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Standard enthalpy of formation of $La_2Te_3O_9$ and $La_2Te_4O_{11}$

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Abstract

Lanthanum tellurites, $La_2Te_3O_9$ and $La_2Te_4O_{11}$, have been prepared by the solid state synthesis route and characterized for their phase and chemical compositions by XRD and ICP-AES analyses. The molar enthalpies of solution of $La_2Te_3O_9(s)$, $La_2Te_4O_{11}(s)$, $La_2O_3(s)$ and $TeO_2(s)$ in 0.150 dm^3 of 10.98 mol dm^{-3} HCl were measured using an isoperibol calorimeter. From these results and other auxiliary data the standard molar enthalpy of formation of $La_2Te_3O_9(s)$ and $La_2Te_4O_{11}(s)$ were derived to be (-2814.6 ± 12.9) kJ mol^{-1} and (-3116.5 ± 17.3) kJ mol^{-1}, respectively, at 298.15 K which are the first reported thermodynamic data on these compounds at 298.15 K.
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1. Introduction

Rare earths (RE) and tellurium are among the fission products formed with burnup of the nuclear fuel. As the oxygen potential inside the oxide fuel generally does not grow beyond the value of Mo/MoO_2 buffer system, tellurium remains alloyed with the metallic fission products whereas the rare earth elements remain dissolved in the fluorite lattice of the fuel matrix. The potential buffering ability of Mo is effective when its oxidation kinetics is high enough to absorb the leftover of fission-generated oxygen. Following uptake by the reactive fission products (RE, Y, Sr, Ba, Zr) the concentration of the left over oxygen in urania-rich fuel is limited by its fast chemical diffusion [1] outwards to the Zircaloy clad. However, the leftover fraction will be high in thoria rich fuels, such as ThO_2–3 mol%UO_2, because of its very poor transport property and limited buffer capacity for oxygen. The oxygen transport in thoria being predominantly governed by the self-diffusion [1] will be orders of magnitude lower as compared to the chemical diffusion in urania. The impediment in transport may lead to a situation where Mo oxidation may not be as fast as the oxygen accumulation rate inside fuel. Under the situation there is possibility that the oxygen potential can be high enough for Te to interact with the RE oxide components forming their tellurite phases. The formation depends on the oxygen potential as well as on the tellurites stabilities. In the context of using thoria rich fuel, it is prudent to have some information regarding the thermodynamic stability of rare earth tellurites.

Recently some DSC studies on the determination of the standard enthalpy of formation of tellurites of yttrium, lanthanum and praseodymium were reported by Gospodinov et al. [2]. The DSC method requires extensive calibration for heat flow and temperature. Moreover, the calibration factors are often complex functions of various parameters like temperature, heating rate, sample mass and rate of its heat absorption/

emission, etc. [3–5]. The DSC measurements were made in the scanning mode [2], which suffers from drawbacks like difficulty in construction of a proper base line when there is change in heat capacities of reactants and products over the whole temperature range [5]. The authors [2] have reported the enthalpy of formation of the rare-earth tellurites at reaction temperatures and not at 298.15 K.

We have taken two compounds in this series, $La_2Te_3O_9$ and $La_2Te_4O_{11}$ and determined their standard enthalpy of formation at 298.15 K using isoperibol solution calorimetry. In an isoperibol solution calorimeter the temperature evolution inside the calorimeter occurs homogeneously under a thermally equilibrated state of its contents, and the heat exchange with the controlled surrounding water bath occurs across the boundary whose transport property has been pre-established.

2. Experimental

2.1. Preparation

The metal tellurites were prepared from high purity La_2O_3 (99.99%) and TeO_2 (Aldrich, purity 99.99%). For preparation of $La_2Te_3O_9$, a mixture of La_2O_3 and TeO_2 were taken in molar proportions of 1:3 and ground. The ground mixture was taken in a sealed quartz ampoule and heated at 900 °C for 3 days. $La_2Te_4O_{11}$ was prepared by heating a mixture of La_2O_3 and TeO_2 in 1:4 molar proportions in a sealed quartz ampoule at 650 °C for 2 days with one intermittent grinding.

2.2. Characterization

The compounds formed were characterized by XRD technique in a Philips X-ray generator PW-1729 with a wide-angle goniometer PW-1820 using Ni filtered Cu Kα radiation. DTA runs for the compounds as well as pure TeO_2 were taken in a commercial TG-DTA apparatus (Setaram, 92-16.18) in pure argon atmosphere at a heating rate of 10 K min^{-1} up to 800 °C. The purity of the compounds formed (single phase) was established from the chemical analysis using ICP-AES technique.

2.3. Calorimetric measurements

The enthalpies of dissolution of $La_2Te_3O_9(s)$ and $La_2Te_4O_{11}(s)$ were measured in an isoperibol calorimeter operated at 298.15 K. The construction and operation of the calorimeter is similar to the one described by Athavale et al. [6]. For each of these compounds the sample was weighed and introduced into a glass bulb, which was then thermally equilibrated in the calorimetric solution. The solvent used was 0.150 dm^3 of

10.98 mol dm^{-3} HCl. The glass bulb was broken to introduce the sample into the solution when a steady state thermal signal was obtained on the strip chart recorder. The energy equivalent of the calorimeter was determined before each measurement by electrical calibration. The enthalpies of dissolution of $La_2O_3(s)$ and $TeO_2(s)$ were also measured in the same solvent. Using these experimental values and other auxiliary data from literature the enthalpies of formation of $La_2Te_3O_9(s)$ and $La_2Te_4O_{11}(s)$ were determined.

3. Results and discussion

The XRD patterns of the compounds $La_2Te_3O_9(s)$ and $La_2Te_4O_{11}(s)$ matched well with that reported in JCPDS file No. 22-0376 and 22-0646, respectively. No lines due to the starting components La_2O_3 and TeO_2 were found.

Thermal analysis of pure TeO_2 gave a sharp melting peak at 733 °C, which corresponds to its reported melting point. For both the compounds no DTA peak was observed up to 800 °C. This proves the absence of TeO_2 as pure phase in the compounds.

The results of the chemical analysis of the telllurites show that the mass percentage of La and Te are 34.7 and 47.6 against the respective calculated values of 34.53 and 47.57 for $La_2Te_3O_9$. For $La_2Te_4O_{11}$ the observed mass percentages for La and Te are 29.0 and 52.5, respectively, against the respective calculated values of 28.81 and 52.93.

The results of the enthalpies of dissolution of $La_2Te_3O_9(s)$, $La_2Te_4O_{11}(s)$, $La_2O_3(s)$ and $TeO_2(s)$ are given in Table 1. Here m denotes the mass of the sample dissolved, ΔH is the measured energy change and $\Delta_{sol}H_m$ is the molar enthalpy of dissolution. Thermochemical cycles from which the standard molar enthalpies of formation of $La_2Te_3O_9(s)$, and $La_2Te_4O_{11}(s)$ have been derived are given in Tables 2 and 3, respectively. The experimentally measured values using the above cycles were combined with other auxiliary data such as the standard enthalpies of formation of $TeO_2(s)$ [7] and $La_2O_3(s)$ [7] to derive the standard molar enthalpies of formation of $La_2Te_3O_9(s)$ and $La_2Te_4O_{11}(s)$ at 298.15 K. The values are (-2814.6 ± 12.9) kJ mol^{-1} and (-3116.5 ± 17.3) kJ mol^{-1} for $La_2Te_3O_9(s)$ and $La_2Te_4O_{11}(s)$, respectively. The molar heats of dissolution for $La_2Te_3O_9(s)$, $La_2Te_4O_{11}(s)$, $La_2O_3(s)$ and $TeO_2(s)$, when plotted against molar concentration show that there is no significant dilution effect and the experiments were carried out effectively under infinite dilution conditions in each case. So in each case the average of four values were taken. A remark can be made that the authors in [2] have not stated the precision of their measurements though they have claimed to have made five measurements for each enthalpy change.

Table 1
The molar enthalpies of dissolution of $La_2Te_3O_9(s)$, $La_2Te_4O_{11}(s)$, $La_2O_3(s)$ and $TeO_2(s)$ in $0.150\ dm^3$ of $10.98\ mol\ dm^{-3}$ of HCl at $T = 298.15\ K$

Solute	m (solute)/g	ΔH/J per solute m	$\Delta_{sol}H_m$/kJ mol^{-1}
$La_2Te_3O_9(s)$ Mol. mass = 804.62	0.19025	−71.43	−302.10
	0.23250	−86.72	−300.11
	0.21200	−80.16	−304.24
	0.17470	−65.64	−302.32
			Ave.: −302.2 ± 1.5
$La_2Te_4O_{11}(s)$ Mol. mass = 964.22	0.067	−23.78	−342.23
	0.1119	−39.61	−341.31
	0.084	−29.21	−335.30
	0.0662	−23.12	−336.75
			Ave.: −338.9 ± 2.9
$La_2O_3(s)$ Mol. mass = 325.82	0.0488	−45.82	−305.92
	0.0482	−45.82	−309.73
	0.0616	−58.12	−307.41
	0.0537	−50.44	−306.04
			Ave.: −307.3 ± 1.5
$TeO_2(s)$ Mol. mass = 159.6	0.2174	−19.72	−14.48
	0.2453	−24.19	−15.74
	0.2548	−24.09	−15.09
	0.2285	−21.93	−15.09
			Ave.: −15.2 ± 0.5

m denotes the mass of the sample dissolved; ΔH is the measured enthalpy change and $\Delta_{sol}H_m$ is the molar enthalpy of solution.

Table 2
Reaction scheme for the standard molar enthalpy of formation of $La_2Te_3O_9(s)$ (sln = $0.150\ dm^3$ of $10.98\ mol\ dm^{-3}$ HCl), $\Delta H_6 = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$

Reaction	ΔH_i	ΔH_m/kJ mol^{-1}	Refs.
$La_2Te_3O_9(s) + 18\ HCl(sln) = (2\ LaCl_3 + 3\ TeCl_4 + 9\ H_2O)(sln)$	ΔH_1	−302.2 ± 1.5	This work
$La_2O_3(s) + 6\ HCl(sln) = (2\ LaCl_3 + 3\ H_2O)(sln)$	ΔH_2	−307.3 ± 1.5	This work
$3\ TeO_2(s) + 12\ HCl(sln) = (3\ TeCl_4 + 6\ H_2O)(sln)$	ΔH_3	−45.6 ± 1.5	This work
$2\ La(s) + 3/2\ O_2(g) = La_2O_3(s)$	ΔH_4	−1793.7 ± 2.0	[7]
$3\ Te(s) + 3\ O_2(g) = 3\ TeO_2(s)$	ΔH_5	−970.2 ± 12.5	[7]
$2\ La(s) + 3\ Te(s) + 9/2\ O_2(g) = La_2Te_3O_9(s)$	ΔH_6	−2814.6 ± 12.9	This work

Table 3
Reaction scheme for the standard molar enthalpy of formation of $La_2Te_4O_{11}(s)$ (sln = $0.150\ dm^3$ of $10.98\ mol\ dm^{-3}$ HCl), $\Delta H_6 = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$

Reaction	ΔH_i	ΔH_m/kJ mol^{-1}	Refs.
$La_2Te_4O_{11}(s) + 22\ HCl(sln) = (2\ LaCl_3 + 4\ TeCl_4 + 11\ H_2O)(sln)$	ΔH_1	−338.9 ± 2.9	This work
$La_2O_3(s) + 6\ HCl(sln) = (2\ LaCl_3 + 3\ H_2O)(sln)$	ΔH_2	−307.3 ± 1.5	This work
$4\ TeO_2(s) + 16\ HCl(sln) = (4\ TeCl_4 + 8\ H_2O)(sln)$	ΔH_3	−60.8 ± 2.0	This work
$2\ La(s) + 3/2\ O_2(g) = La_2O_3(s)$	ΔH_4	−1793.7 ± 2.0	[7]
$4\ Te(s) + 4\ O_2(g) = 4\ TeO_2(s)$	ΔH_5	−1293.6 ± 16.8	[7]
$2\ La(s) + 4\ Te(s) + 11/2\ O_2(g) = La_2Te_4O_{11}(s)$	ΔH_6	−3116.5 ± 17.3	This work

The C_p values for the compounds $La_2Te_3O_9(s)$, and $La_2Te_4O_{11}(s)$ were estimated from the heat capacity values of $La_2O_3(s)$ [7] and $TeO_2(s)$ [7] using the Neumann–Kopp rule [8]. Making use of the heat capacities thus estimated for $La_2Te_3O_9(s)$, and $La_2Te_4O_{11}(s)$, and the values of the heat of reactions leading to the two compounds obtained by Gospodinov [2] the respective standard enthalpies of formation at 298.15 K were found to be −2790.6 kJ mol^{-1} and −3113.2 kJ mol^{-1} by the second-law treatment. These values match well with our results obtained independently by a different technique.

4. Conclusion

The standard enthalpies of formation of $La_2Te_3O_9(s)$, and $La_2Te_4O_{11}(s)$ at 298.15 K are found to be (-2814.6 ± 12.9) kJ mol^{-1} and (-3116.5 ± 17.3) kJ mol^{-1} respectively. This is the first report of the data on these two compounds obtained at 298.15 K.

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