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Thermochimica Acta 467 (2008) 80–85

thermochimica acta

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# Thermodynamic stability of  $Sm<sub>2</sub>TeO<sub>6</sub>$

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Received 3 August 2007; received in revised form 5 November 2007; accepted 6 November 2007 Available online 17 November 2007

#### **Abstract**

The vapour pressure of  $Sm_2TeO_6$  was measured using a thermal analyser with a horizontal arm. This TG based transpiration technique, was validated by measuring the vapour pressure of pure TeO2(s). The temperature dependence of the latter was measured to be log *p* (Pa) = {14.2 − 13321/*T* (K)} (±0.03) in the range 884–987 K. These data yielded a  $\Delta H_{298}^{\circ}$  value of 269.7 ± 0.6 kJ mol<sup>-1</sup> for the enthalpy of sublimation (third-law method) of TeO<sub>2</sub> which compared well with the data reported in the literature. The temperature dependence of the vapour pressure of TeO<sub>2</sub> over the mixture  $\text{Sm}_2\text{TeO}_6(s) + \text{Sm}_2\text{O}_3(s)$  generated by the incongruent vapourisation reaction,

 $Sm_2TeO_6(s) \rightarrow Sm_2O_3(s) + TeO_2(g) + 1/2O_2(g)$ 

could be expressed as

 $\log p$  (Pa) = {18.56 – 25469/T (K)}  $\pm$  0.06 (1374 – 1533 K)

The standard Gibbs energy of formation of  $Sm_2TeO_6(s)$  was derived from the above vapour pressure data in conjunction with auxiliary data for the other coexisting phases. The temperature dependence of the Gibbs energy of formation of  $Sm_2TeO_6$  over the temperature range 1374–1533 K could be represented as

 $\Delta G_f^{\circ}(\text{Sm}_2 \text{TeO}_6)(kJ \text{ mol}^{-1}) = \{-2399.3 + 0.5714 \text{ T} (\text{K})\} \pm 5.8$ 

The Gibbs energy of formation of  $Sm_2TeO_6(s)$  is being reported for the first time. © 2007 Published by Elsevier B.V.

*Keywords:* Samarium tellurate (Sm<sub>2</sub>TeO<sub>6</sub>); TeO<sub>2</sub>; Transpiration technique; Gibbs energy of formation; Vapour pressure; TG

# **1. Introduction**

Tellurium is one of the fission products formed in mixed oxide fuel used in fast breeder reactors (FBRs). It influences the chemistry of the fuel and causes corrosion of the cladding [1,2]. The thermodynamic data on the compounds comprising tellurium and other fission product elements are useful in understanding the fuel-clad chemical interaction in FBR fuel pins. An experimental programme is currently being purs[ued](#page-5-0) [in](#page-5-0) our laboratory with an objective to generate thermodynamic data on multicomponent oxide systems involving tellurium and a fission product element. As a part of this study the systematics in the ternary systems with different lanthanide elements are being investigated. This paper presents the results obtained with the system Sm–Te–O. This ternary system comprises three compounds  $Sm_2TeO_6$ ,  $Sm_2Te_4O_{11}$  and  $Sm_2Te_6O_{15}$ . The thermodynamic stability and vapour pressures of these compounds are yet to be established unambiguously. We measured the vapour pressure of TeO<sub>2</sub>(g) over a mixture containing  $Sm<sub>2</sub>TeO<sub>6</sub>$  and  $Sm<sub>2</sub>O<sub>3</sub>$  and derived the standard Gibbs energy of formation of  $Sm<sub>2</sub>TeO<sub>6</sub>$ from the vapour pressure data.

The vapour pressure of pure  $TeO<sub>2</sub>$  has been determined in the past by many investigators [3–14]. The measurement of the vapour pressure of pure  $TeO<sub>2</sub>$  would be most appropriate for validating the apparatus and procedure, in the context of the lanthanide bearing ternary systems Ln–Te–O. In view of the above, we re-deter[mined](#page-5-0) [th](#page-5-0)e vapour pressure of pure  $TeO<sub>2</sub>$ [15].

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<sup>0040-6031/\$ –</sup> see front matter © 2007 Published by Elsevier B.V. doi:10.1016/j.tca.2007.11.004

#### <span id="page-1-0"></span>**2. Experimental**

#### *2.1. Materials*

Reagent grade  $TeO<sub>2</sub>$  of purity better than 99.9% was procured from Aldrich Chemicals, USA and  $Sm_2O_3$  of purity better than 99.99% was supplied by Indian Rare Earths Ltd., India. High purity  $O_2$  (H<sub>2</sub>O < 2 ppm) and He (O<sub>2</sub> and H<sub>2</sub>O < 2 ppm) were obtained from M/s. Indian Oxygen Limited, Chennai, India.

# *2.2. Preparation of solid solutions*

The ternary oxide  $Sm_2TeO_6$  was prepared by heating an equimolar mixture of  $Sm_2O_3$  and TeO<sub>2</sub>. The temperature suitable for preparing the ternary compound was identified by carrying out a trial experiment in which the above mixture was heated at  $10$  K min<sup>-1</sup> in static air in the thermal analyser (Model Seiko 320, Japan). This experiment revealed an exotherm at 1058 K with an attendant weight gain that continued up to 1223 K. However, no further gain in weight was observed at higher temperatures. The solid mixture was homogenized using an agate mortar and pestle and then compacted into pellets with about 10 mm diameter and 2–3 mm thickness. These pellets were heated at 923 K for 24 h followed by a soak at 1223 K for 48 h. The purity of this ternary oxide  $Sm<sub>2</sub>TeO<sub>6</sub>$  was ascertained by using X-ray diffraction (XRD) analysis. Thus it could be concluded that the amount of impurities in this compound is less than the detection limits of XRD, viz., 2–5 mass%. The heat treated samples were found to contain  $Sm<sub>2</sub>TeO<sub>6</sub>$  (JCPDS XRD file No.40-0332), neither  $Sm_2O_3$  nor TeO<sub>2</sub> was present in them.

#### *2.3. Transpiration set-up*

A horizontal thermal analyser (Model Seiko 320, Japan) was employed as a transpiration apparatus for the vapour pressure investigations. The horizontal disposition of a narrow tubular furnace chamber and the central location of the horizontal dual arm help minimize the errors due to buoyancy, convection and thermomolecular effects. Both the sample temperature and the differential temperature were measured within  $\pm$ 0.5 K by using a Pt–13% Rh/Pt (Type-R) thermocouple. The accuracy in the temperature measurement was testified by determining the freezing points of pure metals viz., Sn, Pb, Sb, Al, Ag and Au. This calibration was found to conform to the ITS-90 [16] scale. Precise flow calibration of the carrier gases viz., He (for the experiments with pure TeO<sub>2</sub>) and O<sub>2</sub> (for the experiments with  $Sm_2TeO_6$ ) was done using a capillary glass flow meter, which in-turn was calibrated by a soap bubble flow meter[.](#page-5-0) [Even](#page-5-0) though the precision in the flow as measured by the glass capillary flow meter was found to be within 0.5%, the overall precision in the integral volume was of the order of  $\pm 1\%$ . Saturation of the carrier gas with the vapour emanating from the sample was ensured by using a finely divided powder of the specimen and by spreading it evenly in a shallow Pt crucible kept in a narrow reaction chamber (furnace tube). Prior to the measurements, blank runs were carried out, in the temperature range 800–1500 K, with empty pans, by maintaining an optimum flow  $(3-18 \text{ dm}^3 \text{ h}^{-1})$  of an appropriate carrier gas  $(He/O<sub>2</sub>)$ . The apparent gain in mass upon heating was found to be about  $10-20 \mu g$  per  $100 \text{ K}$ , over the entire range of flow. A similar drift was observed in the isothermal experiments as well. The "mass loss" values obtained in the isothermal experiments were corrected for this drift. A detailed account on the equipment and methodology could be found elsewhere [17–19].

### *2.4. Vapourisation reaction and intermediates*

The heat effects and mass loss steps [pertainin](#page-5-0)g to the vapourisation of  $\rm Sm_2TeO_6$  were identified using a simultaneous TG-DTA experiment. In a typical experiment, about 85 mg of  $\rm Sm_2TeO_6$  was taken in a Pt crucible and heated in a flowing stream of pure oxygen (flow rate  $8 \text{ dm}^3 \text{ h}^{-1}$ ) at a linear heating rate of  $0.17 \text{ K s}^{-1}$ . In order to identify the intermediates the TG-DTA experiment was interrupted and the specimen was characterized by using XRD.

# **3. Results and discussion**

The apparent pressure of  $TeO<sub>2</sub>(g)$  in equilibrium with either pure TeO<sub>2</sub>(s) or with a mixture of  $Sm<sub>2</sub>TeO<sub>6</sub>(s)$  and  $Sm<sub>2</sub>O<sub>3</sub>(s)$ was calculated from the mass loss of the sample per unit volume of the carrier gas flown over it, using the relation

$$
P^{\rm app} = \frac{WRT_{\rm c}}{MV_{\rm c}}\tag{1}
$$

*W* is the mass loss of the sample,  $V_c$  is the total volume of the carrier gas (saturated with the vapour species) and  $T_c$  is temperature of the carrier gas and *M* is molecular weight of the vapour species. In an earlier study [18] the temperature of the specimen was used in place of  $T_c$ . It is more appropriate to use the latter since the volume measurement is carried out only at *T*<sup>c</sup> Hence, the data presented in ref. [18] should be corrected accordingly.

#### *3.1. Vapour pressure of pu[re](#page-5-0) [soli](#page-5-0)d TeO2*

The vapour pressure of solid  $TeO<sub>2</sub>$  was measured using He as the carrier gas. It was presumed that the vapour comprised only the monomeric  $TeO<sub>2</sub>(g)$  species. The contribution of all other tellurium-bearing species  $[(TeO<sub>2</sub>)<sub>2</sub>, TeO, (TeO)<sub>2</sub>, Te<sub>2</sub>]$  to the total pressure was estimated to be less than 5% from the mass spectrometric studies of Muenow et al. [14].

In the isothermal experiment at 925 K, the mass lost per unit volume of the carrier gas (helium) flown over  $TeO<sub>2</sub>$  was found to remain constant when the flow was between 8 and  $12 \text{ dm}^3 \text{ h}^{-1}$ . This corresponds to the flow [regim](#page-5-0)e (Fig. 1) in which the carrier gas is saturated with vapour species. Data obtained in the isothermal experiments carried out in this flow regime, are presented along with the values of the vapour pressures  $p_{TeO_2}$  derived from them in Table 1.

$$
TeO2(s) \rightarrow TeO2(g)
$$
 (2)

A linear least square regression analysis of the experimen[tal](#page-2-0) [data](#page-2-0) obtained during the congruent vapourisation of  $TeO<sub>2</sub>(s)$ 

<span id="page-2-0"></span>

Fig. 1. Apparent vapour pressure versus flow rate of TeO<sub>2</sub> at 925 K.

shown in Eq. (2) yielded an expression (3) for the temperature dependence of the vapour pressure. These data are also graphically depicted in Fig. 2.

$$
\log p\left(\text{Pa}\right) = \left\{14.2 - \frac{13321}{T\left(\text{K}\right)}\right\} \pm 0.03\left(884 - 987\,\text{K}\right) \tag{3}
$$

The enthalpy of sublimation derived from the slope of the temperature dependence of the vapour pressure at the mean temperature of the measurement (936 K) was found to be  $255 \pm 0.1 \,\mathrm{kJ\,mol^{-1}}$ .

The temperature dependent systematic errors in the measured values of the vapour pressure were examined by using the thirdlaw analysis Eq. (4). The free energy functions (FEF), required for this analysis were derived using the values of  $S_{298}^{\circ}$  and  $C_{p}^{0}$ of  $TeO<sub>2</sub>$  (both solid and gas) obtained from the thermochem-

Table 1 Vapour pressure of  $TeO<sub>2</sub>(s)$ 

Experiment $T(K)$ number		Mass loss $((g))$	$V_c$ (dm <sup>3</sup> )	$T_c$ (K)	Pressure (mPa)
1	884	120	12.414	295	148.7
$\mathfrak{2}$	889	120	10.909	295	169.2
3	895	140	10.909	297	198.7
$\overline{4}$	899	180	10.909	295	253.8
5	905	220	10.909	295	310.2
6	909	232	10.909	295	327.1
7	915	334	10.909	297	474.1
8	925	315	8	297	609.9
9	925	350	9	297	602.3
10	925	400	10.909	297	567.9
11	926	404	10.909	297	573.6
12	935	660	10.909	295	929.5
13	940	820	10.909	295	1154.8
14	941	760	10.909	295	1071.8
15	946	890	10.909	295	1255.1
16	951	1040	10.909	295	1464.6
17	960	1260	9	297	2168.4
18	971	1980	9	297	3407.4
19	976	2160	9	297	3717.2
20	982	2640	9	297	4543.2
21	987	2880	9	297	4956.2





Fig. 2. Temperature dependence of equilibrium vapour pressure of solid  $TeO<sub>2</sub>$ .

ical tables compiled by Knacke et al. [20]. The value of the standard enthalpy of sublimation at 298 K was derived using Eq. (4). The values of  $\Delta H_{sub,298\,\mathrm{K}}^{\circ}$  derived from the experimental data are listed in Table 2. Their temperature dependence is depicted in Fig. 3. The mea[n of th](#page-5-0)ese values was found to be  $(269.7 \pm 0.6)$  kJ mol<sup>-1</sup>.

$$
\Delta H_{\text{sub,298K}}^{\circ} = \Delta G_{\text{vap}}^{\circ} - T \quad \Delta FEF \tag{4}
$$

It is evident from Fig. 3 that the values of  $\Delta H_{\text{sub,298 K}}^{\circ}$  are randomly distributed about the mean. This indicates that the present measurements are devoid of any significant temperature dependent systematic errors.

Mills [3] and Cordfunke and Konings [4] have extensively reviewed the thermochemical data on  $TeO<sub>2</sub>$  which include calorimetric measurements, vapour pressure values and EMF data. The vapour pressure of  $TeO<sub>2</sub>$  was a subject of study from [194](#page-5-0)1 till recent years. Various [exp](#page-5-0)erimental techniques such as Knudsen cell mass loss method [5–8], mass spectrometry [9–11,14] and transpiration [12,13] have been used to measure the vapour pressures. In order to validate the experimental technique used in the present study and to testify the accuracy of the vapour pressure data it w[ould](#page-5-0) [be](#page-5-0) instructive to compare all the [m](#page-5-0)easured values [of vapou](#page-5-0)r pressures with that obtained in this



Fig. 3. Third-law plot of enthalpy of sublimation of TeO<sub>2</sub>; the horizontal line is the mean value of  $\Delta H_{\text{sub,298 K}}^{\circ}$ .

<span id="page-3-0"></span>Table 2 Comparison of vapour pressure data of solid  $TeO<sub>2</sub>$  with the literature

$rac{B}{T(K)}$ Log $p(\text{Pa}) = A -$		$T$ Range $(K)$	$p$ at 900 K (Pa)	$\Delta H_{\text{sub}}^{\circ}$ (mean T) $(kJ \, mol^{-1}) (K)$	$\Delta H_{sub,298\,\mathrm{K}}^{\circ}$ (Third-law) $(kJ \text{ mol}^{-1})$	Method	Ref.
A	B						
13.70	12570	870-930	0.54	240.7 (900)	$266.2 \pm 0.7$	<b>KEML</b>	$[5]$
13.00	12000	846-1006	0.54	229.8 (926)	$261.0 \pm 2.0$	T	$[12]$
14.38	13169	730-981	0.55	252.1 (856)	266.0	<b>KEML</b>	[6]
14.54	13292	873-1006	0.59	254.5 (940)	265.3	<b>KEML</b>	$[7]$
13.78	12650	913-993	0.53	242.2 (953)	266.8	T	$[13]$
14.66	14666	782-903	0.023	280.8 (843)	289.8	<b>KCMS</b>	[14]
14.65	13432	778-906	0.53	257.2 (842)	266.9	<b>KCMS</b>	[9]
15.87	14529	926–970	0.53	278.2 (948)	264.4	<b>KEML</b>	[8]
14.24	13534	750-950	0.16	259.1 (850)	264.0	<b>KCMS</b>	[10]
15.02	13988	805-905	0.3	267.8 (855)	268.6	<b>KCMS</b>	[11]
14.20	13321	884-987	0.25	255.0 (936)	269.7	T	This work
					$264.0 \pm 8.4$	Review	$[3]$
					$266.2 \pm 0.6$	Review	$[4]$

KEML: Knudsen effusion mass loss; T: transpiration; KCMS: Knudsen cell mass spectrometry, Δ $H<sub>sub</sub><sup>°</sup>$  (mean *T*): enthalpy of sublimation [at the m](#page-5-0)ean temperature of the present measurements,  $\Delta H_{sub,298 K}^{\circ}$ : enthalpy of sublimation at 298 K by third-law, *p*: pressure (*p*) at 900 K, *T* range: temperature range.

 $7.5$ 

study. Such a comparison (presented in Table 2) reveals that, by and large, there is a reasonable agreement among the cited values of *p* (Pa) at 900 K and those obtained in the present study. Since the temperature range over which each of these investigations was carried out differ considerably, a comparison of the enthalpy of sublimation at the mean temperature of these measurements is not useful. However, a meaningful comparison of the vapour pressure data (presented in Table 2) could be made with the help of the "third-law" analyses. Mills [3] and Cordfunke and Konings [4] have reviewed the  $\Delta H_{sub,298\,\mathrm{K}}^{\circ}$  values using the mass spectrometric data of Piacente et al. [9]. The value of  $\Delta H_{sub,298 \text{ K}}^{\circ}$  of TeO<sub>2</sub> (269.7 ± 0.6) kJ mol<sup>-1</sup> derived from the present study agrees very w[ell w](#page-5-0)ith that reported by the other [inves](#page-5-0)tigators  $[5-11,13]$  as well as with those recommended by the reveiwers [3,4] within 4 kJ m[ol](#page-5-0)<sup>-1</sup>. In view of the above it could be concluded that the vapour pressures of  $TeO<sub>2</sub>$ obtained in this study are quite reliable. Thus, the present study validates the [reliability o](#page-5-0)f this TG based transpiration technique for measuring [the vap](#page-5-0)our pressures.

# *3.2. Non-isothermal TG of Sm2TeO6*

The simultaneous TG-DTA pertaining to the incongruent vapourisation of  $Sm<sub>2</sub>TeO<sub>6</sub>(s)$  revealed that this compound begins to lose mass from 1373 K in pure  $O_2$ . The X-ray diffraction of a specimen from an interrupted TG-DTA experiment confirmed the presence of the compounds  $Sm<sub>2</sub>TeO<sub>6</sub>(s)$  and  $Sm<sub>2</sub>O<sub>3</sub>(s)$ . Thus the vapourisation of the ternary compound could be represented by Eq. (5).

$$
Sm_2TeO_6(s) \to Sm_2O_3(s) + TeO_2(g) + \frac{1}{2}O_2(g)
$$
 (5)

## *3.3. Vapourisation behaviour of Sm2TeO6 by the transpiration technique*

The dependence of the mass loss on the flow of the carrier gas (pure oxygen) at 1422 K was obtained from the thermogravimetric experiments and is depicted in [Fig.](#page-5-0) 4. This "chair" shaped curve revealed a plateau between the flow values of 7 and 9.5 dm<sup>3</sup> h<sup>-1</sup>, over which the mass loss was independent of the flow. In this flow regime the carrier gas was saturated with  $TeO<sub>2</sub>$ vapour. All the isothermal mass loss measurements were carried out by employing a flow pertaining to this plateau region.

The vapour pressure of TeO<sub>2</sub>(g) over samarium tellurate was calculated at different temperatures from the observed mass loss of the sample,  $m_{\text{total}}$  per unit flow volume of the  $O_2(g)$  at a pressure of 1 bar. Both  $O_2(g)$  and TeO<sub>2</sub>(g) contribute to the total weight loss  $m_{\text{total}}$ . The loss of weight due to the loss of TeO<sub>2</sub>(g) alone was computed from this value using Eq. (6),

$$
m_{\text{TeO}_2} = m_{\text{total}} \left[ \frac{M_{\text{TeO}_2}}{M_{\text{TeO}_2} + 0.5 M_{\text{O}_2}} \right]
$$
 (6)

where *M* is the molecular weight and m is the mass loss of the respective compounds. The vapour pressures,  $p_{TeO_2}$  computed from these experiments are enlisted along with the values of



Fig. 4. Apparent vapour pressure versus flow rate of  $Sm_2TeO_6$  at 1422 K.

<span id="page-4-0"></span>



Initial weight of the sample: 68 mg, *T* (K): temperature corresponding to each experimental measurement,  $V_c$  (dm<sup>3</sup>): volume of the oxygen carrier gas,  $T_c$  (K): temperature of the oxygen carrier gas (*T*<sub>c</sub> = 299 K),  $p_{\text{TeO}_2}^{(a)}$ : calculated by using Eq. (1), *T*<sub>c</sub> = 299 K,  $p_{\text{TeO}_2}^{0}$ : extrapolated values from Eq. (15),  $\Delta G$ ° (Sm<sub>2</sub>TeO<sub>6</sub>)<sup>(b)</sup>: standard Gibbs energy of formation of Sm<sub>2</sub>TeO<sub>6</sub> using Eq. (13),  $\Delta G$ <sub>f</sub> (Sm<sub>2</sub>TeO<sub>6</sub>)<sup>(c)</sup>: standard Gibbs energy of formation of Sm<sub>2</sub>TeO<sub>6</sub> using Eq. (16).



Fig. 5. Temperature dependence of equilibrium vapour pressure of  $Sm_2TeO_6$ .

mass loss, temperature and cumulative volume of the carrier gas *V*c, in Table 3.

The temperature dependence of the vapour pressure is shown in Fig. 5. The linear least squares regression analysis of these data yielded expression (7).

$$
\log p(\text{Pa}) = \{18.56 - 25469/T(\text{K})\}(\pm 0.06)(1374 - 1533 \text{ K})
$$
\n(7)

The standard Gibbs energy change,  $\Delta G^{\circ}_{r(5)}$  for the reaction (5) could be expressed as

$$
\Delta G_{\rm r}^{\circ}(5) = -RT \ln K \quad \text{(where } K = \text{equilibrium constant)} \quad (8)
$$

$$
= -RT \ln \left\{ \frac{a \operatorname{Sm}_2O_3 x p (\operatorname{TeO}_2) x p O_2^{1/2}}{a \operatorname{Sm}_2 \operatorname{TeO}_6} \right\} \tag{9}
$$

where activities of solids ( $a_{\rm Sm_2O_3}$  and  $a_{\rm Sm_2TeO_6}$ ) are equal to one and  $p_{\text{O}_2} = 1$  bar. Hence,

$$
\Delta G_{\rm r}^{\circ}(5) = -RT \ln p_{\rm (TeO_2)} \tag{10}
$$

$$
\Delta G_{\rm r}^{\circ}(5) \, (\text{kJ\,mol}^{-1}) = \{487.7 - 0.2595 \, T \, (\text{K})\} \pm 0.1 \tag{11}
$$

The standard Gibbs energy of formation of  $Sm_2TeO_6$  could be expressed in terms of the equilibrium partial pressure of  $TeO<sub>2</sub>(g)$ and the stabilities of  $Sm_2TeO_6$  and  $Sm_2O_3$  as follows

$$
\Delta G_f^{\circ}(\text{Sm}_2 \text{TeO}_6, s) = \Delta G_f^{\circ}(\text{Sm}_2 \text{O}_3) + \Delta G_f^{\circ}(\text{TeO}_2, g)
$$

$$
+ RT \ln p_{(\text{TeO}_2)} \tag{12}
$$

Combining the expression (11) along with the key data for  $\Delta G_f^{\circ}(\text{Sm}_2\text{O}_3, s)$  and  $\Delta G_f^{\circ}(\text{TeO}_2, g)$  from the literature [20],  $\Delta G_{\rm f}^{\circ}$ (Sm<sub>2</sub>TeO<sub>6</sub>, s) was calculated to be

 $\Delta G_f^{\circ}$ (Sm<sub>2</sub>TeO<sub>6</sub>)(kJ mol<sup>-1</sup>) = {-2399.3 + 0.5714 T (K)}  $\pm$  5.8 (1374 – 15[33](#page-5-0) [K\)](#page-5-0) (13)

 $\Delta G_f^{\circ}$  (Sm<sub>2</sub>TeO<sub>6</sub>, s) with liquid TeO<sub>2</sub> as the reference state is presented in Eq. (14).

$$
\Delta G_f^{\circ}(\text{Sm}_2 \text{TeO}_6, s) = \Delta G_f^{\circ}(\text{Sm}_2 \text{O}_3, s) + \Delta G_f^{\circ}(\text{TeO}_2, l)
$$

$$
+ RT \ln \frac{p_{\text{TeO}_2}}{p_{\text{TeO}_2}^0} \tag{14}
$$

The temperature dependence of vapour pressure of  $TeO<sub>2</sub>(g)$  $(p_{\text{TeO}_2}^0)$  over pure liquid TeO<sub>2</sub> was measured in our laboratory using the same TG based transpiration technique and was found to be [15],

$$
\log p_{\text{TeO}_2}^0 \text{(Pa)} = 12.38 - 11672/T \text{(K)} (1006 - 1070 \text{ K}) \quad (15)
$$

The standard Gibbs energy of formation of  $Sm<sub>2</sub>TeO<sub>6</sub>$  was obtained with the help of Eq. (14) using auxiliary data on the

<span id="page-5-0"></span> $\Delta G_f^{\circ}$  (TeO<sub>2</sub>, 1) and  $\Delta G_f^{\circ}$  (Sm<sub>2</sub>O<sub>3,</sub> s) from the literature [20]. This is shown in Eq. (16)

$$
\Delta G_f^{\circ}(\text{Sm}_2 \text{TeO}_6)(\text{kJ}\,\text{mol}^{-1}) = \{-2394.4 + 0.5711\,T\,\text{(K)}\}
$$
  

$$
\pm 5.8(1374 - 1533\,\text{K})\tag{16}
$$

The slope and intercept of the Eqs. (13) and (16) are related to the standard molar enthalpy and entropy of the formation of  $Sm<sub>2</sub>TeO<sub>6</sub>(s)$ , respectively (valid over the temperature range 1374–1533 K). The Gibbs energy of formation of  $Sm<sub>2</sub>TeO<sub>6</sub>(s)$ is being reported for the first [time. Since no](#page-4-0) information is available on the heat capacity of this compound, the second law and third-law analyses of the vapour pressure data could not be carried out. Hence it was not possible to evaluate and verify the values of the  $\Delta H_{\rm f}^{\circ}$  Sm<sub>2</sub>TeO<sub>6</sub>(s) at 298 K. However, the average enthalpy of formation of  $Sm<sub>2</sub>TeO<sub>6</sub>$  obtained from the present work by using the method of slopes, was found to be  $-2396.9 \pm 5.8 \text{ kJ} \text{ mol}^{-1}$  at the mean temperature of the present measurements.

#### **4. Conclusion**

The applicability of a TG based transpiration technique for measuring vapour pressures was verified by measuring the vapour pressure of pure  $TeO<sub>2</sub>$  over the range 884–987 K yielding a value of  $269.7 \pm 0.6 \text{ kJ} \text{ mol}^{-1}$  for the third-law enthalpy of sublimation which compares well with the literature data. The ternary compound,  $Sm<sub>2</sub>TeO<sub>6</sub>(s)$  was prepared by the solid state reaction of an equimolar mixture of  $Sm_2O_3$ , and  $TeO_2$  and was characterized by X-ray and TG-DTA. The vapour pressure of TeO<sub>2</sub>(g) over  $Sm_2TeO_6(s)$  was derived from these vapour pressure measurements. The values of  $\Delta G_f^{\circ}$  Sm<sub>2</sub>TeO<sub>6</sub>(s) were derived from these vapour pressure measurements and are being reported for the first time. The average enthalpy of formation of  $\rm Sm_2TeO_6$  obtained from the present work was found to be  $-2396.9 \pm 5.8 \text{ kJ} \text{ mol}^{-1}$ .

#### **Acknowledgement**

The authors express their sincere gratitude to Shri. R. Madhavan for recording XRD patterns.

# **References**

- [1] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.
- [2] E.H.P. Cordfunke, R.J.M. Konings, J. Nucl. Mater. 152 (1988) 301.
- [3] K.C. Mills, Thermodynamic Data for Inorgranic Sulphides, Selenides and Tellurides, Butterworths, London, 1974.
- [4] E.H.P. Cordfunke, R.J.M. Konings (Eds.), Thermochemical Data for Reactor Materials and Fission Products, North-Holland, Amsterdam, 1990.
- [5] K. Ueno, J. Chem. Soc. Jpn. 62 (1941) 990 (as quoted in ref. [10,11]).
- [6] V.P. Zlomanov, A.V. Novoselova, A.S. Pashinkin, Yu.P. Simanov, K.N. Semenenko, Zh. Neorg. Khim. 3 (1958) 1473 (as quoted in ref. [10,11]).
- [7] K.E. Prescher, W. Schrodter, Z. Erzbergb, Metallhuett Wes. 16 (1963) 352 (as quoted in ref. [10,11].
- [8] K. Krishnan, G.A. Rama Rao, K.D. Singh Mudher, V. Venugopal, J. Nucl. Mater. 230 (1996) 61.
- [9] V. Piacente, L. Malaspina, G. Bardi, R. Gigli, Rev. Int. Hautes Temp et Refract. 6 (1969) 91 (as quoted in ref. [10,11]).
- [10] T.S. Lakshmi Narasimhan, R. Balasubramanian, S. Nalini, M. Sai Baba, J. Nucl. Mater. 247 (1997) 28.
- [11] T.S. Lakshmi Narasimhan, M. Sai Baba, R. Viswanathan, Thermochim. Acta 427 (2005) 137.
- [12] J.R. Soulen, P. Sthapitanonda, J.L. Margrave, J. Phys. Chem. 59 (1955) 132–352 (as quoted in ref. [10,11]).
- [13] O. Glemser, R.V. Haeseler, A. Muller, Z. Anorg. Allg. Chem. 329 (1964) 352 (as quoted in ref. [10,11]).
- [14] D.W. Muenow, J.W. Hastie, R. Hauge, R. Bautista, J.L. Margrave, Trans. Faraday Soc. 65 (1969) 3210.
- [15] R. Pankajavalli, Private communication, 2007.
- [16] H. Preston-Thomas, Metrologia 27 (1) (1990) 3–10.
- [17] R. Pankajavalli, C. Mallika, O.M. Sreedharan, V.S. Raghunathan, P. Antony Premkumar, K.S. Nagaraja, Chem. Eng. Sci. 57 (2002) 3603.
- [18] R. Pankajavalli, K. Ananthasivan, S. Anthonysamy, P.R. Vasudeva Rao, J. Nucl. Mater. 345 (2005) 96.
- [19] R. Pankajavalli, A. Jain, S. Anthonysamy, K. Ananthasivan, P.R. Vasudeva Rao, Thermochim. Acta 452 (2007) 1.
- [20] O. Knacke, O. Kubaschewski, K. Hesselmann (Eds.), Thermochemical Properties of Inorganic Substances, second ed., Springer-Verlag, Germany, 1991.