Study of (molybdenum + tellurium) by Knudsen-effusion mass spectrometry

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Vaporization of (molybdenum + tellurium) alloys was studied by Knudsen-effusion mass spectrometry. The partial pressures of $Te_2(g)$ and $Te(g)$ over the two-phase field $(Mo_3Te_4 + MoTe_2)$ were determined in the temperature range $T = 820$ K to 950 K. The boundaries of the Mo_3Te_4 phase were delineated by a continuous monitoring of the intensity of Te_2^+ as a function of time, starting with samples having mass fractions 0.67187 and 0.68997 of Te. The phase-boundary compositions correspond to $MoTe_{1.10 \pm 0.03}$ (Mo-rich boundary) and $MoTe_{1.30 \pm 0.04}$ (Te-rich boundary), respectively. By employing the $p(Te_2)$ determined as a function of composition, activities of Te were obtained; and by a Gibbs-Duhem integration, those of Mo were also computed at various compositions within the single-phase Mo_3Te_4. Our previously published $p(Te_2)$ and $p(Te)$ over $(Mo + Mo_3Te_4)$ (*J. Chem. Thermodynamics* **1989**, 21, 1183) were used to obtain revised enthalpy changes for the reaction: $MoTe_x(s) = Mo(s) + (\nu/i)Te_i(g)$, where $i = 1$ or 2, and $\nu = 1.10$, the Mo-rich boundary composition of Mo_3Te_4 determined in this work. The standard molar enthalpies of formation of $MoTe_{1.10}$ and $MoTe_{1.30}$ (Mo- and Te-rich boundaries of the Mo_3Te_4 phase) as well as of $MoTe_{1.89}$ (Mo-rich boundary of the α-modification of the $MoTe_2$ phase) were derived.

1. Introduction

Molybdenum and tellurium are two of the many fission products generated with appreciable yields in a nuclear reactor. Molybdenum is also an alloying element in type AISI-316 stainless-steel cladding commonly used in fast-breeder nuclear reactors. Therefore, thermodynamic properties and phase relations in (molybdenum + tellurium) are essential to understand the chemical interactions between tellurium and molybdenum.

According to the tentative phase diagram of (molybdenum + tellurium) reported by Brewer and Lamoreaux[1] (see figure 1) there are two phases: Mo_3Te_4 and $MoTe_2$, each of which exhibits only a narrow range of homogeneity. We have previously reported a high-temperature mass-spectrometric study of the vaporization of $(Mo + Mo_3Te_4)$.[2] The vapor pressure of $Te_2(g)$ as well as the enthalpy of sublimation determined by us over this two-phase field differed greatly from those reported in the only other vaporization study by Krabbes and Oppermann[3] and Krabbes.[4] Two vaporization studies of $(Mo_3Te_4 + MoTe_2)$ have been reported so

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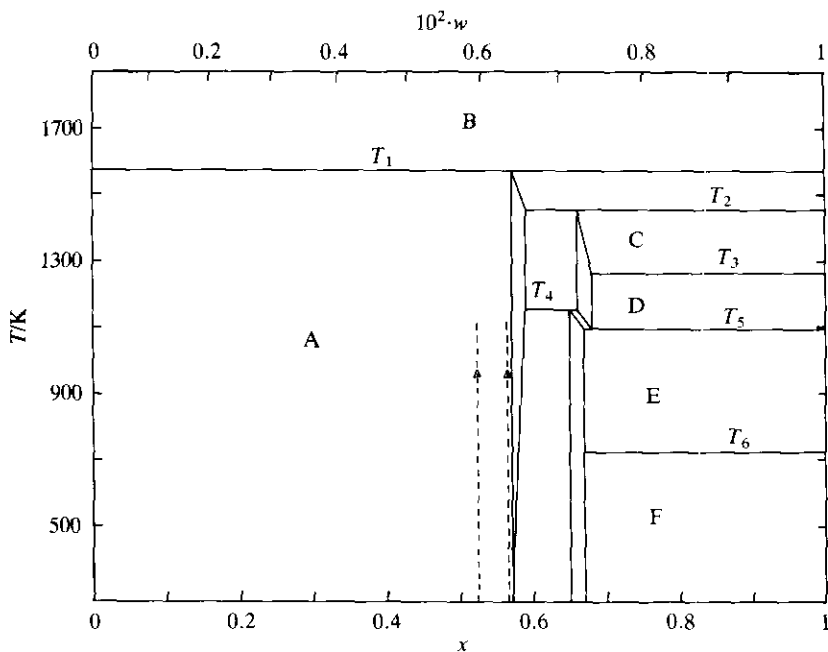

FIGURE 1. Phase diagram of $\{(1-x)Mo+xTe)\}$, taken from reference 1. A: $(Mo+Mo_3Te_4)$; B: $\{Mo+Te_2(g, p° = 101325 \text{ Pa})\}$; C: $\{MoTe_2+Te_2(g, p° = 101325 \text{ Pa})\}$; D: $(\beta\text{-}MoTe_2+l)$; E: $(\alpha\text{-}MoTe_2+l)$; F: $(\alpha\text{-}MoTe_2+Te)$; $T_1 = (1573\pm70) \text{ K}$; $T_2 = (1453\pm70) \text{ K}$; $T_3 = (1261\pm70) \text{ K}$; $T_4 = 1153 \text{ K}$; $T_5 = 1093 \text{ K}$; $T_6 = 722.5 \text{ K}$. The diagram also includes the boundary compositions of the Mo_3Te_4 phase (---△---) obtained in this work at $T \approx 950 \text{ K}$; w denotes mass fraction of Te.

far: one by Opalovskij *et al.*[5] and the other by Krabbes and Oppermann[3] and Krabbes.[4] Though Krabbes and Oppermann claimed that the vapor pressures determined by them were in agreement with those reported by Opalovskij *et al.*, O'Hare,[6] in his review, pointed out the discrepancy between the results of the two studies. Recently, Mallika and Sridharan reported the thermodynamic properties of $MoTe_2$,[7] and Mo_3Te_4,[8] by using e.m.f. measurements, and O'Hare and Hope[9] reported the standard molar enthalpy of formation of $MoTe_2$ by employing fluorine combustion calorimetry.

Closely similar values were obtained for the homogeneity range of $MoTe_2$ by Spiesser *et al.*[10] and Vellinga *et al.*[11] As for the homogeneity range of Mo_3Te_4, Krabbes *et al.*[3, 4] contended that it should be very small, whereas Spiesser *et al.*[10] had earlier reported it to vary between 60.9 mass per cent to 66.0 mass per cent of Te.

The present study, a continuation of our earlier one,[2] was undertaken because of the discrepancies in the published results and to achieve the aims: to determine the partial pressures of the gaseous species over $(Mo_3Te_4+MoTe_2)$; to determine the homogeneity range of Mo_3Te_4; to derive the thermodynamic values for the various reactions involving the vapor and condensed phases; and, finally, to deduce the thermodynamic properties of Mo_3Te_4 and $MoTe_2$.

2. Experimental

Preparation of (molybdenum + tellurium) alloys corresponding to the two-phase field ($Mo_3Te_4 + MoTe_2$) 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 and placed in quartz tubes which were then connected to a vacuum system. Before being finally sealed under a pressure of $\approx 1 \cdot 10^{-4}$ Pa, the quartz tubes were repeatedly filled with high-purity argon and evacuated. The samples were then heated slowly to $T = 680$ K in 7 d, and maintained at this temperature for 7 d. They were subsequently heated at $T = 810$ K for 13 d and at $T = 880$ K for 8 d, and cooled to ambient temperature in 3 d. The starting mass fractions of Te in the two samples prepared were 0.67187 and 0.68997, respectively. That the samples corresponded to the two-phase field ($Mo_3Te_4 + MoTe_2$) was confirmed by X-ray diffraction analysis.

A VG Micromass MM 30 BK mass spectrometer was used to conduct vaporization studies. It consisted of a (Knudsen-cell + furnace) assembly, an electron-impact ionization source, a 305 mm radius magnetic analyzer with a $\pi/2$ sector angle, and a combined (electron multiplier + Faraday ion) collector system.

The samples were taken in alumina Knudsen cells which had the dimensions: i.d., 7.5 mm; o.d., 10.0 mm; height, 10.0 mm; and orifice (knife-edged) diameter, 0.5 mm. The Knudsen cell was placed in a tungsten cup which had a removable but tightly fitting lid made of tungsten with a 3 mm diameter hole collinear with the Knudsen-cell orifice. This assembly was heated by means of electron bombardment from two independent tungsten filaments. Temperatures were measured by a (chromel-to-alumel) thermocouple inserted through the base of the tungsten cup. The thermocouple was calibrated against the melting temperature of silver. The vapor species effusing out from the Knudsen cell were ionized by electron impact. The positive ions, after focussing and acceleration to a potential of 6 kV, were separated according to their mass-to-charge ratio by the magnetic analyzer. Ion currents were measured by a secondary electron multiplier.

Te^+ and Te_2^+ were the only ions observed in the mass spectrum of the vapour over ($Mo_3Te_4 + MoTe_2$). They were identified by their masses and relative isotopic abundances, and were distinguished from the background by interposing a shutter between the Knudsen cell and the ion source. The ionization-efficiency curves for these ions showed that fragmentation occurred at electron-impact energies greater than ≈ 1.9 aJ.

The intensities of the most abundant isotopes of Te^+ ($M = 130$ g·mol^{-1}) and Te_2^+ ($M = 256$ g·mol^{-1}) were measured at an electron impact energy of 1.7 aJ. The conversion of ion intensities $I(Te_i^+)$ to partial pressures of the species $p(Te_i)$ ($i = 1$ or 2) was done in the same way as described in our previous paper.[2]

The experiments can be classified into three groups: the first group in which the sample was kept for most of the time at the same temperature and the ion intensity of Te_2^+ was monitored as a function of time; the second group in which the sample was kept at different temperatures at which ion intensities of Te^+ and Te_2^+ were both

monitored before the sample was cooled, weighed, returned to the mass spectrometer, and the experiment continued as in the first group; and the third group in which ion intensities were monitored as a function of temperature (as in the second group) as well as time (as in the first group). In all the experiments, the total vapor pressure inside the Knudsen cell was always such that flow through the orifice was certain to be molecular. The mass of the condensed phase was measured before and after each vaporization experiment to compute the mass loss which occurred due to effusion of the vapor through the orifice of the Knudsen cell.

The composition of the condensed phase at any time during a quantitative vaporization experiment was deduced by employing the relation between total mass loss and the area under the curve of $I^+ T^{1/2}$ against time for both Te_2^+ and Te^+. The equations and the procedures employed for this purpose were similar to those explained in detail elsewhere.[12, 13] The Te-rich and Mo-rich phase boundaries of Mo_3Te_4 were deduced by identifying the time up to which $p(Te_2)$ corresponded to

TABLE 1. Partial pressures p over $(Mo_3Te_4 + MoTe_2)$, where $\lg(p/Pa) = -A(K/T) + B$

Run no.[a]	T/K	A[b]	B[b]	p/Pa at $T = 885$ K
		Te_2		
1	820 to 920	14587 ± 326	15.261 ± 0.374	$6.01 \cdot 10^{-2}$
2	820 to 920	14928 ± 180	15.724 ± 0.206	$7.18 \cdot 10^{-2}$
3	820 to 935	14898 ± 155	15.740 ± 0.176	$8.04 \cdot 10^{-2}$
4	820 to 920	14362 ± 802	14.934 ± 0.914	$5.07 \cdot 10^{-2}$
5	820 to 935	15637 ± 339	16.554 ± 0.388	$7.67 \cdot 10^{-2}$
6	820 to 920	15015 ± 263	15.932 ± 0.300	$9.25 \cdot 10^{-2}$
7	850 to 950	16161 ± 350	16.958 ± 0.389	$4.98 \cdot 10^{-2}$
8	820 to 950	15126 ± 147	15.785 ± 0.166	$4.93 \cdot 10^{-2}$
9	840 to 950	15430 ± 194	16.233 ± 0.218	$6.27 \cdot 10^{-2}$
10	850 to 950	16092 ± 148	16.873 ± 0.164	$4.90 \cdot 10^{-2}$
11	820 to 950	15602 ± 202	16.369 ± 0.228	$5.50 \cdot 10^{-2}$
Recommended[c]	820 to 950	14979 ± 210	15.722 ± 0.238	$6.26 \cdot 10^{-2}$
		Te		
1	860 to 920	13787 ± 534	12.591 ± 0.160	$1.03 \cdot 10^{-3}$
2	835 to 920	14309 ± 260	13.219 ± 0.295	$1.12 \cdot 10^{-3}$
3	820 to 935	14259 ± 204	13.205 ± 0.232	$1.24 \cdot 10^{-3}$
4	820 to 920	13570 ± 797	12.358 ± 0.903	$1.06 \cdot 10^{-3}$
5	835 to 920	14217 ± 356	13.222 ± 0.402	$1.44 \cdot 10^{-3}$
6	820 to 935	14346 ± 276	13.424 ± 0.311	$1.63 \cdot 10^{-3}$
7	850 to 950	14832 ± 352	13.772 ± 0.392	$1.03 \cdot 10^{-3}$
8	850 to 950	14550 ± 218	13.396 ± 0.242	$9.03 \cdot 10^{-4}$
9	860 to 950	14563 ± 332	13.470 ± 0.369	$1.03 \cdot 10^{-3}$
10	850 to 950	14965 ± 168	13.901 ± 0.187	$9.79 \cdot 10^{-4}$
11	820 to 950	14560 ± 309	13.503 ± 0.349	$1.12 \cdot 10^{-3}$
Recommended[c]	820 to 950	14120 ± 196	13.014 ± 0.220	$1.15 \cdot 10^{-3}$

[a] The first six runs were conducted with the sample having 67.187 mass per cent of Te and the rest with that having 68.997 mass per cent of Te.

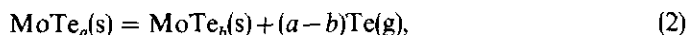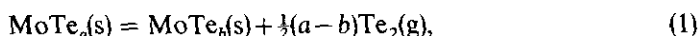[b] The errors quoted for the parameters are standard deviations.

[c] The recommended relations were obtained by a least-squares fitting of all the points from all the runs.

that over $(Mo_3Te_4 + MoTe_2)$ and the time from which $p(Te_2)$ corresponded to that over $(Mo + Mo_3Te_4)$, respectively.

In all, eight runs were conducted to determine the homogeneity range of Mo_3Te_4, and 11 runs to obtain the relations of partial pressure to temperature over $(Mo_3Te_4 + MoTe_2)$. That there was practically no change in the mass of an empty Knudsen cell before and after the vaporization experiments was taken as an indication of absence of reaction between the cell and the sample.

3. Results

Table 1 gives the relations of least-squares-fitted pressure against temperature over $(Mo_3Te_4 + MoTe_2)$ along with the partial pressures at the mean temperature of the investigation ($T = 885$ K) for $Te_2(g)$ and $Te(g)$. From the partial pressures, enthalpy changes for the following reactions were derived by standard methods:[14]

$$MoTe_a(s) = MoTe_b(s) + \tfrac{1}{2}(a-b)Te_2(g), \tag{1}$$

$$MoTe_a(s) = MoTe_b(s) + (a-b)Te(g), \tag{2}$$

$$Te_2(g) = 2Te(g). \tag{3}$$

For this purpose, the value of a (Mo-rich boundary of $MoTe_2$) in equations (1) and (2) was taken as 1.89 as computed from the phase diagram[1] and the value of b (Te-rich boundary of Mo_3Te_4) was taken as 1.30 as computed from the results, given in table 2, of the experiments to determine the homogeneity range of Mo_3Te_4. Each reaction was evaluated by second- and third-law methods and the results are given in table 3. The necessary auxiliary thermodynamic quantities for $Te(g)$,[15] $Te_2(g)$,[15] and molybdenum tellurides[1] were taken from the literature. For the molybdenum

TABLE 2. Te-rich and Mo-rich boundary compositions of Mo_3Te_4 at temperatures T_1 and T_2, respectively; compositions are given as mass fraction w of Te

Run no.	T_1/K	$10^2 \cdot w(T_1)$	T_2/K	$10^2 \cdot w(T_2)$
	Starting composition of the sample: mass fraction 0.67187 of Te			
1[a]	950	63.35	950	59.36
2	920	63.01	975	58.56
3	935	63.10	975	58.71
4	935	63.10	975	58.62
	Starting composition of the sample: mass fraction 0.68997 of Te			
5			950	59.98
6[a]	950	63.33	950	60.00
7[a]	950	63.41	950	60.04
8[a]	975	63.86	975	59.90
Selected[b]		63.31 ± 0.71		59.40 ± 0.67

[a] Results obtained in these runs were employed to deduce Te activities as a function of composition and subsequently Mo activities also (by using Gibbs-Duhem integration) across the homogeneity range of Mo_3Te_4.

[b] Mean values; errors include statistical and estimated uncertainties.

TABLE 3. Standard molar enthalpies of reaction $\Delta_r H_m^\circ$ derived from the partial pressures determined over $(Mo_3Te_4 + MoTe_2)$

Run no.	$\dfrac{T}{K}$	Second law [a]		Third law [b]	Recommended [c]
		$\dfrac{\Delta_r H_m^\circ(T)}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_r H_m^\circ(298.15 \text{ K})}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_r H_m^\circ(298.15 \text{ K})}{kJ \cdot mol^{-1}}$	$\dfrac{\Delta_r H_m^\circ(298.15 \text{ K})}{kJ \cdot mol^{-1}}$
		$MoTe_{1.89}(s) = MoTe_{1.30}(s) + 0.295 Te_2(g)$			
1	870	82.4 ± 1.8	87.1 ± 1.8	78.3 ± 0.3	
2	870	84.3 ± 1.0	89.1 ± 1.0	77.9 ± 0.4	
3	878	84.2 ± 0.9	89.0 ± 0.9	77.6 ± 0.4	
4	870	81.1 ± 4.5	85.9 ± 4.5	78.6 ± 0.6	
5	870	88.3 ± 1.9	93.1 ± 1.9	77.8 ± 0.6	
6	878	84.8 ± 1.5	89.6 ± 1.5	77.3 ± 0.5	84.6 ± 10.6
7	900	91.3 ± 2.0	96.3 ± 2.0	78.3 ± 0.6	
8	885	85.4 ± 0.8	90.3 ± 0.8	78.6 ± 0.5	
9	895	87.2 ± 1.1	92.1 ± 1.1	78.0 ± 0.5	
10	900	90.9 ± 0.8	95.9 ± 0.8	78.4 ± 0.6	
11	885	88.1 ± 1.1	93.0 ± 1.1	78.3 ± 0.7	
$\dfrac{\langle \Delta_r H_m^\circ(298.15 \text{ K}) \rangle}{kJ \cdot mol^{-1}}$:			91.0 ± 3.9	78.1 ± 0.7	
		$MoTe_{1.89}(s) = MoTe_{1.30}(s) + 0.59 Te(g)$			
1	890	155.8 ± 6.0	160.4 ± 6.0	155.0 ± 0.4	
2	878	161.7 ± 2.9	166.2 ± 2.9	154.7 ± 0.4	
3	878	161.1 ± 2.3	165.7 ± 2.3	154.3 ± 0.5	
4	870	153.3 ± 9.0	157.8 ± 9.0	155.0 ± 0.8	
5	878	160.6 ± 4.0	165.2 ± 4.0	153.6 ± 0.5	
6	878	162.1 ± 3.1	166.6 ± 3.1	153.1 ± 0.7	160.7 ± 13.6
7	900	167.6 ± 4.0	172.3 ± 4.0	154.8 ± 0.7	
8	900	164.4 ± 2.5	169.1 ± 2.5	155.4 ± 0.5	
9	905	164.5 ± 3.7	169.3 ± 3.8	154.9 ± 0.5	
10	900	169.1 ± 1.9	173.8 ± 1.9	155.0 ± 0.7	
11	885	164.5 ± 3.5	169.1 ± 3.5	154.6 ± 0.9	
$\dfrac{\langle \Delta_r H_m^\circ(298.15 \text{ K}) \rangle}{kJ \cdot mol^{-1}}$:			166.9 ± 6.4	154.6 ± 0.9	
		$Te_2(g) = 2 Te(g)$			
1	890	252.6 ± 13.8	251.8 ± 13.8	260.8 ± 0.8	
2	878	258.7 ± 7.3	257.9 ± 7.3	260.6 ± 0.7	
3	878	260.8 ± 6.3	260.6 ± 6.2	260.0 ± 0.8	
4	870	245.7 ± 12.9	244.9 ± 12.9	259.1 ± 1.3	
5	878	252.0 ± 10.0	251.2 ± 10.0	257.6 ± 0.9	
6	878	261.9 ± 8.7	261.1 ± 8.7	257.0 ± 1.1	258.2 ± 12.8
7	900	258.5 ± 7.5	257.8 ± 7.5	259.2 ± 0.8	
8	900	261.2 ± 6.3	260.4 ± 6.3	260.9 ± 0.6	
9	905	259.2 ± 9.0	258.4 ± 9.0	260.8 ± 0.6	
10	900	265.0 ± 5.3	264.2 ± 5.3	259.8 ± 0.6	
11	885	258.9 ± 9.3	258.0 ± 9.3	258.7 ± 1.4	
$\dfrac{\langle \Delta_r H_m^\circ(298.15 \text{ K}) \rangle}{kJ \cdot mol^{-1}}$:			256.9 ± 10.6	259.5 ± 1.6	

[a] Errors quoted are standard deviations.

[b] Values of $(\Delta_0^T S_m^\circ - \Delta_{298.15 K}^T H_m^\circ / T)$ for $MoTe_{1.89}$ and $MoTe_{1.30}$ were derived from those given in reference 1 for the nominal compositions $MoTe_2$ and Mo_3Te_4, respectively; errors quoted are standard deviations.

[c] Average of mean second- and third-law values; errors quoted include statistical and estimated uncertainties.
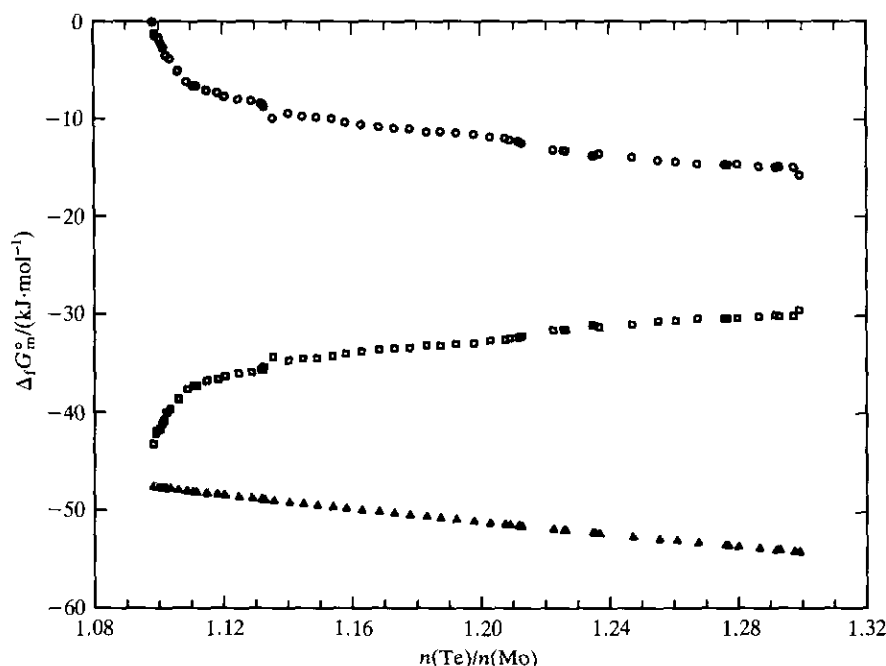
FIGURE 2. Chemical-potential differences: □, of Te and ○, of Mo; molar Gibbs free energy of formation: △, of Mo_3Te_4 as a function of $n(Te)/n(Mo)$ at 950 K.

tellurides, the available values were estimates for the nominal compositions $MoTe_{1.33}$ (Mo_3Te_4 phase) and $MoTe_2$, and not for the compositions used in the present study. While the enthalpy increments were used unchanged by assuming that no significant error would be introduced in deriving $\Delta_r H_m^\circ(298.15$ K) from a second-law $\Delta_r H_m^\circ(T)$, the quantities[1] $(\Delta_0^T S_m^\circ - \Delta_{298.15\,K}^T H_m^\circ/T)$, were slightly modified as described below, and employed in the third-law evaluations.

It is obvious from table 2 that although eight runs were conducted to determine the homogeneity range of Mo_3Te_4, in only four runs was a single constant temperature maintained throughout the period of cross-over of the single phase. In these runs, the activity $a(Te)$ of tellurium was first computed from the $p(Te_2)$ over (molybdenum + tellurium) determined in this work and the $p(Te_2)$ over Te(l) obtained by multiplying the total vapor pressure determined by Kudryavtsev and Ustyugov[16] by $\{p(Te_2)/p(total)\}$ given by Grønvold et al.[15] Then, by setting $a(Mo) = 1$ at the Mo-rich boundary of Mo_3Te_4, and by employing the Gibbs-Duhem integration, $a(Mo)$ at various other compositions richer in tellurium was derived. From the activities, chemical-potential differences and molar Gibbs free energies of formation were obtained across the single phase. Figure 2 shows the results obtained in a typical run. By employing the third-law method, values of $\Delta_f H_m^\circ(298.15$ K) corresponding to both boundary compositions of Mo_3Te_4 were then evaluated. Table 4 gives the thermodynamic quantities of Mo_3Te_4 obtained in this way.

TABLE 4. $\Delta_f G_m^\circ(T)$[a] and $\Delta_f H_m^\circ(298.15\ \text{K})$,[b] for the Mo_3Te_4 phase at Te-rich and Mo-rich boundary compositions

$\dfrac{T}{K}$	$MoTe_\nu$	Te-rich boundary		$MoTe_\nu$	Mo-rich boundary	
		$\dfrac{-\Delta_f G_m^\circ(T)}{kJ\cdot mol^{-1}}$	$\dfrac{-\Delta_f H_m^\circ(298.15\ K)}{kJ\cdot mol^{-1}}$		$\dfrac{-\Delta_f G_m^\circ(T)}{kJ\cdot mol^{-1}}$	$\dfrac{-\Delta_f H_m^\circ(298.15\ K)}{kJ\cdot mol^{-1}}$
		Starting composition of the sample: mass fraction 0.67187 of Te				
950	$MoTe_{1.299}$	54.2	66.6	$MoTe_{1.098}$	47.5	63.1
		Starting composition of the sample: mass fraction 0.68997 of Te				
950	$MoTe_{1.297}$	54.7	67.2	$MoTe_{1.128}$	48.8	63.9
950	$MoTe_{1.304}$	54.9	67.3	$MoTe_{1.130}$	48.9	64.0
975	$MoTe_{1.330}$	54.0	67.0	$MoTe_{1.123}$	47.7	63.9
	$\langle\Delta_f H_m^\circ(298.15\ K)\rangle = -(67.0\pm0.3)\ kJ\cdot mol^{-1}$[c]			$\langle\Delta_f H_m^\circ(298.15\ K)\rangle = -(63.7\pm0.4)\ kJ\cdot mol^{-1}$[d]		

[a] Deduced from $a(Te)$ and $a(Mo)$ at the respective boundary compositions.
[b] Deduced by third-law method from $\Delta_f G_m^\circ(T)$.
[c] Selected value at the Te-rich boundary; assumed to be valid for the composition $MoTe_{1.30}$; error quoted is standard deviation.
[d] Selected value at the Mo-rich boundary; assumed to be valid for the composition $MoTe_{1.16}$; error quoted is standard deviation.

The recommended standard molar enthalpy for reaction (1), the mean standard molar enthalpy of formation of $MoTe_{1.30}$ given in tables 3 and 4, respectively, and the standard molar enthalpy of formation at $T = 298.15\ \text{K}$ of $Te_2(g)$: $(158.0 \pm 6.6)\ kJ\cdot mol^{-1}$,[(17)] were combined to obtain $\Delta_f H_m^\circ(MoTe_{1.89},\ s,\ 298.15\ \text{K}) = -(105.8 \pm 10.8)\ kJ\cdot mol^{-1}$.

4. Discussion

$Te(g)$ and $Te_2(g)$ were the only species detected in the vapor phase over $(Mo_3Te_4 + MoTe_2)$. Hence, the composition of the condensed phase continuously became richer in molybdenum as the vaporization from the Knudsen cell proceeded. The advantage of such vaporization behavior was that we were able to determine the homogeneity range of Mo_3Te_4 starting with samples corresponding to the $(Mo_3Te_4 + MoTe_2)$ phase field. On the other hand, since the sample could not be retained in the $(Mo_3Te_4 + MoTe_2)$ phase field for long, it had to be ensured that the partial pressures given in table 1 actually corresponded to this two-phase field. Not more than three runs were conducted with any fresh charge of the sample so that the mass fraction of Te in the sample at the end of the temperature-dependence runs was certain to lie above 0.635. Attainment of chemical equilibrium inside the Knudsen cell was ascertained by the constancy of ion intensities over a period of time at the highest temperature of each run. Figure 3 represents an experiment in which three temperature-dependence runs over $(Mo_3Te_4 + MoTe_2)$ were conducted and the homogeneity range of Mo_3Te_4 was also determined. In all these runs, $I(Te_2^+)$ at different temperatures was quite reproducible. This, together with the observation that at $T = 935\ \text{K}$ (see figure 3) $I(Te_2^+)$ remained constant for almost 1 h before decreasing continuously, was taken to indicate that the sample was in the $(Mo_3Te_4 + MoTe_2)$ phase field during the temperature-dependence runs. The recommended
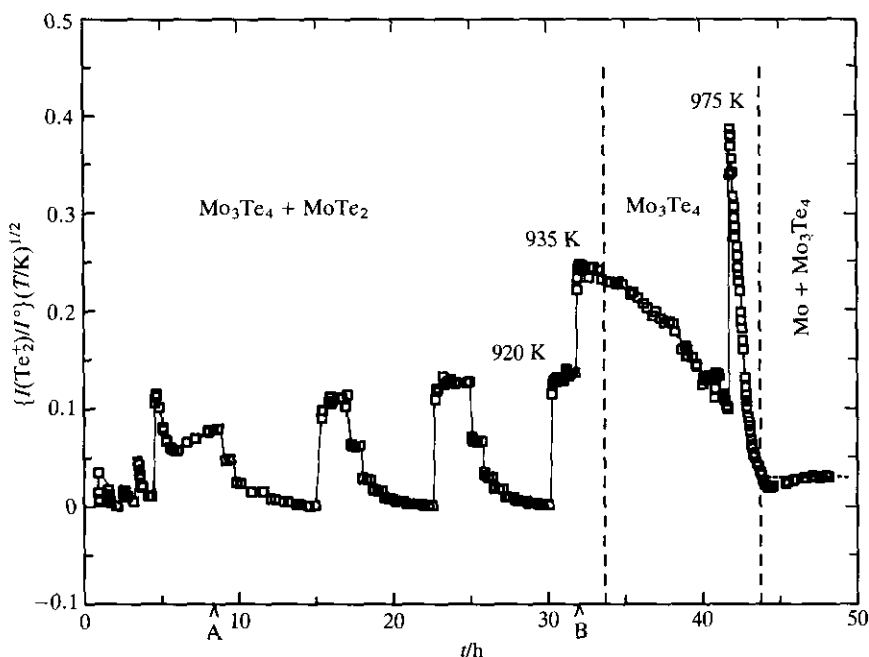
FIGURE 3. $\{I(\text{Te}_2^+)/I^\circ\}(T/\text{K})^{1/2}$ as a function of time. Between A and B, three temperature-dependence runs (from $T = 820$ K to 920 K) were conducted over the $(\text{Mo}_3\text{Te}_4 + \text{MoTe}_2)$ two-phase field. Te-rich and Mo-rich phase boundaries of Mo_3Te_4 were determined at $T = 935$ K and 975 K, respectively. Initial mass fraction of Te in the sample: 0.67187; initial mass: 0.26588 g; total mass loss: 0.05633 g.

pressure equations given in table 1 were obtained by pooling together all the points from all such temperature-dependence runs conducted over the $(\text{Mo}_3\text{Te}_4 + \text{MoTe}_2)$ two-phase region.

There were only two previous investigations in which attempts were made to determine the total vapor pressure over $(\text{Mo}_3\text{Te}_4 + \text{MoTe}_2)$ and in both cases a manometric method was used. Opalovskij et al.[5] did not give the pressure equation explicitly in their paper, and therefore we derived the pressure equation $(T = 1182$ K to 1254 K), from the thermodynamic quantities given in it, as

$$\lg\{p(\text{Te}_2)/\text{Pa}\} = -9745(\text{K}/T) + 11.714. \tag{4}$$

Although Krabbes[4] detected through d.t.a. measurements the phase transformation from α-MoTe_2 to β-MoTe_2 at 1153 K, he preferred to represent the vapor pressures measured in the temperature range $T = 1100$ K to 1300 K by a single vapor-pressure equation:

$$\lg\{p(\text{Te}_2)/\text{Pa}\} = -11790(\text{K}/T) + 13.398. \tag{5}$$

The total vapor pressure $\{p(\text{Te}_2) + p(\text{Te})\} = 544$ Pa at 1153 K, computed by extrapolating the recommended partial-pressure equations given in table 1, is lower by about a factor of three than the values of Opalovskij et al.: 1827 Pa from equation (4), and of Krabbes and Oppermann[3] or Krabbes:[4] 1488 Pa from equation (5).

Although the total pressures reported by both previous investigators seem to agree well, as Krabbes and Oppermann[3] also mentioned in support of their results, a careful examination of the representative pressure equations (4) and (5) reveals discrepancies in the coefficients. The fact that the apparent enthalpies of sublimation of $Te_2(g)$ derived from the results of Krabbes and Oppermann[3, 4] and Opalovskij *et al.*[5] (225.8 kJ·mol^{-1} and 186.6 kJ·mol^{-1}, respectively) are not consistent has already been pointed out by O'Hare[6] and O'Hare and Hope.[9]

Mallika and Sreedharan[8] also attempted to derive the vapor pressures over $(Mo_3Te_4 + MoTe_2)$, though indirectly, from the standard molar Gibbs free energies of formation of $MoTe_2$ and Mo_3Te_4 deduced by them from e.m.f. measurements of molybdenum activities in $(MoTe_2 + Te)$ and $(Mo_3Te_4 + MoTe_2)$, respectively. They chose to present the computed values in the form of a plot. According to this plot, the vapor pressures deduced by them are higher than those reported by Krabbes.[4] We derived an equation from the same set of values that must have been employed by them:

$$\lg\{p(Te_2)/Pa)\} = -10618(K/T) + 11.802. \tag{6}$$

The plot presented by Mallika and Sreedharan does not seem to correspond to the above expression. Besides, $p(Te_2) = 391$ Pa, computed from the above expression at $T = 1153$ K, is much lower than the vapor pressure reported by Krabbes and in fact seems to agree with the value obtained in the present study. This agreement should also be considered as only apparent, just as that between the results of Opalovskij *et al.*[5] and Krabbes and Oppermann,[3, 4] since the parameters in equation (6) and in our recommended equation for $p(Te_2)$ in table 1 are different. An apt comparison may, instead, be that between the values of $a(Mo)$, since that is what Mallika and Sreedharan had measured in $(Mo_3Te_4 + MoTe_2)$ and which we can also derive by employing the Gibbs-Duhem integration. Our $a(Mo)$ values (0.15 ± 0.01) *(three runs at $T = 950$ K)* and 0.11 (one run at $T = 975$ K) at the Te-rich boundary of Mo_3Te_4 are not significantly different from those (0.069 at $T = 950$ K and 0.075 at $T = 975$ K) reported by Mallika and Sreedharan.

All homogeneity-range experiments were characterized by the presence of a period during which there was a continuous decrease in $I(Te_2^+)$. Furthermore, before and after such a period, $I(Te_2^+)$ not only remained steady for a considerable time but also corresponded to $p(Te_2)$ which were in accord with the recommended values for either $(Mo_3Te_4 + MoTe_2)$ (table 1) or $(Mo + Mo_3Te_4)$.[2] The above observations together with the fact that the total vapor pressure inside the Knudsen cell was never above 2.3 Pa formed the basis of our assumption that equilibrium existed throughout the period of the homogeneity-range experiment.

The phase-boundary compositions of Mo_3Te_4 given in table 2 were deduced in the same way for $(Cr + Te)$[13] except that $I(Te^+)$ in the present work was not measured as often as $I(Te_2^+)$ was. Instead, it was computed from $I(Te_2^+)$ and the equilibrium constant for dissociation reaction (3) derived from $p(Te)$ and $p(Te_2)$ obtained in the present study and those reported previously by us for $(Fe + Te)$,[18] $(Ni + Te)$,[19] $(Cr + Te)$,[13] and $(Mo + Te)$.[2] That such an indirect method of deriving $I(Te^+)$ has obviously not caused any great uncertainty in the computed compositions could be

inferred from the fact that the maximum difference between the compositions deduced by neglecting the presence of Te(g) in the vapor phase, *i.e.* by employing $I(\text{Te}_2^+)$ alone, and those deduced by employing both $I(\text{Te}_2^+)$ and the derived $I(\text{Te}^+)$ was mass fraction 0.0003 of Te. This is so because effusion of Te(g) makes very little contribution to the total amount of tellurium lost from the samples. At $T = 950$ K, for instance, Te(g) constitutes only mole fractions ≈ 0.03 of the vapor phase over $(\text{Mo}_3\text{Te}_4 + \text{MoTe}_2)$, and ≈ 0.10 of the vapor phase over $(\text{Mo} + \text{Mo}_3\text{Te}_4)$.

The uncertainties in the phase-boundary compositions could result from the errors in the starting compositions of the sample loaded into the Knudsen cell as well as in the assignment of the time of cross over of the condensed phase from the two-phase region to the single-phase region (Te-rich boundary) or from the single-phase region to the two-phase region (Mo-rich boundary). The starting compositions of the samples were deduced from the masses of the elements used in the preparation by assuming that oxygen, a common non-metallic impurity, was present in them only at very low levels. This assumption was supported by the observation that the boundary compositions obtained with samples of different initial compositions and different initial masses showed no great disagreement. Uncertainty in the assignment of the actual time at which the sample might have been at either boundary introduces much more error in the composition of the Te-rich boundary than in that of Mo-rich boundary since the vapor pressure at the entry point into the single phase is much more than that at the exit point from the single phase.

The recommended phase-boundary compositions given in table 2 were obtained by taking a mean of the values obtained in all the runs, though the boundaries were determined at temperatures which varied from $T = 920$ K to 975 K. The overall uncertainty in the recommended phase-boundary compositions includes the statistical uncertainty (standard deviation of the mean value) as well as the estimated uncertainty in the boundary compositions in each run. In those runs in which Te-rich boundary compositions were determined at $T = 920$ K or 935 K, the temperature was increased to 975 K when the samples were in the middle of the single phase because it would have otherwise taken much more time to reach the Mo-rich boundary. Figure 3, for instance, represents an experiment in which the sample entered and left the Mo_3Te_4 phase at different temperatures.

The homogeneity range of Mo_3Te_4 extends from $\text{MoTe}_{1.10\pm0.03}$ to $\text{MoTe}_{1.30\pm0.04}$ with a mass fraction width of (0.039 ± 0.010) of Te. The values given by Spiesser *et al.*[10] (from $\text{MoTe}_{1.17}$ to $\text{MoTe}_{1.46}$) showed only a slightly larger mass-fraction width of 0.051 of Te. On the contrary, Krabbes[4] reported the homogeneity range to be very small: from $\text{MoTe}_{1.31\pm0.01}$ to $\text{MoTe}_{1.325\pm0.005}$. However, in the case of MoTe_2, Krabbes predicted a very narrow and negligible homogeneity range, $\text{MoTe}_{2\pm0.01}$, while Spiesser *et al.*[10] and Vellinga *et al.*[11] gave a much larger range of homogeneity, which makes us believe that the results of Krabbes contain some error.

The composition $\text{MoTe}_{1.10}$ corresponding to the Mo-rich boundary Mo_3Te_4 determined in this work is obviously different from the nominal composition $\text{MoTe}_{1.33}$ employed in our earlier paper for deriving the thermodynamic quantities from the partial pressures over $(\text{Mo} + \text{Mo}_3\text{Te}_4)$.[2] An immediate consequence is that

the good agreement observed by us previously between the second- and third-law enthalpies for the reactions

$$MoTe_v(s) = Mo(s) + (v/i)Te_i(g), \tag{7}$$
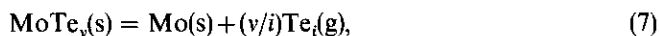
with $v = 1.33$ no longer exists if the evaluations are performed by employing the same $p(Te_i)$ ($i = 1$ or 2) over $(Mo + Mo_3Te_4)$ but with $v = 1.10$. The same auxiliary thermodynamic quantities given by Brewer and Lamoreaux[1] (strictly applicable to the nominal composition $MoTe_{1.33}$) when employed also for $MoTe_{1.10}$ cause more error in the $\Delta_r H_m^\circ(298.15\ K)$ derived by the third-law method than in that derived by the second-law method. That is because the only auxiliary thermodynamic quantities employed in a second-law evaluation are the enthalpy increments which may show a negligible composition dependence, whereas in a third-law evaluation the entropies, which may show a large composition dependence, are also used. Moreover, in the second-law method, the auxiliary thermodynamic functions are employed only to convert $\Delta_r H_m^\circ(T)$ to $\Delta_r H_m^\circ(298.15\ K)$ and the difference between these two values is usually not very large. Therefore, by assuming that the enthalpy increments do not vary much across the homogeneity range, the $\Delta_{T'}^T H_m^\circ$ ($T' = 298.15\ K$) values given by Brewer and Lamoreaux have been retained. The $S_m^\circ(T)$s for $MoTe_{1.10}$ were computed by multiplying those for $MoTe_{1.33}$[1] by a constant factor. This factor f was estimated from the $S_m^\circ(298.15\ K)$s for the constituent elements $Mo(s)$,[20] and $Te(s)$,[15] as follows:

$$f = \{S_m^\circ(Mo, s) + 1.10 S_m^\circ(Te, s)\}/\{S_m^\circ(Mo, s) + 1.33 S_m^\circ(Te, s)\}. \tag{8}$$

Good agreement between the second- and third-law values was once again observed, although the values were lower than those obtained with $v = 1.33$. In table 5, we have shown how the choice of the boundary compositions and the auxiliary

TABLE 5. Second- and third-law enthalpies for the reaction: $MoTe_v(s) = Mo(s) + (v/i)Te_i(g)$, evaluated from the partial pressures determined over $(Mo + Mo_3Te_4)$[a]

		$\Delta_r H_m^\circ(298.15\ K)/(kJ \cdot mol^{-1})$	
v	i	second-law	third-law
1.33[b]	2	178.7 ± 3.1	179.0 ± 0.4
	1	345.2 ± 6.2	347.5 ± 0.9
1.10[c]	2	152.1 ± 2.5	133.2 ± 1.0
	1	289.4 ± 5.1	272.3 ± 1.1
1.10[d]	2	152.1 ± 2.5	154.0 ± 0.6
	1	289.4 ± 5.1	293.0 ± 0.9

[a] $p(Te_2)$ and $p(Te)$ obtained in our previous study over $(Mo + Mo_3Te_4)$[2] (table 1: run no. 6 at 1.7 aJ) were employed in the evaluations.

[b] Mo-rich boundary composition assumed as $MoTe_{1.33}$; enthalpy increments and $(\Delta_0^T S_m^\circ - \Delta_{298.15\ K}^T H_m^\circ/T)$ from reference 1 for $MoTe_{1.33}(s)$.

[c] Mo-rich boundary composition obtained in this work ($MoTe_{1.10}$) was used; enthalpy increments and $(\Delta_0^T S_m^\circ - \Delta_{298.15\ K}^T H_m^\circ/T)$ from reference 1 for $MoTe_{1.33}(s)$.

[d] Mo-rich boundary composition obtained in this work ($MoTe_{1.10}$) was used. While enthalpy increments given in reference 1 for $MoTe_{1.33}$ were retained for $MoTe_{1.10}$, $(\Delta_0^T S_m^\circ - \Delta_{298.15\ K}^T H_m^\circ/T)$ given in the same reference were modified as described in the text.

thermodynamic quantities for those compositions alter the results derived from the same set of partial pressures. On the basis of the above discussion, we have reevaluated the partial pressures over $(Mo + Mo_3Te_4)$ reported by us previously, and the following thermodynamic quantities were obtained: $\Delta_r H_m^\circ (298.15 \text{ K}) = (153.3 \pm 4.7) \text{ kJ} \cdot \text{mol}^{-1}$ for the reaction:

$$MoTe_{1.10}(s) = Mo(s) + 0.55Te_2(g), \tag{9}$$
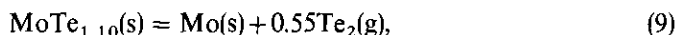
and $\Delta_r H_m^\circ (298.15 \text{ K}) = (291.8 \pm 11.0) \text{ kJ} \cdot \text{mol}^{-1}$ for the reaction:

$$MoTe_{1.10}(s) = Mo(s) + 1.10Te(g). \tag{10}$$

The entropies of $MoTe_{1.30}$ and $MoTe_{1.89}$ were derived from those of $MoTe_{1.33}$ and $MoTe_2$,[1] respectively, by the method shown in equation (8): $S_m^\circ(T)$ for $MoTe_{1.30}$ was obtained by multiplying $S_m^\circ(MoTe_{1.33})$,[1] by 0.9843 and $S_m^\circ(T)$ for $MoTe_{1.89}$ was obtained by multiplying $S_m^\circ(MoTe_2)$,[1] by 0.9574. Despite the use of such modified entropies, the agreement between the second- and third-law values given in table 3 for reactions (1) and (2) can only be termed as fair. We believe that the discrepancy, though not significant, can be due either to the inadequacy of the approach employed by us to estimate the entropies for $MoTe_{1.89}$ or to the possibility that the Mo-rich boundary composition of $MoTe_2$ might not correspond to $MoTe_{1.89}$. The good agreement seen in the same table for reaction (3) evidently removes any doubts about the reliability of the partial pressures. The recommended reaction enthalpies given in table 3 were computed by taking the average of the second- and third-law values. Use of the auxiliary thermodynamic functions given by Brewer and Lamoureaux without any modification has resulted in greater disagreement between the second- and the third-law values for reactions (1) and (2). The agreement was no better when the calculations were performed by assuming the Mo-rich boundary of $MoTe_2$ to be $MoTe_2$ and the Te-rich boundary of Mo_3Te_4 to be $MoTe_{1.33}$.

Table 6 summarizes the values of $\Delta_f H_m^\circ(298.15 \text{ K})$ for Mo_3Te_4 and $MoTe_2$ deduced from the results obtained in this work as well as our previous work on $(Mo + Mo_3Te_4)$.[2] We have also included in this table the values reported by other workers. The following inferences may be drawn from table 6: in the case of Mo_3Te_4, our value that corresponds to the Te-rich boundary composition $MoTe_{1.30}$ is in good agreement with that reported by Mallika and Sreedharan[8] for the nominal composition $MoTe_{1.33}$; the recalculation by O'Hare and Hope[9] of the vapor pressure over $(Mo + Mo_3Te_4)$ determined by Krabbes[4] yields a value for $\Delta_f H_m^\circ(MoTe_{1.33}, s, 298.15 \text{ K})$ that is $\approx 9 \text{ kJ} \cdot \text{mol}^{-1}$ higher than that obtained by us;[2] and our results for α-$MoTe_2$ show a higher stability for this phase than the value of Mallika and Sreedharan[7] suggests.

While comparing the results, it should be borne in mind that the values, if derived from measurements over two-phase fields, may be influenced by the compositions assumed for the co-existing phases (in other words, the phase-boundary compositions) as well as by the auxiliary thermodynamic quantities employed in the calculations. Furthermore, while computing the thermodynamic quantities for the individual phases from the results obtained over the two-phase regions, the variation in the values of thermodynamic quantities across the homogeneity range of the single

TABLE 6. Enthalpies of formation of $MoTe_v$ determined by different methods. KEMS denotes Knudsen-effusion mass spectrometry

v	$\dfrac{-\Delta_f H_m^\circ(298.15\ \text{K})}{\text{kJ} \cdot \text{mol}^{-1}}$	Method
	Mo_3Te_4 phase	
1.33	70.5 ± 4.6[2]	KEMS[a,b,c]
1.10	63.5 ± 4.7	KEMS results from reference 2 re-evaluated in this work[a,d,c]
1.10	66.4 ± 5.9	KEMS results from reference 2 re-evaluated in this work[a,d,e]
1.10	63.7 ± 0.4	KEMS; this work[f]
1.30	67.0 ± 0.3	KEMS; this work[f]
1.33	65.2 ± 3.3[4]	Bourdon manometric technique[a,b]
1.33	61.7 ± 3.3[9]	Results from reference 4 re-evaluated[b,c]
1.33	69.7 ± 3.3[8]	e.m.f. studies[g]
	$MoTe_2$ phase (α-modification)	
1.89	103.5 ± 10.6	KEMS; this work[g,h,c]
1.89	105.0 ± 10.8	KEMS; this work[g,h,e]
2.00	90.3 ± 1.0[7]	e.m.f. studies[i]
	$MoTe_2$ phase (β-modification)	
2.00	85.0 ± 10[4]	Bourdon manometric technique[g,j]
2.00	84.2 ± 4.6[9]	Combustion calorimetry

[a] Measurements over $(Mo + Mo_3Te_4)$ two-phase region.
[b] Mo-rich boundary of Mo_3Te_4 taken as $MoTe_{1.33}$.
[c] Derived by using $\Delta_f H_m^\circ(Te_2, g, 298.15\ K) = 163.2\ kJ \cdot mol^{-1}$.[15]
[d] Mo-rich boundary of Mo_3Te_4 taken as $MoTe_{1.10}$.
[e] Derived by using $\Delta_f H_m^\circ(Te_2, g, 298.15\ K) = (158.0 \pm 6.6)\ kJ \cdot mol^{-1}$.[17]
[f] The selected values in table 4 reproduced.
[g] Measurements over $(Mo_3Te_4 + MoTe_2)$ two-phase region.
[h] Te-rich boundary of Mo_3Te_4 taken as $MoTe_{1.30}$; Mo-rich boundary of $MoTe_2$ taken as $MoTe_{1.89}$.
[i] Measurements over $(MoTe_2 + Te)$ two-phase region.
[j] Te-rich boundary of Mo_3Te_4 taken as $MoTe_{1.33}$; Mo-rich boundary of $MoTe_2$ taken as $MoTe_{2.00}$.

phase is, more often than not, ignored. For instance, Krabbes[4] first derived thermodynamic quantities for Mo_3Te_4 from $p(Te_2)$ over $(Mo + Mo_3Te_4)$, and subsequently, by using these values and $p(Te_2)$ over $(Mo_3Te_4 + MoTe_2)$, derived those for $MoTe_2$. Similarly Mallika and Sreedharan[7, 8] first derived thermodynamic quantities for $MoTe_2$ from the $a(Mo)$ in $(MoTe_2 + Te)$, and subsequently, by using these values and $a(Mo)$ in $(Mo_3Te_4 + MoTe_2)$, derived those for Mo_3Te_4. Our results for Mo_3Te_4 (see table 4) show that there could exist a difference of $6\ kJ \cdot mol^{-1}$ to $7\ kJ \cdot mol^{-1}$ in $\Delta_f G_m^\circ(T)$ and $3\ kJ \cdot mol^{-1}$ to $4\ kJ \cdot mol^{-1}$ in $\Delta_f H_m^\circ(298.15\ K)$ across the homogeneity range. However, since differences of this magnitude might well be comparable to errors associated with the derived values, neglect of compositional dependence is perhaps not serious.

A determination of high-temperature heat capacities of Mo_3Te_4 and $MoTe_2$ is highly desirable so as to be able to deduce reliable second- and third-law values. In the meantime, we recommend the following values obtained by us: $\Delta_f H_m^\circ(MoTe_{1.10}, s, 298.15\ K) = -(66.4 \pm 5.9)\ kJ \cdot mol^{-1}$ and $\Delta_f H_m^\circ(MoTe_{1.30}, s, 298.15\ K) = -(67.0 \pm 0.3)\ kJ \cdot mol^{-1}$ for the Mo_3Te_4 phase; and

$\Delta_f H_m^\circ(\text{MoTe}_{1.89}, \text{s}, 298.15 \text{ K}) = -(105.0 \pm 10.8) \text{ kJ} \cdot \text{mol}^{-1}$ for the MoTe_2 phase (α-modification).

The authors wish to thank Mr M. Sai Baba for valuable discussions, Mr K. V. G. Kutty and his group (X-ray group) for the characterization of the samples, and Mr K. C. Srinivas and his group (Instrumentation and Mechanical Services) for the maintenance of the mass spectrometer.

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