STANDARD GIBBS ENERGY OF FORMATION OF Mo_3Te_4 BY EMF MEASUREMENTS

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The emf of the galvanic cells

Pt, Mo, MoO_2 | 8 YSZ | 'FeO', Fe, Pt   (I) and

Pt, Fe, 'FeO' | 8 YSZ | MoO_2, Mo_3Te_4, $MoTe_2(\alpha)$, C, Pt   (II)

were measured over the temperature ranges 837 to 1151 K and 775 to 1196 K, respectively, using 8 mass% yttria-stabilized zirconia (8 YSZ) as the solid electrolyte. From the emf values, the partial molar Gibbs energy of solution of molybdenum in $Mo_3Te_4/MoTe_2(\alpha)$, $\Delta \overline{G}_{Mo}$, was found to be

$$\Delta \overline{G}_{Mo} \pm 1.19 \quad (kJ/mol) = -025.08 + 0.00420 T(K).$$

Using the literature data for the Gibbs energy of formation of $MoTe_2(\alpha)$, the expression

$$\Delta G_f^\circ (Mo_3Te_4, s) \pm 5.97 \quad (kJ/mol) = -253.58 + 0.09214 T(K)$$

was derived for the range 775 to 1196 K. A third-law analysis yielded a value of -209 ± 10 kJ/mol for $\Delta H_{f,298}^\circ$ of $Mo_3Te_4(s)$.

1. Introduction

Molybdenum tellurides were of interest to materials scientists as high temperature lubricants [1]. These elements are also among the predominant fission products in the metallic precipitates of spent fast-reactor fuel pins [2]. Moffatt [3] has computed the phase diagram of the Mo–Te system based on the thermodynamic data estimated by Brewer et al. [4]. In this phase diagram Mo_3Te_4 and $MoTe_2$ are the two congruently melting phases and the solubility of Mo in Te is negligible. These two tellurides have been studied by Kiwia and Westrum [5] using low temperature heat capacity measurements, by Opalovskii et al. [6], Krabbes and Oppermann [7] and Krabbes [8] employing vapour pressure measurements and the Gibbs energy data on $MoTe_2(\alpha)$ by Mallika and Sreedharan [9] using oxide electrolyte emf measurements. O'Hare [10] has critically estimated the standard molar enthalpy of formation, $\Delta H_{f,298}^\circ$, of $MoTe_2(s)$ and $Mo_3Te_4(s)$ in a review on inorganic chalcogenides. Mills [11] has also made an estimate of the thermodynamic data of these tellurides based on their similarity to the corresponding sulphides. Since the emf method was demonstrated to yield precise thermodynamic values even on tellurides like Sb_2Te_3 and $MoTe_2$ coexisting with Te (s or *l*) [12,9] this technique was

chosen in the present investigation to determine the standard molar Gibbs energy of formation, ΔG_f° of Mo_3Te_4 coexisting with $MoTe_2$ and MoO_2 over a wide range of temperature.

2. Experimental

2.1. Materials and synthesis

Molybdenum powder (purity better than 99.9%, Alfa Ventron, USA) and tellurium granules (purity greater than 99.99%, BDH, UK) were the starting materials. Stoichiometric quantities of Mo and Te in the mole ratios of 3:4 and 1:2 were blended together and compacted at a pressure of 100 MPa into cylindrical pellets of 10 mm diameter and 2 to 3 mm thickness. The pellets of these two compositions were separately encapsulated in evacuated and sealed silica ampoules. For the synthesis of Mo_3Te_4, the appropriate ampoules were gradually heated to 623 K and maintained there for 24 h followed by subsequent isothermal heat treatments at 700 and 750 K for 36 and 24 h, respectively. Likewise, for the synthesis of $MoTe_2(\alpha)$, the ampoules of the other composition were gradually heated and maintained at iso-

thermal temperatures of 623, 773 and 873 K for 24, 24 and 30 h, respectively. In all these isothermal heat treatment steps it was necessary to ensure that the ampoules were of short length and were positioned in the isothermal zone of the furnace to prevent isopiestic transpiration of Te. The products were identified by powder X-ray diffraction technique (XRD) to be pure Mo_3Te_4 and pure $MoTe_2(\alpha)$ which were free from other impurity phases to the 5 mass% limit of detection by XRD. The compounds Mo_3Te_4, $MoTe_2$ and MoO_2 (purity better than 99%, Alfa products, USA) were mixed in the mass ratio 2 : 2 : 1, and were compacted into cylindrical pellets as described above in order to serve as test electrodes. Iron sponge (99.9% pure, Cerac, USA) and Fe_2O_3 (purity greater than 99.99%, Johnson Matthey Chemicals, UK) were mixed in the mass ratio of 8 : 1 followed by compaction into pellets as mentioned earlier and were heated in vacuum to 900 K (above the eutectoid temperature range of 790 to 840 K) [13,14]. These pellets were used as reference electrodes. A mixture containing Mo and MoO_2 in the mass ratio of 4 : 1 was used for making pellets of Mo/MoO_2 electrode.
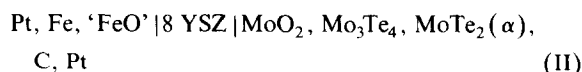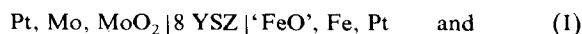
2.2. Emf measurements

Circular discs of 10 mm diameter and 3 mm thickness made of 8 mass% yttria-stabilized zirconia (YSZ) (density better than 98% theoretical, Friedrichsfeld, FRG) were used as the solid electrolyte. He gas purified by passing through a trap containing refrigerated molecular sieve at a very low flow rate (less than 1 dm^3/h) provided the inert gas blanket for the open cell stacked-pellet assembly [15–17] employed in these measurements. In addition, titanium sponge was employed as an in-situ getter of oxygen in the vicinity of the stacked pellets. The temperature was measured by a Pt–10% Rh/Pt thermocouple calibrated at the freezing points of high purity Sn, Zn, Bi and Ag. A symmetric galvanic cell with identical Fe/'FeO' electrodes sandwitching a disc of YSZ was used to check the absence of asymmetric potentials. A cell voltage of less than 0.5 mV was measured in this arrangement over the range 700 to 1200 K showing the absence of asymmetric potentials and verifying the location of the pellets in the isothermal zone (as otherwise large thermo-emfs might be noticed). A high purity graphite spacer was used to prevent the attack of platinum disc and lead wire by the constituents of the electrode namely Mo and Te. Absence of thermo-emf contributions by this spacer by virtue of its being in the constant temperature zone was again verified with the help of an otherwise symmetric

cell configuration. Only those cell voltages which did not drift by more than 1×10^{-3} V/h and reproducible during the subsequent heating cycles were taken into account. The other experimental details are discussed elsewhere [12,15–18].

3. Results

The galvanic cells studied were

Pt, Mo, MoO_2 | 8 YSZ | 'FeO', Fe, Pt   and   (I)

Pt, Fe, 'FeO' | 8 YSZ | MoO_2, Mo_3Te_4, $MoTe_2(\alpha)$,

C, Pt   (II)

(8 YSZ denotes 8 mass% yttria-stabilized zirconia).

To check the consistency in the emf of the cells (I) and (II), the emf of the following galvanic cell was also measured at one temperature approximately in the middle of the temperature range covered by the above cells:

Pt, Mo, MoO_2 | 8 YSZ | MoO_2, Mo_3Te_4, $MoTe_2(\alpha)$, Pt. (III)
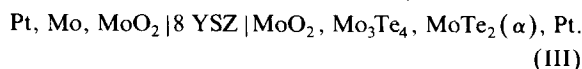
The emf of the galvanic cells (I) and (II) shown in figs. 1(a) and (b) and summarised in tables 1 and 2 could be represented by the following least-squares eqs. (1) and (2) which are valid over the ranges of 837 to 1151 K and 775 to 1196 K, respectively.

$$(E_I \pm 1.49) \quad (mV) = (120.58 \pm 3.1)$$
$$- (0.09966 \pm 0.0016)T(K), \quad (1)$$

$$(E_{II} \pm 1.60) \quad (mV) = -(55.61 \pm 3.2)$$
$$+ (0.08877 \pm 0.0017)T(K). \quad (2)$$

For the passage of four faradays of electricity, the reaction for the cell (I) could be represented as

$$Mo + 2'FeO' \rightleftharpoons MoO_2 + 2Fe. \quad (3)$$
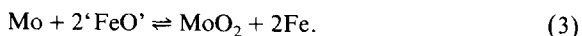
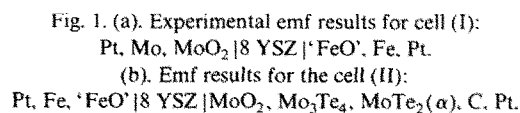For this reaction, the standard Gibbs energy change, $\Delta G_r^\circ(1)$ was calculated from eq. (1) to be

$$\Delta G_r^\circ(1) \pm 0.58 \quad (kJ/mol) = -46.54 + 0.03846T(K). \quad (4)$$

To derive the standard Gibbs energy of formation of $MoO_2(s)$, the following expression for the ΔG_f° of 'FeO', critically assessed by Giddings and Gordon [19] was made use of:

$$\Delta G_f^\circ('FeO') \pm 1.0 \quad (kJ/mol)$$
$$= -261.3 + 0.0633T(K)(835–1476 K). \quad (5)$$

Combining eqs. (4) and (5), one obtains the ΔG_f° of MoO_2.

$$\Delta G_f^\circ(MoO_2) \pm 2.58 \quad (kJ/mol)$$
$$= -569.14 + 0.16506T(K). \quad (6)$$

Fig. 1. (a). Experimental emf results for cell (I):
Pt, Mo, MoO_2 |8 YSZ| 'FeO', Fe, Pt.
(b). Emf results for the cell (II):
Pt, Fe, 'FeO' |8 YSZ| MoO_2, Mo_3Te_4, $MoTe_2(\alpha)$, C, Pt.

Many workers have reported $\Delta G_f^\circ (MoO_2)$ from solid oxide electrolyte emf studies in the temperature range of present interest [20–28]. However, there are variations in the choice of reference electrodes for use with Mo/MoO_2 electrode. Among the later publications, Kleykamp and Supawan [28] had made a critical comparison of the results on the ΔG_f° of MoO_2 from the earlier reports wherein mainly emf technique was employed. Hence, a comparison of the ΔG_f° of MoO_2 derived from eq. (1) is made here (fig. 2), with those reported by Kleykamp and Supawan [28] and Chatto-

padhyay et al. [26] who had employed Fe/'FeO' as the reference electrode. To avoid redundancy the earlier works reviewed by Kleykamp and Supawan are not included here. It is seen from fig. 2 that there is excellent agreement in the ΔG_f° of MoO_2 between the three works, the present one appearing as somewhat an average of the other two. The cross-over temperature for the reversal of the direction of the spontaneous reaction (3) (corresponding to zero emf of cell (I)) is found to be 1210 K from fig. 1(a) as compared to 1206 and 1248 K from the reports by Kleykamp and Supawan [28] and

Table 1
Experimental results for cell (I):
Pt, Mo, MoO_2 |8 YSZ| 'FeO', Fe, Pt,

where 8 YSZ denotes 8 mass% yttria-stabilized zirconia

Run	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)
1	836.6	37.91	901.6	32.53	965.0	24.18	1016.7	20.24
	995.0	21.76						
2	919.5	25.58	955.5	26.15	1029.5	19.85	1117.7	9.64
3	928.7	26.89	1059.7	17.09	1145.9	2.87	952.8	26.54
	1093.5	12.08						
4	991.6	23.24	1038.1	14.05	915.4	28.49	1085.9	12.74
	1121.7	10.13	1150.8	6.24				
5	1008.9	18.51	1056.7	16.25	968.4	23.17		
6	989.5	22.21	1019.1	20.39	1004.5	19.88	1033.6	16.27
	1063.8	14.41						

Table 2
Experimental emf results for cell (II):

Pt, Fe, 'FeO' |8 YSZ |MoO_2, Mo_3Te_4, $MoTe_2(\alpha)$, C, Pt

Run	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)
1	903.8	23.57	1115.1	46.35	986.7	34.07	1153.9	46.21
2	791.4	15.54	919.4	27.83	1096.3	44.26	1019.1	36.92
	1122.7	43.39	1168.7	47.48				
3	1062.3	37.91	888.4	23.68	955.8	28.58	1041.4	36.26
	1093.3	40.48	1138.2	44.70				
4	1053.0	35.88	1113.5	43.95	1196.0	50.38		
5	774.7	10.87	1054.6	35.49	1140.7	47.88	1076.6	39.89
	916.9	27.88						
6	1054.2	35.07	1170.8	49.62	1085.0	41.92	1107.9	41.75
7	1086.1	40.31	1068.9	37.47	1099.8	44.34	1183.6	47.85
	1071.4	38.30						

Chattopadhyay et al. [26], respectively, showing a better agreement between this work and that of Kleykamp and Supawan.

To eliminate the uncertainty due to the scatter in ΔG_f° of MoO_2 and to minimize the systematic errors if any in the galvanic cell results, the least-squares eqs. (1) and (2) were combined to give the following expression for E_{III} of cell (III):

$$(E_{III} \pm 3.09) \quad (\text{mV}) = 64.98 - 0.01089T(\text{K}). \tag{7}$$

This could be taken to be valid over the range 775 to 1196 K of cell (II). In order to check the internal consistency of the results from cells (I) and (II), cell (III) was actually assembled and measured at one particular temperature of 922.7 K, for about a day and was found to yield a value of 54.5 ± 1.0 mV. This is in good agreement with the value of 54.9 ± 3.1 mV calculated

from eq. (7). Since this cell was somewhat sluggish to equilibrate apart from considerable attack of both Pt electrodes by Mo (despite the use of graphite spacers) no attempt was made to measure the emf of cell (III) at higher temperatures. Hence, thermodynamic data for $Mo_3Te_4(s)$ was derived only by using eq. (7).

For the passage of four faradays of electricity through cell (III), the galvanic cell reaction could be written as

$$2MoTe_2(\alpha) + Mo(s) \rightleftharpoons Mo_3Te_4(s). \tag{8}$$
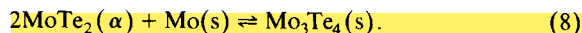
The ΔG_r° for reaction (8) could be written as

$$\Delta G_r^\circ(8) = -4FE_{III} = RT \ln a_{Mo}, \tag{9}$$

$$(\Delta G_r^\circ(8) \pm 1.19) \quad (\text{kJ/mol})$$

$$= -25.08 + 0.00420T(\text{K}), \tag{10}$$

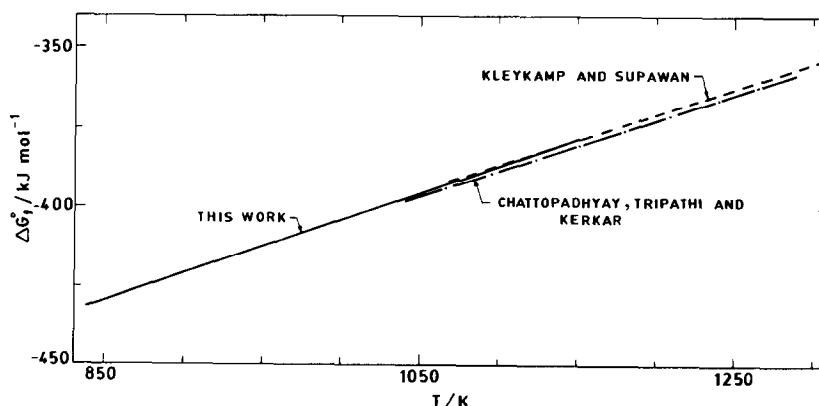where a_{Mo} is the activity of Mo in $Mo_3Te_4/MoTe_2(\alpha)$ assuming the stoichiometry of MoO_2 to be the same in

Fig. 2. Comparison of the standard Gibbs energy of formation of $MoO_2(s)$.

both the electrodes of cell (III). This assumption is justifiable in view of the cell temperature being lower than 1273 K; further for a difference of less than one order of magnitude in equilibrium oxygen pressure of the two MoO_2 bearing electrodes, the oxygen stoichiometry would vary only insignificantly at lower temperatures [29]. The $\Delta G_r^\circ(8)$ could be equated to the ΔG_f° terms as follows:

$$\Delta G_r^\circ(8) = \Delta G_f^\circ(Mo_3Te_4) - 2\Delta G_f^\circ(MoTe_2, \alpha). \quad (11)$$

Recently Mallika and Sreedharan [9] have reported the following expression for the ΔG_f° of $MoTe_2(\alpha)$ from their emf measurements over the range 728 to 1065 K:

$$\left(\Delta G_f^\circ(MoTe_2, \alpha) \pm 2.39\right) \quad (kJ/mol)$$

$$= -114.25 + 0.04397T(K). \quad (12)$$

The upper limit of temperature for eq. (12) was restricted by the detrimental effects of the higher tellurium pressures. However, measurements on cell (II) could be extended to 1196 K owing to lower tellurium activity of the $Mo_3Te_4/MoTe_2(\alpha)$ phase boundary. Krabbes and Oppermann [7] and Krabbes [8] had reported an α to β transition in $MoTe_2$ at about 1173 K attended by a standard enthalpy change of transition, ΔH_t° of about 4.8 kJ mol^{-1}. However, no discernable break could be observed in the emf curve for cell (II) in fig. 1(b) up to 1196 K within the limits of quoted precision. Hence, by combining eqs. (10) and (12) the following equation could be derived for the ΔG_f° of Mo_3Te_4 which is valid up to 1196 K:

$$\left(\Delta G_f^\circ(Mo_3Te_4) \pm 5.97\right) \quad (kJ/mol)$$

$$= -253.58 + 0.09214T(K). \quad (13)$$

Combining eqs. (12) and (13) the activity of tellurium for the following equilibrium between the tellurides could be derived:

$$Mo_3Te_4(s) + 2Te(g) \rightleftharpoons 3MoTe_2(\alpha), \quad (14)$$
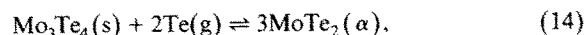
$$\Delta \bar{G}_{Te} = RT \ln a_{Te}$$

$$= \frac{3}{2}\Delta G_f^\circ(MoTe_2, \alpha) - \frac{1}{2}\Delta G_f^\circ(Mo_3Te_4), \quad (15)$$

$$\Delta \bar{G}_{Te}(kJ/mol) = -44.59 + 0.01989T(K). \quad (16)$$

Brooks [30] has reported the following expression for the total tellurium equilibrium pressure, $P_{Te(total)}^\circ$ for $Te(l)$ over the temperature range 919 to 1263 K:

$$\log P_{Te(total)}^\circ(atm) = 4.719 - 5960/T(K). \quad (17)$$

Combining eqs. (16) and (17), the log $P_{Te(total)}$ over the equilibrium mixture $Mo_3Te_4/MoTe_2$ was computed and is plotted in fig. 3. For a comparison, the expression

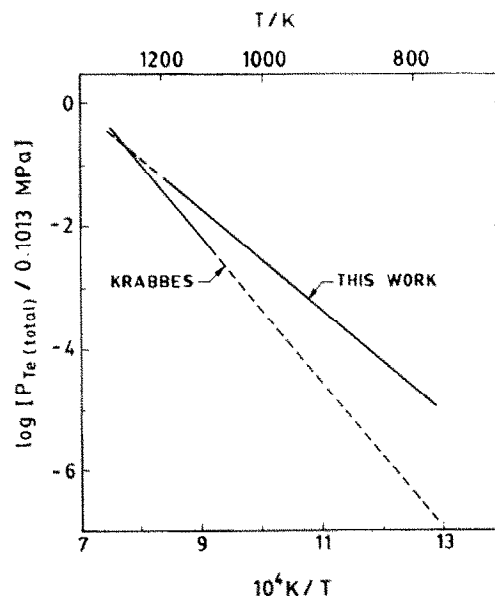$$\log\left(P_{Te_2}/10^5 \text{ Pa}\right) = 8.398 - 11790/T(K) \quad (18)$$

Fig. 3. Plot of the total equilibrium partial pressure of Te_2 over the mixture $Mo_3Te_4(s)-Te_2(g)-MoTe_2(\alpha)$ against reciprocal temperature.

by Krabbes [8] for the vapour pressure of tellurium (P_{Te_2}) over $Mo_3Te_4/MoTe_2(\beta)$ was combined with the ratio of $P_{Te_2}/P_{Te(total)}$ listed by Grønvold et al. [31] (as an approximation) to compute log $P_{Te(total)}$ which is also shown in the same figure. Apart from the difference in the slopes, the values of the vapour pressure are also lower than the ones estimated by the present study. Since emf data help to compute the equilibrium partial pressures more closely, the lower value of the vapour pressure of Te by Krabbes could be attributed to lack of attainment of true equilibrium in manometric measurements owing to the experimental difficulties associated with it. Further, the values of $P_{(Te_2)}/P_{(total)}$ given by Grønvold et al. are only for liquid tellurium. As the activity of Te is reduced, more dissociation of Te_2 into monomer might occur which should be taken into consideration for the calculation of $P_{(total)}$. In view of these two difficulties, the differences in the vapour pressures computed from the present emf studies and the manometric data by Krabbes [8] can be considered as tolerable.

To assess the extent of temperature dependent errors in the values of ΔG_f° of Mo_3Te_4, a third-law analysis of the emf data in fig. 1(b) was carried out at the actual temperatures of measurement. To facilitate this, the free-energy functions listed in table 3 were made use of. From the third-law plot in fig. 4, a value of $-209.0 \pm$

-195500-298*268 =-275 364J
while (13) gives -226 12228J
error of +-25kJ

Table 3

Values of free-energy functions used for computing ΔH_f° (Mo₃Te₄,s) at 298.15 K

Element/ compound	Free-energy function (J K⁻¹ mol⁻¹)			Ref.
	800 K	1000 K	1200 K	
Mo(s)	− 37.69	− 41.59	− 45.15	[4],[35]
Te(*l*)	− 62.17	− 71.38	− 78.88	[34–36]
Mo₃Te₄(s)	− 333.94	− 361.71	− 386.65	[4]

10.0 kJ mol⁻¹ could be derived for $\Delta H_{f,298}^\circ$ of Mo₃Te₄(s) which compares well with a value of − 195.5 ± 10.0 kJ mol⁻¹ reported by Krabbes [8] and − 211.5 ± 13.8 kJ mol⁻¹ reported by Viswanathan et al. [32] very recently by employing Knudsen cell mass spectrometry. O'Hare and Hope [33] have determined the standard enthalpy of formation of MoTe₂(β) at 298.15 K by fluorine-combustion calorimetry recently and combining it with the data from Krabbes [8] estimated a value of − 185 ± 10 kJ mol⁻¹ for $\Delta H_{f,298}^\circ$ of Mo₃Te₄(s). Since their estimate is based on Krabbes data and not a direct determination, the discrepancy between − 185 ± 10 kJ mol⁻¹ and the present value of − 209 ± 10 kJ mol⁻¹ could be ignored for the reasons stated earlier. Further, reliable heat capacity data even on liquid tellurium are not available in the literature. For instance, a constant value of 37.66 J K⁻¹ mol⁻¹ independent of temperature is given for the C_p of liquid tellurium by Hultgren et al. [34], Barin and Knacke [35] and Pankratz [36]. Likewise, the C_p data for Mo₃Te₄ and MoTe₂(α) are available only up to 344 K [5] which was extrapolated to 1600 K by Brewer et al. [4]. Therefore a critical analysis of the enthalpy and the entropy terms would be possible only if the relevant heat capacity data are generated over the desired range of temperature.

References

[1] P.A.G. O'Hare, Argonne National Laboratory, Illinois, USA, private communication.

[2] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.

[3] W.G. Moffatt, in: The Handbook of Binary Phase Diagrams, Vol. III (Genium, New York, 1986) p. 7/82.

[4] L. Brewer, R.H. Lamoreaux, R. Ferro, R. Marazza and K. Girgis, in: Molybdenum: Physico-Chemical Properties of its Compounds and Alloys, Special Issue No. 7, Chap. I, II, Ed. L. Brewer (International Atomic Energy Agency, Vienna, 1980).

[5] H.L. Kiwia and E.F. Westrum, Jr., J. Chem. Thermodyn. 7 (1975) 683.

[6] A.A. Opalovskii, V.E. Fedorov, E.U. Lobkov and B.I. Tsikanovskii, Zh. Fiz. Khim. 45 (1971) 1864.

[7] G. Krabbes and H. Oppermann, in: Problemi Kalorimetrii i Khimicheskoi Termodinamiki, Proc. of the Tenth All-Union Conference on Calorimetry and Chemical Thermodynamics (Akad. Nauk SSSR, Inst. Vys. Temp., Moscow, 1984) Vol. 2, pp. 32, 33.

[8] G. Krabbes, Z. Anorg. Allg. Chem. 543 (1986) 97.

[9] C. Mallika and O.M. Sreedharan, J. Chem. Thermodyn. 20 (1988) 769.

[10] P.A.G. O'Hare, J. Chem. Thermodyn. 19 (1987) 675.

[11] K.C. Mills, in: Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides (Butterworths, London, 1974) p. 438.
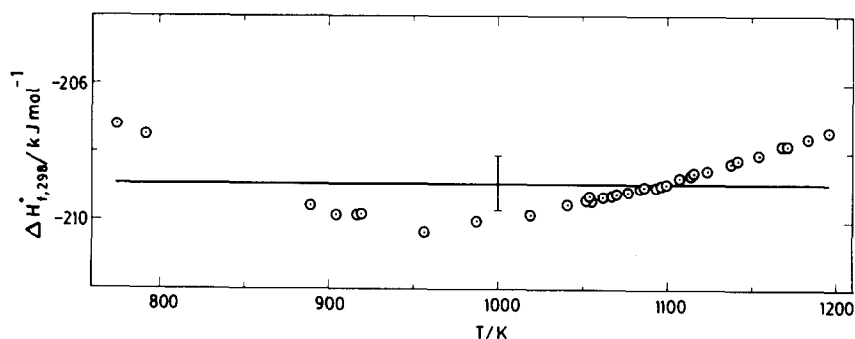

Fig. 4. The ΔH_f° (Mo₃Te₄, s) at 298.15 K determined by third-law computations from the Gibbs energy data.

[12] C. Mallika and O.M. Sreedharan, J. Chem. Thermodyn. 18 (1986) 727.

[13] N. Birks, Nature 210 (1966) 407.

[14] C. Mallika, R. Pankajavalli and O.M. Sreedharan, Electrochim. Acta 31 (1986) 885.

[15] E.S. Ramakrishnan, O.M. Sreedharan and M.S. Chandrasekharaiah, J. Electrochem. Soc. 122 (1975) 328.

[16] A.M. Azad and O.M. Sreedharan, J. Appl. Electrochem. 17 (1987) 949.

[17] A.M. Azad, O.M. Sreedharan and J.B. Gnanamoorthy, J. Nucl. Mater. 151 (1988) 293.

[18] O.M. Sreedharan, E. Athiappan, R. Pankajavalli and J.B. Gnanamoorthy, J. Less-Comm. Met. 68 (1979) 143.

[19] R.A. Giddings and R.S. Gordon, J. Am. Ceram. Soc. 56 (1973) 111.

[20] R.A. Rapp, Trans. Metall. Soc. AIME 227 (1963) 371.

[21] V.N. Drobyshev, T.N. Rezukhina and L.A. Tarasova, Zh. Fiz. Khim. 39 (1965) 70.

[22] E.J. McIver and S.S. Teale, AERE Report-4942 (1965).

[23] S. Berglund and P. Kierkegward, Acta Chem. Scand. 23 (1969) 329.

[24] W.A. Fischer and G. Pateisky, Arch. Eisenhüttenwe. 41 (1970) 661.

[25] I. Katayama and Z. Kozuka, Technol. Rep. Osaka Univ. 23 (1973) 411.

[26] G. Chattopadhyay, S.N. Tripathi and A.S. Kerkar, J. Am. Ceram. Soc. 67 (1984) 610.

[27] C.B. Alcock and J.C. Chan. Can. Met. Quarterly 11 (1972) 559.

[28] H. Kleykamp and A. Supawan, J. Less-Comm. Met. 63 (1979) 237.

[29] S. Zador, in: Electromotive Force Measurements in High-Temperature Systems, Ed. C.B. Alcock (The Institution of Mining and Metallurgy, London, 1968) p. 145.

[30] L.S. Brooks, J. Am. Chem. Soc. 74 (1952) 227.

[31] F. Grønvold, J. Drowart and E.F. Westrum, Jr., in: The Chemical Thermodynamics of Actinide Elements and Compounds, Part 4: The Actinide Chalcogenides (Excluding Oxides) (International Atomic Energy Agency, Vienna, 1984).

[32] R. Viswanathan, R. Balasubramanian and C.K. Mathews. J. Chem. Thermodyn., in press.

[33] P.A.G. O'Hare and G.A. Hope, J. Chem. Thermodyn. 21 (1989) 701.

[34] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, in: Selected Values of the Thermodynamic Properties of Elements (American Society for Metals, Metals Park, Ohio, 1973) p. 508.

[35] I. Barin and O. Knacke, in: Thermochemical Properties of Inorganic Substances (Springer-Verlag, Berlin, 1973) p. 736.

[36] L.B. Pankratz, in: Thermodynamic Properties of Elements and Oxides, Bulletin 672 (United States Department of the Interior Bureau of Mines, Washington, 1982) p. 414.