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Note

HEATS OF FORMATION OF SOME METAL TELLURITES

G.G. GOSPODINOV and B.G. BOGDANOV

Department of Inorganic Chemistry and Central Investigation Laboratory, Higher Institute of Chemical Technology, Bourgas 8010 (Bulgaria)

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Experimental data concerning the thermodynamic functions of tellurites are limited to data on the standard heats of formation of the tellurites of lead [1] and bismuth [2].

The heats of formation of the tellurites of Cu, Ag, Zn, Cd, Hg, Pb and Bi under standard conditions was estimated by Buketov et al. [3] by employing Reznitsky's method of approximation [4]. He established a linear dependence of ΔH on the normal electrode potentials of the elements contained in the compounds in the form of cations, viz.

$$-\Delta H^0_{298} = A - BE$$

The values of E for the elements in different oxidation states were obtained in refs. 5 and 6 and used in calculations. The coefficients A and B of the tellurites were determined from experimental values of ΔH^0_{298} for the tellurites of sodium, lead and bismuth by the method of least squares and were found to be 66.59 and 20.93, respectively.

Recently, the tellurites of bismuth, lead and copper have been a subject of interest as possible materials for use in devices for operation control of laser beams [7,8]. In addition, some tellurites play an important role in the chemistry and technology of tellurium which is a valuable element. Therefore, it is expedient to obtain data on the thermodynamic properties of tellurites.

The present work aims to determine the heats of formation of eleven metal tellurites.

EXPERIMENTAL

In order to determine the heats of formation of metal tellurites, eleven compositions of a metal oxide and tellurous oxide were prepared, their compositions corresponding to the stoichiometry of the tellurites under study (Table 1). The mixtures were subjected to thorough homogenization in an agate mortar. The degree of homogenization was determined by employing two methods.

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TABLE 1

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

Compound	Calcd. (%)		Found (%)	
	Metal oxide	Tellurous oxide	Metal oxide	Tellurous oxide
$CuTeO_3$	33.26	66.74	33.30, 33.24, 33.50	66.69, 66.78, 66.75
$ZnTeO_3$	33.77	66.23	33.84, 33.53, 33.78	66.19, 66.30, 66.25
$CdTeO_3$	44.58	55.42	44.62, 44.57, 44.60	55.38, 55.42, 55.40
$Al_2(TeO_3)_3$	17.56	82.44	17.54, 17.43, 17.60	82.39, 82.44, 82.52
$Ga_2(TeO_3)_3$	28.13	71.87	28.15, 28.12, 28.20	71.90, 71.85, 71.86
$In_2(TeO_3)_3$	36.70	63.30	36.68, 36.72, 36.70	63.63, 63.72, 63.70
$Tl_2(TeO_3)_3$	48.82	51.18	48.84, 48.82, 48.80	51.23, 51.16, 51.18
$Ge(TeO_3)_2$	24.68	75.32	24.72, 24.69, 24.67	75.20, 75.35, 75,32
$Sn(TeO_3)_2$	32.07	67.93	32.05, 32.10, 32.08	68.00, 67.91, 67.94
$PbTeO_3$	58.31	41.69	58.40, 58.30, 58.32	41.70, 41.69, 41.68
$Bi_2(TeO_3)_3$	49.32	50.68	49.32, 49.30, 49.34	50.70, 50.67, 50.68

(1) Chemical method. The mechanical mixture was chemically analysed and the content of the metal oxide and tellurous oxide in the sample was determined. GeO_2 was analytically determined by employing mannitol and a titrimetric technique [9]. All other metal oxides were determined by direct or inverse complexometric titrations [10]. TeO_2 was determined iodometrically [11]. The results obtained were compared with theoretical data (Table 1).

(2) X-Ray analysis. Part of the mechanical mixture was inserted into a quartz ampoule, which was evacuated and then sealed: the mixture was then subjected to synthesis. The X-ray pattern of the tellurite obtained was taken and compared with data from the ASTM card-index. Its composition was considered to be homogeneous if all the lines in the X-ray pattern belonged to the tellurite studied, or if the X-ray pattern did not contain lines of the initial metal oxide and tellurous oxide. In order to determine the heat of formation, a differential scanning calorimeter DSC-111 (Seteram, France) was used.

For this purpose, the mechanical mixture of a metal oxide and tellurous oxide corresponding to the stoichiometry of the tellurite under study was heated and the reaction heat of formation of the metal tellurite was registered. Then the reaction heat obtained was summed up with the heat of formation of the metal oxide and tellurous oxide obtained from the literature [12,13]. The heats of formation of the metal tellurites with oxidation states +2, +3 and +4 were calculated from the expressions

$$MTeO_{3(crys.)} \quad \Delta H^0_{form.} = \Delta H_{MO(crys.)} + \Delta H_{TeO_2(crys.)} + \Delta H_{reac.}$$

$$M_2(TeO_3)_{3(crys.)} \quad \Delta H^0_{form.} = \Delta H_{M_2O_3(crys.)} + 3\Delta H_{TeO_2(crys.)} + \Delta H_{reac.}$$

TABLE 2

Heats of formation of some metal tellurites. ΔH values are given in kcal mole^{-1}

Compound	Literature data			Present data		
	$-\Delta H^0_{\text{form.}}$ of metal oxide [13]	$-\Delta H^0_{\text{form.}}$ of TeO_2 [12]	$-\Delta H^0_{\text{form.}}$ of metal tellurites	$-\Delta H$ of reaction	Transition Temp. (°C)	$-\Delta H^0_{\text{form.}}$ of metal tellurites
$CuTeO_3$	39.50	76.90	119.10 [a]	0.42 ± 0.01	409, 509	116.82
$ZnTeO_3$	83.80	76.90	165.10 [a]	2.72 ± 0.07	424	163.42
$CdTeO_3$	61.90	76.90	150.00 [b]	6.88 ± 0.2	526	145.68
$Al_2(TeO_3)_3$	396.00	230.70		4.88 ± 0.1	556	631.58
$Ga_2(TeO_3)_3$	260.30	230.70		3.15 ± 0.1	507	494.15
$In_2(TeO_3)_3$	221.30	230.70		6.52 ± 0.2	514, 620	458.52
$Tl_2(TeO_3)_3$	93.30	230.70		8.82 ± 0.3	346, 380	332.82
$Ge(TeO_3)_3$	129.00	153.80		2.43 ± 0.06	622	285.23
$Sn(TeO_3)_3$	139.80	158.80		2.20 ± 0.06	558	295.80
$PbTeO_3$	52.07	76.90	132.40 [b]	3.73 ± 0.1	506, 533, 579	132.70
$Bi_2(TeO_3)_3$	138.10	230.70	388.50 [c]	16.25 ± 0.4	536, 604	385.05

[a] Ref. 3.
[b] Ref. 1.
[c] Ref. 2.

$M(TeO_3)_{2(crys.)}\ \Delta H^0_{form.} = \Delta H_{MO_2(crys.)} + 2\Delta H_{TeO_2(crys.)} + \Delta H_{reac.}$

where M represents a metal.

RESULTS AND DISCUSSION

The results obtained are presented in Table 2. As is seen from these data, the obtained heats of formation of $PbTeO_3$ and $Bi_2(TeO_3)_3$ are in good agreement with those determined experimentally [1,2]. The heats of formation of $CuTeO_3$, $ZnTeO_3$ and $CdTeO_3$ differ by 2–5 kcal $mole^{-1}$ from that calculated by Reznitsky's method of approximation [3].

It was established from DSC curves that the formation of some tellurites takes place in stages which makes it possible to assume the existence of basic tellurites. Thus it is known from the literature that copper forms $CuTeO_3$ as well as basic copper tellurite, $CuO \cdot CuTeO_3$, while lead, besides forming $PbTeO_3$, has two basic lead tellurites, $2\ PbO \cdot PbTeO_3$ and $4\ PbO \cdot PbTeO_3$. Therefore, the existence of two temperature intervals of formation registered for copper and three temperature intervals of formation registered for lead confirms the idea that this method can be used to determine the number of possible tellurites in a given system. This study confirms the presence of basic tellurites of In, Tl and Bi in the systems $MO–TeO_2$.

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