

## Standard molar Gibbs energy of formation of MoTe<sub>2</sub> from e.m.f. measurements

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The e.m.f. of the galvanic cell:



(where  $p^\circ = 1 \times 10^5$  Pa and YSZ denotes 15 mass per cent of Y<sub>2</sub>O<sub>3</sub> stabilizing ZrO<sub>2</sub>) was measured over the range 654 to 1065 K. From these e.m.f. results, the following least-squares expression was derived for the standard molar Gibbs free energy of formation of MoTe<sub>2</sub>(s) from Mo(s) and Te(l) over the range 728 to 1065 K:

$$\Delta_f G_m^\circ(\text{MoTe}_2, \text{s}, \alpha)/(\text{kJ} \cdot \text{mol}^{-1}) = -(114.25 - 0.04397T/\text{K}) \pm 2.39.$$

Using a value of 13.88 for  $S_m^\circ/R$  for MoTe<sub>2</sub>(s) at 298.15 K reported in the literature, a value of  $-(90.32 \pm 1.00) \text{ kJ} \cdot \text{mol}^{-1}$  was calculated by the third-law method for the standard molar enthalpy of formation of MoTe<sub>2</sub>(s,  $\alpha$ ) at 298.15 K.

### 1. Introduction

Molybdenum and tellurium are among the predominant fission products in the metallic precipitates of spent fast-reactor fuel pins.<sup>(1)</sup> They are found along with (uranium + plutonium), the noble metals, antimony, and tin. For a thermodynamic analysis of these metallic precipitates, precise thermodynamic values for the constituent binary mixtures are required.<sup>(1, 2)</sup> Not only the thermodynamic values, but even the phase diagram, are not reliably known for (molybdenum + tellurium). Moffatt<sup>(3)</sup> has computed the phase diagram based on the thermodynamic values estimated by Brewer *et al.*<sup>(4)</sup> According to this phase diagram, the solubility of molybdenum in tellurium(s or l) is negligible and Mo<sub>3</sub>Te<sub>4</sub> and MoTe<sub>2</sub> are the congruently melting phases. Opalovskii *et al.*<sup>(5)</sup> have reported the thermodynamic stability of Mo<sub>3</sub>Te<sub>4</sub> and MoTe<sub>2</sub> over the temperature range 909 to 981 K using dissociation-pressure measurements. On the basis of pressure measurements of Te<sub>2</sub>(g) over (Mo + Mo<sub>3</sub>Te<sub>4</sub>), (Mo<sub>3</sub>Te<sub>4</sub> + MoTe<sub>2</sub>), and {MoTe<sub>2</sub> + Te(l)} reported by Krabbes and Oppermann,<sup>(6)</sup> and Krabbes<sup>(7)</sup> using a Bourdon manometer and on the calorimetric results reported by Kiwia and Westrum,<sup>(8)</sup> O'Hare *et al.*<sup>(9)</sup> have assessed the standard molar enthalpy of formation  $\Delta_f H_m^\circ$  and  $S_m^\circ$  of MoTe<sub>2</sub> at

298.15 K. More recently O'Hare<sup>(10)</sup> has again revised the value of  $\Delta_f H_m^\circ$  of  $\text{MoTe}_2(\text{s}, \alpha)$  in a critical review on inorganic chalcogenides. Another estimate of these quantities was made by Mills<sup>(11)</sup> on the basis of thermodynamic values for molybdenum sulphides. Since the e.m.f. method was demonstrated to yield precise thermodynamic values even on a telluride phase like  $\text{Sb}_2\text{Te}_3$  coexisting with tellurium(s),<sup>(12)</sup> this technique was chosen in the present investigation to determine the standard molar Gibbs free energy of formation of  $\text{MoTe}_2$  over a wide range of temperature.

## 2. Experimental

Molybdenum ditelluride  $\text{MoTe}_2$  was synthesized from powdered molybdenum (purity greater than 99.9 mass per cent, supplied by Alfa Ventron, U.S.A.) and tellurium granules (purity better than 99.99 mass per cent, supplied by B.D.H., U.K.). An intimate mixture of these powders in the stoichiometric ratio required for the preparation of  $\text{MoTe}_2$  was compacted at a pressure of 100 MPa into cylindrical pellets of 10.0 mm diameter and 2 to 3 mm thickness. These pellets were sealed in evacuated silica ampoules and were gradually heated in stages at 623 K for 24 h, 773 K for 24 h, and finally at 873 K for 30 h. The compound was found to be pure  $\text{MoTe}_2(\alpha)$  free from other phases within the limits (5 mass per cent) of detection by X-ray diffractometry.  $\text{MoO}_2(\text{s})$  was also of purity better than 99.0 mass per cent, and was supplied by Alfa products, U.S.A.

The electrodes were made from  $(0.687\text{MoTe}_2 + 0.187\text{Te} + 0.126\text{MoO}_2)$  compacted at a pressure of 100 MPa into cylindrical pellets of 6.0 mm diameter and 2 to 3 mm thickness. Pre-fired graphite cups were used to contain the electrode pellets as was done in the previous studies on systems bearing free tellurium.<sup>(12)</sup>

In the first series of e.m.f. measurements, the galvanic cell:



was used, where  $p^\circ = 1 \times 10^5$  Pa and YSZ denotes 15 mass per cent of  $\text{Y}_2\text{O}_3$  stabilizing  $\text{ZrO}_2$ . The absence of asymmetric potentials due to the graphite cup was verified as discussed in earlier studies.<sup>(12-14)</sup> However, the platinum lead wire was found to snap off frequently owing to embrittlement by tellurium vapour, though it was not contributing any serious error arising from thermal e.m.f. Nevertheless it was necessary to extend the life of the cell by replacing Pt with Chromel lead wires in a series of measurements. As the use of Chromel wire leads to a thermal e.m.f., values of the thermal e.m.f. for Chromel-to-platinum were measured independently over the range of temperatures employed in the e.m.f. runs. These values were fitted into an expression to facilitate interpolation for correcting the e.m.f. results:

$$E(\text{Chromel-to-platinum})/\text{mV} = -(10.43 - 0.03371T/\text{K}), \quad (551 \text{ to } 1092 \text{ K}). \quad (1)$$

The volatilization of tellurium was reduced as far as possible by employing a nearly static purified argon atmosphere. The method of purification and other experimental details are identical as described in the earlier publications.<sup>(12, 14, 15)</sup>

The temperature was measured using a platinum-to-(platinum + 10 mass per cent of rhodium) thermocouple calibrated at the freezing temperatures of high-purity metals such as Sn, Zn, Sb, and Ag. The hot junction of this thermocouple was placed in the same isothermal zone of the galvanic cell in the reference (air) electrode compartment. To reach stable e.m.f. values (fluctuating by less than 1 mV around the mean value) the cells required 10 to 20 h at lower temperatures and about 2 h at higher temperatures after attaining constancy ( $\pm 1$  K) of temperature. The cell potentials were tested for reversibility by thermal cycling and by micropolarization.<sup>(16)</sup> Since the temperature coefficient of the e.m.f. is about  $0.5 \text{ mV} \cdot \text{K}^{-1}$ , whenever the temperature of the cell was raised to the next isothermal setting there would be a drift in the e.m.f. When this drift followed the thermal oscillation in a more or less sinusoidal manner, around a mean value not deviating by more than 1 mV, it was recorded as a reading. Absence of electrical pick-up from the a.c. field of the furnace was verified by momentarily switching off the furnace and confirming an identical value of the e.m.f.

### 3. Results and discussion

The e.m.f. results on cell (I) after correcting for the thermal e.m.f. contributions of the Chromel-to-platinum lead wire whenever necessary {using equation (1)} are presented in table 1 and figure 1. It might appear from figure 1 that the e.m.f. results obtained with a Pt lead wire are slightly lower than those obtained with a Chromel lead wire though the reason is not at present understood. However, the difference between the results obtained with Pt and Chromel lead wires is well within the experimental scatter. Two least-squares lines could be drawn for the two temperature ranges, 654 to 713 K and 728 to 1065 K, corresponding to the temperature ranges over which tellurium coexists with  $\text{MoTe}_2(\text{s}, \alpha)$  and  $\text{MoO}_2(\text{s})$  in the solid and in the liquid states, respectively. The least-squares expressions for these

TABLE 1. Experimental results for the cell (I):  
Pt or Chromel|C| $\text{MoTe}_2(\text{s}, \alpha)$ |Te(s or l)| $\text{MoO}_2(\text{s})$ |YSZ|air  $\{p(\text{O}_2) = 0.21 p^\circ\}$ |Pt, where  $p^\circ = 1 \times 10^5$  Pa and  
YSZ denotes 15 mass per cent of  $\text{Y}_2\text{O}_3$  stabilizing  $\text{ZrO}_2$

Run	T/K	E/mV	T/K	E/mV	T/K	E/mV	T/K	E/mV	T/K	E/mV	T/K	E/mV
1 <sup>a</sup>	708.4	934.70	751.4	913.33	819.9	884.74	977.9	833.69	727.7	925.02		
2 <sup>a</sup>	773.1	903.86	948.7	841.09	796.2	893.93						
3 <sup>b</sup>	864.0	881.43	844.3	880.48	924.1	854.36	712.6	938.17	1001.8	829.31		
	810.0	894.14	920.0	857.95	933.1	849.95	1016.9	824.59				
4 <sup>b</sup>	745.5	923.27	825.1	884.05	876.2	870.21	962.9	842.73	993.4	831.31	1040.1	818.72
	653.6	973.46	944.0	848.82	770.6	913.30	1064.7	812.15	908.1	856.66		
5 <sup>b</sup>	674.1	950.65	977.5	836.13	969.5	838.38	875.7	869.25				
	818.6	891.77	895.9	867.91	957.6	842.37						
6 <sup>b</sup>	777.6	908.06	939.2	847.28	866.7	870.50	1009.9	829.64	786.3	897.47	910.9	857.29

<sup>a</sup> Runs with Pt as the lead wire.

<sup>b</sup> Runs with Chromel lead wire {after correcting for the thermal e.m.f. contributions by the (Chromel-to-platinum) couple using equation (1)}.

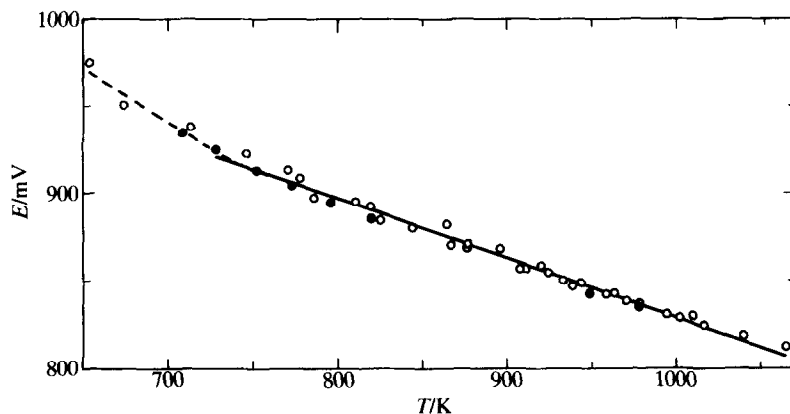


FIGURE 1. Experimental results  $E$  for cell (I):

Pt or Chromel|C|MoTe<sub>2</sub>|Te(s or l)|MoO<sub>2</sub>|ysz|air{ $p(\text{O}_2) = 0.21p^\circ$ }|Pt, where  $p^\circ = 1 \times 10^5$  Pa and ysz denotes 15 mass per cent of Y<sub>2</sub>O<sub>3</sub> stabilizing ZrO<sub>2</sub>. ●, Results with Pt lead wire; ○, results with Chromel lead wire; ---, Te(s) as the coexisting phase.

two ranges for the measured potentials of cell I are represented by

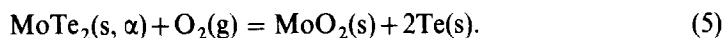
$$E(\text{I})/\text{mV} = (1357.13 - 0.59357T/\text{K}) \pm 4.40, \quad (654 \text{ to } 713 \text{ K}); \quad (2)$$

$$E(\text{I})/\text{mV} = (1168.45 - 0.33937T/\text{K}) \pm 3.35, \quad (728 \text{ to } 1065 \text{ K}). \quad (3)$$

After correcting for the standard pressure of oxygen in the reference air electrode in cell (I), the standard molar Gibbs free energy change  $\Delta_r G_m^\circ$  for the passage of four electrons in equation (2) is represented as

$$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -(523.78 - 0.21608T/\text{K}) \pm 1.70, \quad (654 \text{ to } 713 \text{ K}), \quad (4)$$

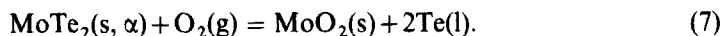
corresponding to the reaction:



Similarly  $\Delta_r G_m^\circ$  corresponding to equation (3) is given by

$$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -(450.96 - 0.11797T/\text{K}) \pm 1.29, \quad (728 \text{ to } 1065 \text{ K}), \quad (6)$$

for the reaction:



Solving equations (4) and (6) for reactions (5) and (7), the molar enthalpy and temperature of melting of tellurium are calculated to be  $36.4 \text{ kJ} \cdot \text{mol}^{-1}$  and  $742 \text{ K}$  in very poor agreement with the  $17.5 \text{ kJ} \cdot \text{mol}^{-1}$  and  $723 \text{ K}$  tabulated by Kubaschewski and Alcock.<sup>(17)</sup> At least one set of experimental results is in serious error. Equations (2) and (4) corresponding to the temperature range of existence of tellurium in the solid state, are based on just four experimental points over a rather narrow temperature span from 654 to 713 K. It was pointed out by Kubaschewski<sup>(18)</sup> and Sreedharan *et al.*<sup>(16)</sup> that e.m.f. results are more reliable with reference to the standard molar Gibbs free energies, but when one is concerned to

split the results into enthalpy and entropy terms, measurements should be made over a wide enough range of temperature. Further, at temperatures below 700 K, the micropolarization tests required much longer annealing periods to reach the original values after each application of a bucking potential. Such a difficulty was not experienced when Te was in the molten state in the three-phase electrode. For these reasons the results in the lower temperature range should not be considered for the calculation of the molar enthalpy change or the melting temperature  $T_m$  of Te since an error of just  $2 \text{ kJ} \cdot \text{mol}^{-1}$  could shift  $T_m$  by 20 K. This is further justified from entropy considerations in the subsequent analysis of the results leading to equations (2) and (4). Moreover, the least-squares expressions (3) and (6) for  $\text{Te(l)}$  are based on 37 experimental points over a much wider range, namely from 728 to 1065 K, apart from their consistency with the entropy analysis made later in this section.

To calculate the standard molar Gibbs free energy of formation of  $\text{MoTe}_2(\text{s}, \alpha)$ , the expression for  $\Delta_f G_m^\circ$  of  $\text{MoO}_2(\text{s})$  was used:<sup>(19, 20)</sup>

$$\Delta_f G_m^\circ(\text{MoO}_2, \text{s})/(\text{kJ} \cdot \text{mol}^{-1}) = -(565.21 - 0.16194T/\text{K}) \pm 1.10, \quad (1070 \text{ to } 1320 \text{ K}). \quad (8)$$

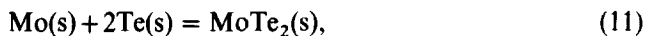
Justification for the selection of equation (8) which is based upon the recent e.m.f. measurements and assessment by Kleykamp and Supawan,<sup>(19)</sup> and the later e.m.f. measurements by Chattopadhyay *et al.*<sup>(20)</sup> might be necessary. These authors have reported a value of  $(162 \pm 1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for the second-law entropy  $\Delta_f S_m^\circ(\text{MoO}_2, T)$  in the temperature range of their measurements. This value is more reasonable than the 176 and  $(173 \pm 25) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  tabulated by Pankratz,<sup>(21)</sup> and Kubaschewski and Alcock,<sup>(17)</sup> respectively, on the basis of calorimetric results published in the sixties. The relation between  $\Delta_f G_m^\circ(\text{MoTe}_2, \text{s})$  and  $\Delta_f G_m^\circ(4)$  can be represented by

$$\Delta_f G_m^\circ(\text{MoTe}_2, \text{s}) = \Delta_f G_m^\circ(\text{MoO}_2, \text{s}) - \Delta_f G_m^\circ(4). \quad (9)$$

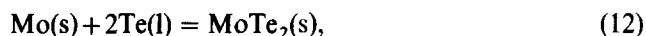
Thus equations (4), (8), and (9) may be combined:

$$\Delta_f G_m^\circ(\text{MoTe}_2, \text{s}, \alpha)/(\text{kJ} \cdot \text{mol}^{-1}) = -(41.43 + 0.05414T/\text{K}) \pm 2.80, \quad (10)$$

for the reaction:



over the range 654 to 713 K. Similarly, for the reaction:



one may derive:

$$\Delta_f G_m^\circ(\text{MoTe}_2, \text{s}, \alpha)/(\text{kJ} \cdot \text{mol}^{-1}) = -(114.25 - 0.04397T/\text{K}) \pm 2.39 \quad (13)$$

for the range 728 to 1065 K.

To check which of these results represented by expressions (10) and (13) is correct, the following expression for the molar Gibbs free energy of fusion was added to equation (13) to get equation (11) for the (solid + solid) reaction; the

difference in the molar heat capacities of solid and liquid tellurium on extrapolation over a narrow range of temperature was ignored.

$$\Delta_{\text{fus}} G_m^\circ(\text{Te}, \text{s})/(\text{kJ} \cdot \text{mol}^{-1}) = (35.00 - 0.04841 T/\text{K}). \quad (14)$$

Thus by adding equations (13) and (14) one obtains

$$\Delta_f G_m^\circ(\text{MoTe}_2, \text{s})/(\text{kJ} \cdot \text{mol}^{-1}) = -(79.25 + 0.00444 T/\text{K}). \quad (15)$$

Comparison of equations (10) and (15) shows an unreasonably large value of  $54 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for the (solid + solid) reaction (11). Therefore, equation (10) was rejected and, thus, equations (2) and (4). The entropy term in equation (15) is a reasonably small positive value as expected.

Further, assessment of the temperature-dependent error may be made by calculating the standard molar enthalpy of formation  $\Delta_f H_m^\circ$  of  $\text{MoTe}_2(\text{s})$  at 298.15 K. We have used  $\Delta_0^T S_m^\circ/R = 13.88$  for  $\text{MoTe}_2(\text{s})$  ( $R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) and  $(\Delta_0^T S_m^\circ - \Delta_{298.15 \text{ K}}^T H_m^\circ/T)$  assessed by Brewer *et al.*<sup>(4)</sup> This calculation has yielded  $\Delta_f H_m^\circ = -(90.32 \pm 1.00) \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{MoTe}_2(\text{s})$  at 298.15 K without any discernible temperature dependence of the individual values. The estimate of  $(\Delta_0^T S_m^\circ - \Delta_{298.15 \text{ K}}^T H_m^\circ/T)$  by Brewer *et al.*<sup>(4)</sup> for  $\text{MoTe}_2(\text{s}, \alpha)$  over the range 298 to 1260 K has been made on the basis of the  $C_{p,m}^\circ$  values up to 344 K reported by Kiwia and Westrum.<sup>(8)</sup> Using the  $C_{p,m}^\circ$  values of  $\text{MoTe}_2(\text{s}, \alpha)$  by Kiwia and Westrum,<sup>(8)</sup> and those of  $\text{Mo}(\text{s})$  and  $\text{Te}(\text{s or l})$  by Barin and Knacke,<sup>(22)</sup> and  $\Delta_{\text{fus}} H_m^\circ$  of  $\text{Te}$  by Barin and Knacke, a value of  $-80.0 \text{ kJ} \cdot \text{mol}^{-1}$  was computed for the second-law molar enthalpy of formation of  $\text{MoTe}_2(\text{s}, \alpha)$  at 298.15 K. These second- and third-law values of  $-80.0$  and  $-(90.32 \pm 1.00) \text{ kJ} \cdot \text{mol}^{-1}$  respectively for  $\Delta_f H_m^\circ(\text{MoTe}_2, \text{s}, \alpha)$  at 298.15 K from the present study are in the same range as those of  $-91.1 \text{ kJ} \cdot \text{mol}^{-1}$  in an earlier estimate by O'Hare *et al.*,<sup>(9)</sup>  $-(89.5 \pm 11.0) \text{ kJ} \cdot \text{mol}^{-1}$  reported by Krabbes,<sup>(7)</sup>  $-(83 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$  in a recent review by O'Hare,<sup>(10)</sup> and  $-(77.32 \pm 14.96) \text{ kJ} \cdot \text{mol}^{-1}$  estimated by Brewer *et al.*<sup>(4)</sup>

For a better assessment as well as better agreement between the second- and the third-law values of the  $\Delta_f H_m^\circ$  of  $\text{MoTe}_2(\text{s}, \alpha)$  at 298.15 K, precise  $C_{p,m}^\circ$  values for  $\text{MoTe}_2(\text{s}, \alpha)$  should be measured above 344 K up to the temperature range of interest.

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