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Vaporisation studies on tellurium dioxide: A Knudsen effusion mass spectrometric study.

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Abstract

The vaporisation of $TeO_2(s)$ was studied by Knudsen effusion mass spectrometry. The vapour phase was found to consist of $(TeO_2)_n$ ($n = 1$–3)(g), $(TeO)_n(g)$ ($n = 1$–3) and $Te_2(g)$. The p–T relations of $TeO_2(g)$, $(TeO_2)_2(g)$ and $(TeO_2)_3(g)$ were derived to be $\log(p/\mathrm{Pa}) = (-13534 \pm 78)/T + (14.241 \pm 0.09)$ (750–950 K), $\log(p/\mathrm{Pa}) = (-14823 \pm 212)/T + (14.373 \pm 0.242)$ (825–950 K) and $\log(p/\mathrm{Pa}) = (-19074 \pm 540)/T + (17.337 \pm 0.606)$ (850–921 K) respectively. From the partial pressures, $\Delta_r H^0_{298.15}$ of $n\mathrm{TeO_2(s)} = (\mathrm{TeO_2})_n(\mathrm{g})$ ($n = 1$–3) were evaluated by second and third law methods. Also, enthalpy of the pressure independent reaction $TeO_2(s) + TeO_2(g) = (TeO_2)_2(g)$ has been evaluated. Using the $\Delta_f H^0_{298.15}$ of $TeO_2(s)$, $\Delta_f H^0_{298.15}$ of $(TeO_2)_n(g)$ ($n = 1$–3) were calculated. The partial pressure and enthalpy data for $(TeO_2)_3(g)$ have been obtained for the first time. © 1997 Elsevier Science B.V.

1. Introduction

It is believed that tellurium is one of the hazardous fission products, which could attack the cladding material of a nuclear reactor, forming binary and multi component compounds. In continuation of our thermodynamic investigations on M–Te systems (M = Stainless steel components: Fe, Cr, Ni, Mo and Mn) [1–5], to understand the role played by tellurium in fuel-clad chemical interactions in fast reactors, vaporisation studies on M–Te–O systems have been initiated. It is reported that metal tellurides might vaporise mainly as $TeO_2(g)$ [6,7] and that, tellurium may evolve as $TeO(g)$ and $TeO_2(g)$, from the damaged core of a pressurised water reactor [8]. Therefore, a study of vaporisation behaviour of $TeO_2(s)$ is essential. Mills [9] and Cordfunke and Konings [10] have reviewed the thermodynamic studies on TeO_2(s, l), which include vapour pressure, calorimetric and emf measurements. Vaporisation studies on $TeO_2(s)$ by Knudsen effusion mass spectrometry have been reported by Muenow et al. [11] and Piacente et al. [12]. Muenow et al. [11] have observed the molecular species $(TeO)_n(g)$ and $(TeO_2)_n(g)$ ($n = 1$ to 4), $Te_2(g)$ and $O_2(g)$ in the temperature range 788–903 K and Piacente et al. [12] have observed $TeO_2(g)$, $TeO(g)$ and $(TeO_2)_2(g)$ in the range 778–906 K. The partial pressures and the enthalpy of vaporisation of $TeO_2(g)$, obtained by Muenow et al. [11], are in disagreement with the results reported by others in the literature [9,10]. In order to resolve this discrepancy, we reinvestigated the vaporisation of $TeO_2(s)$ by Knudsen effusion mass spectrometry. In this paper, we report our results on the partial pressures of $(TeO_2)_n(g)$ ($n = 1$–3) over $TeO_2(s)$ and the thermodynamic quantities deduced from them for different chemical equilibria.

2. Experimental

A VG Micromass 30 BK mass spectrometer has been used for the vaporisation study. $TeO_2(s)$ was obtained from M/s Leico Industries (99.99% purity). The Knudsen cell assembly consisted of a Mo cup housing a alumina cell (O.D. = 10.0 mm; I.D. = 7.5 mm; height = 10.0 mm; orifice dia = 0.51 mm; knife edge). The cell was heated by electron bombardment and the temperatures were measured by a chromel–alumel thermocouple inserted through the base of the Mo cup and touching the bottom of the alumina cell. The thermocouple was calibrated against the melting temperature of silver. The vapour effusing from

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the Knudsen cell was ionised by electrons emitted from a variable electron energy source. The positive ions produced were accelerated to 6 kV, mass analysed by a 90° sector single focusing magnetic analyser and detected by secondary electron multiplier/Faraday cup. The details of electron energy calibration and other instrumental parameters are given elsewhere [13].

2.1. Mass spectrometric measurements

The mass spectrum of the equilibrium vapour was found to consist of peaks corresponding to the following ions: Te^+, Te_2^+, TeO^+, $Te_2O_2^+$, $Te_3O_3^+$, TeO_2^+, $Te_2O_4^+$, $Te_3O_6^+$, $Te_2O_3^+$ and Te_2O^+. The ions were identified from their masses and isotopic abundances. The relative intensities of these ions at 900 K are 25:7:40:3: 0.001:100:6:0.1:0.8:0.1. The ion intensities were recorded as a function of electron energy to determine the appearance energies (AE) of these ions. The AE values (+0.5 eV) are: 11.4 (Te^+), 8.9 (Te_2^+), 10.7 (TeO^+), 12.9 ($Te_2O_2^+$), 11.9 (TeO_2^+), 11.9 ($Te_2O_4^+$), 11.7 ($Te_3O_6^+$), 14.3 ($Te_2O_3^+$), 12.7 ($Te_3O_3^+$) and 13.9 (Te_2O^+) eV respectively. From the AE values, the neutral species were ascertained to be Te_2(g), TeO(g), $(TeO)_2$(g), $(TeO)_3$(g), TeO_2(g), $(TeO_2)_2$(g), and $(TeO_2)_3$(g). The ions pertinent to this paper are, TeO_2^+, $(TeO_2)_2^+$ and $(TeO_2)_3^+$. Their intensities at an electron energy of 48 eV were measured as a function of temperature in the range 750–950 K for TeO_2^+, 825–950 K for $(TeO_2)_2^+$ and 850–950 K for $(TeO_2)_3^+$. The fragmentation corrections were not considered in the measured ion intensities. The experiments were conducted both in ascending and descending temperature cycles. In each experiment, the sample was kept at the first temperature for long period (~ 2 h) to ascertain equilibrium inside the Knudsen cell, which was indicated by the constancy of ion intensities. The measured ion intensities were converted to partial pressures using

$$p_i = k/(\sigma s h)_i I_i T, \tag{1}$$

where p_i is the partial pressure of species 'i', k, the

Table 1

Partial pressures of $(TeO_2)_n$(g) (n = 1–3) over TeO_2(s)

Sample	Expt	Run	Temp range (K)	$\log(p_i/\mathrm{Pa}) = -A/T(\mathrm{K}) + B$	(p/Pa) at 875 K	
				$-A$	B	
$i = TeO_2$(g)						
1	1	1	825–921	13630 ± 75	14.227 ± 0.086	4.5×10^{-2}
	2	1	825–921	13718 ± 101	14.411 ± 0.115	5.4×10^{-2}
		2	825–921	13827 ± 75	14.544 ± 0.086	5.5×10^{-2}
	3	1	825–921	13410 ± 166	14.060 ± 0.191	5.4×10^{-2}
		2	825–921	13482 ± 101	14.130 ± 0.116	5.3×10^{-2}
2	1	1	825–921	14222 ± 286	15.087 ± 0.324	6.8×10^{-2}
		2	825–921	13491 ± 96	14.231 ± 0.110	6.5×10^{-2}
	2	1	825–921	13796 ± 103	14.602 ± 0.117	6.8×10^{-2}
		2	825–921	13906 ± 77	14.714 ± 0.087	6.6×10^{-2}
	3	1	825–950	13030 ± 172	13.685 ± 0.196	6.2×10^{-2}
	4	1	825–950	13295 ± 232	13.949 ± 0.261	5.7×10^{-2}
		2	825–950	13110 ± 258	13.712 ± 0.290	5.4×10^{-2}
3	1	1	750–875	13995 ± 31	14.823 ± 0.037	6.7×10^{-2}
		2	750–875	13737 ± 74	14.523 ± 0.091	6.7×10^{-2}
Recommended			750–950	13534 ± 78	14.241 ± 0.090	5.9×10^{-2}
$i = (TeO_2)_2$(g)						
1	1	1	850–921	14920 ± 274	14.511 ± 0.311	2.9×10^{-3}
	3	1	825–921	14843 ± 311	14.460 ± 0.357	3.1×10^{-3}
2	2	1	825–921	14577 ± 586	14.072 ± 0.670	2.6×10^{-3}
	3	1	825–950	14445 ± 364	13.965 ± 0.412	2.9×10^{-3}
	4	1	825–950	15274 ± 477	14.802 ± 0.540	2.2×10^{-3}
		2	825–950	14578 ± 414	14.053 ± 0.468	2.5×10^{-3}
Recommended			825–950	14823 ± 212	14.373 ± 0.242	2.7×10^{-3}
$i = (TeO_2)_3$(g)						
1	3	1	875–921	17971 ± 2009	16.097 ± 2.236	3.6×10^{-5}
2	2	1	875–921	18501 ± 886	16.743 ± 0.986	4.0×10^{-5}
	3	3	850–921	18787 ± 290	17.081 ± 0.328	4.1×10^{-5}
	4	1	850–921	19669 ± 417	17.924 ± 0.471	2.8×10^{-5}
Recommended			850–921	19074 ± 540	17.337 ± 0.606	3.5×10^{-5}

Table 2
Reaction enthalpies (kJ/mol)

Sample	Expt	Run	T_m [a] (K)	II law [b]		III law [b]	Recommended [c]
				$\Delta_r H_T^0$	$\Delta_r H_{298.15}^0$	$\Delta_r H_{298.15}^0$	
$TeO_2(s) = (TeO_2)(g)$							
1	1	1	873	261.0 ± 1.4	272.6 ± 1.4	274.8 ± 0.1	272.5 ± 3.8
	2	1	873	262.7 ± 1.9	274.3 ± 1.9	273.4 ± 0.1	
		2	873	264.8 ± 1.4	276.4 ± 1.4	273.2 ± 0.1	
	3	1	873	256.8 ± 3.2	268.4 ± 3.2	273.4 ± 0.1	
		2	873	258.2 ± 1.9	269.7 ± 1.9	273.6 ± 0.1	
2	1	1	873	272.3 ± 5.5	283.9 ± 5.5	271.6 ± 0.3	
		2	873	258.3 ± 1.8	269.9 ± 1.8	272.1 ± 0.1	
	2	1	873	264.2 ± 2.0	275.8 ± 2.0	271.7 ± 0.1	
		2	873	266.3 ± 1.5	277.9 ± 1.5	271.9 ± 0.1	
	3	1	888	249.5 ± 3.3	261.4 ± 3.3	272.5 ± 0.2	
	4	1	888	254.6 ± 4.4	266.5 ± 4.4	273.2 ± 0.2	
		2	888	251.0 ± 4.9	262.9 ± 4.9	273.7_0.3	
3	1	1	813	268.0 ± 0.6	278.2 ± 0.6	272.2 ± 0.1	
		2	813	263.0 ± 1.4	273.3 ± 1.4	272.0 ± 0.1	
				Mean:	272.2 ± 6.2	272.8 ± 0.9	
$2(TeO_2)(s) = (TeO_2)_2(g)$							
1	1	1	886	285.7 ± 5.2	296.4 ± 5.2	320.4 ± 0.3	307.2 ± 20.8
	3	1	873	284.2 ± 6.0	294.6 ± 6.0	319.5 ± 0.3	
2	2	1	873	279.1 ± 11.0	289.5 ± 11.0	321.0 ± 0.6	
	3	1	888	276.6 ± 7.0	287.3 ± 7.0	320.7 ± 0.6	
	4	1	888	292.5 ± 9.1	303.2 ± 9.1	322.3 ± 0.5	
		2	888	279.1 ± 7.9	289.9 ± 7.9	321.7 ± 0.6	
				Mean:	293.5 ± 5.8	320.9 ± 1.0	
$3(TeO_2)(s) = (TeO_2)_3(g)$							
1	3	1	898	344.1 ± 38.5	353.9 ± 38.5	378.1 ± 0.7	373.1 ± 18.7
2	2	1	898	354.2 ± 17.0	364.1 ± 17.0	377.1 ± 0.4	
	3	1	886	359.7 ± 5.6	369.2 ± 5.6	376.7 ± 0.2	
	4	1	886	376.6 ± 8.0	386.1 ± 8.0	379.3 ± 0.2	
				Mean:	368.3 ± 13.4	377.8 ± 1.2	

[a] T_m is the mean temperature of each run.
[b] Errors quoted are standard deviations.
[c] Average of mean of second and third law values; errors quoted include statistical and estimated uncertainties.

instrument calibration constant, σ, the ionisation cross-section, s, the multiplier yield and h, the isotopic abundance. The values of 'k' were obtained from calibration experiments with Ag(s) (three runs) and Te(s) (one run). The ionisation cross-sections for the elements were taken from Mann's compilation [14] [1]. For $(TeO_2)_n(g)$ ($n = 1$–3), the σ values were taken to be $0.75\ (n\sigma_{Te} + 2n\sigma_O)$. The multiplier yield was assumed to be inversely proportional to the square root of individual masses.

3. Results

Table 1 gives pressure–temperature relations obtained by a least square fitting for each run, along with the recommended pressure equations, for $(TeO_2)_n(g)$ ($n = 1$–3). The partial pressures, based on pressure calibration with Ag(s), were employed to deduce these relations. The recommended equation was obtained by pooling all the points of the individual runs and fitting the combined data. Fig. 1 shows the plot of partial pressure against inverse temperature for all the three species. From the partial pressures, the enthalpy changes for the following reactions were evaluated by second- and third-law methods:

$$TeO_2(s) = TeO_2(g), \tag{2}$$

$$2TeO_2(s) = (TeO_2)_2(g), \tag{3}$$

$$3TeO_2(s) = (TeO_2)_3(g). \tag{4}$$

The values are given in Table 2. The necessary auxiliary thermodynamic quantities were taken from Knacke et al. [15] for $TeO_2(s)$,$TeO_2(g)$ and $(TeO_2)_2(g)$. Since no ther-

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[1] Ionisation cross-section tables can be obtained on request.

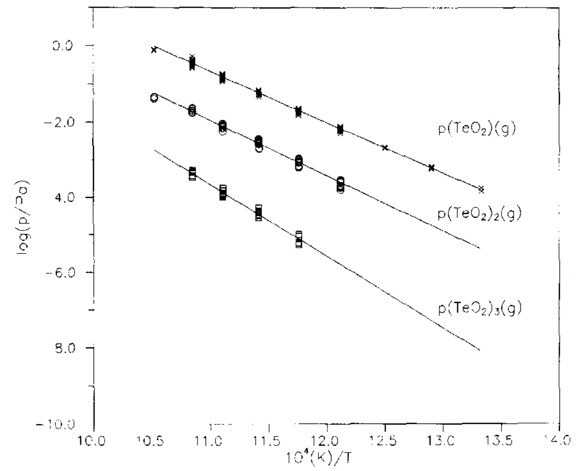

Fig. 1. Plot of log(p/Pa) against $1/T$ for $(TeO_2)_n(g)$ ($n = 1$–3).

modynamic functions were available for $(TeO_2)_3(g)$, only very crudely estimated values, based on the enthalpy and Gibbs free energy functions of monomer and dimer were used. The difference between the thermodynamic functions of monomer and dimer was added to the dimer functions to obtain the values for the trimer.

Based on the data obtained for the reactions 2 to 4, the enthalpy changes for the following reactions were evaluated:

$$(TeO_2)_2(g) = 2(TeO_2)(g), \qquad (5)$$

$$(TeO_2)_3(g) = 3(TeO_2)(g). \qquad (6)$$

Using the partial pressures obtained for the individual data points, for the monomer and dimer, the following pressure independent reaction was evaluated:

$$TeO_2(s) + TeO_2(g) = (TeO_2)_2(g). \qquad (7)$$

The enthalpy values for reactions 5 to 7 are given in Table 3 along with those for reactions 1 to 3 and compared with those available in the literature.

Table 3
Comparison of enthalpies of different reactions (kJ/mol)

Reaction no. [a]	$\Delta_r H^0_{298.15}$ (kJ/mol)	Reference
2	272.5 ± 3.8	present work
	264.0 ± 8.4	Mills [9]
	266.2 ± 0.6	Cordfunke and Konings [10]
	289.9 ± 8.4	Muenow et al. [11] [b]
3	307.2 ± 20.8	present work
	299.5 ± 30.5	Mills [9] [c]
	308.5 ± 10.0 [d]	Cordfunke and Konings [10]
4	373.1 ± 18.7	present work
5	237.8 ± 22.1	present work [e]
	228.5 ± 34.8	Mills [9] [e]
	223.9 ± 10.0	Cordfunke and Konings [10] [e]
	282.4 ± 8.4	Muenow et al. [11] [b]
6	444.4 ± 21.9	present work
7	47.6 ± 0.2	present work [f]
	42.3	Piacente et al. [12]

[a] Refers to equation number given in text.
[b] Average of II and III law values.
[c] Calculated from $\Delta_f H^0_{298.15}$ of $TeO_2(s)$ and $(TeO_2)_2(g)$.
[d] The error given for $\Delta_f H^0_{298.15}$ $(TeO_2)_2(g)$ was used.
[e] Calculated from the values of reaction 2 and 3, from the respective references.
[f] The third law value has been given.

4. Discussion

The pressure calibrations with Ag(s) and Te(s) yielded reasonably consistent partial pressures. For $TeO_2(g)$, at 875 K, for example, while Ag calibration gave a value of 0.06 Pa, Te calibration gave a value of 0.04 Pa. As mentioned already, only the pressures based on Ag calibration were chosen in all our evaluations. To compare our $p(TeO_2)$ with those obtained by others, we made use of the total pressure–temperature relations tabulated by Mills [9]. Our value is higher by a factor of ~ 7.4 than that of Muenow et al. [11], but in general lower by a factor ~ 3.5 than those of others [9]. The contributions from TeO(g) and other gaseous species to the total vapour pressure may slightly narrow down the discrepancy, but not account for the difference as high as a factor of 3.5. It is interesting to note that the plot of log(p/atm) against $1/T$ given by Muenow et al. [11] show values of $p(TeO_2)$, that are lower than our values, only by a factor of 1.7. For $(TeO_2)_2(g)$, the pressures read from the plot of Muenow et al. [11] are lower than our values by a factor of 3.2.

For $(TeO_2)_3(g)$, the partial pressures and the thermodynamic data are reported for the first time. The results presented for this species include those data points only up to 921 K. This is because the data point at $T = 950$ K showed a large negative deviation from the least squares fit of rest of the points. (by as much as ~ 40 kJ/mol). The deviations in the case of $TeO_2(g)$ and $(TeO_2)_2(g)$ were not as distinct and within experimental uncertainty. We do not know the reason for the negative deviation at 950 K. No phase transformation in solid TeO_2 is reported in the literature in the temperatures near 925 K. It might be worth mentioning here, that in those experiments, where the sample was heated to 950 K, the alumina cell got stuck to the Mo cup and only with difficulty, the two could be separated.

Table 2 shows that there is a good agreement between second and third law values for reaction 2. For the reaction

Table 4
Enthalpies of formation of $(TeO_2)_n(g)$, $n = 1–3$

Species	$\Delta_f H^0_{298.15}$ (kJ/mol)	Reference
$(TeO_2)(g)$	-48.5 ± 4.5	present work [a]
	-54.8 ± 2.6	Cordfunke and Konings [10] [a]
	-59.4 ± 8.4	Mills [9]
$(TeO_2)_2(g)$	-334.8 ± 21.4	present work [a]
	-333.5 ± 10.0	Cordfunke and Konings [10] [a]
	-408.8 ± 8.4	Muenow et al. [11]
	-347.3 ± 29.4	Mills [9]
$(TeO_2)_3(g)$	-589.9 ± 20.1	present work [a]

[a] Obtained using the $\Delta_f H^0_{298.15}$ of $TeO_2(s)$ given by Cordfunke and Konings [10] (-321.0 ± 2.5 kJ/mol).

3, the third law values are slightly higher than the second law enthalpies. The recommended values were obtained by taking the average of mean of second and third law values. As can be seen from Table 3, our values obtained for reactions 2 and 3, in the present work, agree well with those recommended by Cordfunke and Konings [10] and Mills [9]. The value from Muenow et al. [11] is somewhat high, for the reaction 2.

For reaction 7, the individual data points of the monomer and dimer were used to obtain the equilibrium constant. The enthalpy values obtained by second and third law methods are 27.5 ± 4.6 and 47.6 ± 0.2 kJ/mol). The third law value is comparable with the value obtained by Piacente et al. [12].

Using the value $\Delta_f H^0_{298.15}$ for $TeO_2(S)$ given by Cordfunke et al. (-321.0 kJ/mol) [9], enthalpies of formation of $(TeO_2)_n(g)$ ($n = 1–3$) were calculated and presented in Table 4 along with other available data in the literature.

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