Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 885–888

ENTHALPIES OF FORMATION OF THE TELLURITES OF THE RARE EARTHS Gd, Tb, Dy, Tm AND Yb

G. G. Gospodinov and G. Baikusheva-Dimitrova

Prof. Assen Zlatarov University, Bourgas 8010, Bulgaria

(Received May 19, 1999; in revised form December 21, 1999)

Abstract

By using a DSK of the French firm Seteram, the standard enthalpies of formation of 5 tellurites and 5 tetratellurites of the rare earths Gd, Tb, Dy, Tm and Yb were determined for the first time.

Three parallel determinations for each sample were compared. The results are very similar, which is an indication of the great reliability of the method used and the correctness of the data obtained.

Keywords: calorimetry, enthalpies of formation, rare earth, tellurites, thermodynamic data, X-ray analysis

Introduction

The enthalpies of formation are important thermodynamic characteristics of compounds. They are successfully used in general physical and analytical chemistry and also in studies of a number of technological processes.

No data are available concerning the enthalpies of formation of the tellurites of the rare earths. The present study was carried out to fill this gap.

Experimental

The oxides Gd_2O_3, Tb_2O_3, Dy_2O_3, Tm_2O_3, Yb_2O_3 and TeO_2, with purities of at least 99.999%, were used to study the enthalpies of formation of the rare earth tellurites. The parameters of the elementary cells of the initial oxides were established. They all crystallize in the cubic crystal system of type Mn_2O_3, with the parameters a=5.4061 Å for Gd_2O_3; a=5.3653 Å for Tb_2O_3; a=5.3332 Å for Dy_2O_3; a=5.2441 Å for Tm_2O_3; and a=5.2203 Å for Yb_2O_3. These parameters are very close to those in the literature. Weighed quantities of the oxides of the rare earths and tellurrous oxide, corresponding to the stoichiometry of the tellurite under study, were placed into an agate mortar and subjected to thorough homogenization.

The degree of homogenization and the stoichiometry of the mechanical mixture obtained were determined by two methods:

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

A) X-ray phase analysis: Samples of each mechanical mixture were sealed in vacuum quartz ampoules. Solid-phase synthesis was carried out at a temperature 50°C lower than the melting temperature of the corresponding tellurite. X-ray patterns were obtained with a URD-6 apparatus (Germany), with a Cu anode for K_α emission and a nickel filter for β emission. The mixtures were considered homogeneous if the interplanar distances and the intensities of all peaks in the X-ray patterns coincided with those of the corresponding tellurites. When no X-ray data were available, the mixture was assumed to be homogeneous if the X-ray patterns of the tellurites obtained exhibited no bands characteristic of the starting metal oxides or tellurous oxide.

B) Chemical analysis: A thoroughly homogenized mechanical mixture was subjected to chemical analysis. A known quantity of the solid phase was dissolved, and the quantities of metal oxide and tellurous oxide were determined. The metal oxide was analysed by reverse complexometric titration, using Eriochrome black T as indicator [1]. Tellurous oxide was determined iodometrically and gravimetrically [2]. Chemical analysis data and the theoretical calculations for the corresponding tellurites are presented in Table 1.

Table 1 Results of chemical analysis of the mechanical mixture of a metal oxide and tellurous oxide corresponding to the stoichiometry of the compound

Compound	Calculated/%		Found/%	
	Metal oxide	Tellurous oxide	Metal oxide	Tellurous oxide
$Gd_2(TeO_3)_3$	43.09	56.91	43.12; 43.06; 43.10	57.00; 56.88; 56.93
$Gd_2Te_4O_{11}$	36.22	63.78	36.19; 36.22; 36.20	63.81; 63.75; 63.79
$Tb_2(TeO_3)_3$	43.31	59.69	43.33; 43.29; 43.30	56.70; 56.73; 56.78
$Tb_2Te_4O_{11}$	36.43	63.57	36.44; 36.40; 36.43	63.60; 63.55; 63.57
$Dy_2(TeO_3)_3$	43.79	56.21	43.80; 43.81; 43.78	56.20; 56.23; 56.21
$Dy_2Te_4O_{11}$	36.88	63.12	36.92; 36.85; 36.88	63.08; 63.10; 63.15
$Tm_2(TeO_3)_3$	44.63	55.37	44.60; 44.64; 44.62	55.40; 55.39; 55.35
$Tm_2Te_4O_{11}$	37.67	62.33	37.71; 37.68; 37.66	62.35; 62.33; 62.28
$Yb_2(TeO_3)_3$	45.15	54.85	45.18; 45.15; 45.14	54.80; 54.88; 54.84
$Yb_2Te_4O_{11}$	38.17	61.83	38.20; 38.16; 38.18	61.69; 61.77; 61.85

In order to determine the standard enthalpies of formation, mixtures of metal oxides and tellurous oxide corresponding to the stoichiometry of the tellurites were sealed in ampoules, which were inactive as regards the metal oxides, tellurous oxide and the tellurites obtained DSC curves were obtained as described in reference 3 by using a DSC-111 calorimeter (Seteram, France). In order to determined the temperature interval, derivatographic analysis was performed from room temperature up to 1300 K.

The DSC curves were used to determine the enthalpies of the reactions. On summation of the data obtained and the enthalpies of formation of the metal oxides [4–10] and tellurous oxide [10–12] (taking into account their mole ratios), the standard enthalpies of formation of the metal tellurites under study were calculated via the equations:

for $M_2(TeO_3)_3$:

$$\Delta H^{\circ}_{298} = \Delta H^{\circ}_{298\,\mathrm{M_2O_3}} + 3\Delta H^{\circ}_{298\,\mathrm{TeO\,2}} + \Delta H\ \text{peak}$$

for $M_2Te_4O_{11}$:

$$\Delta H^{\circ}_{298} = \Delta H^{\circ}_{298\,\mathrm{M_2O_3}} + 4\Delta H^{\circ}_{298\,\mathrm{TeO\,2}} + \Delta H\ \text{peak}$$

In order to ensure maximum accuracy in calculating the standard enthalpies of formation, particular attention was paid to accurate determination of the enthalpies of the chemical reactions.

Accurate determination of the standard enthalpies of formation of metal tellurites depends on the completion of the chemical reactions between the metal oxides and tellurous oxide. This was proved by two methods: repeated DSC analysis and X-ray phase analysis.

Table 2 Heats of formation of some metal tellurites. ΔH values are given in kJ mol^{-1}

Compound	Literature data		Present data	
	$-\Delta H$ °(form) of metal oxide	$-\Delta H$ °(form) of TeO_2	$-\Delta H$ of reaction	$-\Delta H$ (form) of metal tellurites
$Gd(TeO_3)_3$	1805.64	966.63	64.26	2836.53
$Gd_2Te_4O_{11}$	1805.64	1288.84	70.66	3165.15
$Tb_2(TeO_3)_3$	1830.19	966.63	79.49	2876.31
$Tb_2Te_4O_{11}$	1830.19	1288.84	114.19	3233.24
$Dy_2(TeO_3)_3$	1864.55	966.63	83.22	2914.41
$Dy_2Te_4O_{11}$	1864.55	1288.84	99.16	3253.80
$Tm_2(TeO_3)_3$	1891.37	966.63	81.30	2939.30
$Tm_2Te_4O_{11}$	1891.37	1288.84	99.74	3279.94
$Yb_2(TeO_3)_3$	1933.27	966.63	55.07	2954.96
$Yb_2Te_4O_{11}$	1933.27	1988.84	117.24	3339.35

In the first method involves obtaining repeated DSC curves. The lack of exothermal peaks in these indicates that the reactions are completed and that the areas of the exothermal peaks provide accurate quantitative characteristics of the enthalpies of the chemical reactions between the initial metal oxides and tellurous oxide.

The second method involves performing X-ray phase analysis of the products of the interactions between the metal oxides and tellurous oxide. The lack of peaks in the X-ray patterns corresponding to the initial oxides is indicative of the completion of the chemical reactions and the accuracy of the data obtained.

The results from determinations of the standard enthalpies of formation of the metal tellurites and the enthalpies of formation of the initial metal oxides and tellurous oxide are presented in Table 2. The reliability of the results obtained by the authors is assessed highly in reference [13].

References

1 G. Charlo, Metodi Analiticheskoi Chimii, Chimia, Moscow, 1969.

2 J. T. Nazarenko and E. I. Ermakov, Analiticheskaia Chimia Selena, Tellura, Nauka, Moscow 1977, pp. 5 and 59.

3 I. L. McNaughton and C. T. Mortimer, Differential Scanning Calorimetry, Perkin Elmer Corporation, Norvalk Conektion, 1975, p. 11.

4 D. Ch. Cagareichvily, G. G. Gvalesiani and T. S. Iachvili, J. Phys. Chem. Russ., 43 (1969) 882.

5 E. F. Westrum and B. H. Justice, J. Phys. Chem., 67 (1963) 659.

6 B. H. Justice, E. F. Westrum, E. Chang and R. Radebaugh, J. Phys. Chem., 73 (1969) 333.

7 D. Ch. Cagareichvily and G. G. Gvalesiani, J. Neorg. Chem. Russ., 10 (1965) 319.

8 S. P. Gordienko, B. V. Fenotachka and G. Ch. Viksman, Termodinamika Soedinenii Lantanoidou, Naukova Dumka, Kiev 1979.

9 Termicheskie Konstanti Vechtestv, Izd. ,'VINITI', Moskva 1985.

10 Ihsan Barin, Thermochemical Data of Pure Substances, Parts I and II, VCH, 1993.

11 A. S. Pashinkin, I. B. Rabinovich, M. S. Sheiman, V. P. Mistratov and D. J. Vorobjova, J. Chem. Thermodynamics, 17 (1985) 43.

12 E. H. P. Gordeunke, R. Clustra and J. Van Miltenburg, J. Chem. Thermodynamics, 17 (1985) 1079.

13 A. S. Pashinkin and V. A. Dolgih, J. Neorg. Chem. Russ., 42 (1997) 190.