



The standard molar Gibbs energy of formation of $\text{CeTe}_2\text{O}_6(\text{s})$ and $\text{R}_2\text{TeO}_6(\text{s})$ ($\text{R} = \text{La}, \text{Nd}, \text{Dy}, \text{Y}$)

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ABSTRACT

Ternary oxides $\text{CeTe}_2\text{O}_6(\text{s})$, $\text{La}_2\text{TeO}_6(\text{s})$, $\text{Nd}_2\text{TeO}_6(\text{s})$, $\text{Dy}_2\text{TeO}_6(\text{s})$ and $\text{Y}_2\text{TeO}_6(\text{s})$ have been prepared by solid-state reaction technique and characterized by X-ray powder diffraction method. The standard molar Gibbs energy of formation of these compounds have been determined by measuring $\text{TeO}_2(\text{g})$ over required biphasic equilibrium mixture using a transpiration technique. The standard molar Gibbs energy of formation of these compounds were calculated from the measured $\text{TeO}_2(\text{g})$ pressures and are given as:

$$\begin{aligned} \{\Delta_f G_m^\circ(\text{CeTe}_2\text{O}_6, \text{s}, T) \pm 9\} / \text{kJ mol}^{-1} &= -1683.0 + 0.4944(T/\text{K}) \quad (922 \leq T/\text{K} \leq 1074), \\ \{\Delta_f G_m^\circ(\text{La}_2\text{TeO}_6, \text{s}, T) \pm 8\} / \text{kJ mol}^{-1} &= -2308.6 + 0.5776(T/\text{K}) \quad (993 \leq T/\text{K} \leq 1158), \\ \{\Delta_f G_m^\circ(\text{Nd}_2\text{TeO}_6, \text{s}, T) \pm 7\} / \text{kJ mol}^{-1} &= -2309.1 + 0.5802(T/\text{K}) \quad (983 \leq T/\text{K} \leq 1213), \\ \{\Delta_f G_m^\circ(\text{Dy}_2\text{TeO}_6, \text{s}, T) \pm 6\} / \text{kJ mol}^{-1} &= -2343.7 + 0.5852(T/\text{K}) \quad (944 \leq T/\text{K} \leq 1089), \\ \{\Delta_f G_m^\circ(\text{Y}_2\text{TeO}_6, \text{s}, T) \pm 7\} / \text{kJ mol}^{-1} &= -2391.2 + 0.5694(T/\text{K}) \quad (1017 \leq T/\text{K} \leq 1102). \end{aligned}$$

The Gibbs energies of formation of $\text{La}_2\text{TeO}_6(\text{s})$, $\text{Dy}_2\text{TeO}_6(\text{s})$ and $\text{Y}_2\text{TeO}_6(\text{s})$ have been reported for the first time.

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1. Introduction

Tellurium is one of the highly corrosive fission products and its interaction with other fission products influences the chemistry of the fuel [1–3]. The prediction of chemical state of fission products in various stages of nuclear fuel cycle is possible with the help of thermodynamic data-base containing relevant tellurium compounds. The thermodynamic studies of tellurium compounds with other fission products are currently being pursued in our laboratory. As a part of study, a systematic investigation on rare earth–tellurium–oxygen systems has been taken up. These systems have been characterized by a number of ternary compounds. In general, rare earth oxides are highly soluble in fuel matrix to form solid solutions. To know whether rare earth tellurates will form in any stage of nuclear fuel cycle, thermodynamic properties of these ternary compounds are required. In $\text{R}_2\text{O}_3\text{–TeO}_2$ system, $\text{R}_2\text{TeO}_6(\text{s})$ coexists with $\text{R}_2\text{O}_3(\text{s})$ and $\text{CeTe}_2\text{O}_6(\text{s})$ coexists with $\text{CeO}_2(\text{s})$ in $\text{CeO}_2\text{–TeO}_2$ system. The literature survey gave limited thermodynamic data [4–7] on rare earth–tellurium–oxygen system and showed strong similarity of yttrium to rare earths. Fission yield of yttrium in U or Pu fission is normally grouped with rare earths due

to its strong chemical similarities with rare earths. As in R–Te–O system, $\text{Y}_2\text{TeO}_6(\text{s})$ also coexists with $\text{Y}_2\text{O}_3(\text{s})$ in $\text{Y}_2\text{O}_3\text{–TeO}_2$ system. This paper gives the standard molar Gibbs energy of formation of $\text{La}_2\text{TeO}_6(\text{s})$, $\text{CeTe}_2\text{O}_6(\text{s})$, $\text{Nd}_2\text{TeO}_6(\text{s})$, $\text{Dy}_2\text{TeO}_6(\text{s})$ and $\text{Y}_2\text{TeO}_6(\text{s})$ by measuring $\text{TeO}_2(\text{g})$ pressures over the equilibrium phase fields using transpiration method in the temperature range 922–1213 K.

2. Experimental

2.1. Material preparation

$\text{CeTe}_2\text{O}_6(\text{s})$ and $\text{R}_2\text{TeO}_6(\text{s})$ were prepared by mixing respective rare earth oxides with $\text{TeO}_2(\text{s})$ and heating the mixture in air at required temperature as per the method reported in the literature [7]. $\text{CeTe}_2\text{O}_6(\text{s})$ was prepared by mixing $\text{CeO}_2(\text{s})$ and $\text{TeO}_2(\text{s})$ in the mole ratio 1:2. $\text{La}_2\text{TeO}_6(\text{s})$, $\text{Nd}_2\text{TeO}_6(\text{s})$, $\text{Dy}_2\text{TeO}_6(\text{s})$ and $\text{Y}_2\text{TeO}_6(\text{s})$ were synthesized by a solid-state reaction between $\text{R}_2\text{O}_3(\text{s})$ and $\text{TeO}_2(\text{s})$ in the mole ratio of 1:1. Rare earth oxides, yttrium oxide and $\text{TeO}_2(\text{s})$ with mass fraction purity of 0.995 were taken from Aldrich, USA. Before weighing, rare earth oxides were calcined at 1173 K in air for 2 h to remove adsorbed moisture and $\text{CO}_2(\text{g})$ and $\text{TeO}_2(\text{s})$ at 500 K to remove moisture. These mechanical mixtures were separately pressed into pellet at 100 MPa pressure and pellets were kept in separate alumina boats. The phase mixture: $\{\text{CeO}_2(\text{s}) + 2\text{TeO}_2(\text{s})\}$ and $\{\text{R}_2\text{O}_3(\text{s}) + \text{TeO}_2(\text{s})\}$ were separately heated at 500 K for 100 h. Then $\{\text{CeO}_2(\text{s}) + 2\text{TeO}_2(\text{s})\}$ was heated at 800 K for 100 h and $\{\text{R}_2\text{O}_3(\text{s}) + \text{TeO}_2(\text{s})\}$ was heated at 1073 K for 200 h with intermediate grindings. The reaction products were analyzed by STOE, Germany, X-ray diffractometer using $\text{Cu K}\alpha$ radiation. These compounds were identified as $\text{CeTe}_2\text{O}_6(\text{s})$, file number 80-1879 [8], $\text{La}_2\text{TeO}_6(\text{s})$ [8], file number 78-0998, $\text{Nd}_2\text{TeO}_6(\text{s})$ [8], file number 50-0255 [8], $\text{Dy}_2\text{TeO}_6(\text{s})$ [8], file number 50-0259 and $\text{Y}_2\text{TeO}_6(\text{s})$ [9]. Separate homogeneous biphasic mixture $\{\text{CeO}_2(\text{s}) + \text{CeTe}_2\text{O}_6(\text{s})\}$ and $\{\text{R}_2\text{TeO}_6(\text{s}) + \text{R}_2\text{O}_3(\text{s})\}$ were made and

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Table 1
Pressures of TeO₂(g) over {CeTe₂O₆(s)+CeO₂(s)} and Δ_rG^o_m(CeTe₂O₆,s,T) values as a function of temperature.

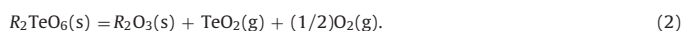
(T/K)	Mass (TeO ₂) × 10 ³ gm	V(O ₂) dm ³	V(O ₂) _{STP} dm ³	p(TeO ₂) × 10 ⁴ kPa	Δ _r G ^o _m (T) kJ mol ⁻¹	Δ _r G ^o _m (T) kJ mol ⁻¹
922	2.69	211.73	192.78	1.986	201.5	-1226.2
976	11.89	233.85	215.07	7.867	190.9	-1202.7
1008	16.63	121.48	110.24	21.47	180.4	-1184.5
1022	27.92	126.21	114.53	34.69	174.7	-1175.4
1036	32.08	119.74	108.66	42.01	173.8	-1171.2
1037	36.08	130.13	118.09	43.47	173.4	-1170.5
1044	42.17	133.75	122.60	48.94	172.5	-1167.9
1048	54.16	138.64	126.23	61.05	169.3	-1163.8
1055	32.94	71.95	65.51	71.55	167.7	-1160.5
1065	50.79	93.5	85.42	84.61	166.3	-1156.7
1074	44.02	66.46	60.31	103.9	164.0	-1152.3

V(O₂) is total volume of carrier gas (oxygen) collected at gas outlet temperature. V(O₂)_{STP} is total volume of oxygen at 273.15 K.

annealed at 800 K for 50 h and these mixtures were stored in desiccators for the transpiration measurements.

2.2. Experimental set-up

Transpiration apparatus was consisted of a 20 mm i.d. quartz reaction tube with 'O' ring sealed end couplings. The end couplings had provisions for carrier gas entry and insertion of a thermo-well at one side and a condenser at other side. The condenser was made of quartz with an orifice of 0.5 mm. Equilibrium biphasic mixture was kept in an alumina boat in the isothermal zone (20 mm) of the Kanthal wire-wound horizontal furnace. The system was repeatedly evacuated and flushed with dry oxygen as carrier gas for the transpiration measurements. The condenser was inserted into one end of the isothermal zone of the furnace as the furnace temperature became constant and carrier gas oxygen was flown over the sample from the other end. Carrier gas oxygen was used to stabilize tellurium to TeO₂(g) over equilibrium phase mixture. It gets saturated with TeO₂(g) which was generated due to one of the following reactions:



Carrier gas along with TeO₂(g) was then entered the quartz condenser where TeO₂(s) deposited in the cooler portion. The carrier gas then flown into the wet test meter for measurement of volume of O₂(g) passed over equilibrium phase mixture at a required temperature. The mass of the condensate TeO₂(s) per dm³ of the carrier gas flown at each experimental temperature was measured at the ambient temperature at which the carrier gas was collected for the measurement of its volume. Prior to the experiment, transpiration apparatus was calibrated by measuring flow rate plateau for TeO₂(s). The oxygen carrier gas was flown over pure TeO₂(s) at different flow rates (1.8–6 dm³ per hour) at 800 K. The mass of TeO₂(s) collected inside condenser was measured for these flow rates. The mass of TeO₂(s) collected per unit volume was found to be independent of the flow rate in the region of 2.4–3.6 dm³ per hour which was the flow rate plateau region for TeO₂(g). Thus, measurements were carried out at oxygen carrier gas flow rate at 2.7 dm³ per hour.

3. Results

The apparent equilibrium vapour pressure of TeO₂(g) at each experimental temperature was calculated for Eq. (1) and is given as:

$$p(\text{TeO}_2, \text{g}) = \frac{n(\text{TeO}_2, \text{s})}{\{n(\text{TeO}_2, \text{s}) + n(\text{carrier gas})\}} P \quad (3)$$

and that for Eq. (2) at each experimental temperature was calculated from following relation.

$$p(\text{TeO}_2, \text{g}) = \frac{n(\text{TeO}_2, \text{s})}{\{n(\text{TeO}_2, \text{s}) + n(\text{O}_2, \text{g}) + n(\text{carrier gas})\}} P \quad (4)$$

where P is the total pressure over the system ($p(\text{O}_2) = 101.325$ kPa), $n(\text{TeO}_2, \text{s})$, $n(\text{O}_2, \text{g})$ and $n(\text{carrier gas})$ are the respective number of moles. $\{n(\text{O}_2, \text{g}) + n(\text{carrier gas})\}$ can be calculated from the total volume of oxygen flown to the wet test meter at STP ($T = 273$ K, $P = 101.325$ kPa). One mole of carrier gas oxygen occupies 22.4 dm³ at STP.

3.1. Δ_fG^o_m(CeTe₂O₆,s,T)

The vapour pressures of TeO₂(g) over {CeTe₂O₆(s)+CeO₂(s)} have been calculated from Eq. (3) and are given in Table 1 and shown in Fig. 1. The linear least squares regression analysis of these data yielded following expression:

$$\{\ln(p(\text{TeO}_2, \text{g}) \pm 0.02/\text{kPa})\} = 19.903 - 26260(\text{K}/T) \quad (5)$$

The standard molar Gibbs energy change for Eq. (1) is expressed by the equation:

$$\Delta_r G^o_m(T) = -RT \ln K = -2RT \ln p(\text{TeO}_2) \quad (6)$$

The standard molar Gibbs energy change for reaction (1) can also be given as:

$$\Delta_r G^o_m(T) = \Delta_f G^o_m(\text{CeO}_2, \text{s}, T) + 2\Delta_f G^o_m(\text{TeO}_2, \text{g}, T) - \Delta_f G^o_m(\text{CeTe}_2\text{O}_6, \text{s}, T) \quad (7)$$

Δ_fG^o_m(CeTe₂O₆,s,T) can be given as:

$$\Delta_f G^o_m(\text{CeTe}_2\text{O}_6, \text{s}, T) = \Delta_f G^o_m(\text{CeO}_2, \text{s}, T) + 2\Delta_f G^o_m(\text{TeO}_2, \text{g}, T) + 2RT \ln p(\text{TeO}_2) \quad (8)$$

Δ_fG^o_m(CeTe₂O₆,s,T) has been calculated by incorporating Eq. (5) and Δ_fG^o_m(T) values for CeO₂(s) and TeO₂(g) from the literature [10] (given in Table 2) in Eq. (8) and corresponding expression is:

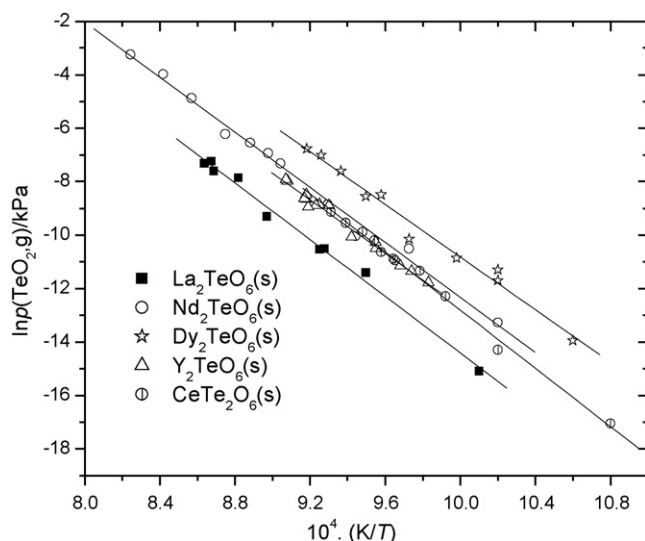


Fig. 1. Temperature dependence of equilibrium vapour pressure of CeTe₂O₆(s), La₂TeO₆(s), Nd₂TeO₆(s), Dy₂TeO₆(s) and Y₂TeO₆(s).

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