys. Chem., 46 (1972) 617.
[26] L.A. Vnuchkova, A.P. Bayanov and V.V. Serebrennikov, Russ. J. Phys. Chem., 46 (1972) 618.
[27] V.V. Serebrennikov, E.I. Perov, T.M. Shkolnikova and V.A. Novozhenov, Russ. J. Phys. Chem., 45 (1971) 790.
[28] I. Katayama, S. Igi and Z. Kozuka, J. Jpn. Inst. Met., 38 (1973) 332.
[29] A.P. Bayanov, N.A. Soboleva and E.N. Ganchenko, Izv. Akad. Nauk, SSSR, Metally, 1 (1975) 198.
[30] L.F. Yamshchikov, V.A. Lebedev, I.F. Nichkov, S.R. Raspopin and O.K. Kokoulin, Russ. J. Phys. Chem., 53 (1979) 657.
[31] B. Mitrovic, E. Schachinger and J.P. Carbotte, Phys. Rev., B29 (1984) 6187.
[32] T.B. Massalski, H. Okamoto, P.R. Subramanian and L. Kacprzak (Eds.), Binary Alloy Phase Diagrams, ASM, Metals Park, OH, 2nd edn. (1990).
[33] A.K. Niessen, F.R. deBoer, R. Boom, P.F. deChatel, W.C.M. Mattens and A.R. Miedema, Calphad, 7 (1983) 51.
[34] O.J. Kleppa and L. Topor, Thermochim. Acta, 139 (1989) 291.
[35] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, Selected Values of the Thermodynamic Properties of the Elements, ASM, Metals Park, OH (1973).
[36] P. Villars and L.D. Calvert, Eds., Pearson's Handbook of Crystallographic Data for Intermetallic Phases, ASM, Metals Park, OH (1985).