

Vaporization thermodynamics of the metal-rich molybdenum telluride Mo_3Te_4 : a high-temperature mass-spectrometric study

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Vaporization of (molybdenum + tellurium) alloys corresponding to the two-phase field ($\text{Mo} + \text{Mo}_3\text{Te}_4$) was studied by using Knudsen-effusion mass spectrometry. The two samples used had initial compositions of 40.3 and 50.1 mass per cent of tellurium, respectively. The vapour phase was found to consist of Te_2 and Te . Relations of partial pressure against temperature were determined to be $\lg(p/\text{Pa}) = -(13631 \pm 97)(\text{K}/T) + (12.999 \pm 0.095)$ for $\text{Te}_2(\text{g})$, and $\lg(p/\text{Pa}) = -(13238 \pm 116)(\text{K}/T) + (11.674 \pm 0.113)$ for $\text{Te}(\text{g})$, respectively, in the temperature range 960 to 1110 K. Enthalpy changes were derived from the partial pressures for the equilibria: $\text{MoTe}_x(\text{s}) = \text{Mo}(\text{s}) + (x/i)\text{Te}_i(\text{g})$ and $\text{Te}_2(\text{g}) = 2\text{Te}(\text{g})$, where $x = 1.3334$ with $i = 1$ or 2. The standard molar enthalpy and standard molar Gibbs free energy of formation of $\text{MoTe}_{1.3334}$ were derived.

1. Introduction

Tellurium is a major fission product which is believed to be responsible for the internal corrosion of the stainless-steel cladding of mixed-oxide fuel used in fast-breeder reactors.⁽¹⁾ To assess the possible chemical reactions between tellurium and the constituents of stainless steel, thermodynamic properties of the relevant compounds of tellurium are essential. Our previous measurements on the tellurides of Fe ,^(2,3) Ni ,⁽⁴⁾ and Cr ,⁽⁵⁾ employing high-temperature mass-spectrometry, yielded accurate thermodynamic quantities. The tellurides of molybdenum are also interesting since molybdenum is not only an alloying element in the stainless-steel cladding of type AISI-316 but is also a major fission product with a yield of ≈ 22.3 per cent in the fission of ^{239}Pu .⁽⁶⁾

A tentative phase diagram of (molybdenum + tellurium) was reported by Brewer and Lamoreaux,⁽⁷⁾ on the basis of the results of Spiesser *et al.*,⁽⁸⁾ Vellinga *et al.*,⁽⁹⁾ and Opolovskii *et al.*,⁽¹⁰⁾ as well as by a comparison with (molybdenum + selenium). O'Hare⁽¹¹⁾ recently reviewed the results of the vaporization studies by Krabbes and

Oppermann⁽¹²⁾ and by Opolovskii *et al.*,⁽¹⁰⁾ and suggested further study in view of the discrepancies between them. Hence, a detailed investigation of the vaporization behaviour of different phase fields in (molybdenum + tellurium) using Knudsen-effusion mass spectrometry was taken up, and this paper reports the results obtained by us over the two-phase field ($\text{Mo} + \text{Mo}_3\text{Te}_4$). It is this phase field which is important in (fuel + clad) chemical interactions. The only other vaporization study reported previously in this phase field was that by Krabbes and Oppermann⁽¹²⁾ using a manometric method and covering a temperature range of 1173 to 1333 K.

2. Experimental

Preparation of (molybdenum + tellurium) alloys that corresponded to the two-phase field ($\text{Mo} + \text{Mo}_3\text{Te}_4$) was carried out by direct reaction of molybdenum powder (Metallwerk Plansee, Austria, purity 99.99 mass per cent) and tellurium powder (Leico Industries, Inc., U.S.A., purity 99.999 mass per cent). The required amounts of the two powders were mixed intimately, flushed several times with high-purity argon, sealed in quartz tubes under a pressure of 1×10^{-4} Pa, and heated at 700 K for 12 d, at 780 K for 4 d, and at 890 K for 7 d, before finally being cooled to ambient temperature. The starting compositions of the two samples prepared were 40.3 and 50.1 mass per cent of tellurium, respectively. The presence of Mo and Mo_3Te_4 and the absence of any other phase in these samples were confirmed by X-ray diffraction analysis.

A VG Micromass MM 30 BK mass spectrometer was used to conduct vaporization studies. An alumina Knudsen cell containing about 400 mg of the sample was placed in a tantalum cup and heated by electron bombardment. The temperatures were measured by a (chromel-to-alumel) thermocouple inserted through the base of the tantalum cup. The thermocouple was calibrated against the melting temperature of silver. The intensities of Te^+ and Te_2^+ , the only ions observed in the mass spectra of the equilibrium vapour, were measured as a function of electron-impact energy. That these ions were produced directly by the ionization of $\text{Te}(\text{g})$ and $\text{Te}_2(\text{g})$, respectively, below an electron-impact energy of 1.9 aJ, and that fragmentation of $\text{Te}_2(\text{g})$ occurred above this energy, were ascertained in the same way as in earlier studies.^(2, 4, 5) The ion intensities were measured as a function of the temperature of the Knudsen cell in the range 960 to 1110 K at electron-impact energies of 1.7 and 6.2 aJ. Attainment of chemical equilibrium inside the Knudsen cell was ascertained by ensuring the constancy of the ion intensities for at least 2 h at the highest temperature of a run, and by maintaining the subsequent temperatures for 20 min each before making measurements. The samples were annealed at different temperatures before the highest temperature was reached. This not only facilitated the removal of traces, if any, of unreacted tellurium or any volatile oxytelluride which would otherwise enhance the ion intensities, but also ensured that Knudsen-flow conditions were always maintained.

The partial pressures of $\text{Te}_2(\text{g})$ and $\text{Te}(\text{g})$ were computed from the ion intensities

by using the equations:

$$p(\text{Te}_2) = kI(\text{Te}_2^+)T, \quad (1)$$

$$p(\text{Te}) = kI(\text{Te}^+)T\{\sigma(\text{Te}_2)/\sigma(\text{Te})\}\{\gamma(\text{Te}_2^+)/\gamma(\text{Te}^+)\}\{n(\text{Te}_2^+)/n(\text{Te}^+)\}, \quad (2)$$

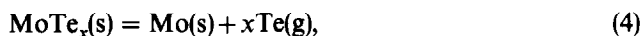
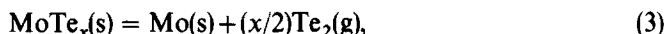
where k is the pressure calibration constant, and σ , γ , and n are the ionization cross section of the species, the relative detector response, and the abundance of the isotope measured, respectively. The pressure calibration constant was determined through a calibration run with Te(s) in the same Knudsen cell used for the measurements over $(\text{Mo} + \text{Mo}_3\text{Te}_4)$. The measured intensities of Te_2^+ and the previously known partial pressures of $\text{Te}_2(\text{g})$ over Te(s) ,⁽¹³⁾ were employed to obtain k . The ratio $\sigma(\text{Te}_2)/\sigma(\text{Te})$ was taken as 1.44 as suggested by Pottier,⁽¹⁴⁾ and $\gamma(\text{Te}_2^+)/\gamma(\text{Te}^+)$ was assumed to be $\{M(\text{Te}^+)/M(\text{Te}_2^+)\}^{1/2}$, where $M(\text{Te}^+) = 130 \text{ g} \cdot \text{mol}^{-1}$ and $M(\text{Te}_2^+) = 256 \text{ g} \cdot \text{mol}^{-1}$. The correction for the contribution to $I(\text{Te}^+)$ arising from dissociative ionization of $\text{Te}_2(\text{g})$ at 6.2 eV was deduced from $I(\text{Te}^+)/I(\text{Te}_2^+)$ over elemental tellurium in the calibration runs at much lower temperatures (620 to 650 K) where Te^+ arose solely due to fragmentation.^(13, 15) In all, seven runs were conducted: four runs with the sample with 40.3 mass per cent of Te , and three runs with the other sample.

To confirm the reliability of the partial pressures and reaction enthalpies obtained in this work, measurements have also been made using silver (National Bureau of Standards) for pressure calibration. A Knudsen cell made of molybdenum, with an orifice of diameter 0.3 mm was used to contain the condensed phases. The experimental procedure used was essentially the same as that employed in experiments with tellurium for pressure calibration. Vapour pressures of silver recommended by N.B.S.⁽¹⁶⁾ were used to compute a pressure calibration constant. The ionization cross sections for Ag(g) and Te(g) were taken from Mann's tables⁽¹⁷⁾ and a value of 1.44 $\sigma(\text{Te})$ was assumed for $\text{Te}_2(\text{g})$.

3. Results

Table 1 gives the relations of least-squares-fitted pressure against temperature over $(\text{Mo} + \text{Mo}_3\text{Te}_4)$ along with the partial pressures at the mean temperature of the investigation (1035 K) for $\text{Te}_2(\text{g})$ and Te(g) . The results given in table 1 are those obtained by using tellurium for pressure calibration. The partial-pressure equations obtained in the set of measurements where silver was used for pressure calibration are given in table 2. The errors quoted for the coefficients in tables 1 and 2 are standard deviations.

From the partial pressures, enthalpy changes for the following reactions were derived by standard methods:⁽¹⁸⁾



and



TABLE 1. Partial pressures of Te_2 and of Te over $(\text{Mo} + \text{Mo}_3\text{Te}_4)$, where $\lg(p/\text{Pa}) = -A(K/T) + B$; known $p(\text{Te}_2)$ over Te(s) was used for pressure calibration

Run no.	T/K	A	B	p/Pa^a
$p(\text{Te}_2)$				
Electron impact energy: 1.7 aJ				
1	960 to 1110	13287 ± 141	12.661 ± 0.137	0.67
2	960 to 1060	13981 ± 139	13.363 ± 0.138	0.71
3	970 to 1060	14030 ± 79	13.368 ± 0.078	0.65
4	975 to 1060	13030 ± 191	12.407 ± 0.190	0.66
5	995 to 1110	13544 ± 334	12.945 ± 0.318	0.72
6	995 to 1110	13505 ± 242	12.849 ± 0.234	0.63
7	960 to 1110	13830 ± 93	13.200 ± 0.090	0.69
Recommended	960 to 1110	13631 ± 97	12.999 ± 0.095	0.67
Electron impact energy: 6.2 aJ				
1	960 to 1110	13284 ± 134	12.625 ± 0.129	0.62
2	960 to 1060	13693 ± 181	13.071 ± 0.180	0.69
3	970 to 1060	13570 ± 173	12.910 ± 0.171	0.63
4	975 to 1100	12941 ± 104	12.290 ± 0.101	0.61
5	995 to 1110	13692 ± 317	13.147 ± 0.301	0.83
6	960 to 1110	13569 ± 231	12.976 ± 0.224	0.73
7	960 to 1110	13880 ± 107	13.232 ± 0.104	0.66
$p(\text{Te})$				
Electron-impact energy: 1.7 aJ				
1	960 to 1110	13096 ± 154	11.544 ± 0.148	0.078
2	960 to 1060	13653 ± 151	12.127 ± 0.150	0.086
3	970 to 1060	13871 ± 158	12.293 ± 0.157	0.078
4	975 to 1060	12907 ± 100	11.376 ± 0.099	0.080
5	995 to 1110	13476 ± 384	11.888 ± 0.365	0.074
6	995 to 1110	13288 ± 242	11.677 ± 0.234	0.069
7	960 to 1110	13524 ± 89	11.959 ± 0.087	0.078
Recommended	960 to 1110	13238 ± 116	11.674 ± 0.113	0.077
Electron-impact energy: 6.2 aJ				
1	960 to 1110	13262 ± 162	11.985 ± 0.157	0.15
2	960 to 1060	13570 ± 135	12.330 ± 0.134	0.17
3	970 to 1060	13550 ± 197	12.290 ± 0.194	0.16
4	975 to 1100	13140 ± 153	11.869 ± 0.148	0.15
5	995 to 1110	13364 ± 417	12.118 ± 0.397	0.16
6	960 to 1110	13260 ± 273	11.986 ± 0.264	0.15
7	960 to 1110	13972 ± 140	12.665 ± 0.136	0.15

^a $\langle T \rangle = 1035 \text{ K}$.

For this purpose, the value of x in equations (3) and (4) was taken as 1.3334, computed from the nominal formula of Mo_3Te_4 , assigned by Brewer and Lamoreaux.⁽⁷⁾ To derive the enthalpy changes for the above reactions, the auxiliary thermodynamic quantities for Mo(s) ,⁽¹⁹⁾ Te(g) , $\text{Te}_2(\text{g})$ ⁽²⁰⁾ and $\text{MoTe}_{1.3334}(\text{s})$ ⁽⁷⁾ were taken from the literature.

Reaction enthalpies derived are given in table 3. Table 4 gives the results of third-law evaluations for a typical run. The errors quoted are standard deviations. The

TABLE 2. Partial pressures over $(\text{Mo} + \text{Mo}_3\text{Te}_4)$ determined by using known $p(\text{Ag})$ over Ag(s) for pressure calibration; starting composition of the sample, 40.3 mass per cent of Te; $\lg(p/\text{Pa}) = -A(K/T) + B$

Run no.	T/K	A	B	p/Pa^a
$\text{Te}_2(\text{g})$; electron-impact energy = 1.7 aJ				
1	965 to 1100	13296 ± 246	13.015 ± 0.235	1.48
2	980 to 1080	13058 ± 196	12.728 ± 0.189	1.30
$\text{Te}_2(\text{g})$; electron-impact energy = 6.2 aJ				
1	965 to 1100	13092 ± 215	12.629 ± 0.208	0.95
2	980 to 1080	12945 ± 261	12.441 ± 0.252	0.86
$\text{Te}(\text{g})$; electron-impact energy = 1.7 aJ				
1	965 to 1100	13025 ± 253	11.534 ± 0.242	0.089
2	980 to 1080	13116 ± 276	11.580 ± 0.267	0.081
$\text{Te}(\text{g})$; electron-impact energy = 6.2 aJ				
1	965 to 1100	13481 ± 235	12.086 ± 0.227	0.12
2	980 to 1080	13351 ± 298	11.921 ± 0.288	0.11

^a $\langle T \rangle = 1035 \text{ K}$.

recommended standard molar enthalpy for reaction (3) given in table 3, and the standard molar enthalpy of formation of $\text{Te}_2(\text{g})$,⁽²⁰⁾ were combined to give $\Delta_f H_m^\circ(\text{MoTe}_{1.3334}, \text{s}, 298.15 \text{ K}) = -(70.5 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$. This value as well as $S_m^\circ(298.15 \text{ K})$ values for Mo ,⁽¹⁹⁾ Te ,⁽²⁰⁾ and $\text{MoTe}_{1.3334}$,⁽⁷⁾ were used to derive $\Delta_f G_m^\circ(\text{MoTe}_{1.3334}, \text{s}, 298.15 \text{ K}) = -(72.0 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$.

4. Discussion

Table 1 shows that while good agreement exists between $p(\text{Te}_2)$ obtained from measurements at 6.2 and 1.7 aJ, $p(\text{Te})$ from measurements at the higher electron energy are higher by a factor of two than those obtained at 1.7 aJ. A possible reason for the discrepancy in $p(\text{Te})$ is the inadequate correction for the dissociative contribution to $I(\text{Te}^+)$ at 6.2 aJ. On the other hand, it is also probable that $p(\text{Te})$ at 1.7 aJ has a larger uncertainty, since $\sigma(\text{Te}_2)/\sigma(\text{Te}) = 1.44$ is more valid at energies corresponding to maximum ionization E_{max} and may not be applicable at energies less than E_{max} . It was not possible to determine E_{max} from the ionization-efficiency curve for Te^+ as reliably as in other studies,^(4, 5) and even an application of the approximate correction formula to estimate E_{max} ⁽¹⁸⁾ would cause only a small increase in $\sigma(\text{Te}_2)/\sigma(\text{Te})$ that would raise $p(\text{Te})$ at 1.7 aJ by not more than about 50 per cent. These facts, together with the better agreement between second- and third-law enthalpies for reaction (5) observed at 1.7 aJ than between those observed at 6.2 aJ, make $p(\text{Te})$ at 1.7 aJ more reliable than that at 6.2 aJ. The fragmentation of $\text{Te}_2(\text{g})$ at higher electron-impact energies obviously does not affect $p(\text{Te}_2)$ as much as $p(\text{Te})$ since Te_2 is the major species in the vapour phase and the resulting decrease in $I(\text{Te}_2^+)$ is very small. Further, $p(\text{Te}_2)$ and $I(\text{Te}_2^+)$ over Te(s) were used to compute the

TABLE 3. Standard molar reaction enthalpies $\Delta_r H_m^\circ(T)$ derived from the partial pressures at each of two electron-impact energies; known $p(\text{Te}_2)$ over $\text{Te}(\text{s})$ was used for pressure calibration. ($p^\circ = 101325 \text{ Pa}$)

Run no.	T K	Second law		Third law	Recommended
		$\Delta_r H_m^\circ(T)$ kJ·mol ⁻¹	$\Delta_r H_m^\circ(298.15 \text{ K})$ kJ·mol ⁻¹	$\Delta_r H_m^\circ(298.15 \text{ K})$ kJ·mol ⁻¹	$\Delta_r H_m^\circ(298.15 \text{ K})$ kJ·mol ⁻¹
Electron-impact energy = 1.7 aJ					
MoTe _{1.3334} (s) = Mo(s) + 0.6667Te ₂ (g)					
1	1035	169.6 ± 1.8	175.9 ± 1.8	178.7 ± 0.3	179.3 ± 4.6
2	1010	178.5 ± 1.8	184.7 ± 1.8	178.5 ± 0.3	
3	1015	179.1 ± 1.0	185.3 ± 1.0	179.0 ± 0.2	
4	1018	166.3 ± 2.4	172.6 ± 2.4	178.7 ± 0.2	
5	1053	172.9 ± 4.3	179.3 ± 4.3	178.3 ± 0.4	
6	1035	172.4 ± 3.1	178.7 ± 3.1	179.0 ± 0.4	
7	1035	176.6 ± 1.2	182.9 ± 1.2	178.5 ± 0.3	
Mean:			179.9 ± 5.3	178.7 ± 0.4	
MoTe _{1.3334} (s) = Mo(s) + 1.3334Te(g)					
1	1035	334.3 ± 3.9	340.3 ± 3.9	346.2 ± 0.6	347.2 ± 10.3
2	1010	348.6 ± 3.8	354.4 ± 3.8	345.3 ± 0.5	
3	1015	354.1 ± 4.0	360.0 ± 4.0	346.5 ± 0.5	
4	1018	329.5 ± 2.5	335.4 ± 2.5	345.5 ± 0.4	
5	1053	344.0 ± 9.8	350.1 ± 9.8	346.7 ± 1.0	
6	1035	339.2 ± 6.2	345.2 ± 6.2	347.5 ± 0.9	
7	1035	345.3 ± 2.3	351.2 ± 2.3	346.1 ± 0.4	
Mean:			348.1 ± 9.9	346.3 ± 1.0	
Te ₂ (g) = 2Te(g)					
1	1035	247.1 ± 3.6	246.6 ± 3.6	251.2 ± 0.5	251.9 ± 9.8
2	1010	255.2 ± 4.9	254.6 ± 4.9	250.2 ± 0.4	
3	1015	262.6 ± 6.7	262.0 ± 6.7	251.2 ± 0.5	
4	1018	244.8 ± 3.3	244.2 ± 3.3	250.3 ± 0.3	
5	1053	256.7 ± 9.3	256.2 ± 9.3	252.8 ± 0.9	
6	1035	250.3 ± 5.1	249.7 ± 5.1	252.8 ± 0.7	
7	1035	253.1 ± 2.2	252.6 ± 2.2	251.4 ± 0.3	
Mean:			252.3 ± 8.2	251.4 ± 1.2	
Electron-impact energy = 6.2 aJ					
MoTe _{1.3334} (s) = Mo(s) + 0.6667Te ₂ (g)					
1	1035	169.6 ± 1.7	175.9 ± 1.7	179.2 ± 0.3	
2	1010	174.8 ± 2.3	181.0 ± 2.3	178.6 ± 0.2	
3	1015	173.2 ± 2.2	179.4 ± 2.2	179.1 ± 0.2	
4	1038	165.2 ± 1.3	171.5 ± 1.3	179.2 ± 0.4	
5	1053	174.8 ± 4.0	181.2 ± 4.0	177.4 ± 0.4	
6	1035	173.2 ± 3.0	179.6 ± 3.0	178.2 ± 0.4	
7	1035	177.2 ± 1.4	183.5 ± 1.4	178.8 ± 0.3	
Mean:			178.9 ± 4.7	178.6 ± 0.7	
MoTe _{1.3334} (s) = Mo(s) + 1.3334Te(g)					
1	1035	338.6 ± 4.1	344.6 ± 4.1	338.8 ± 0.6	
2	1010	346.4 ± 3.4	352.2 ± 3.4	337.9 ± 0.6	
3	1015	345.9 ± 5.0	351.8 ± 5.0	338.3 ± 0.6	
4	1038	335.5 ± 3.9	341.4 ± 3.9	338.7 ± 0.4	
5	1053	341.2 ± 10.6	347.3 ± 10.6	337.7 ± 1.1	
6	1035	338.5 ± 7.0	344.5 ± 7.0	338.7 ± 1.0	
7	1035	356.7 ± 3.6	362.7 ± 3.6	338.9 ± 1.2	
Mean:			349.2 ± 9.3	338.4 ± 1.0	

TABLE 3—continued

Run no.	$\frac{T}{\text{K}}$	Second law		Third law	Recommended
		$\frac{\Delta_r H_m^\circ(T)}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_r H_m^\circ(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_r H_m^\circ(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_r H_m^\circ(298.15 \text{ K})}{\text{kJ} \cdot \text{mol}^{-1}}$
Te ₂ (g) = 2Te(g)					
1	1035	253.5 ± 4.1	253.0 ± 4.1	239.4 ± 0.9	
2	1010	257.5 ± 2.5	256.9 ± 2.5	239.0 ± 0.7	
3	1015	259.1 ± 7.5	258.5 ± 7.5	238.9 ± 0.8	
4	1038	255.4 ± 5.9	254.9 ± 5.9	239.3 ± 0.9	
5	1053	249.6 ± 10.9	249.1 ± 10.9	240.4 ± 1.1	
6	1035	248.0 ± 6.5	247.5 ± 6.5	240.8 ± 1.0	
7	1035	269.3 ± 5.2	268.8 ± 5.2	240.3 ± 1.5	
Mean:			255.5 ± 9.6	239.5 ± 0.8	

pressure calibration constant. Table 2 shows that in the set of measurements where silver was used for pressure calibration $p(\text{Te}_2)$ at 1.7 aJ is higher than that at 6.2 aJ. This could be due to $\sigma(\text{Te}_2)/\sigma(\text{Te})$ at 1.7 aJ being approximately 2 rather than 1.44. Good agreement is observed, within error limits, between the partial pressures given in table 2, with the exception of $p(\text{Te}_2)$ at 1.7 aJ, and those recommended in table 1. The recommended pressure equations given in table 1 were obtained by pooling all the points from all the runs conducted at the electron-impact energy only of 1.7 aJ. The aim of the measurements with two pressure calibration procedures and at two energies, in fact, was more to obtain reliable Te_2 pressures than to make measurements with different calibration procedures and at different energies, as will be seen from the following discussion.

TABLE 4. Third-law evaluation of standard molar reaction enthalpies (run 6); electron-impact energy = 1.7 aJ; ($p^\circ = 101325 \text{ Pa}$)

$\frac{T}{\text{K}}$	$\frac{\Delta_r H_m^\circ(298.15 \text{ K})^a}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_r H_m^\circ(298.15 \text{ K})^b}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta_r H_m^\circ(298.15 \text{ K})^c}{\text{kJ} \cdot \text{mol}^{-1}}$
1110	179.2	347.7	252.8
1095	179.1	348.1	253.4
1080	179.3	348.2	253.4
1060	178.3	346.0	251.6
1040	178.6	346.6	252.0
1025	179.5	348.6	253.6
1010	179.6	348.6	253.6
995	178.6	347.1	252.7
980	178.9	347.5	252.9
960	179.1	347.1	252.0
Mean:	179.0 ± 0.4	347.5 ± 0.9	252.8 ± 0.7

^a $\text{MoTe}_{1.3334}(\text{s}) = \text{Mo}(\text{s}) + 0.6667\text{Te}_2(\text{g})$.

^b $\text{MoTe}_{1.3334}(\text{s}) = \text{Mo}(\text{s}) + 1.3334\text{Te}(\text{g})$.

^c $\text{Te}_2(\text{g}) = 2\text{Te}(\text{g})$.

Values of $p(\text{Te}_2)$ obtained in this work are lower by a factor of about 10 than those computed by extrapolating to the temperatures of the present study the pressure equation reported earlier by Krabbes and Oppermann.⁽¹²⁾ Since the ionization cross-section was not necessary to compute $p(\text{Te}_2)$ from equation (1), any systematic error in our $p(\text{Te}_2)$ values can be caused only by the pressure calibration constant k . This method of calibration was also used in our earlier studies,⁽²⁻⁵⁾ where good results were obtained. Furthermore, the equilibrium constant determined in this work for reaction (5) at 1100 K, for example, 4.7×10^{-2} Pa agrees well with values computed from the results of our previous investigations:^(2,4,5) 3.10×10^{-2} Pa, 2.7×10^{-2} Pa, and 2.8×10^{-2} Pa, respectively, as well as with that extrapolated from the results of Budininkas *et al.*:⁽²¹⁾ 3.9×10^{-2} Pa. Hence, we believe that the partial pressures reported in this work are reliable.

Indirect evidence suggesting that the actual pressures cannot be as high as those derived from the equation reported by Krabbes and Oppermann was obtained from the magnitude of the mass loss in the condensed phase due to the effusion of vapour through the orifice of the Knudsen cell. The condensed phase should have been completely depleted of tellurium under the conditions of the present study (vaporization time, temperature, orifice dimensions) had the pressures been as high as those suggested by Krabbes and Oppermann.

The observations in the present work, as well as those over cerium monotelluride by Koyama and Yamawaki,⁽²²⁾ suggest that there is a possibility of overestimating the pressures if volatile impurities such as an oxytelluride,⁽²²⁾ or even traces of unreacted tellurium, are not removed by annealing in vacuum at a high temperature. In the present study, there was a continuous decrease of $I(\text{Te}_2^+)$ during the annealing process (eightfold in one sample) until the intensity became constant after 4 h. Krabbes and Oppermann did not state that attempts had been made to remove volatile impurities before making pressure measurements; this omission might have contributed to the apparently high pressures reported.

The apparent enthalpy of sublimation computed from the pressure equation given by Krabbes and Oppermann: $189 \text{ kJ} \cdot \text{mol}^{-1}$, is about $70 \text{ kJ} \cdot \text{mol}^{-1}$ less than that computed from the recommended partial-pressure equation for $\text{Te}_2(\text{g})$ obtained in the present study. One might be tempted to attribute such a large difference to a hitherto unknown phase transformation over $(\text{Mo} + \text{Mo}_3\text{Te}_4)$ between the temperature ranges of the two studies. Even then, the vapour pressures reported by Krabbes and Oppermann would be too high by a factor of five or more in comparison with those obtained in the present study.

Reaction enthalpies given in table 3 show generally good agreement between second- and third-law evaluations, except where tellurium pressures at 6.2 aJ are used. Table 4 shows that no obvious trend could be observed in the third-law values at different temperatures. On the contrary, there is a difference of $\approx 30 \text{ kJ} \cdot \text{mol}^{-1}$ between the second- and third-law enthalpies for reaction (3) derived from the pressure equation given by Krabbes and Oppermann.⁽¹²⁾ The third-law evaluation of the results showed a regular increase of $\approx 0.6 \text{ kJ} \cdot \text{mol}^{-1}$ for each 20 K increase in temperature.

The recommended enthalpies given in table 3 are the averages of the mean second-

and third-law values. The overall errors in the recommended values were computed by considering statistical errors as well as the estimated errors in the partial pressures and temperatures. The uncertainties in the partial pressures were estimated to be ≈ 30 per cent for $\text{Te}_2(\text{g})$ and ≈ 75 per cent for $\text{Te}(\text{g})$. An absolute error in temperature of ± 3 K and a differential error of ± 1.5 K were assumed for the second-law treatments, while an absolute error of only ± 3 K was considered for third-law evaluations.

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