

Vaporization behaviour and thermodynamic stabilities of strontium tellurites, SrTeO₃ and SrTe₂O₅

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Abstract

The TeO₂ vapour pressure of the strontium tellurites SrTeO₃ and SrTe₂O₅ measured by the transpiration technique using a micro-thermobarometer in the temperature ranges 1254 ≤ T/K ≤ 1289 and 1000 ≤ T/K ≤ 1079 can be given by the expressions $\ln(p/\text{Pa})(\pm 0.02) = -38933.2/T + 30.99$ and $\ln(p/\text{Pa})(\pm 0.05) = -33455.6/T + 32.21$, respectively. The Gibbs energy of formation of SrTeO₃ and SrTe₂O₅ derived from the measured vapour pressure of the two compounds and other auxiliary data for the coexisting phases in the vaporization reactions can be given by the relations $\Delta_f G^0(\text{SrTeO}_3)(\pm 6.2 \text{ kJ mol}^{-1}) = -1008.8 + 0.288T$ and $\Delta_f G^0(\text{SrTe}_2\text{O}_5)(\pm 7.1 \text{ kJ mol}^{-1}) = -1375.5 + 0.481T$ respectively. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The prediction of chemical states of fission products in various stages of the nuclear fuel cycle is possible with the help of the thermodynamic data base for the relevant system [1]. The thermodynamic data base for the compounds of the reactive elements in this context, is therefore, very essential. Tellurium is one of the fission products with high reactivity and the thermodynamic stabilities of its compounds with the other fission products draws special attention [2]. The thermochemistry of the compounds of tellurium with other fission products like strontium provides relevant information on its chemical state in irradiated fuel. In this paper we present our data on the vapour pressures of strontium tellurites (SrTeO₃ and SrTe₂O₅) and their standard Gibbs energy and the enthalpy of formation derived from these data. The present work forms the part of our investigations to obtain thermodynamic stabilities of alkaline earth tellurites and tellurates

and to establish a systematic trend in their thermodynamic properties.

2. Experimental

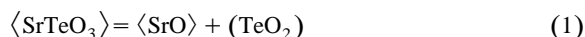
The compound SrTeO₃ was prepared by heating thoroughly ground mixtures of SrCO₃ (99.995%, Aldrich Chemical) and TeO₂ (99.995%, Aldrich Chemical) in the molar ratios 1:1, contained in a platinum boat in flowing argon for 8 h at 925 K followed by heating at 1200 K for 30 min. SrTe₂O₅ was prepared by heating a 1:2 molar mixture at 1000 K under similar conditions. The procedure involved heating of the mixtures at 2 K/min to the required temperatures, followed by isothermal heating for 8 h. The mixtures maintained at these temperatures were withdrawn intermittently from the furnace and reheated after repeated grinding. The completion of the reactions was confirmed from the X-ray powder diffraction patterns of the products. Differential thermal analysis (DTA) results obtained in this laboratory [3] on these compounds show that SrTeO₃ undergoes two reversible crystallographic transitions around the temperatures 1105 K and 1246 K. SrTe₂O₅ undergoes a reversible phase transition at temperature 894 K. The reverse transformations in SrTeO₃ are quite slow and are accompanied by a considerable temper-

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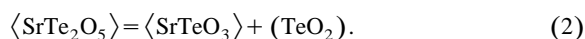
ature hysteresis. The room-temperature phase obtained depends very much on the method of preparation, i.e., the temperature to which the reaction mixture has been heated and the rate at which the product has been cooled. In the present work, the X-ray powder pattern of SrTeO₃ prepared as mentioned above and cooled slowly agreed with the XRD pattern reported by Mal'yutin et al. [4] for the product which they obtained by heat treating SrTeO₃ · H₂O at 330°C, i.e., after dehydration. The XRD pattern of SrTe₂O₅ agreed with that reported in the JCPDS file No. 43-344. The X-ray pattern for SrTeO₃ showed no lines due to SrO or TeO₂ indicating that the stoichiometric reaction between the 1:1 mixture of SrCO₃ and TeO₂ was complete below 1000 K. In the case of SrTe₂O₅, lines due to SrTeO₃, TeO₂ and SrCO₃ were totally absent in the product obtained by heating a 1:2 mixture of SrCO₃ and TeO₂.

The thermogravimetric (TG), differential thermal analysis (DTA) and X-ray diffraction investigations carried out independently on these mixtures in our laboratory [3] indicated that the reactions between SrCO₃ and TeO₂ began around 750 K and were completed much below the temperature at which pure TeO₂ begins to vaporize at a significant rate. Thus, the preferential volatilization of TeO₂, which could result in the contamination of the product by a less volatile component, is ruled out. The stoichiometries of the compounds were established independently by chemical analysis.

⟨SrTeO₃⟩ and ⟨SrTe₂O₅⟩ vaporized incongruently according to the reactions



and



The vapour pressure of (TeO₂) over ⟨SrTeO₃⟩ and ⟨SrTe₂O₅⟩ was measured using the novel thermogravimetric transpiration apparatus described elsewhere [5]. The experimental details involving the measurement of temperature and flow rate are given in Refs. [6,7]. The mass loss of the sample per unit volume of the carrier gas (argon) swept over it was monitored as a function of flow rate at 1270 K in the case of ⟨SrTeO₃⟩. It was found to remain constant in the range of flow rates between 3.15 and 3.50 l/h, indicating thereby the saturation of the carrier gas by the vapour. The measurements at different temperatures were carried out employing the flow rate of 3.36 l/h. Similar mass-loss experiments carried out for ⟨SrTe₂O₅⟩ as a function of flow rate at 1060 K indicated that the carrier gas (argon) was saturated with TeO₂ vapour between 3.20 and 3.49 l/h. A flow rate of 3.39 l/h was employed in the measurements carried out at different temperatures.

3. Results and discussion

The coexistence of the solid equilibrium phases indicated by vaporization reactions in Eqs. (1) and (2) was confirmed on the lines similar to those in our earlier work [8]. The X-ray diffraction analysis of the residue obtained by partial vaporization of SrTe₂O₅ indicated the presence of SrTeO₃ in addition to SrTe₂O₅ in accordance with the phase diagram reported in the literature [9]. The coexistence of SrO with SrTeO₃ during the vaporization reaction was inferred likewise from the X-ray diffraction pattern of the residue obtained from the partially vaporized compound. The mixture of SrCO₃ and TeO₂ corresponding to SrO:TeO₂ ratio 3:2 on heating to 1275 K yielded the mixture of SrO and SrTeO₃. The SrO obtained in this method and by thermal decomposition of pure SrCO₃ at 1275 K had no measurable difference in its lattice parameters, indicating negligible solubility of SrTeO₃ in SrO. JCPDS X-ray diffraction file No. 37-1458 and the reference given therein [10] report a phase Sr₂Te₃O₈, which could be the phase coexisting with SrTe₂O₅ when it vaporizes to give TeO₂ vapour. Our attempts to prepare and characterise this compound was not successful. We always ended up with a mixture of SrTeO₃ and SrTe₂O₅ when an SrCO₃ and TeO₂ mixture in the ratio 2:3 was heated slowly to 775°C according to the method described by Elerman and Kocak [10]. Moreover, the DTA pattern of the compound prepared according to this procedure gave the transition due to SrTe₂O₅, indicating that the compound Sr₂Te₃O₈ was not formed and it was only a mixture of SrTeO₃ and SrTe₂O₅. In view of these observations, Eq. (2) was assumed to be correct and the Gibbs energy of formation of SrTe₂O₅ was calculated accordingly.

The apparent pressures of tellurium bearing species in equilibrium with ⟨SrTeO₃ + SrO⟩ and ⟨SrTe₂O₅ + SrTeO₃⟩ were calculated from the mass loss of the sample per unit volume of the carrier gas swept over it from the relation

$$p_{\text{app}} = (W/V_c)(RT_c/M) \quad (3)$$

where W is the mass transported, V_c is the total volume of the carrier gas passed over the sample, T_c is the ambient temperature (in the case of SrTeO₃ the ambient temperature was 300.0 ± 0.5 K and in the case of SrTe₂O₅, 300.5 ± 0.5 K) at which volume of the carrier gas is measured and M is the molecular weight of the vapour species. The vapour species in the temperature range of the present measurements are assumed to be predominantly (TeO₂). The contribution of all other tellurium-bearing species [(TeO₂)₂, TeO, (TeO)₂, and Te₂] to the total pressure was estimated to be less than 5% from the mass spectrometric studies of Muenow et al. [11] which is well below the error involved in the pressure measurements (10%) in the present studies. The values of the vapour pressure of (TeO₂) over ⟨SrTeO₃⟩ + ⟨SrO⟩ at different temperatures are listed in Table 1. The corresponding least

Table 1
The standard Gibbs energy of formation of SrTeO₃ ($\Delta_f G^0\langle\text{SrTeO}_3\rangle$)

Temperature (K)	Mass loss (mg l ⁻¹)	$p(\text{TeO}_2)^a$ (Pa)	$\Delta_f G^{0b}$ (kJ mol ⁻¹)
1254.0	0.060	0.938	-647.6
1259.0	0.069	1.078	-646.2
1264.0	0.078	1.219	-644.8
1267.0	0.087	1.360	-643.9
1272.0	0.091	1.422	-642.5
1275.0	0.100	1.563	-641.6
1278.0	0.109	1.703	-640.7
1281.0	0.114	1.782	-639.9
1286.0	0.133	2.078	-638.4
1288.5	0.141	2.203	-637.7

^aVapour pressure of (TeO₂) above $\langle\text{SrO}\rangle + \langle\text{SrTeO}_3\rangle$.

^b $\Delta_f G^0\langle\text{SrTeO}_3\rangle$ calculated using Eq. (7).

square equation for the tabulated data could be expressed as (Fig. 1)

$$\ln(p(\text{TeO}_2)/\text{Pa})(\pm 0.02) = -38933.2/T + 30.99 \quad (4)$$

(1254 < T/K < 1289)

The values of vapour pressure of (TeO₂) above $\langle\text{SrTe}_2\text{O}_5\rangle + \langle\text{SrTeO}_3\rangle$ at different temperatures are listed in Table 2. The corresponding least square equation for the tabulated data could be expressed as (Fig. 2)

$$\ln(p(\text{TeO}_2)/\text{Pa})(\pm 0.05) = -33455.6/T + 32.21 \quad (5)$$

(1000 < T/K < 1079)

3.1. The standard Gibbs energy of formation of $\langle\text{SrTeO}_3\rangle$

The standard Gibbs energy of formation of $\langle\text{SrTeO}_3\rangle$ could be expressed in terms of the partial pres-

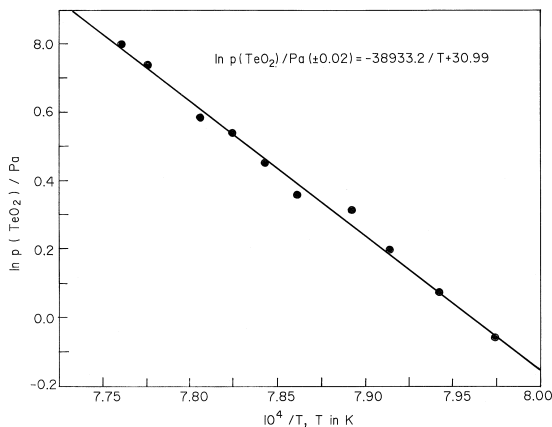


Fig. 1. $\ln p(\text{TeO}_2)/\text{Pa}$ vs. $1/T$ of SrTeO₃.

sure of (TeO₂) over a mixture of $\langle\text{SrTeO}_3\rangle$ and $\langle\text{SrO}\rangle$ by the equation

$$\Delta_f G^0\langle\text{SrTeO}_3\rangle = \Delta_f G^0\langle\text{SrO}\rangle + \Delta_f G^0(\text{TeO}_2) + RT \ln p\text{TeO}_2 \quad (6)$$

The key data for $\Delta_f G^0\langle\text{SrO}\rangle$ and $\Delta_f G^0(\text{TeO}_2)$ used in Eq. (6) were taken from the compilation of Barin [12]. Table 1 presents $\Delta_f G^0\langle\text{SrTeO}_3\rangle$ values calculated from Eq. (6), using the measured vapour pressure of the compound from Eq. (4) and the values of $\Delta_f G^0\langle\text{SrO}\rangle$ and $\Delta_f G^0(\text{TeO}_2)$ from Ref. [12]. These values could be expressed by the equation

$$\Delta_f G^0\langle\text{SrTeO}_3\rangle(\pm 6.2 \text{ kJ/mol}) = -1008.8 + 0.288T \quad (7)$$

3.2. The standard Gibbs energy of formation of $\langle\text{SrTe}_2\text{O}_5\rangle$

The standard Gibbs energy of formation for the compound $\langle\text{SrTe}_2\text{O}_5\rangle$ could be expressed in terms of the partial pressure of (TeO₂) over a mixture of $\langle\text{SrTeO}_3\rangle$ and $\langle\text{SrTe}_2\text{O}_5\rangle$ by

$$\Delta_f G^0\langle\text{SrTe}_2\text{O}_5\rangle = \Delta_f G^0\langle\text{SrTeO}_3\rangle + \Delta_f G^0(\text{TeO}_2) + RT \ln p\text{TeO}_2 \quad (8)$$

The key data for $\Delta_f G^0\langle\text{SrTeO}_3\rangle$ and $\Delta_f G^0(\text{TeO}_2)$ used in Eq. (8) were taken from Eq. (7) and Barin [12] respectively. Table 2 presents $\Delta_f G^0\langle\text{SrTe}_2\text{O}_5\rangle$ values calculated from Eq. (8), using the measured vapour pressure of the compound (Eq. (5)) and the values of $\Delta_f G^0\langle\text{SrTeO}_3\rangle$ and $\Delta_f G^0(\text{TeO}_2)$ from Eq. (7) and Ref.

Table 2
The standard Gibbs energy of formation of SrTe₂O₅ ($\Delta_f G^0\langle\text{SrTe}_2\text{O}_5\rangle$)

Temperature (K)	Mass loss (mg l ⁻¹)	$p(\text{TeO}_2)^a$ (Pa)	$\Delta_f G^{0b}$ (kJ mol ⁻¹)
1000.0	0.020	0.313	-894.5
1006.0	0.021	0.329	-891.6
1012.0	0.026	0.407	-888.7
1022.0	0.037	0.579	-883.9
1031.0	0.053	0.830	-879.6
1041.0	0.066	1.033	-874.8
1045.0	0.074	1.158	-872.9
1047.0	0.087	1.362	-872.0
1056.0	0.102	1.597	-867.6
1057.0	0.117	1.831	-867.1
1065.0	0.139	2.176	-863.2
1079.0	0.216	3.381	-856.5

^aVapour pressure of (TeO₂) above $\langle\text{SrTeO}_3\rangle + \langle\text{SrTe}_2\text{O}_5\rangle$.

^b $\Delta_f G^0\langle\text{SrTe}_2\text{O}_5\rangle$ calculated using Eq. (9).

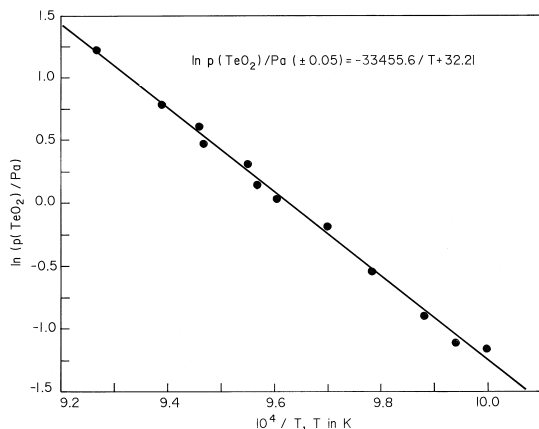


Fig. 2. $\ln p(\text{TeO}_2)/\text{Pa}$ vs. $1/T$ of SrTe_2O_5 .

[12] respectively. These values could be expressed by the equation

$$\Delta_f G^0(\text{SrTe}_2\text{O}_5)(\pm 7.1 \text{ kJ/mol}) = -1375.5 + 0.481T \quad (9)$$

4. Conclusion

The Gibbs energy of formation of strontium tellurites derived from vapour pressure measurements, presented in this paper are the first measurements on the thermodynamic properties of these compounds. The average second-law heat of formation for $\langle \text{SrTeO}_3 \rangle$ and $\langle \text{SrTe}_2\text{O}_5 \rangle$ obtained from Eqs. (7) and (9) at the mean temperatures of the measurements were found to be (-1008.8 ± 6.2) and $(-1375.5 \pm 7.1) \text{ kJ mol}^{-1}$, respectively. The standard enthalpy of formation $\Delta_f H_{298.15}^0$ of $\langle \text{SrTeO}_3 \rangle$ derived from the enthalpy of formation of the compound at the mean temperature of the measurements, the approximate value of the enthalpy of phase transformations obtained by DTA in this laboratory (approximately $(5 \pm 2) \text{ kJ mol}^{-1}$ for the first at 1106 K and about $(10 \pm 5) \text{ kJ mol}^{-1}$ for the second at 1246 K) and its estimated heat capacity by the Neumann and Kopp rule [13] was found to be $(-1016.4 \pm 10.0) \text{ kJ}$

mol^{-1} . Similarly, the standard enthalpy of formation of $\langle \text{SrTe}_2\text{O}_5 \rangle$ derived from the enthalpy of formation of the compound at the mean temperature of the vapour pressure measurements, the approximate value of the enthalpy of phase transformation obtained by DTA in this laboratory (approximately $(15 \pm 5) \text{ kJ mol}^{-1}$ at 894 K) and by making use of the estimated heat capacity as in the case of $\langle \text{SrTeO}_3 \rangle$ was found to be $(-1373.5 \pm 12.3) \text{ kJ mol}^{-1}$. These values are in excellent agreement with the standard enthalpy of formation $\Delta_f H_{298.15}^0$ of $\langle \text{SrTeO}_3 \rangle$ $(-1026.8 \pm 9.2 \text{ kJ mol}^{-1})$ and $\langle \text{SrTe}_2\text{O}_5 \rangle$ $(-1381.2 \pm 10.7 \text{ kJ mol}^{-1})$ obtained in our laboratory [14] employing the isoperibol calorimeter.

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