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Vaporization behavior of $TeO_2(s)$: a quantitative vaporization—Knudsen effusion mass spectrometric study

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Abstract

A high temperature mass spectrometric study of solid tellurium-di-oxide was conducted in conjunction with the 'quantitative vaporization method'. This study differs from our previous work [J. Nucl. Mater. 247 (1997) 28] essentially on two accounts: in situ pressure calibration and partial pressures from ion intensities corresponding to a low electron-impact energy of 13 eV. Focus was on the species $TeO_2(g)$, $TeO(g)$, $Te_2(g)$, $(TeO_2)_2(g)$, and $(TeO)_2(g)$. When compared to the results deduced from our previous measurements, no significant change was observed in the relative abundance of these gaseous species, but the absolute partial pressures were higher by a factor of 1.8. The p–T relations were obtained for these gaseous species in the temperature range 805–905 K. Enthalpies of various homogeneous gas-phase and heterogeneous gas–solid reactions were deduced, and so were the enthalpies of formation of (Te + O) gaseous species. The discrepancies amongst different mass spectrometric studies with regard to the absolute partial pressures and the $p(TeO)/p(TeO_2)$ and $p(Te_2)/p(TeO)$ ratios are brought out.

Keywords: $TeO_2(s)$; Quantitative vaporization; Knudsen effusion mass spectrometry; Partial pressures; Enthalpies

1. Introduction

Tellurium is one of the volatile and reactive fission products generated in nuclear reactors, and its behavior is of concern under normal and in transient conditions. During reactor operation, it can form a host of compounds with the components of fuel and cladding materials [1]. Under off-normal conditions, apart from the chemical reactivity, its vaporization behavior can also become complex and might vaporize as $Te_2(g)$ and Te–O bearing species [2]. To understand the role played by tellurium in the fuel clad interaction in the case of fast reactors, we have systematically conducted vaporization and thermodynamic studies on binary M–Te systems (M = SS components Fe, Cr, Ni, Mo and Mn) [3–13]. Recently, we have initiated the studies on ternary M–Te–O systems [14–16], which are of relevance for oxide fuelled fast reactors. Since the compounds in these systems vaporize to give Te–O bearing species in the vapor phase, detailed vaporization studies on TeO_2 would help gain a better understanding of their vaporization behavior and obtain reliable partial pressures of TeO_2, the major gaseous species over solid TeO_2.

Mills [17] and Cordfunke and Konings [18] have reviewed the vaporization and thermodynamic data on $TeO_2(s)$ quite extensively. Vapor pressure measurements over $TeO_2(s)$ have been carried out by Knudsen effusion mass loss [19–22] and transpiration methods [23,24] covering a temperature range from 730 to 1006 K. There is, in general, good agreement in the reported total pressures. The mass spectrometric investigations include those by Muenow et al. [25] (using tantulum Knudsen cell with Lucalox (alumina) liner), Piacente et al. [26] (using platinum Knudsen cell), and recently by us [27] (using alumina Knudsen cell) as well as almost concurrently by Kazenas and Bol'shikh [28] (using platinum Knudsen cell). Muenow et al. [25] investigated this system in the temperature range 782–903 K, observed $(TeO_2)_n(g)$, $(TeO)_n(g)$ (n = 1–4), $Te_2(g)$ and $O_2(g)$, and reported the partial

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pressures of species excluding the trimers and tetramers. Piacente et al. [26] observed $(TeO_2)_n$(g) ($n = 1$–2) and (TeO)(g), and reported $p(TeO_2)$ in the temperature range 778–906 K. The $p(TeO_2)$ obtained by these two earlier mass spectrometric studies [25,26] disagree by a factor of ∼5, the value of Piacente et al. [26] being higher and close to the total pressure [19–24] over TeO_2(s). Our previous Knudsen effusion mass spectrometric study [27] was aimed at resolving this discrepancy, rather huge for a major gaseous which is TeO_2(g). We reported the partial pressures of $(TeO_2)_n$(g) ($n = 1$–3) based on ion intensities measured at an electron energy of 48 eV in the temperature range 750–950 K. Kazenas and Bol'shikh [28] reported the partial pressure of TeO_2(g) in the temperature range 840–940 K and those of other species viz., TeO(g), $(TeO)_2$(g), $(TeO_2)_2$(g), Te_2(g) and O_2(g) only at 940 K. There is a good agreement, in general, amongst the values of enthalpy of sublimation of TeO_2(g) reported in the literature. Both Cordfunke and Konings [18] and Mills [17] who reviewed the third-law values disregarded the value of Muenow et al. [25] which is high and differs considerably from all other measurements. For $(TeO_2)_2$(g), the values selected [17,18] were based on the vapor pressure measurements by mass spectrometric methods [25,26].

In our previous paper [27], we showed that there was a reasonable agreement in the $p(TeO_2)$ obtained through pressure calibrations using elemental silver or tellurium and that our value, however, was between those obtained by Muenow et al. [25] and Piacente et al. [26]. Interestingly, Kazenas and Bol'shikh [28] obtained a value of $p(TeO_2)$ that was between our value and that of Piacente et al. [26]. For TeO(g), the second major gaseous species in the equilibrium vapor over TeO_2(s), the only p–T relation available in the literature is from Muenow et al. [25]. In the other two mass spectrometric investigations [26,28], only its relative composition at one temperature is given. Our interest in this system got rekindled upon evaluation of TeO^+ data from our previous measurements [27] and comparison of the results with others': the $p(TeO)/p(TeO_2)$ ratio, as deduced from our study (≈0.7 at 885 K), was many times higher than the other three mass spectrometric results (≈0.05 at 940 K [28] and 0.09 at 885 K [25,26]). Furthermore, the ratio deduced for Muenow et al. [25] and Piacente et al. [26] was strikingly similar despite a huge discrepancy observed in the values of partial pressures for each species. Such anomalies, perhaps, have been mainly caused by error in any one or more of the factors such as pressure calibrations, fragmentation corrections, and ionization cross-sections. It is also possible that variation in $p(O_2)$ could cause the discrepancies. With these consideration in mind, we investigated this system once again, but in conjunction with a long isothermal quantitative vaporization method (an absolute method that permits in situ pressure calibration and also attainment of congruently effusing composition that will fix the oxygen pressure) and by making measurements at lower electron-impact energy (13.0 eV) as well (to minimize fragmentation and possibly the errors in fragmentation correction). While this method gave partial pressures that are higher by a factor of ≈1.8, the relative abundance of TeO(g) as well as those of other gaseous species remained practically the same as those deduced from our previous measurements [14,27]. The paper discusses the above-mentioned aspects and presents the results in detail.

2. Experimental

TeO_2(s), supplied by Leico Industries, Inc., U.S.A. (purity 99.99%) was used for the experiments. For the vaporization studies, a VG micro-mass Knudsen effusion mass spectrometer was used. The samples, contained in platinum lined-alumina Knudsen cell, were heated by electron bombardment and the vapor species effused through a knife edged orifice of 0.5 mm diameter. Temperatures were measured by a chromel–alumel thermocouple inserted through one of the holes at the bottom of the molybdenum cup housing the Knudsen cell, and touching the latter. The molecules in the vapor beam were ionized by electron-impact, and the ions produced were accelerated by applying a negative potential of 6000 V. Mass analysis of the ions was carried out by a single focussing 90° magnetic sector analyzer and the ion currents were measured by a secondary electron multiplier. For determining the detector response, ion currents were measured with a Faraday cup as well at the highest temperature of measurements.

Amongst the various ions detected in the mass spectra of the equilibrium vapor over TeO_2(s) [27], we paid attention in the present study to: Te^+, Te_2^+, TeO^+, TeO_2^+, $Te_2O_2^+$, and $Te_2O_4^+$, and O_2^+. The ion intensities were recorded as a function of electron energy to obtain ionization efficiency curves. Because of high background at mass number 32, O_2^+ was not considered for any data evaluation. Two series of vaporization experiments were conducted. In series 1, vaporization experiments on TeO_2(s) were conducted by quantitative mass loss method. Ion intensities of $^{130}Te^+$, $^{256}Te_2^+$, $^{146}TeO^+$ and $^{162}TeO_2^+$ were measured continuously as a function of time at 885 K and at an electron energy of 37.3 eV. Ion intensities were measured at 13 eV also, at regular intervals throughout the duration of the experiment. The samples were weighed before and after the vaporization experiment to deduce the mass loss. Totally three experiments were carried out and for each experiment, a fresh lot of sample was used. At the end of experiment 3, temperature dependence measurement of ion intensities of Ag^+, over Ag(s) was also carried out.

In series 2, ion intensities of $^{130}Te^+$, $^{256}Te_2^+$, $^{146}TeO^+$, $^{288}(TeO)_2^+$, $^{162}TeO_2^+$, $^{320}(TeO_2)_2^+$ were measured at an electron energy of 37.3 eV, in the temperature range 805–905 K, and also at 13.0 eV at a few temperatures. Three experiments, each consisting of one run, was conducted with one sample. Table 1 gives the values of ion intensities. The $p(TeO_2)$ obtained at 885 K in series 1 was used to deduce the pressure calibration constant for each run.

Table 1
Ion intensities measured at 37.3 eV on three separate experiments conducted on successive days in series 2

T (K)	$I(\mathrm{Te}^+)$	$I(\mathrm{Te_2}^+)$	$I(\mathrm{TeO}^+)$	$I(\mathrm{TeO_2}^+)$	$I(\mathrm{Te_2O_2}^+)$	$I(\mathrm{Te_2O_4}^+)$
Day 1: experiment 1						
885	2.05×10^{-3}	2.15×10^{-4}	3.33×10^{-3}	6.35×10^{-3}	2.89×10^{-4}	4.05×10^{-4}
870	1.16×10^{-3}	1.18×10^{-4}	1.87×10^{-3}	3.56×10^{-3}	1.47×10^{-4}	2.09×10^{-4}
845	4.27×10^{-4}	4.18×10^{-5}	6.54×10^{-4}	1.25×10^{-3}	3.83×10^{-5}	6.59×10^{-5}
820	1.51×10^{-4}	1.62×10^{-5}	2.17×10^{-4}	3.98×10^{-4}	1.23×10^{-5}	1.84×10^{-5}
805	6.96×10^{-5}	7.82×10^{-6}	9.66×10^{-5}	1.79×10^{-4}	4.76×10^{-6}	7.53×10^{-6}
830	2.23×10^{-4}	2.19×10^{-5}	3.40×10^{-4}	6.17×10^{-4}	2.04×10^{-5}	3.04×10^{-5}
855	6.41×10^{-4}	6.07×10^{-5}	1.02×10^{-3}	1.95×10^{-3}	7.23×10^{-5}	1.16×10^{-4}
905	4.31×10^{-3}	5.05×10^{-4}	7.52×10^{-3}	1.36×10^{-2}	7.21×10^{-4}	9.93×10^{-4}
Day 2: experiment 2						
885	2.02×10^{-3}	2.24×10^{-4}	3.43×10^{-3}	6.57×10^{-3}	3.02×10^{-4}	4.30×10^{-4}
870	1.14×10^{-3}	1.42×10^{-4}	1.90×10^{-3}	3.59×10^{-3}	1.50×10^{-4}	2.26×10^{-4}
845	4.08×10^{-4}	4.26×10^{-5}	6.47×10^{-4}	1.25×10^{-3}	4.43×10^{-5}	6.82×10^{-5}
820	1.51×10^{-4}	1.73×10^{-5}	2.07×10^{-4}	3.90×10^{-4}	1.21×10^{-5}	1.90×10^{-5}
805	6.97×10^{-5}	1.24×10^{-5}	9.67×10^{-5}	1.83×10^{-4}	5.82×10^{-6}	8.16×10^{-6}
830	2.08×10^{-4}	2.10×10^{-5}	3.41×10^{-4}	6.39×10^{-4}	2.09×10^{-5}	3.80×10^{-5}
855	6.65×10^{-4}	6.92×10^{-5}	1.07×10^{-3}	2.03×10^{-3}	6.39×10^{-5}	1.22×10^{-4}
905	4.18×10^{-3}	5.16×10^{-4}	7.15×10^{-3}	1.36×10^{-2}	7.01×10^{-4}	1.04×10^{-3}
Day 3: experiment 3						
885	1.99×10^{-3}	2.45×10^{-4}	3.56×10^{-3}	7.01×10^{-3}	3.14×10^{-4}	5.00×10^{-4}
865	9.54×10^{-4}	1.13×10^{-4}	1.66×10^{-3}	3.30×10^{-3}	1.25×10^{-4}	2.07×10^{-4}
835	2.75×10^{-4}	3.18×10^{-5}	4.52×10^{-4}	9.00×10^{-4}	2.88×10^{-5}	4.68×10^{-5}
805	7.10×10^{-5}	8.63×10^{-6}	8.64×10^{-5}	1.92×10^{-4}	4.90×10^{-6}	9.42×10^{-6}
820	1.28×10^{-4}	1.56×10^{-5}	2.05×10^{-4}	4.13×10^{-4}	1.20×10^{-5}	2.06×10^{-5}
850	4.99×10^{-4}	5.60×10^{-5}	8.58×10^{-4}	1.71×10^{-3}	5.83×10^{-5}	9.31×10^{-5}
875	1.33×10^{-3}	1.58×10^{-4}	2.41×10^{-3}	4.76×10^{-3}	1.96×10^{-4}	2.95×10^{-4}
905	4.19×10^{-3}	5.53×10^{-4}	7.77×10^{-3}	1.48×10^{-2}	7.45×10^{-4}	1.08×10^{-3}

Ion intensities corresponding to 13.0 eV were deduced from these and the mean values of [I^+ (at 37.3 eV)/I^+ (at 13.0 eV)] ratios. Mean of five to seven values of [I^+ (at 37.3 eV)/I^+ (at 13.0 eV)] ratios: 8.28 (Te^+); 1.66 ($\mathrm{Te_2}^+$); 8.18 (TeO^+); 5.25 ($\mathrm{TeO_2}^+$); 9.02 ($\mathrm{Te_2O_2}^+$); 4.59 ($\mathrm{Te_2O_4}^+$).

3. Results

Fig. 1 shows pertinent portions of the ionization efficiency curves for the ions Te^+, $\mathrm{Te_2}^+$, TeO^+, $\mathrm{TeO_2}^+$, $\mathrm{Te_2O_2}^+$, and $\mathrm{Te_2O_4}^+$. The appearance energies derived from these curves by linear extrapolation method were: 11.4 (Te^+), 8.9 ($\mathrm{Te_2}^+$), 8.8 (TeO^+), 11.3 ($\mathrm{TeO_2}^+$), 11.5 ($\mathrm{Te_2O_2}^+$), and 11.2 ($\mathrm{Te_2O_4}^+$). From mass, isotopic abundance and the appearance energy

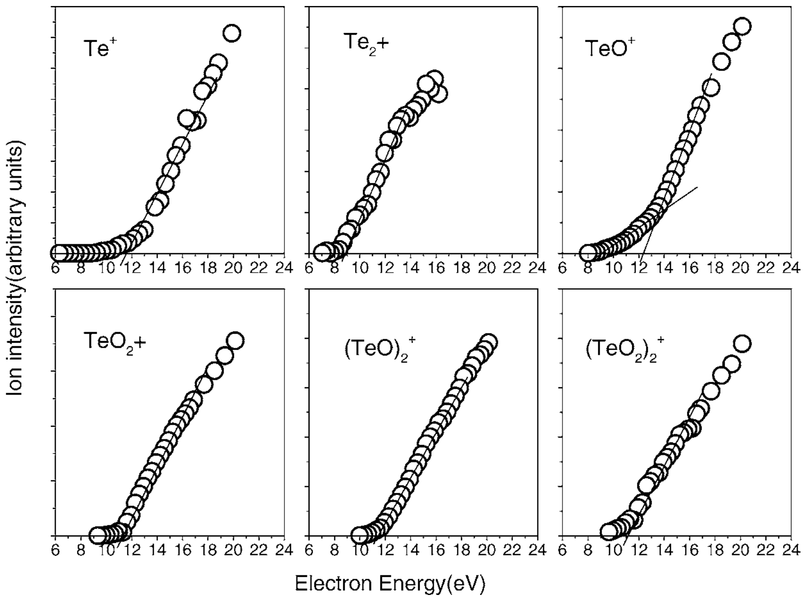

Fig. 1. Pertinent portions of ionization efficiency curves for Te^+, $\mathrm{Te_2}^+$, TeO^+, $\mathrm{TeO_2}^+$, $(\mathrm{TeO})_2{}^+$, $(\mathrm{TeO_2})_2{}^+$.

values, the neutral species (as discussed in Section 4.1) were ascertained to be Te_2(g), $(TeO_2)_n$(g), $(TeO)_n$(g) ($n = 1$–2). O_2(g) was also assumed to be a neutral species over TeO_2(s), although no serious data evaluation was done for O_2^+.

3.1. Determination of partial pressures

3.1.1. Series 1: quantitative vaporization experiments

The equations relating mass loss and partial pressure is given by Hertz–Knudsen equation [29]:

$$\Delta w(i) = p(i) a_0 C \Delta t \sqrt{\frac{M(i)}{2\pi RT}} \quad (1)$$

and the equation relating ion intensity and partial pressures is given by [29]:

$$p(i) = k'(i) I(i^+) T \quad (2)$$

where

$$k'(i) = \frac{k}{\sigma(i)\gamma(i)n(i)}$$

Combining relations 1 and 2 and on rearranging we get

$$\Delta W_{\text{tot}} = \sum_i \Delta w(i) = \varphi \left\{ \sqrt{M(\text{TeO}_2)} A(\text{TeO}_2) + \sum_{i=\text{TeO},\text{Te}_2} \times \sqrt{M(i)} A(i) \frac{\sigma(\text{TeO}_2)\gamma(\text{TeO}_2{}^+) n(\text{TeO}_2{}^+)}{\sigma(i)\gamma(i^+) n(i^+)} \right\} \quad (3)$$

and

$$\varphi = a_0 C \sqrt{\frac{1}{2\pi R}} k'(\text{TeO}_2)$$

where ΔW_{tot} is the total mass loss, $\Delta w(i)$, mass loss due to effusion of species i, a_0, the orifice area, C, the Clausing factor, $A(i)$, the area under the curve $I(i^+)T^{1/2}$ versus time and $M(i)$, the molecular weights for the individual species. $p(i)$ is the partial pressure of the species i, k, the instrument calibration constant, σ, the ionization cross-section of species i, γ, the multiplier yield and n, the isotopic abundance of the ionic species of i^+.

The ion intensities measured at 37.3 eV were converted to those at 13 eV by the following relations:

$$I(i^+)_{13\,\text{eV}} = I(i^+)_{37.3\,\text{eV}} \chi(i^+) \quad (i = \text{TeO}_2, \text{Te}_2) \quad (4)$$

and

$$I(\text{TeO}^+)_{13\,\text{eV}} = I(\text{TeO}^+)_{37.3\,\text{eV}} \chi(\text{TeO}^+) + I(\text{Te}^+)_{37.3\,\text{eV}} \chi(\text{Te}^+) \frac{\gamma(\text{TeO}^+) n(\text{TeO}^+)}{\gamma(\text{Te}^+) n(\text{Te}^+)} \quad (5)$$

where

$$\chi(i^+) = \frac{I(i^+)_{13\,\text{eV}}}{I(i^+)_{37.3\,\text{eV}}}$$

$I(\text{Te}^+)$, since mainly contributed by dissociation of TeO(g) was added to $I(\text{TeO}^+)$.

The details of mass loss etc., for series 1 experiments are given in Table 2. The higher polymers of TeO(g) and TeO_2(g) were not considered in the area calculations as they contribute to <5% of total vapor pressure.

From the values of A_i for each species and the total mass loss during the experiment, the factor φ was calculated. From this constant, φ, the mass loss due to vaporization of individual species was obtained. The orifice area a_0 was calculated from the dimensions measured employing an optical microscope while the corresponding Clausing factor for the knife edged orifice was taken from the literature [29]. The ionization cross-section $\sigma(\text{Te}_x\text{O}_y)$ was assumed to be $0.75[x\sigma(\text{Te}) + y\sigma(\text{O})]$. The corresponding cross-sections for the elements were taken from Mann's compilation [30]. The multiplier gains were deduced from the relative ratios of ion intensities measured using secondary electron multiplier and Faraday cup. Using these constants and the mass loss data of individual species, the partial pressures (corresponding to ion intensities at 13 eV) for each species was calculated by the application of Hertz–Knudsen relation (Eq. (1)), and are given in Table 2.

The $p(O_2)$ was calculated by assuming TeO_2(s) to effuse congruently (that is, the Te-to-O atomic flow ratio in the

Table 2
Details of quantitative vaporization experiments[a,b] and partial pressures (in Pa) derived in series 1

Experiment	Initial mass (g)	Mass loss, Δw_{tot} (g)	Time, t (s)	Area (A_i)				$p(i)$			
				$i = TeO_2$	i = TeO	$i = Te_2$	i = Te	$i = TeO_2$	i = TeO	$i = Te_2$	$i = O_2$[c]
1	0.13680	0.00676	61020	258.24	102.36	61.68	65.1	0.164	0.109	0.032	0.048
2	0.13000	0.01488	111660	777.48	317.82	268.20	198.78	0.185	0.126	0.053	0.067
3	0.11512	0.01031	109800	775.62	276.00	193.86	142.26	0.147	0.081	0.030	0.040
Mean[d]								0.165 ± 0.019	0.105 ± 0.023	0.038 ± 0.011	0.052 ± 0.014

$T = 885$ K, electron energy = 13 eV.

[a] $\sigma(\text{TeO}_2) = 2.23 \times 10^{-16}$ cm^2; $\sigma(\text{TeO}) = 2.23 \times 10^{-16}$ cm^2; $\sigma(\text{Te}_2) = 4.46 \times 10^{-16}$ cm^2; $\gamma(\text{TeO}_2) = 3.89 \times 10^{-6}$; $\gamma(\text{TeO}) = 3.80 \times 10^{-6}$; $\gamma(\text{Te}_2) = 3.54 \times 10^{-6}$; $\gamma(\text{Te}) = 3.40 \times 10^{-6}$; $n({}^{162}\text{TeO}_2) = 0.338$; $n({}^{146}\text{TeO}) = 0.338$; $n({}^{256}\text{Te}_2) = 0.229$; $n({}^{130}\text{Te}) = 0.338$.

[b] Orifice diameter = 0.05 cm; $a_0 C = 1.93 \times 10^{-3}$ cm^2.

[c] Estimated by applying congruency condition (Eq. (6)).

[d] Errors quoted are the standard deviation of mean.

Table 3
p–T relations obtained in series 2 (805–905 K)

Species	Experiment	$\log p$ (Pa)[a] = $-A/T$(K) + B		p (Pa) at 855 K
		A	B	
TeO_2(g)	1	13964 ± 114	15.002 ± 0.135	4.68×10^{-2}
	2	14083 ± 114	15.130 ± 0.134	4.56×10^{-2}
	3	13952 ± 137	14.973 ± 0.161	4.52×10^{-2}
	Recommended[b]	13988 ± 72	15.021 ± 0.085	4.58×10^{-2}
TeO(g)	1	13715 ± 87	14.518 ± 0.103	3.00×10^{-2}
	2	13703 ± 133	14.501 ± 0.157	2.98×10^{-2}
	3	13847 ± 113	14.643 ± 0.132	2.80×10^{-2}
	Recommended[b]	13738 ± 79	14.535 ± 0.093	2.93×10^{-2}
Te_2(g)	1	13319 ± 209	13.319 ± 0.246	5.51×10^{-3}
	2	13606 ± 372	13.624 ± 0.439	5.14×10^{-3}
	3	13433 ± 178	13.422 ± 0.210	5.14×10^{-3}
	Recommended[b]	13443 ± 151	13.444 ± 0.178	5.26×10^{-3}
$(TeO_2)_2$(g)	1	15586 ± 113	15.650 ± 0.132	2.64×10^{-3}
	2	15460 ± 190	15.483 ± 0.222	2.52×10^{-3}
	3	15491 ± 155	15.536 ± 0.183	2.62×10^{-3}
	Recommended[b]	15499 ± 89	15.541 ± 0.104	2.59×10^{-3}
$(TeO)_2$(g)	1	16055 ± 131	15.780 ± 0.154	1.00×10^{-3}
	2	15717 ± 148	15.360 ± 0.173	9.50×10^{-4}
	3	15752 ± 453	15.410 ± 0.532	9.70×10^{-4}
	Recommended[b]	15840 ± 153	15.515 ± 0.180	9.74×10^{-4}

[a] Errors quoted are the standard deviation.
[b] Recommended equation was obtained by least-squares-fitting of all the data points from all the runs.

effusate = 0.5) and by employing the following expression which is based on congruent effusion principle [14]:

$$\frac{p(\mathrm{TeO_2})/\sqrt{M(\mathrm{TeO_2})} + p(\mathrm{TeO})/\sqrt{M(\mathrm{TeO})} + 2p(\mathrm{Te_2})/\sqrt{M(\mathrm{Te_2})}}{2p(\mathrm{TeO_2})/\sqrt{M(\mathrm{TeO_2})} + p(\mathrm{TeO})/\sqrt{M(\mathrm{TeO})} + 2p(\mathrm{O_2})/\sqrt{M(\mathrm{O_2})}} = 0.5 \qquad (6)$$

Since at the end of experiment 3, pressure calibration experiment using solid silver was also carried out, the $p(TeO_2)$ at 885 K corresponding to this set of pressure calibration constants at 37.3 and 13.0 eV were deduced: 0.05 and 0.047 Pa, respectively.

3.1.2. Series 2: temperature dependence of partial pressures

Ion intensities at 13.0 eV derived using Eqs. (4) and (5) were converted to partial pressures using Eq. (2). The value of $k'(TeO_2)$ was calculated from the mean of $p(TeO_2)$ obtained at 885 K, in series 1 experiments. Using $k'(TeO_2)$ and the ratios $[(\sigma\gamma n)_{TeO_2}/(\sigma\gamma n)_i]$ (where $i = Te_2$, TeO, Te_2O_2, Te_2O_4), pressure calibration constants $k'(i)$ for other species were obtained, and subsequently their partial pressures. The p–T relation for each run was obtained from $p(i)$s at different temperatures. The recommended equation was obtained by pooling all the data points from all the runs. The p–T relations thus obtained are given in Table 3, and shown in Fig. 2.

3.2. Thermodynamic quantities

3.2.1. Reaction enthalpies

From the partial pressures derived, enthalpies of various solid–gas and gas-phase reactions (see Tables 4 and 5) were evaluated by second- and/or third-law methods. The necessary auxiliary functions were taken from the literature [31].

The least-squares-fitted equilibrium constant (K°)–temperature relations for the gas-phase reactions 3–5 ($P^0 = 101\,325$ Pa; see Table 4) in the temperature range 805–905 K

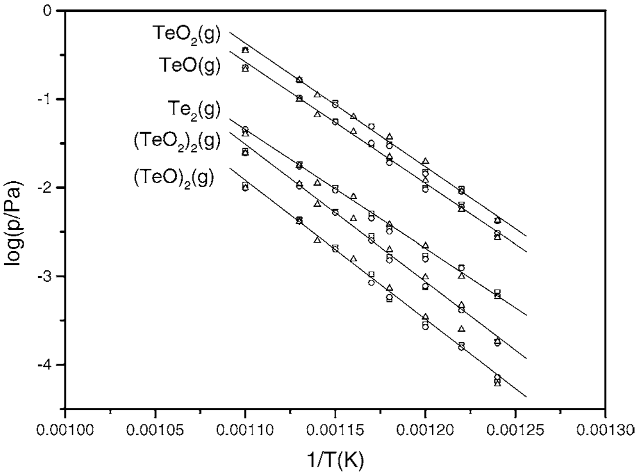

Fig. 2. Partial pressures of different vaporizing species as a function of temperature. (□) Experiment 1; (○) Experiment 2; (△) Experiment 3.

Table 4
Reaction enthalpies[a] (kJ/mol)

Experiment	Second law[b]		Third law[b]	Recommended[c,d]
	$\Delta_r H^\circ_m$ (T_m)[e]	$\Delta_r H^\circ_m$ (298.15 K)	$\Delta_r H^\circ_m$ (298.15 K)	
Reaction 1: $TeO_2(s) = TeO_2(g)$				
1	267.4 ± 2.2	278.4 ± 2.2	268.5 ± 0.1	268.6 ± 2.7
2	269.7 ± 2.2	280.6 ± 2.2	268.7 ± 0.1	
3	267.1 ± 2.6	278.1 ± 2.6	268.7 ± 0.1	
Mean		279.0 ± 1.4	268.6 ± 0.1	
Reaction 2: $2TeO_2(s) = (TeO_2)_2(g)$				
1	298.4 ± 2.2	308.2 ± 2.2	313.7 ± 0.1	313.9 ± 5.1
2	296.0 ± 3.6	305.7 ± 3.6	314.1 ± 0.2	
3	296.6 ± 3.0	306.3 ± 3.0	313.7 ± 0.1	
Mean		306.7 ± 1.3	313.9 ± 0.2	
Reaction 3: $(TeO_2)_2(g) = 2TeO_2(g)$				
1	236.1 ± 3.5	248.3 ± 3.5	223.3 ± 0.4	223.4 ± 6.6
2	241.7 ± 5.3	253.9 ± 5.3	223.3 ± 0.5	
3	238.6 ± 8.7	250.9 ± 8.7	223.6 ± 0.5	
Mean		251.0 ± 2.8	223.4 ± 0.2	
Reaction 4: $(TeO)_2(g) = 2TeO(g)$				
1	217.1 ± 4.3	221.7 ± 4.3	211.8 ± 0.2	212.0 ± 6.6
2	225.2 ± 7.6	229.7 ± 7.6	211.5 ± 0.4	
3	235.9 ± 13.4	240.4 ± 13.4	212.6 ± 0.6	
Mean		230.6 ± 9.4	212.0 ± 0.6	
Reaction 5: $TeO_2(g) + 0.5Te_2(g) = 2TeO(g)$				
1	130.1 ± 3.5	131.3 ± 3.5	116.2 ± 0.3	116.2 ± 6.4
2	125.7 ± 4.8	126.9 ± 4.8	115.8 ± 0.3	
3	134.0 ± 3.2	135.2 ± 3.2	116.5 ± 0.3	
Mean		131.1 ± 4.2	116.2 ± 0.4	

[a] Derived from partial pressures obtained in series 2.
[b] Errors quoted are standard deviation of the mean.
[c] Mean of third-law value is recommended.
[d] Errors quoted include statistical as well as estimated uncertainties.
[e] $T_m = 855$ K, mean temperature of the runs.

were deduced to be

$$\log(K^\circ)\,(\text{reaction 3}) = \left(\frac{-12\,459}{T\,(\text{K})} \pm 180\right) + (9.478 \pm 0.211) \qquad (7)$$

$$\log(K^\circ)\,(\text{reaction 4}) = \left(\frac{-11\,775}{T\,(\text{K})} \pm 308\right) + (8.708 \pm 0.362) \qquad (8)$$

$$\log(K^\circ)\,(\text{reaction 5}) = \left(\frac{-6770}{T\,(\text{K})} \pm 150\right) + (4.825 \pm 0.176) \qquad (9)$$

Using the value of $\Delta_f H^\circ_m$ (298.15) of $TeO_2(s) = -(321.0 \pm 2.5)$ kJ/mol [18], and enthalpies of reactions 1 and 2, enthalpies of formation of $(TeO_2)_n(g)$ ($n = 1$–2) were derived. Using $\Delta_f H^\circ_m$ (298.15) $TeO_2(g)$ thus derived and taking $\Delta_f H^\circ_m$ (298.15) of $Te_2(g)$ (163.2 ± 0.5 kJ/mol) from literature [32], $\Delta_f H^\circ_m$ (298.15) of TeO(g) was deduced using reaction 5. Subsequently, $\Delta_f H^\circ_m$ (298.15) $(TeO)_2(g)$ was also calculated using the enthalpy of reaction 4. All these values are listed in Table 6 along with those available in literature.

4. Discussion

4.1. Neutral species, partial pressures, and total pressure

The appearance energies (AEs) determined in the present work have an uncertainty of ±0.5 eV, and, in general, agree with those available in the literature [25] and those obtained by us earlier [27]. The ionization efficiency curves shown in Fig. 1 indicate that at 13 eV, the ions Te_2^+, TeO^+ and TeO_2^+ originated wholly from their respective neutral species, and so did $Te_2O_2^+$ and $Te_2O_4^+$. Contribution to TeO^+, if any, from fragmentation of $TeO_2(g)$ should be negligibly small as shown by the ionization efficiency curves for TeO^+ and TeO_2^+: the positive deviation from linearity in the case of TeO^+ begins at an electron energy ≥13 eV, while the corresponding negative deviation in the case of TeO_2^+ is not readily

Table 5
Comparison of enthalpies (kJ/mol) of different solid–gas and gas-phase reactions

Reaction	$\Delta_r H^\circ_m$(298.15 K)	Reference
(1) $TeO_2(s) = TeO_2(g)$	264.0 ± 8.4	[17] (review)
	266.2 ± 0.6	[18] (review)
	288.7 ± 8.4^{a}	[25]
	268.2 ± 1.7^{a}	[26]
	271.2 ± 2.1^{a}	[28]
	268.6 ± 2.7^{a}	Present work
(2) $2TeO_2(s) = (TeO_2)_2(g)$	308.5	[18]
	$296.7 \pm 8.4^{a,b}$	[25]
	288.7 ± 12.6^{a}	[28]
	313.9 ± 5.1^{a}	Present work
(3) $(TeO_2)_2(g) = 2(TeO_2)(g)$	280.7 ± 8.4^{a}	[25]
	266.1^{a}	[28]
	225.9 ± 7.2^{c}	[26]
	223.4 ± 6.6^{a}	Present work
(4) $(TeO)_2(g) = 2TeO(g)$	258.6 ± 8.4^{a}	[25]
	246.4^{a}	[28]
	212.0 ± 6.6^{a}	Present work
(5) $TeO_2(g) + 0.5Te_2(g) = 2TeO(g)$	$125.2 \pm 11.9^{a,d}$	[25]
	62.3^{d}	[28]
	133.6 ± 6.8^{e}	[34]
	153.8 ± 4.2^{f}	[35]
	116.2 ± 6.4^{a}	Present work
(6) $TeO_2(s) + TeO_2(g) = (TeO_2)_2(g)$	8.0 ± 11.9^{b}	[25]
	42.3 ± 5.8	[26]
	5.1 ± 2.1^{b}	[28]
	45.3 ± 0.4^{a}	Present work

[a] Third-law value.

[b] Calculated from the enthalpies of reactions 1 and 3.

[c] Derived from enthalpies of reactions 1 and 6.

[d] Derived from the enthalpies of the reactions $TeO_2(g) = 0.5Te_2(g) + O_2(g)$ and $TeO(g) = 0.5Te_2(g) + 0.5O_2(g)$ given by them.

[e] Calculated from the enthalpies of reactions $TeO_2(g) = TeO(g) + 0.5O_2(g)$ and $Te(g) + 0.5O_2(g) = TeO(g)$ as given by Cordfunke and Konings [18], based on the data given by Staley [34] and taking the enthalpy of dissociation of $Te_2(g)$ from [36].

[f] Derived from the enthalpy of reaction $TeO_2(g) + Te(g) = 2TeO(g)$ (of Zmbov and Miletic [35] as given by Cordfunke and Konings [18]) and the enthalpy of dissociation of $Te_2(g)$ from [36].

Table 6
Comparison of enthalpies of formation (kJ/mol) of different gaseous species

Species	$\Delta_f H^\circ_m$ (298.15 K)	Reference
$TeO_2(g)$	-63.2 ± 8.4	[25]
	-52.8 ± 3.0^{a}	[26]
	-51.5	[28]
	-59.4 ± 8.4	[17] (review)
	-54.8 ± 2.6	[18] (review)
	-52.4 ± 3.7^{a}	Present work
$(TeO_2)_2(g)$	-408.8 ± 8.4	[25]
	-348.9	[28]
	$-331.5 \pm 7.0^{a,b}$	[26]
	-347.3 ± 29.3	[17] (review)
	-333.0 ± 10.0	[18] (review)
	-328.1 ± 5.7^{a}	Present work
$TeO(g)$	72.4 ± 8.4	[25]
	70.7	[28]
	66.3 ± 5.2^{c}	[34]
	93.2 ± 2.3^{d}	[34]
	89.8 ± 1.8^{e}	[35]
	69.0 ± 21	[37]
	74.5	[17] (review)
	92.0 ± 5.0	[18] (review)
	72.7 ± 7.4	Present work
$(TeO)_2(g)$	-112.5 ± 8.4	[25]
	-105.0	[28]
	-108.8 ± 12.6	[17] (review)
	-66.6 ± 9.9	Present work

[a] $\Delta_f H^\circ_m$ (298.15 K) of $TeO_2(s) = -321.0 \pm 2.5$ [18].

[b] $\Delta_f H^\circ_m$ (298.15 K) of reaction $9 = 42.3 \pm 5.8$ [26].

[c] Using $\Delta_r H^\circ_m$ (298.15 K) of $TeO_2(g) = TeO(g) + 0.5O_2(g)$.

[d] Using $\Delta_r H^\circ_m$ (298.15 K) of $TeO(g) = Te(g) + 0.5O_2(g)$.

[e] Using $\Delta_r H^\circ_m$ (298.15 K) of $TeO_2(g) + Te(g) = 2TeO(g)$ and enthalpy of dissociation of $Te_2(g)$ from [36] (c–e as given by Cordfunke and Konings [18]).

noticeable. The AEs of Te_2O^+ and $Te_2O_3^+$ being only above 13 eV [27], no fragmentation corrections were necessary for $(TeO)_2(g)$ and $(TeO_2)_2(g)$.

The reasons for resorting to ion intensity measurements at 37.3 eV as well as 13.0 eV are the following: (1) to be able to compare the present results with those of our previous study (which was done only at high electron energy) and (2) ion intensities at 13.0 eV would be too low at low temperatures for reliable measurements and therefore use of conversion factors (deduced at high temperatures and given in footnote of Table 1) will render it possible to have ion-intensity data at 13.0 eV for the entire temperature range.

We considered Te^+ as a fragment ion since its appearance energy (11.4 eV) was much higher than the first ionization energy of Te(g) [33]. Though Te^+ could originate from both TeO(g) and $Te_2(g)$, its contribution from the latter at 13 eV was considered negligible because of the following reasons: (1) the $I(Te_2^+)$ over $TeO_2(s)$ itself is only ~30% of $I(TeO^+)$ and (2) the ratio of Te^+/Te_2^+ over Te(s), where Te^+ arises almost solely from $Te_2(g)$ is ~0.005 [4] whereas the ratio of Te^+/Te_2^+ over $TeO_2(s)$ is 1.4 (see Table 1).

Our identification of the neutral species over $TeO_2(s)$ in the present and previous work [27] are in accord with those reported by Muenow et al. [25], who in addition, observed tetramers of $TeO_2(g)$ and TeO(g). Piacente et al. [26] confirmed the presence of TeO(g) by an additional experiment in which a ~1:1 mixture of $TeO_2(s)$ and Te(s) was heated to have enhanced amount of $(TeO)_i(g)$ in the vapor phase. Staley [34] found Te(g), TeO(g), $TeO_2(g)$, and $O_2(g)$ along with Na–Te–O species over a pre-melted mixture of $TeO_2(s)$ and $Na_2CO_3(s)$ heated in an iridium Knudsen cell that had a gas inlet.

The $p(TeO_2)$ derived in the present work by quantitative vaporization method is higher by a factor of ~1.8, than that obtained by us earlier [27]. However, the $p(TeO_2)$ deduced at 885 K for experiment 3, at 37.3 eV electron energy using pressure calibration constant for silver was in reasonable agreement with that obtained in earlier work [27]. We seek to explain this discrepancy as follows: Apart from the way pressure calibrations were performed, the two methods differ in the way the ionization cross-sections were used. While in the case of silver calibration method, we need to use absolute ionization cross-sections (σ's) for Te_xO_y(g) and Ag(g) [30], with quantitative vaporization method we need to use only $\sigma(Te_xO_y)/\sigma(TeO_2)$. Thus any error in $\sigma(Te_xO_y)$ (due to use of empirical relation $0.75[x\sigma(Te) + y\sigma(O)]$ will introduce less error in the latter method. The lower value of $p(TeO_2)$ reported in our previous study [27] might be attributed to an underestimated $\sigma(Ag)/\sigma(TeO_2)$ ratio. Furthermore, errors due to fragmentation contribution have been largely avoided in the present study with the conversion of all ion intensities to those at an electron energy (13 eV) where fragmentation is minimal, and also because correction for fragmentation of TeO(g) to Te^+ was made for calculating p(TeO). We consider the partial pressures obtained in the present work as more reliable since it was obtained by an absolute method, which as mentioned above is relatively less prone to errors due to estimated ionization cross-sections.

Fig. 3 compares the $p(TeO_2)$ recommended in the present study with those available in the literature. There is excellent agreement with the values of Kazenas and Bol'shikh [28]. Our values continue to be between those obtained by Muenow et al. [25] and Piacente et al. [26], relatively closer to the latter. In comparison with our values, the $p(TeO_2)$ of Muenow et al. [25] is lower by a factor of 3.5, while that of Piacente et al. [26] is higher by a factor of ∼1.8.

As for the partial pressure of TeO, the next major species observed in the present study, our result is higher by a factor of ∼12 compared to that of Kazenas and Bol'shikh [28] (who have given the value only at 940 K); our values are also higher than those of Muenow et al. [25] and Piacente et al. [26] by a factor of ≈25 and ≈4, respectively. In terms of $p(TeO)/p(TeO_2)$ ratio, the values are: 0.085 [25], 0.09 [26], 0.72 (from our previous measurements [27]), and 0.63 (present study) at 885 K; and 0.05 [28] and 0.60 (present study) at 940 K. Our value is easily 7–12 times higher than the values from other mass spectrometric studies. This anomaly perplexes us, especially because the $[p(TeO)/p(TeO_2)]$ ratio will be totally unaffected by errors in pressure calibration or affected, if at all, by not more than a factor of 2 due to differences in $[\sigma(TeO_2)/\sigma(TeO)]$. Not even the fragmentation correction that had been applied in this study for deducing the p(TeO) could be responsible because without this correction, our p(TeO) (and thus the ratio) would at best have been only 1.5 times lower. Should there be any doubt as to whether contribution to TeO^+ from fragmentation of TeO_2(g) could have given rise to the high values of p(TeO) in the present study, it is sought to be removed by following reasoning: (1) we deduced the partial pressures from I^+ corresponding to 13 eV, and the ionization efficiency curve for TeO^+ (see Fig. 1) clearly shows that the onset of contribution to TeO^+ due to fragmentation starts only at energy ≥13 eV and (2) the value estimated (from thermochemical data for the pertinent gaseous species and AE of TeO^+) for the dissociative ionization of TeO_2(g) to TeO^+ is ≈12.6 eV (Muenow et al.'s [25] value being 13.4 eV), and hence at 13 eV, the fragmentation of TeO_2(g) could be ignored as insignificant, as was also evidenced by the ionization efficiency curve for TeO_2^+.

We did not measure the $p(O_2)$ in the present study, but as described already, we deduced it by assuming congruent effusion. Our value is 25 times higher than that measured by Muenow et al. [25] and 30 times higher than that measured by Kazenas and Bol'shikh [28]. In terms of $p(O_2)/p(TeO_2)$, our values is ≈0.2, whereas the value of Muenow et al. [25] is ≈0.04 (at 885 K) and that of Kazenas and Bol'shikh [28] is ≈0.008 (at 940 K).

As for Te_2(g), our value of $p(Te_2)$ is 14 times higher than that of Muenow et al. [25], but in reasonable agreement (within ∼33%) with that of Kazenas and Bol'shik [28]. In terms of $p(Te_2)/p(TeO_2)$, our value is 0.11, while that of Muenow et al. [25] is 0.03 and that of Kazenas and Bol'shik [28] is 0.08.

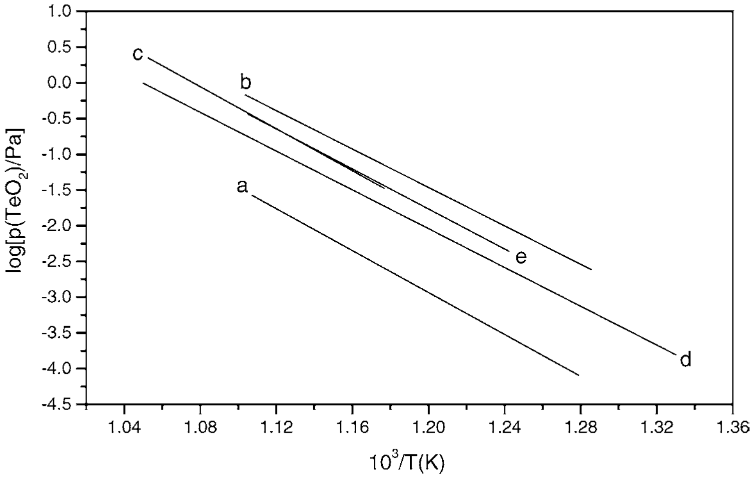

Fig. 3. Comparison of $p(TeO_2)$ over TeO_2(s): (a) Muenow et al. [25], (b) Piacente et al. [26], (c) Kazenas and Bol'shikh [28], (d) our earlier work [27] and (e) present work.

Interestingly, the Te-to-O ratio in the effusate, calculated by using partial pressures of just four species TeO_2(g), TeO(g), Te_2(g), and O_2(g) (left-hand side of the Eq. (6)) is ∼0.50 for Muenow et al. [25], in perfect accord with the requirement for congruent effusion of TeO_2(s). The value deduced for Kazenas and Bol'shik [28] is 0.56. TeO_2(g) being the most dominant species, the Te-to-O ratio in the effusate will hover around 0.50 irrespective of how high or low is the $p(TeO_2)$ measured by different authors. Nevertheless, the positive deviation of its value from 0.5 can provide some indication of consistency in the $p(Te_2)/p(O_2)$ or $p(Te_2)/p(TeO)$ ratios. Not surprisingly is thus the $p(Te_2)/p(O_2)$ ratio of Muenow et al. (0.6) consistent with the value obtained in the present study (0.7), but the value of Kazenas and Bol'shik (10.5) is relatively very high. The situation is nearly similar with regard to the $p(Te_2)/p(TeO)$ ratio also. The values are 0.32 (Muenow et al.), 0.17 (present study), and 1.57 (Kazenas and Bol'shik). Such analysis was not done in the case of Piacente et al. [26] who did not report $p(O_2)$ or $p(Te_2)$.

The total pressure $[p(TeO_2) + p(TeO) + p(Te_2) + p(O_2) + p(TeO_2)_2 + p(TeO)_2]$ obtained in the present work is in reasonable agreement (within 25%) with those obtained by transpiration, Knudsen effusion mass loss methods [17–24] and the mass spectrometric data of Piacente et al. [26]. The total pressure for the latter was calculated from the partial pressure ratio given by them for TeO_2(g), TeO(g) and $(TeO_2)_2$(g) (100:9:9). However, the value of Muenow et al. [25] at 885 K and Kazenas and Bol'shikh [28] at 940 K are lower, respectively, by a factor ∼6.0 and ∼1.8. Though Muenow et al. [25] did not give partial pressures for individual species, the same were read from the log(p) versus $1/T$ plot given by them.

Our ascription of the results obtained in the present study to congruently effusing composition of TeO_2(s) was based on the observation that the ion intensities were reasonably stable at a constant temperature for long durations (mass-loss experiments lasting for ∼30 h) and were reproducible from run to run conducted on different days on the same sample (temperature-dependence experiments). X-ray diffraction analysis of samples before and after vaporization experiments did not show presence of phases other than TeO_2. The low $p(Te_2)$ values provided evidence that the samples never were in the two phase region of Te(l) + TeO_2(s), a situation which could also give rise to stable ion intensities with time.

4.2. Reaction enthalpies

4.2.1. Heterogeneous solid–gas reactions

Table 4 shows that there exists a difference of ∼10 kJ/mol between second- and third-law values for the sublimation of TeO_2(s) to TeO_2(g). On account of the fact that the number of runs are less and that the temperature range of measurement is only 100 K, the mean of third-law values is recommended for this reaction as well as for other reactions. The uncertainty quoted for the recommended value was deduced from the estimated uncertainty in the temperature measurement (±3 K) and in the measured partial pressures (30% for TeO_2(g) and TeO(g) and 50% for other species).

Table 5 compares the enthalpies of different solid–gas and gas-phase reactions obtained in the present study with those available in the literature [17,18,25,26,28,34,35]. With no access to complete partial pressures data at different temperatures, no reevaluation was performed with uniform thermal functions, and therefore, only the values as given by authors were used for comparison. The value recommended in the present study for the reaction 1 agrees well with that selected by Mills [17] and Cordfunke and Konings [18]. Both reviewers have mainly considered total vapor pressure values and the mass spectrometric data of Piacente et al. [26], while giving their selected value.

Our value of enthalpy of sublimation of $(TeO_2)_2$(g) is in good agreement with that selected by Cordfunke and Konings [18], who calculated, based on their selected value of enthalpy of sublimation of TeO_2(g) and the enthalpy of reaction 6 for Piacente et al. [26]. The value of Muenow et al. [25] is lower by about 16 kJ/mol and that of Kazenas and Bol'shikh [28] by about 25 kJ/mol.

For the pressure independent reaction 6, our recommended third-law value agrees well with that given by Piacente et al. [26], but the value deduced for Muenow et al. [25] from values for reactions 1 and 3 is 37 kJ/mol lower.

4.2.2. Homogeneous gas-phase reactions

Table 5 also compares the enthalpies of different gas-phase reactions available in or deduced from the literature. The details are given in footnote of the table. For reaction 3, our recommended value is in accord with Piacente et al.'s value [26]. For reaction 5, our value is closest to that calculated from Muenow et al.'s [25] data. For reaction 4, our value is the lowest, consistent with relatively high p(TeO) reported by us.

Third-law evaluation of reactions $TeO_2(g) = TeO(g) + 0.5O_2(g)$ and $TeO_2(g) = 0.5\ Te_2(g) + O_2(g)$ helped us to infer that our results agree much better with those of Staley [34] than with Muenow et al. [25] or Kazenas and Bol'shik [28]. For the former reaction, the third-law enthalpy values (in kJ/mol at T = 298.15 K) are 118 (present study), 121 (Staley), 144 (Muenow et al.), 151 (Kazenas and Bol'shik). The values for the latter reaction are 122 (present study), 110 (Staley), 145 (Muenow et al.), 150 (Kazenas and Bol'shik). The fact that Staley undertook measurements under controlled oxygen pressures reconfirms the discrepancy between our results and those obtained by Muenow et al. and Kazenas and Bol'shik, especially for TeO(g) and Te_2(g).

4.2.3. Formation reactions

Table 6 compares the enthalpies of formation of various gaseous species derived in the present work with those available in the literature. $\Delta_f H^\circ{}_m$ (298.15) of TeO_2(g) and $(TeO_2)_2$(g) agree reasonably with those selected by Mills

[17] and Cordfunke and Konings [18] in their reviews. For $(TeO_2)_2$(g), the value of Muenow et al. [25] is higher than that reported by others. In the case of TeO(g), the values attributed to Staley [34] and Zmbov and Miletic [35] were those derived by Cordfunke and Konings [18], which, however, are different from that given by Pedley and Marshall [36] in their compilation of data on gaseous monoxides. The value obtained in the present work compares well with that selected by Mills [17]. For $(TeO)_2$(g) the present work yields lower stability than others.

5. Conclusions

The present mass spectrometric study, undertaken in conjunction with the quantitative evaporation method, gave very reliable partial pressures which are, however, higher by a factor of 1.8 than our previous study [27]. It also led to the reconfirmation of the relative abundance of the gaseous species (with respect to TeO_2(g)), deducible from our previous measurements. A rather huge and unexplainable discrepancy exists with regard to the relative abundance of TeO(g) with respect to TeO_2(g) (between our results on one side and those from all other mass spectrometric studies [25,26,28] on the other side). The relative abundance of Te_2 with respect to TeO or O_2 obtained by us agrees well with the first mass spectrometric study of this system by Muenow et al. [25], but differ hugely from the most recent mass spectrometric study by Kazenas and Bol'shikh [28].

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References

[1] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.

[2] B.R. Bowsher, S. Dickinson, A.L. Nichols, R.A. Gomme, J.S. Ogden, Anon.-American Chemical Society, Division of Nuclear Chemistry and Technology, Washington, DC (U.S.A.), in: Proceedings of the Symposium on Chemical Phenomenon Associated with Radioactivity Releases During Severe Nuclear Plant Accidents, Anaheim, CA, American Chemical Society, September 8–12, 1986.

[3] B. Saha, R. Viswanathan, M. Sai Baba, D. Darwin Albert Raj, R. Balasubramanian, D. Karunasagar, C.K. Mathews, J. Nucl. Mater. 130 (1985) 316.

[4] M. Sai Baba, R. Viswanathan, R. Balasubramanian, D. Darwin Albert Raj, B. Saha, C.K. Mathews, J. Chem. Thermodyn. 20 (1988) 1157.

[5] R. Viswanathan, M. Sai Baba, D. Darwin Albert Raj, R. Balasubramanian, B. Saha, C.K. Mathews, J. Nucl. Mater. 149 (1987) 302.

[6] R. Viswanathan, M. Sai Baba, D. Darwin Albert Raj, R. Balasubramanian, B. Saha, C.K. Mathews, J. Nucl. Mater. 167 (1989) 94.

[7] R. Viswanathan, M. Sai Baba, T.S. Lakshmi Narasimhan, R. Balasubramanian, D. Darwin Albert Raj, C.K. Mathews, J. Alloys Compd. 206 (1994) 201.

[8] R. Viswanathan, R. Balasubramanian, C.K. Mathews, J. Chem. Thermodyn. 21 (1989) 1183.

[9] R. Viswanathan, D. Darwin Albert Raj, T.S. Lakshmi Narasimhan, R. Balasubramanian, C.K. Mathews, J. Chem. Thermodyn. 25 (1993) 533.

[10] M. Sai Baba, T.S. Lakshmi Narasimhan, R. Balasubramanian, C.K. Mathews, J. Nucl. Mater. 201 (1993) 147.

[11] T.S. Lakshmi Narasimhan, R. Viswanathan, R. Balasubramanian, J. Phys. Chem. B 102 (1998) 10586.

[12] T.S. Lakshmi Narasimhan, M. Sai Baba, R. Balasubramanian, S. Nalini, R. Viswanathan, J. Chem. Thermodyn. 34 (2002) 103.

[13] M. Sai Baba, R. Viswanathan, C.K. Mathews, Rapid Commun. Mass Spectrom. 10 (1996) 691.

[14] T.S. Lakshmi Narasimhan, Ph.D. Thesis, University of Madras, Madras, India, 2000 (Chapter 2B for congruent vaporization processes and equations).

[15] T.S. Lakshmi Narasimhan, M. Sai Baba, R. Viswanathan, J. Phys. Chem. B 106 (2002) 6762.

[16] T.S. Lakshmi Narasimhan, M. Sai Baba, S. Nalini, R. Viswanathan, Thermochim. Acta 410 (2004) 149.

[17] K.C. Mills, Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides, Butterworths, London, 1974.

[18] E.H.P. Cordfunke, R.J.M. Konings (Eds.), Thermochemical Data for Reactor Materials and Fission Products, North-Holland, Amsterdam, 1990.

[19] K. Ueno, J. Chem. Soc. Jpn. 62 (1941) 990 (as quoted in Ref. [17]).

[20] J.R. Soulen, P. Sthapitanonda, J.L. Margrave, J. Phys. Chem. 59 (1955) 132 (as quoted in Ref. [17]).

[21] V.P. Zlomanov, A.V. Novoselova, A.S. Pashinkin, Y. Simanov, K. Semenenko, Zhur. Neorg. Khim. 3 (1958) 1473 (as quoted in Ref. [17]).

[22] K. Krishnan, G.A. Rama Rao, K.D. Singh Mudher, V. Venugopal, J. Nucl. Mater. 230 (1996) 61.

[23] O. Glemser, R.V. Haeseler, A. Muller, Z. Anorg. Allg. Chem. 329 (1964) 51 (as quoted in Ref. [17]).

[24] K.E. Prescher, W. Schrodter, Z. Erzbergb. Metallhuett Wes. 15 (1962) 299;
K.E. Prescher, W. Schrodter, Z. Erzbergb. Metallhuett Wes. 16 (1963) 352 (as quoted in Ref. [17]).

[25] D.W. Muenow, J.W. Hastie, R. Hauge, R. Bautista, J.L. Margrave, Trans. Faraday Soc. 65 (1969) 3210.

[26] V. Piacente, L. Malaspina, G. Bardi, R. Gigli, Rev. Int. Hautes Temp. Refract. 6 (1969) 91.

[27] T.S. Lakshmi Narasimhan, R. Balasubramanian, S. Nalini, M. Sai Baba, J. Nucl. Mater. 247 (1997) 28.

[28] E.K. Kazenas, M.A. Bol'shikh, Metallurgy 2 (1996) 9.

[29] R.A. Rapp (Ed.), Physicochemical Measurements in Metals Research, Part I, in: R.F. Bunshah (Ser. Ed.), Techniques in Metal Research, vol. IV, Wiley, New York, 1970.

[30] J.B. Mann, Recent developments in mass spectrometry, in: K. Ogata, T. Hayakawa (Eds.), Proceedings of the International Conference on Mass Spectrometry, University of Tokyo Press, Tokyo, Japan, 1970, p. 814.

[31] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd ed., Springer-Verlag, Berlin, 1991.

[32] F. Grønvold, J. Drowart, E.F. Westrum Jr., The chemical thermodynamics of actinide elements and compounds, Part 4, in: The Actinide Chalcogenides (Excluding Oxides), IAEA, Vienna, 1984.

[33] C.E. Moore, Ionization potentials and ionization limits derived from the analyses of optical spectra, Nat. Bur. Stand. U. S. NSRDS-NBS 34 (1970) 22.
[34] H.G. Staley, J. Chem. Phys. 52 (1970) 4311.
[35] K.F. Zmbov, M.M. Miletic, Bull. Soc. Chim. (Beograd) 43 (1978) 521 (as quoted in Ref. [18]).
[36] R. Viswanathan, M. Sai Baba, D. Darwin Albert Raj, R. Balasubramanian, T.S. Lakshmi Narasimhan, C.K. Mathews, Spectrochim. Acta 49B (1994) 243.
[37] J.B. Pedley, E.M. Marshall, J. Phys. Chem. Ref. Data 12 (1983) 967.