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Thermodynamic characterization of lanthanum tellurate

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ABSTRACT

The standard Gibbs energy of formation of lanthanum tellurate, La_2TeO_6 was derived from its vapour pressure measurements in the temperature range 1420–1520 K employing TG based transpiration method. The temperature dependence of vapour pressure of TeO_2 vapour over the mixture La_2TeO_6 (s) + La_2O_3 (s) generated by the incongruent vapourisation reaction, $La_2TeO_6\ (s) \rightarrow La_2o_3\ (s) + TeO_2\ (g) + 1/2O_2\ (g)$ could be represented as: $\log p\ (\mathrm{Pa}) = [18.47 - 27127/T\,(\mathrm{K})] \pm 0.03$ (1420–1520 K). Enthalpy increments on La_2TeO_6 were determined by using inverse drop calorimetry in the temperature range 583–1287 K and the thermodynamic functions, namely, heat capacity, entropy and Gibbs energy functions were derived. The mean value of $-2381.3 \pm 2.0\ \mathrm{kJ\,mol^{-1}}$ was obtained for $\Delta_f H^\circ_{298}$ (La_2TeO_6) by combining the value of $\Delta_f G^\circ$ (La_2TeO_6) derived from vapour pressure data and the free energy functions of La_2TeO_6 derived from the drop calorimetry data.

1. Introduction

Data on the thermodynamic properties of the compounds that could be formed through the possible interactions between fuel, fission products and the constituents of the clad and coolant are important in evaluating the performance of the mixed oxides of uranium and plutonium as fuels for fast breeder reactors [1,2]. Rare earths and tellurium are among the major fission products formed during the burn up of a fast reactor fuel [1–3]. To predict the chemical behavior of the above fission products, a study is being undertaken on the thermochemical properties of compounds in rare earth–tellurium–oxygen system. As a part of the ongoing thermodynamic investigations on the rare earth tellurates, we report the values of the vapour pressure of lanthanum tellurate measured by using a transpiration technique employing a horizontal beam type thermal analyser. From the measured partial pressure of TeO_2 (g) over the mixture La_2TeO_6 and La_2O_3, the standard Gibbs energy of formation of La_2TeO_6 was determined for the first time.

In addition, enthalpy increments of La_2TeO_6 were measured by employing the method of inverse drop calorimetry in the temperature range 583–1287 K for the first time. The measured data were fitted into a polynomial equation and from this fit, other thermodynamic functions viz. heat capacity, entropy and free energy function were derived in the temperature range 298–1300 K.

2. Experimental

2.1. Materials

Analytical reagent grade TeO_2 of purity greater than 99.9% was procured from M/s. Aldrich Chemicals, USA. La_2O_3 with a purity of 99.99% was supplied by M/s. Indian Rare Earths Ltd, India. High purity O_2 ($H_2O < 2$ ppm) was obtained from M/s. Indian Oxygen Ltd, India.

The ternary oxide La_2TeO_6 was prepared by a solid state reaction between an equimolar mixture of La_2O_3 and TeO_2. This mixture was prepared by homogenizing the two oxides intimately followed by cold compaction into cylindrical pellets of 10 mm diameter and 2–3 mm thickness. These green compacts were heated in air at 923 K for 24 h and then at 1200 K for 60 h. These pellets were withdrawn intermittently during the heat treatment from the furnace. Compacts were powdered, re-compacted and then heat treated again. This cycle was repeated twice to ensure the complete formation of La_2TeO_6. The purity of the final product was ascertained by powder XRD using XPERT MPD system supplied by M/s. Philips, The Netherlands.

2.2. Apparatus used in the transpiration experiments

A horizontal beam type thermal analyser (model Seiko 320, Japan) was adopted as a transpiration apparatus for carrying out the vapour pressure measurements. A Pt–13% Rh/Pt thermocouple, which formed an arm of the balance beam was used for measuring the temperature of the sample as well as the temperature

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differential. The accuracy of temperature measurement in this study was determined by measuring the melting points of pure metals such as In, Sn, Al, Au and was found to be ±0.5 K. The calibration was found to conform to ITS-90 [4] scale. High purity oxygen was used as the carrier gas. The flow was monitored by using a glass capillary flow meter. This flow meter in turn was calibrated with the help of a soap bubble flow meter which was constructed using a horizontal calibrated burette. A wet test meter (M/s. Toshniwal, India) was used for total volume measurement at the outlet and was in turn calibrated with a capillary flow meter. The furnace was purged with the carrier gas at room temperature prior to heating.

2.3. Procedure for transpiration experiment

Non-isothermal TG experiments were carried out on La_2TeO_6 using TG/DTA thermal analyser in order to identify the mass loss steps and to determine the decomposition temperature of La_2TeO_6 for vapour pressure measurements. In a typical experiment, ~75 mg of La_2TeO_6 was taken in a Pt crucible and was heated in a flowing stream of pure oxygen (flow rate: 8 $dm^3\ h^{-1}$) at a linear heating rate of 0.07 $K\ s^{-1}$.

To carry out transpiration experiment initially, a few blank runs were carried out by maintaining the oxygen flow in the range of 3–12 $dm^3\ h^{-1}$. To study the vapour pressure of TeO_2 vapour over the mixture $La_2TeO_6 + La_2O_3$, the sample was spread in a flat platinum crucible in order to maximize the surface area exposed to the gas. At each flow rate or at each measurement temperature a fresh sample was taken instead of recycling the same sample to avoid errors arising from sintering, surface depletion and oxidation.

2.4. High temperature drop calorimetry

A "multi-detector" High Temperature Calorimeter (MHTC-96) with a drop detector of M/s. SETARAM, France was employed for measuring the enthalpy increments of La_2TeO_6. This tubular calorimetric detector consisted of a thermopile having 36 thermocouples in which a sample crucible and an empty reference crucible were positioned one above the other. These thermocouples covered the whole surface enabling the measurement of an integrated heat exchange between the crucibles. In the present study, a drop detector, made up of Pt–30% Rh/Pt–6% Rh thermocouples were employed. The detector was placed in a gas-tight alumina tube which in turn was placed in the resistively heated graphite furnace. In a typical experiment, pellets of reference α-alumina (SRM 720) and pellets of La_2TeO_6 (4 mm diameter and 1–2 mm thickness) were dropped alternatively from the specimen holder, maintained at the ambient temperature, into the sample crucible at the experimental temperature '*T*'. From the areas of the peaks corresponding to the alumina reference and the sample, the enthalpy increments of the La_2TeO_6 samples were determined by using the critically assessed enthalpy increment values of alpha alumina reported in reference [5].

3. Results and discussion

3.1. Purity of the starting materials

The purity of La_2TeO_6 was ascertained by powder XRD, comparing the powder XRD pattern obtained with the specimen with that reported in JCPDS X-ray diffraction files (No. 78-0998). Thus the presence of La_2TeO_6 and absence of La_2O_3 and TeO_2 were ascertained. Peaks pertaining to La_2TeO_6 were only observed. 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%.

3.2. Non-isothermal thermogravimetric analysis

The mean variation in mass obtained from the blank run was found to be of the order of 10–20 µg for about 100 K raise in temperature over the entire range of flow rate (3–12 $dm^3\ h^{-1}$) employed in this study. Similar variation in mass was also observed for isothermal experiment for a period of one hour. The mass loss obtained from the blank run was subtracted from all the recorded isothermal mass losses. The validity of this transpiration technique was already established on well characterized materials such as pure TeO_2 [6]. The details of the experimental design and the method of measurement of the vapour pressure are described elsewhere [7,8].

The simultaneous TG/DTA curves revealed that the sample started losing mass at a temperature pertaining to the inception of the decomposition of La_2TeO_6 (s) viz. 1410 K in pure O_2. The X-ray diffraction analysis of the decomposition product indicated the presence of the compounds La_2TeO_6 (s) and La_2O_3 (s). These observations lead to the conclusion that the volatilization of the ternary compound takes place through the following chemical reaction:

$$La_2TeO_6\ (s) \rightarrow La_2O_3\ (s) + TeO_2\ (g) + 1/2O_2\ (g). \qquad (1)$$

From the foregoing discussion it is evident that in presence of oxygen, La_2TeO_6 incongruently vapourises above 1410 K. The apparent vapour pressure of the TeO_2 (g) (p^{app}) in equilibrium with a mixture of La_2TeO_6 (s) and La_2O_3 (s) was calculated from the mass loss of the sample per unit volume of the carrier gas (pure oxygen) swept over it, using the relation:

$$P^{app} = WRT_c/MV_c, \qquad (2)$$

where '*W*' is the mass loss of the sample, '*R*' is the universal gas constant, 'T_c' is the ambient temperature of the carrier gas (297.15 K) and '*M*' is the molecular weight of the vapour species, 'V_c' is the total volume of the carrier gas (saturated with the vapour species).

The mass loss of the sample per unit volume of the carrier gas (pure oxygen) swept over it was monitored as a function of flow rate at 1471 K. In order to establish the measured values of p^{app} to be the equilibrium vapour pressure at 1471 K, it was necessary to demonstrate the existence of a chair-shaped curve in the plot of p^{app} against flow rate. Such a plot at 1471 K is shown in Fig. 1. The existence of a plateau over the flow rates region 6–8.6 $dm^3\ h^{-1}$ shows that the vapourisation rate was adequate to saturate the

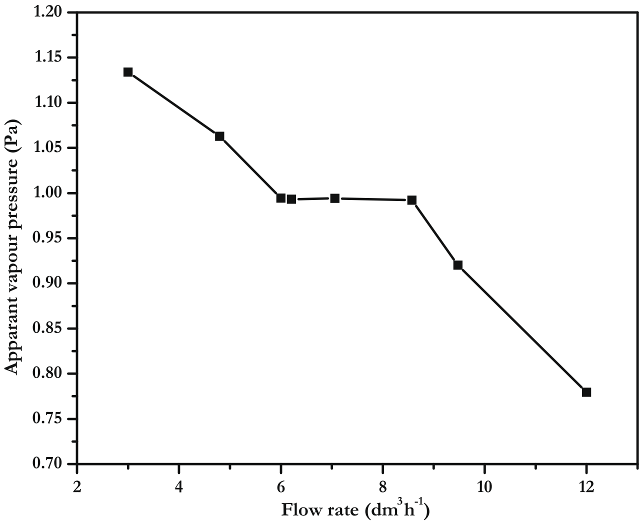

Fig. 1. A plot of apparent vapour pressure vs flow rate of gas at 1471 K.

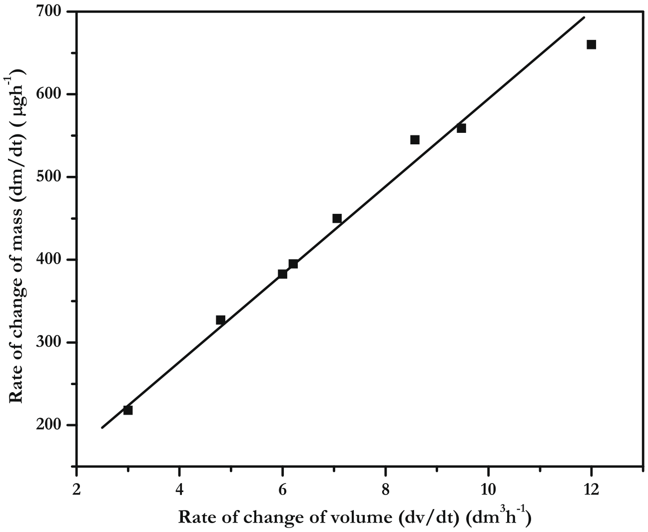

Fig. 2. A plot of rate of mass loss (dm/dt) vs rate of flow of oxygen (dv/dt).

carrier gas for any flow rate within this range. The rate of mass loss (dm/dt) vs flow rate (dv/dt) is depicted in Fig. 2. It was found that the mass loss increased with flow rate thus conforming to true transpiration. The transpiration experiments were carried out at different temperatures by employing a flow that pertained to the plateau region. The vapour species were assumed to be predominantly monomeric TeO_2 (g) species. This assumption is in agreement with the observations made by Muenow et al. [9], who estimated the contribution of all other tellurium-bearing species [TeO, $(TeO)_2$, Te_2] to the total pressure to be less than 5%.

The vapour pressure of TeO_2 (g) over a mixture of La_2TeO_6 (s) and La_2O_3 (s) was derived from the measured values of mass loss of the sample, m_{total} per unit volume of O_2 (g) at one atmosphere pressure. As the mass loss was due to the volatilization of both TeO_2 and O_2, m_{total} values were corrected for the contribution of O_2 to obtain the value of '*W*' as:

$$W = m_{TeO_2} = m_{Total} \times \left[(M_{TeO_2})/(M_{TeO_2} + 0.5M_{O_2})\right] \quad (3)$$

$$P^{app} = p_{TeO_2} = (m_{TeO_2} \times R \times T_c)/(M \times V_c).$$

The mass loss (W), temperature (T_c), volume of the gas (V_c) and the values of the vapour pressure p_{TeO_2} at the experimental temperature are given in Table 1. The temperature dependence of vapour pressure as plotted in Fig. 3 could be represented by the following least square expression:

$$\log p \text{ (Pa)} = [18.47 - 27127/T \text{ (K)}](\pm 0.03) \quad (1421\text{–}1520\text{ K}). \quad (4)$$

The standard Gibbs energy change, $\Delta G^\circ_{r(1)}$ for the reaction (1) could be expressed by the following expression:

$$\Delta G^\circ_{r(1)} = -RT \ln K \text{ where } K \text{ is the equilibrium constant,} \quad (5)$$

$$= -RT \ln\left\{\left[a_{La_2O_3} \times p_{TeO_2} \times p^{1/2}_{O_2}\right] \big/ a_{La_2TeO_6}\right\}, \quad (6)$$

where La_2O_3 and La_2TeO_6 are at unit activity and p_{O_2} is one atmosphere. Hence,

$$\Delta G^\circ_{r(1)} = -RT \ln p_{TeO_2}, \quad (7)$$

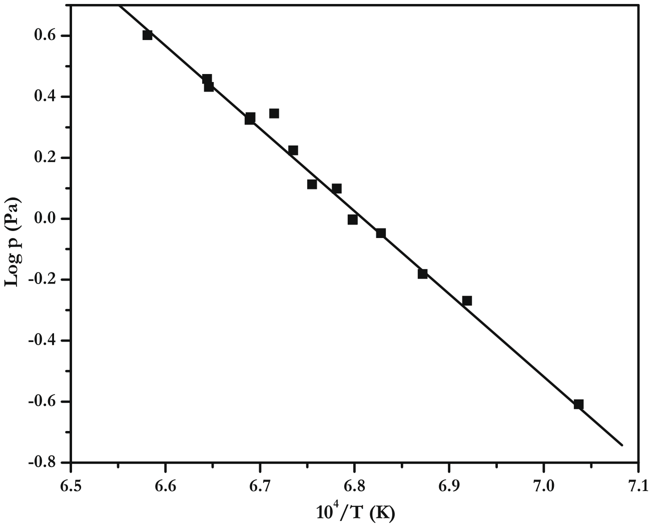

Fig. 3. Temperature dependence of vapour pressure of TeO_2 vapour over the mixture La_2TeO_6 (s) + La_2O_3 (s).

Table 1
Vapour pressure data and calculation of standard free energy of formation of La_2TeO_6.

T (K)	Mass loss (µg)	V_c (dm^3)	p_{TeO_2} (Pa)	$p^\circ_{TeO_2}$ (Pa)	$\Delta_fG^\circ(La_2TeO_6)^{(a)}$ (kJ mol^{-1})	$\Delta_fG^\circ(La_2TeO_6)^{(b)}$ (kJ mol^{-1})
1421.2	136.3	8.571	0.2464	14697	−1604.5	−1602.0
1445.3	245.4	7.059	0.5384	20145	−1590.5	−1588.6
1455.2	299.9	7.059	0.6581	22862	−1586.1	−1583.1
1464.8	409.0	7.059	0.8974	25803	−1580.4	−1577.8
1471.0	382.7	6.0	0.9945	27878	−1577.9	−1574.3
1471.0	395.0	6.207	0.9932	27878	−1577.9	−1574.3
1471.0	450	7.059	0.9940	27878	−1577.9	−1574.3
1471.0	545	8.571	0.9921	27878	−1577.9	−1574.3
1474.8	572.6	7.059	1.2563	29222	−1574.3	−1572.2
1480.4	654.4	7.815	1.2969	31307	−1572.8	−1569.1
1484.9	763.5	7.059	1.6751	33078	−1568.7	−1566.6
1489.2	996.8	7.059	2.2137	34853	−1565.3	−1564.2
1494.9	981.6	7.059	2.1537	37335	−1563.5	−1561.1
1495.0	1064.4	7.815	2.1075	38380	−1563.7	−1561.0
1504.7	1363.3	7.815	2.7019	41973	−1558.6	−1555.6
1505.2	1308.8	7.059	2.8716	42223	−1557.7	−1555.4
1519.6	2017.7	7.815	3.9988	50007	−1550.5	−1547.4

Initial weight of the sample: 75 mg.
$\Delta G^\circ_f(La_2TeO_6)(a) = \Delta G^\circ_f(La_2O_3, s) + \Delta G^\circ_f(TeO_2, g) + RTp_{TeO_2}$.
$\Delta G^\circ_f(La_2TeO_6)(b) = \Delta G^\circ_f(La_2O_3, s) + \Delta G^\circ_f(TeO_2, l) + RT \ln\left(p_{TeO_2}/p^\circ_{TeO_2}\right)$.

$$\Delta G^{\circ}_{r(1)}\ (\mathrm{kJ\ mol^{-1}}) = [519.4 - 0.2578T\ (\mathrm{K})] \pm 0.1 \quad (1421\text{–}1520\ \mathrm{K}). \tag{8}$$

The standard Gibbs energy of formation of La_2TeO_6 could be expressed in terms of the partial pressure of TeO_2 (g) over a mixture of La_2TeO_6 and La_2O_3 by the following equation,

$$\Delta_f G^{\circ}(\mathrm{La_2TeO_6,s}) = \Delta_f G^{\circ}(\mathrm{La_2O_3,s}) + \Delta_f G^{\circ}(\mathrm{TeO_2,g}) - \Delta G^{\circ}_{r(1)}, \tag{9}$$

$$= \Delta_f G^{\circ}(\mathrm{La_2O_3,s}) + \Delta_f G^{\circ}(\mathrm{TeO_2,g}) + RT\ \ln p_{\mathrm{TeO_2}}. \tag{10}$$

Combining the expression (8) along with the key data for $\Delta_f G^{\circ}$ (La_2O_3, s) and $\Delta_f G^{\circ}$ (TeO_2, g) obtained from Ref. [10], the temperature dependence of $\Delta_f G^{\circ}$ (La_2TeO_6, s) was calculated to be,

$$\Delta_f G^{\circ}(\mathrm{La_2TeO_6,s})(\mathrm{kJ\ mol^{-1}}) = [-2395.4 + 0.5563T\ (\mathrm{K})] \quad (\pm 5.0) \quad (1421\text{–}1520\ \mathrm{K}). \tag{11}$$

Table 1 also presents $\Delta_f G^{\circ}$ (La_2TeO_6, s) values calculated from Eq. (11) for each experimental temperature.

The $\Delta_f G^{\circ}$ (La_2TeO_6, s) could also be expressed in terms of the partial pressures of the TeO_2 vapour over La_2TeO_6 and pure liquid TeO_2 as the reference state as given in the following equation:

$$\Delta_f G^{\circ}(\mathrm{La_2TeO_6,s}) = \Delta_f G^{\circ}(\mathrm{La_2O_3,s}) + \Delta_f G^{\circ}(\mathrm{TeO_2,l}) + RT\ \ln\left(p_{\mathrm{TeO_2}}/p^{\circ}_{\mathrm{TeO_2}}\right), \tag{12}$$

The vapour pressure of TeO_2 (g) over the pure liquid TeO_2 was taken from our recent study [6]. Other auxiliary data viz., $\Delta_f G^{\circ}$ (TeO_2, l) and $\Delta_f G^{\circ}$ (La_2O_3, s) were taken from the Ref. [10]. The *Delta*$_f G^{\circ}$ (La_2TeO_6, s) calculated by using Eq. (12) are also listed in Table 1 and could be expressed as:

$$\Delta_f G^{\circ}(\mathrm{La_2TeO_6,s})(\mathrm{kJ\ mol^{-1}}) = [-2390.6 + 0.5549T\ (\mathrm{K})] \quad (\pm 5.8) \quad (1421\text{–}1520K). \tag{13}$$

The slope and intercept of Eqs. (9) and (11) are proportional to the standard molar enthalpy and entropy of formation of La_2TeO_6 (s) respectively from the elements in the temperature range 1421–1520 K. The standard Gibbs energy of formation of La_2TeO_6 (s) is being reported for the first time. The average "second law" enthalpy of formation of La_2TeO_6 obtained was found to be -2393 ± 5.8 kJ mol^{-1} at the mean temperature of the present measurement.

3.3. Measurement of enthalpy increments by drop calorimetry

The enthalpy increments of La_2TeO_6 (s) was measured by the drop calorimetric method in the temperature range 583–1287 K. The measured values were fitted into a 4-term polynomial function using the least-squares method.

$$H^{\circ}_T - H^{\circ}_{298}(\mathrm{J\ mol^{-1}}) = 236.602T + 0.236 \times 10^{-3}T^2 + 39.978 \times 10^5/T\ (\mathrm{K}) - 83973. \tag{14}$$

The following constraints were used for fitting the data: (a) $H^{\circ}_T - H^{\circ}_{298} = 0$ at 298 K and (b) the derivative of the function at 298 K is equal to the value of heat capacity of La_2TeO_6 at 298 K (191.77 J K^{-1} mol^{-1}). The latter was estimated from the values of $C^{\circ}_{p,298K}$ pertaining to La_2O_3 [11] and TeO_3 [12] by applying Neuman–Kopp's molar additivity rule. The value of S°_{298K} of TeO_3 was estimated by combining the values of S°_{298K} of TeO_2 [10] and the difference between the values of S°_{298K} pertaining to A_2TeO_3 and A_2TeO_4 (where A = alkali metal) from Ref. [13]. The value of S°_{298K} (La_2TeO_6) was computed by combining the S°_{298K} (TeO_2) thus obtained with that of La_2O_3 [11] using Neuman–Kopp's molar additivity rule. The standard error of this fit was 1.7% and the estimated standard deviation of this fit was 2.5 kJ mol^{-1}. The val-

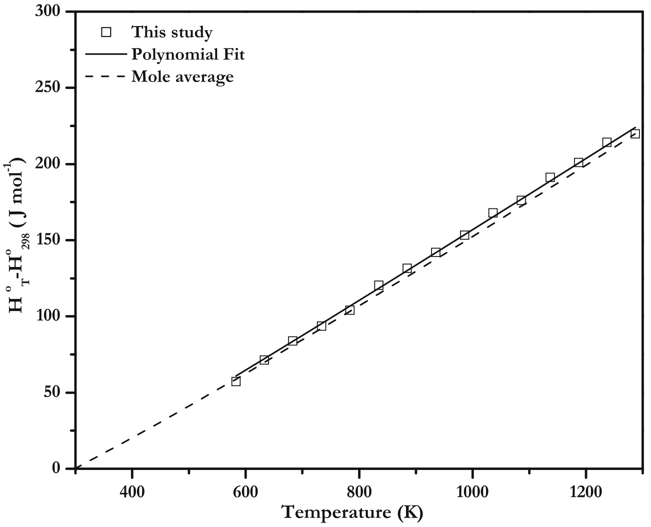

Fig. 4. Measured value of the enthalpy increments on La_2TeO_6.

Table 2
Thermodynamic functions of La_2TeO_6.

T (K)	$H^{\circ}_T - H^{\circ}_{298}$ (kJ mol^{-1})		T (K)	$H^{\circ}_T - H^{\circ}_{298}$ (kJ mol^{-1})	C°_P (J K^{-1} mol^{-1})	S°_T (J K^{-1} mol^{-1})	$-(G_T - H^{\circ}_{298})/T$ (J K^{-1} mol^{-1})
	Measured	Fit					
583	57.236	60.904	298	0	191.77	205.127	205.127
633	71.329	72.207	300	0.355	192.32	206.315	205.131
683	83.907	83.590	400	20.701	211.81	264.712	212.960
734	93.537	95.267	500	42.383	220.85	313.057	228.291
784	104.079	106.768	600	64.737	225.78	353.799	245.905
835	120.363	118.543	700	87.476	228.77	388.846	263.880
885	131.625	130.123	800	110.458	230.73	419.531	281.459
935	141.959	141.732	900	133.603	232.09	446.790	298.343
986	153.292	153.601	1000	156.864	233.08	471.297	314.434
1036	167.956	165.260	1100	180.210	233.82	493.548	329.721
1086	176.046	176.937	1200	203.622	234.39	513.919	344.234
1137	191.245	188.866	1300	227.085	234.85	532.699	358.018
1187	200.914	200.575	–	–	–	–	–
1237	214.239	212.298	–	–	–	–	–
1287	219.701	224.030	–	–	–	–	–

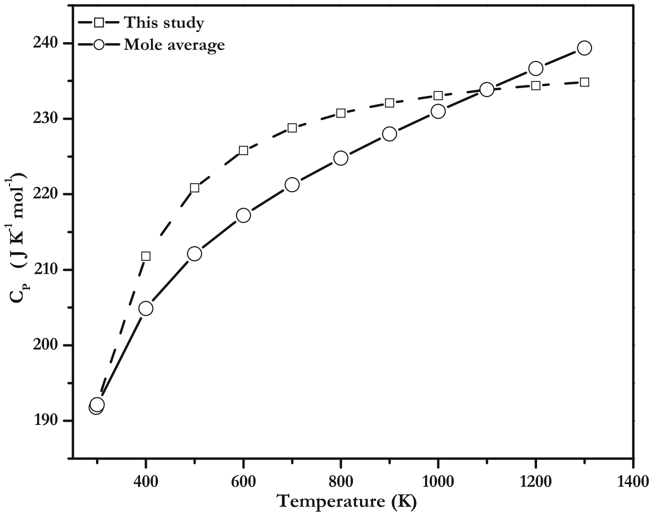

Fig. 5. Temperature dependence of the *Cp* values derived from the measured values of the enthalpy increments pertaining to the La_2TeO_6 specimens.

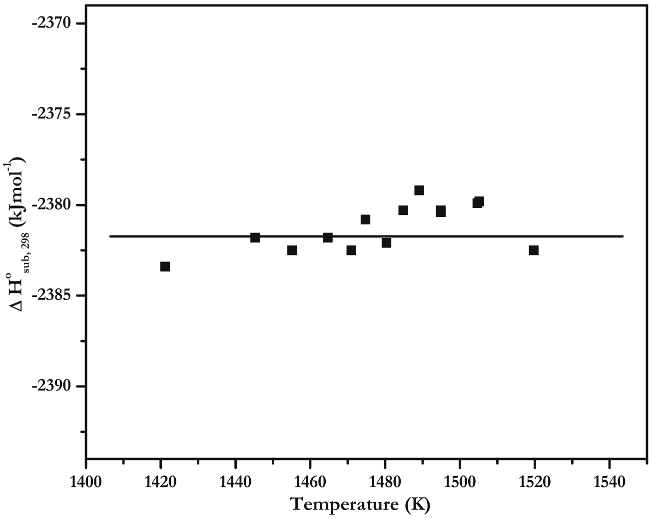

Fig. 6. Third law analysis of the experimental data for La_2TeO_6.

ues of the enthalpy increment obtained through measurement as well as by interpolation at a desired temperature by using the above fit are given in Table 2. In addition, the calculated values of enthalpy increments and other thermodynamic functions viz. heat capacity, entropy and free energy functions at regular intervals of temperature are also presented in Table 2.

In Fig. 4, the measured values and those obtained by interpolating the fit values of the enthalpy increments obtained in present study are compared with the values cited in the literature. As can be seen from Fig. 4, the present enthalpy increment data are in agreement with those cited in the literature [10,12] within 3.3%. In Fig. 5, the heat capacity values from the present study are compared with the mole average values. The mole average values of heat capacity of La_2TeO_6 were obtained from the constituent binary oxides La_2O_3 [11] and TeO_3 [12] by applying Newman–Kopp's additivity rule. The agreement in the present heat capacity data is within 3.5% at temperatures below 800 K and within 1% for temperatures above 800 K.

3.4. Third-law analysis of the vapour pressure data

In order to determine the temperature dependent errors in the values of the vapour pressure obtained in this study, "third-law analysis" of the data was carried out. The free energy functions of La_2TeO_6 derived from the present drop calorimetric data (Table 2) were used in conjunction with the free energy functions of the elements La, Te and O_2 [14] in order to derive the change in free energy function (Δfef) for the formation of La_2TeO_6. For the computation of $\Delta_f H^{\circ}_{298}$ (La_2TeO_6), expression (13) was used.

$$\Delta_f H^{\circ}_{298}(La_2TeO_6) = \Delta_f G^{\circ}(La_2TeO_6) - T \times (\Delta \text{fef}). \qquad (15)$$

The Δfef values interpolated at the actual temperatures at which the vapour pressure measurements were carried out were combined with the values of $\Delta_f G^{\circ}$of La_2TeO_6 in order to obtain $\Delta_f H^{\circ}_{298}$ corresponding to each experimental measurement. A plot of $\Delta_f H^{\circ}_{298}$ vs temperature is shown in Fig. 6. The mean value of $\Delta_f H^{\circ}_{298}$ was found to be -2381.3 ± 2.0 kJ mol^{-1}. The random scatter of values of $\Delta_f H^{\circ}_{298}$ around its mean value in Fig. 6 indicates the absence of temperature dependent errors in the vapour pressure measurements.

3.5. Errors in measurement

The precision in the values of the flow rate measured by the capillary flow meter was ±5%, which resulted in an overall precision in the integral volume of ±1% of the total volume of the carrier gas. The uncertainty in the measurement of temperature is ±0.5 K and the error in the measurement of vapour pressure of TeO_2 vapour over the mixture La_2TeO_6 (s) + La_2O_3 (s) was found to be ±0.03%. These two factors introduce an error ±5 kJ mol^{-1} in the measurement of Gibbs energy of formation of La_2TeO_6.

4. Conclusion

The ternary oxide, La_2TeO_6 (s) was prepared by the solid state reaction of an equimolar mixture of La_2O_3, and TeO_2 and was characterized by X-ray and TG/DTA. The vapour pressure of TeO_2 (g) over the mixture La_2TeO_6 (s) + La_2O_3 (s) was measured by the TG based transpiration method. The values of $\Delta_f G^{\circ}$ of La_2TeO_6 (s) were calculated from these vapour pressure measurements and reported for the first time. The average second law enthalpy of formation of La_2TeO_6 obtained from the present work was found to be -2393 ± 5.8 kJ mol^{-1}. Enthalpy increments on La_2TeO_6 have been measured in the temperature range 583–1769 K for the first time by inverse drop calorimetry. Other thermodynamic functions of La_2TeO_6, namely, heat capacity, entropy and free energy functions were computed in the temperature range 298–1300 K. A third-law analysis of the vapour pressure data yielded a mean value of -2381.3 ± 2.0 kJ mol^{-1} for $\Delta_f H^{\circ}_{298}$ (La_2TeO_6).

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References

[1] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221–246.
[2] E.H.P. Cordfunke, R.J.M. Konings, J. Nucl. Mater. 152 (1988) 301–309.
[3] Y. Abbas, Thesis, University of Grenoble (1976), cited in T. Thevenin, J. Jove, M. Pages, Mater. Res. Bull. 20 (1985) 1075–1080.
[4] H. Preston-Thomas, Metrologia 27 (1) (1990) 3–10.
[5] Synthetic Sapphire Al_2O_3, Certificate of Standard Reference Materials, SRM 720, National Bureau of Standards, US Department of Commerce, Washington, DC 20234, USA, 1982.
[6] S. Balakrishnan, R. Pankajavalli, K. Ananthasivan, S. Anthonysamy, Thermochim. Acta 467 (2008) 80–85.
[7] R. Pankajavalli, C. Mallika, O.M. Sreedharan, V.S. Raghunathan, P. Antony Premkumar, K.S. Nagaraja, Chem. Eng. Sci. 57 (2002) 3603–3610.

[8] R. Pankajavalli, Ashish Jain, S. Anthonysamy, K. Ananthasivan, P.R. Vasudeva Rao, Thermochim. Acta 452 (2007) 1–6.
[9] D.W. Muenow, J.W. Hastie, R. Hauge, R. Bautista, J.L. Margrave, Trans. Faraday Soc. 65 (1969) 3210–3220.
[10] O. Knacke, O. Kubaschewski, K. Hesselmann (Eds.), Thermochemical Properties of Inorganic Substances, second ed., Springer-Verlag, Germany, 1991.
[11] M.W. Chase, NIST-JANAF Thermochemical Tables, fourth ed., American Institute of Physics for the National Institute of Standards and Technology, USA, 1998.
[12] R. Agarwal, Z. Singh, J. Alloys Compd. 414 (2006) 230–234.
[13] T. B Lindemer, T.M. Bessman, J. Nucl. Mater. 100 (1981) 178–226.
[14] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, Selected Values of the Thermodynamic Properties of Elements, American Society for Metals, Metals Park, Ohio, 1973.