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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.
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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 vapor-ize 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

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 par-

tial 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.