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Thermodynamic properties of tungsten ditelluride (WTe_2)

II. Standard molar enthalpy of formation at the temperature 298.15 K

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The standard molar enthalpies of formation of WTe_2(cr) and TeF_6(g) have been determined by combustion calorimetry in high-pressure fluorine: $\Delta_f H^\circ_m(WTe_2, cr, 298.15\ K) = -(38 \pm 5)\ kJ \cdot mol^{-1}$, and $\Delta_f H^\circ_m(TeF_6, g, 298.15\ K) = -(1380.7 \pm 1.3)\ kJ \cdot mol^{-1}$. Two high-temperature investigations of the vaporization of WTe_2 give derived enthalpies of formation that agree with this result, but which have rather large uncertainties that arise from estimated thermodynamic properties used in the calculations. The enthalpy of formation of TeF_6 replaces an earlier determination, now thought to be in error.

1. Introduction

This investigation represents the final part of an effort to determine accurate values for the standard molar enthalpies of formation $\Delta_f H^\circ_m$ of the dichalcogenides (excluding oxides) of molybdenum and tungsten by the technique of fluorine-combustion calorimetry. Similar previous studies have yielded enthalpies of formation at $T = 298.15$ K for MoS_2,(1) $MoSe_2$,(2) $MoTe_2$,(3) WS_2,(4) and WSe_2.(5)

Although practical applications of WTe_2 have been described in connection with a number of modern technologies including, for example, as a cathode component of photorechargeable batteries,(6) very little reliable information is available concerning its thermodynamic properties. In a review article (7) published about five years ago, we were able to list only two thermodynamic investigations of WTe_2. Since that time, Weir and Callanan(8) have measured the low-temperature heat capacity of the same sample of telluride used in the present study, and they also reported the usual derived thermodynamic properties to $T = 360$ K. Apart from that work, no other research on WTe_2 of a thermodynamic nature has been subsequently described in the literature.

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Previous fluorine-combustion calorimetric studies of the molybdenum and tungsten dichalcogenides were performed at Argonne National Laboratory. Those activities have since been terminated, but a new similar effort has been underway at the National Institute of Standards and Technology (NIST) since early 1990. This paper reports the first results of the NIST investigations.

The standard molar enthalpy of formation $\Delta_f H_m^\circ(\mathrm{WTe_2, cr, 298.15\ K})$ determined in the present study is based upon the standard molar energy of combustion at $T = 298.15$ K of WTe_2 in F_2 according to the reaction:

$$\mathrm{WTe_2(cr) + 9F_2(g) = WF_6(g) + 2TeF_6(g)}, \qquad (1)$$

combined with the standard molar enthalpies of formation at $T = 298.15$ K of $WF_6(g)$ and $TeF_6(g)$. Upon completion of the measurements of the energy of combustion of WTe_2, we found the calculated result for $\Delta_f H_m^\circ(\mathrm{WTe_2})$ to be surprisingly small when compared with similar values for the other Mo and W dichalcogenides. There were no apparent difficulties with the determination of the energy of combustion, and $\Delta_f H_m^\circ(\mathrm{WF_6})$ has been reported by several investigators(9 11) with concordant results. Therefore, it was suspected that our published value(12) for $\Delta_f H_m^\circ(\mathrm{TeF_6, g, 298.15\ K})$ might be in error. This suspicion has now been confirmed by our current measurements of the energy of combustion of Te in F_2, according to:

$$\mathrm{Te(cr) + 3F_2(g) = TeF_6(g)}. \qquad (2)$$

This new result, which is based on a combustion technique that is rather different, and better defined, than that used previously, is believed to be more reliable, and leads to a much more reasonable value for $\Delta_f H_m^\circ(\mathrm{WTe_2})$.

2. Experimental

Tungsten ditelluride was prepared at Griffith University by direct combination of stoichiometric amounts of the elements. Fine details of the method used have been given in reference 8. The tellurium was part of the same batch that had been used earlier(3) for the synthesis of $MoTe_2$. Powdered tungsten, of nominal purity 99.99 mass per cent, was purchased from Electronic Space Products, Inc.† This powder was heated to redness in a tungsten boat in a high vacuum in order to remove any oxide that might have been present. A two-stage crystal-growth technique was used: first, the elements were combined in a sealed tube; then the resulting crystals, still in the tube, were shaken vigorously and distributed along the tube bottom to grow the final sparkling crystalline product by vapor transport. The transport agent was 0.3 mass per cent of $TeCl_4$. The tube was broken under water, and approximately 20 g of crystals was gathered on a filter and dried in a desiccator. This material was sealed in a glass tube and shipped, by way of NIST, to R. D. Weir at the Royal Military College of Canada, Kingston, Canada.

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† Certain commercial equipment, instruments, or materials are identified to describe the experimental conditions completely, but in no way should this be construed as an endorsement by the National Institute of Standards and Technology.

Subsequent treatment of the WTe_2, including removal of about 80 mg of water by pumping in a high vacuum, as well as the measurement of the heat capacity, has been described by Weir and Callanan.(8) After completion of those measurements, the calorimetric specimen was returned to NIST for the fluorine-bomb experiments.

A portion of the WTe_2 was examined in a scanning tunnelling microscope; there was no evidence for the presence of an oxide layer on the surface of the material, nor was there any indication of adsorbed oxygen. The positions of the atoms fitted precisely the published(13) X-ray structure for the 001 plane.

In trial experiments, it soon became clear that, similar to $MoTe_2$,(3) neat WTe_2 did not react to completion in fluorine. It was necessary to use a tungsten saucer as an auxiliary combustion aid, in conjunction with a sulfur fuse, to bring about complete conversion of WTe_2 to WF_6 and $2TeF_6$ according to reaction (1). High-purity tungsten sheet, of thickness 0.025 mm, was purchased from Schwarzkopf Development and formed into saucers approximately 4 cm in diameter. The sulfur fuse was part of U.S. Bureau of Mines sample USBM-P1b. High-purity tellurium, taken from a fragmented zone-refined ingot (catalog no. 12607), was purchased from Johnson-Matthey (Aesar/Alfa).

Fluorine of 99.99 mass per cent purity, prepared at Argonne National Laboratory by distillation in a low-temperature still, was shipped in 0.25 kg masses to NIST.

As we have pointed out earlier in this paper, a new laboratory for fluorine-combustion calorimetry has been set up at NIST. It is quite similar to the previous arrangement at Argonne. A manifold for handling high-pressure fluorine was constructed from 316-stainless-steel lines and valves (Autoclave Engineers, Inc.) and was kept under vacuum with rotary oil pumps (Alcatel). Waste fluorine and gaseous fluorides were passed through a copper column filled with activated alumina spheres (Alcoa). The glovebox and associated purification unit were purchased from T. M. Vacuum Products, Inc. Both the oxygen and water compositions of the glovebox nitrogen atmosphere were continually monitored. Typically, mass fractions of $1 \cdot 10^{-6}$ and $5 \cdot 10^{-6}$ were observed for H_2O and O_2, respectively. All operations in which the combustion bomb was open were performed in the glovebox. Calorimetric specimens were also permanently stored there. An automatic electronic balance (Sartorius R160P), capable of weighing calorimetric samples with an accuracy of approximately $3 \cdot 10^{-5}$ g, had been installed in the glovebox. The (bomb + fluorine storage tank) reaction vessel, calorimeter (ANL-R-2), and quartz-crystal based temperature-measuring system were the same as those used in earlier work(3) at Argonne. The temperature of the calorimetric laboratory was maintained at approximately 293 K.

The calorimetric system was calibrated by combustion in oxygen of standard reference material NIST SRM 39i benzoic acid, which has a certified specific energy of combustion of $-(26434 \pm 3)\ \mathrm{J \cdot g^{-1}}$ under prescribed conditions. This value becomes $-26413\ \mathrm{J \cdot g^{-1}}$ under standard conditions at 298.15 K.

As with $MoTe_2$,(3) complete combustion of WTe_2 could be achieved only with the assistance of tungsten as an auxiliary substance. We have mentioned that there was reason to suspect an error in our earlier calorimetric study(12) of reaction (2). In the course of that investigation, we observed that tellurium, unlike its chemical analogs sulfur and selenium, did not combine readily, or completely, with high-pressure fluorine, and we therefore employed a disk of boron carbide B_4C as a thermal insulator to promote essentially complete reaction to TeF_6. Upon reconsideration of that work, we now believe that the most likely source of error was the correction used to allow for the combustion of approximately 1 mg masses of the B_4C sample support. Consequently, we decided upon tungsten as an auxiliary material for the present experiments with tellurium, and deliberately avoided the use of B_4C. It turns out, then, that essentially identical techniques were used for the experiments with WTe_2 and Te: the material to be reacted was placed on an approximately 0.7 g saucer made from tungsten sheet, a small quantity of sulfur was added as fuse, and the assemblage was placed on top of a 25.8 g prefluorinated nickel crucible whose sides were perforated with 0.5 cm holes (to allow rapid circulation of the fluorine around the sample as combustion proceeded) and which rested on the head of the bomb. A similar arrangement was used to determine the energy of combustion of tungsten, sulfur being used here also as a fuse. In order to improve the combustions of tellurium, a ≈ 6 g quartz disk was interposed between the crucible and the bomb head; the disk, almost completely protected from direct exposure to hot fluorine, did not react chemically to any significant extent.

The fluorine storage tank was charged ($T \approx 293$ K) to a pressure of 1000 kPa for the experiments with WTe_2 and to 1500 kPa for the experiments with Te and W. The prefluorinated (bomb + tank) assembly was placed in the water bucket of the calorimeter and, after completion of the fore-rating period, the tank valve was opened remotely. Upon entry of the fluorine into the bomb, the sulfur fuse ignited spontaneously, and that, in turn, initiated the reaction of the tungsten and the materials resting upon it.

Combustions proceeded as expected: of WTe_2 to WF_6 and $2TeF_6$, and of W to WF_6; no solids were observed in the crucible. However, after each combustion of Te a small, white-colored substance, $\approx 2\ \text{mm}^2$ in area and of approximate mass 1 mg, was found in the crucible; these residues were too small to recover for X-ray diffraction analysis and were assumed to consist of TeF_4. This assumption is based on previous experience with the combustion calorimetry of tellurium-containing compounds, and our experimental observations that, in the reaction vessel with initial fluorine pressures of approximately 1 MPa, lower fluorides of W do not form.

3. Results

Because the calorimeter has been relocated, the quartz-crystal thermometer reset, and other minor alterations made, detailed numerical particulars of the calibration experiments are set out in table 1. The standard deviation of ε(calor), $\pm 0.00005 \cdot \varepsilon$(calor), is similar to previous such results for this calorimetric system obtained at Argonne National Laboratory.

Details of the individual quantities used to derive the energies of combustion of tungsten, tungsten ditelluride, and tellurium are given in tables 2, 3, and 4. Many of the symbols are common to those tables and to table 1, and have been defined by Hubbard.(14) Masses of material placed in the bomb are denoted by *m*; they were

TABLE 1. Results for benzoic acid calibration of the calorimeter[a]

m'/g	1.00060	0.99962	0.99772	0.99970	0.99971	0.99994	1.00007	0.99990
m''/g	0.00277	0.00315	0.00345	0.00331	0.00308	0.00269	0.00285	0.00281
$\Delta\theta_{\mathrm{corr}}/\mathrm{K}$	0.01256	0.01050	0.01245	0.01743	0.01613	0.01381	0.01456	0.01246
$\{m'\Delta_c U_m/M\}/\mathrm{J}$	−26450.5	−26424.6	−26374.3	−26426.7	−26426.9	−26433.0	−26435.9	−26432.0
$\Delta U(\mathrm{fuse})/\mathrm{J}$	−47.8	−54.4	−59.6	−57.1	−53.2	−46.4	−49.2	−48.5
$\Delta U(\mathrm{cont})\mathrm{J}$	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9
$\Delta U(\mathrm{ign})/\mathrm{J}$	−0.5	−0.5	−0.5	−0.5	−0.5	−0.5	−0.5	−0.5
$\Delta\theta_c/\mathrm{K}$	1.90129	1.89961	1.89682	1.90008	1.89994	1.90014	1.90078	1.89964
$\varepsilon(\mathrm{calor})/(\mathrm{J \cdot K^{-1}})$	13917.9	13920.0	13916.7	13919.1	13918.2	13916.3	13914.7	13920.6

$\langle\varepsilon(\mathrm{calor})\rangle = (13917.9 \pm 0.7)\ \mathrm{J \cdot K^{-1}}$

[a] The symbols in the table have the following meanings: m' is the mass of benzoic acid; m'' is the mass of thread; θ^i, θ^f, and $\Delta\theta_{\mathrm{corr}}$ are the initial and final temperatures of the experiment and the correction to the observed temperature increase, respectively; $m'\Delta_c U_m/M$ is the energy of combustion of the benzoic acid sample; ΔU(fuse) is the energy of combustion of the thread; ΔU(cont) is the correction for the contents of the bomb (crucible, electrodes, water); ΔU(ign) is the contribution of the electrical ignition energy; $\Delta\theta_c = \theta^f - \theta^i - \Delta\theta_{\mathrm{corr}}$; and ε(calor) is the energy equivalent of the calorimetric system with an uncertainty given as the standard deviation of the mean.

TABLE 2. Energy of combustion of tungsten in fluorine ($T = 298.15$ K, $p^\circ = 101.325$ kPa)

$m(\mathrm{W})/\mathrm{g}$	1.16278	1.26812	1.18091	1.15353	1.16751	1.24741
$m(\mathrm{S})/\mathrm{g}$	0.00212	0.00253	0.00471	0.00133	0.00109	0.00107
$\Delta\theta_c/\mathrm{K}$	0.78880	0.86098	0.80791	0.77996	0.78872	0.84253
$\varepsilon(\mathrm{calor})(-\Delta\theta_c)/\mathrm{J}$	−10978.4	−11983.0	−11244.4	−10855.4	−10977.3	−11726.2
$\Delta U(\mathrm{S})/\mathrm{J}$	80·4	96·0	178.6	50.4	41.3	40.6
$\Delta U(\mathrm{cont})/\mathrm{J}$	−11.8	−12.9	−12.1	−11.7	−11.8	−12.6
$\Delta U(\mathrm{gas})/\mathrm{J}$	0.0	0.0	0.0	0.0	0.0	0.0
$\Delta U(\mathrm{blank})/\mathrm{J}$	−7.5	−7.5	−7.5	−7.5	−7.5	−7.5
$\{\Delta_c U^\circ_m/M(\mathrm{sample})\}/(\mathrm{J \cdot g^{-1}})$	−9389.0	−9389.8	−9387.2	−9383.5	−9383.5	−9384.0

$\langle\{\Delta_c U^\circ_m/M(\mathrm{sample})\}\rangle = -(9386.2 \pm 1.2)\ \mathrm{J \cdot g^{-1}}$

TABLE 3. Summary of combustion results for WTe_2 ($T = 298.15$ K, $p^\circ = 101.325$ kPa)

$m(\mathrm{WTe_2})/\mathrm{g}$	1.03766	1.01460	0.51312	0.50540	0.72988
$m(\mathrm{W})/\mathrm{g}$	0.80387	0.78757	0.69208	0.76782	0.76297
$m(\mathrm{S})/\mathrm{g}$	0·00317	0·00236	0·00371	0·00169	0·00181
$\Delta\theta_c/\mathrm{K}$	1.30245	1.27225	0.84878	0.88844	1.04791
$\varepsilon(\mathrm{calor})(-\Delta\theta_c)/\mathrm{J}$	−18127.4	−17707.0	−11813.2	−12365.2	−14584.7
$\Delta U(\mathrm{cont})/\mathrm{J}$	−18.3	−17.8	−10.1	−13.3	−15.8
$\Delta U(\mathrm{gas})/\mathrm{J}$	0.9	0.9	0.9	2.2	2.2
$\Delta U(\mathrm{blank})/\mathrm{J}$	6.7[a]	6.7[a]	6.7[a]	5.4[b]	5.4[b]
$\Delta U(\mathrm{W})/\mathrm{J}$	7545.3	7392.3	6496.0	7206.9	7161.4
$\Delta U(\mathrm{S})/\mathrm{J}$	120.3	89.5	140.8	64.1	68.7
$\{\Delta_c U^\circ_m/M(\mathrm{sample})\}/(\mathrm{J \cdot g^{-1}})$	−10092.4	−10088.1	−10093.0	−10090.8	−10087.7

$$\langle\{\Delta_c U^\circ_m/M(\mathrm{sample})\}\rangle = -(10090.4 \pm 1.1)\ \mathrm{J \cdot g^{-1}}$$
$$\Delta_c U^\circ_m(\mathrm{WTe_2}) = -(4430.2 \pm 1.1)\ \mathrm{kJ \cdot mol^{-1}}$$
$$\Delta_c H^\circ_m(\mathrm{WTe_2}) = -(4445.1 \pm 1.1)\ \mathrm{kJ \cdot mol^{-1}}$$

[a] Experiments performed with a tank pressure of 1000 kPa at $T \approx 293.5$ K.

[b] Experiments performed with a tank pressure of 1500 kPa at $T \approx 293.5$ K.

TABLE 4. Summary of combustion results for Te ($T = 298.15$ K, $p^\circ = 101.325$ kPa)

$m(\mathrm{Te})/\mathrm{g}$	0.61741	0.62720	0.61932	0.62723	0.56079
$m(\mathrm{W})/\mathrm{g}$	0.73296	0.82839	0.85586	0.71411	0.75797
$m(\mathrm{S})/\mathrm{g}$	0.00233	0.00166	0.00173	0.00067	0.00083
$\Delta\theta_c/\mathrm{K}$	0.97804	1.04815	1.06050	0.96822	0.94689
$\varepsilon(\mathrm{calor})(-\Delta\theta_c)/\mathrm{J}$	−13612.3	−14588.0	−14759.9	−13475.6	−13178.7
$\Delta U(\mathrm{cont})/\mathrm{J}$	−19.2	−20.6	−20.8	−19.0	−18.6
$\Delta U(\mathrm{gas})/\mathrm{J}$	2.2	2.3	2.2	2.2	2.3
$\Delta U(\mathrm{blank})/\mathrm{J}$	5.4	5.4	5.4	5.4	5.4
$\Delta U(\mathrm{W})/\mathrm{J}$	6879.7	7775.4	8033.3	6702.8	7114.5
$\Delta U(\mathrm{S})/\mathrm{J}$	88.4	63.0	65.6	25.4	31.5
$\Delta U(\mathrm{TeF_4})/\mathrm{J}$	−1.8	−2.5	−0.7	−2.9	−0.8
$\{\Delta_c U^\circ_m/M(\mathrm{sample})\}/(\mathrm{J\cdot g^{-1}})$	−10783.1	−10786.0	−10777.8	−10780.3	−10778.4

$$\langle\{\Delta_c U^\circ_m/M(\mathrm{sample})\}\rangle = -(10781.1 \pm 1.5)\ \mathrm{J\cdot g^{-1}}$$

$$\Delta_c U^\circ_m(\mathrm{Te}) = -(1375.7 \pm 0.6)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_c H^\circ_m(\mathrm{Te}) = \Delta_f H^\circ_m(\mathrm{TeF_6},\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -(1380.7 \pm 1.3)\ \mathrm{kJ\cdot mol^{-1}}$$

TABLE 5. Auxiliary quantities ($T = 298.15$ K) used in the calculations

	W	Te	$\mathrm{WTe_2}$	Ni	S	$\mathrm{SiO_2}$
$\rho/(\mathrm{g\cdot cm^{-3}})$	19.25[a]	6.23[a]	7.5[b]	8.9[a]	2.07[a]	2.66[a]
$c^\circ_p/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$	0.132[c]	0.202[d]	0.18[e]	0.443[c]	0.707[c]	0·742[c]
	$\mathrm{F_2}$	$\mathrm{WF_6}$	$\mathrm{TeF_6}$	$\mathrm{SF_6}$		
$C^\circ_{p,m}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	22.99[c]	119.03[c]	109.23[f]	88.66[c]		

[a] *Crystal Data Determinative Tables, 3rd Edition, Volume II: Inorganic Compounds*, Donnay, J. D. H.; Ondik, H. M.: editors. U.S. National Bureau of Standards and the Joint Committee on Powder Diffraction Standards, U.S.A., 1973.

[b] Reference 13. [c] Reference 28. [d] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, 11. Supplement no. 2.

[e] Reference 8. [f] Reference 20.

converted from apparent masses by means of the densities given in table 5. In table 1, ε(calor) applies to the *empty* bomb. Thus, ΔU(cont) in tables 2, 3, and 4 is a correction that allows for the contents of the bomb, such as sample supports, fluorine, and fluoride gases formed during the experiments; values of the heat capacities used to calculate ΔU(cont) are to be found in table 5. Hubbard(14) has also defined ΔU(gas) and described its calculation; for that purpose, we have used intermolecular-force constants from the literature for $\mathrm{F_2(g)}$,(15) $\mathrm{WF_6(g)}$,(16) and $\mathrm{TeF_6(g)}$;(17) the small amounts of $\mathrm{SF_6}$ present were ignored. The quantity ΔU(blank), measured in separate experiments by expansion of $\mathrm{F_2(g)}$ into an evacuated bomb, was calculated as outlined in an earlier publication.(18) Contributions to the overall measured energy of the reaction from the energy of combustion of tungsten and sulfur are denoted by ΔU(W) and ΔU(S), respectively; put simply, $\Delta U(\mathrm{W})/\mathrm{J} = -9386.2\cdot m(\mathrm{W})/\mathrm{g}$ (see table 2), and $\Delta U(\mathrm{S})/\mathrm{J} = -37944\cdot m(\mathrm{S})/\mathrm{g}$.(19) Finally, $\Delta U(\mathrm{TeF_4})$ is the correction for the (hypothetical) conversion of the $\mathrm{TeF_4}$ residue to $\mathrm{TeF_6}$; it is based on the standard molar enthalpy of formation of $\mathrm{TeF_4}$,(20) and is given by

$\Delta U(TeF_4)/J = -1.8 \cdot m(TeF_4)/mg$. For the conversion of specific energies of combustion to molar energies of combustion, we have used molar masses of $439.05\ g \cdot mol^{-1}$ for WTe_2 and $127.60\ g \cdot mol^{-1}$ for Te.

4. Discussion

The present result for $\Delta_f H_m^\circ(TeF_6, g, 298.15\ K)$, $-(1380.7 \pm 1.3)\ kJ \cdot mol^{-1}$, is given in table 4. It is $8.9\ kJ \cdot mol^{-1}$ more negative than the value of $-(1371.8 \pm 1.8)\ kJ \cdot mol^{-1}$ recommended by us in reference 3. Bousquet *et al.*(21) reported $\Delta_f H_m^\circ(TeF_6) = -(1381 \pm 25)\ kJ \cdot mol^{-1}$ which, because of the large uncertainty, agrees with both values. In our earlier study, a disk of B_4C was used to support the calorimetric specimens of tellurium in order to promote complete combustion. After each of six combustion experiments, it was observed that the mass of the disk had decreased (by between 2.12 mg and 0.69 mg). Consequently, the measured overall energy of each reaction was reduced, on the basis of the assumption that B_4C had reacted with fluorine to yield $4BF_3(g)$ and $CF_4(g)$. In retrospect, such an assumption might not have been valid. It is possible that the loss in mass of the disk could have been due, in part, to the evaporation of a volatile impurity or to the combustion of binders used to enhance the mechanical strength of the B_4C. Unfortunately, we are unable now to check the validity of those hypotheses. Nevertheless, because of the improved technique used for the present determination and the lack of ambiguity in the interpretation of the reaction products, we are confident that the new value for $\Delta_f H_m^\circ(TeF_6)$ is reliable.

The standard molar enthalpy of formation of WTe_2 was obtained from the enthalpy of reaction $\Delta_r H_m$ by means of the equation:

$$\Delta_f H_m^\circ(WTe_2, cr, 298.15\ K) = \Delta_f H_m^\circ(WF_6, g, 298.15\ K) + 2\Delta_f H_m^\circ(TeF_6, g, 298.15\ K) - \Delta_r H_m^\circ. \quad (3)$$

The $\Delta_f H_m^\circ$ values for WF_6 and TeF_6 were taken to be $-(1721.7 \pm 1.7)\ kJ \cdot mol^{-1}$,(9) and $-(1380.7 \pm 1.3)\ kJ \cdot mol^{-1}$, and $\Delta_r H_m^\circ$ is given in table 3. Thus, we calculate $\Delta_f H_m^\circ(WTe_2, cr, 298.15\ K) = -(38 \pm 5)\ kJ \cdot mol^{-1}$, for the formation reaction:

$$W(cr) + 2Te(cr) = WTe_2(cr). \quad (4)$$

There has been no previous direct determination of $\Delta_f H_m^\circ(WTe_2)$, but there have been two investigations from which this value may be estimated. Opalovskii *et al.*(22) used a quartz-membrane null manometer to measure the equilibrium vapor pressure of $Te_2(g)$ over WTe_2 in the temperature range 1080 K to 1162 K. No details were given of the method of calculation nor of the constants of the vapor-pressure equation. However, for the reaction:

$$W(s) + Te_2(g) = WTe_2(s), \quad (5)$$

Opalovskii *et al.* reported $\Delta_r H_m^\circ = -(196.6 \pm 2.1)\ kJ \cdot mol^{-1}$ which, we assume, may be applied to the approximate mean temperature of 1100 K. The enthalpy increments $\{H_m^\circ(T) - H_m^\circ(298.15\ K)\}$ are well established for W(s) and $Te_2(g)$, but there is no such information for WTe_2. We know from published results that enthalpy increments at the same temperature are approximately equal for the pairs of analogs MoS_2 and WS_2 ($\approx 59\ kJ \cdot mol^{-1}$)(23, 24) and $MoSe_2$ and WSe_2 ($\approx 65\ kJ \cdot mol^{-1}$).(24, 25) Equations are also available to represent the estimated heat capacities of $MoSe_2$ and $MoTe_2$. Brewer and Lamoreaux(26) obtained them by extrapolating the low-temperature heat-capacity results of Kiwia and Westrum;(27) integration of those equations gives polynomial expressions for the enthalpy values. Thus, for $MoSe_2$ at $T = 1100\ K$, the enthalpy increment is estimated to be $64\ kJ \cdot mol^{-1}$, close to the experimental result(24) of $64.9\ kJ \cdot mol^{-1}$. This good agreement gives us confidence that the estimated enthalpy increment for $MoTe_2$ at 1100 K, $66\ kJ \cdot mol^{-1}$, is probably also quite reasonable, and we assume that a value of $(65 \pm 3)\ kJ \cdot mol^{-1}$ for WTe_2, the other member of the pair, should not be seriously in error. Combination of this estimate with the enthalpy increments for W, $21.0\ kJ \cdot mol^{-1}$,(28) and $Te_2(g)$, $33.1\ kJ \cdot mol^{-1}$,(29) yields $\Delta\{H^\circ_m(1100\ K) - H^\circ_m(298.15\ K)\} = (11 \pm 3)\ kJ \cdot mol^{-1}$ for reaction (5). From $\Delta_r H^\circ_m(1100\ K)$ given earlier, and $\Delta_f H^\circ_m(Te_2, g, 298.15\ K) = (163.2 \pm 0.5)\ kJ \cdot mol^{-1}$,(29) we deduce $\Delta_f H^\circ_m(WTe_2, s, 298.15\ K) = -(44 \pm 4)\ kJ \cdot mol^{-1}$, which is in quite good agreement with the present determination.

The dissociation pressure of WTe_2 to $Te_2(g)$ as a function of temperature has also been measured by Obolonchik and Nesterovskaya.(30) They studied the decomposition of WTe_2 in a flowing stream of argon between 973 K and 1173 K and for the reaction:

$$WTe_2(cr) = W(cr) + Te_2(g), \tag{6}$$

gave the relation:

$$\lg(p/p^\circ) = -6503.3(K/T) + 4.67. \tag{7}$$

At $T = 1100\ K$, a convenient intermediate temperature, equation (7) implies $\Delta_r G^\circ_m(1100\ K) = 26.2\ kJ \cdot mol^{-1}$. At this point in the calculation, in the absence of high-temperature thermodynamic properties for WTe_2, the quantity $(\Delta_0^T S^\circ_m - \Delta_{T'}^T H^\circ_m/T)$, where $T' = 298.15\ K$, has to be estimated. An approximate value: $162.2\ J \cdot K^{-1} \cdot mol^{-1}$, is obtained for $MoTe_2$ from the Brewer and Lamoreaux(26) polynomial. We believe that the corresponding quantity for WTe_2 should be somewhat larger and accordingly estimate $(170 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}$. From the literature, we take values of $47.3\ J \cdot K^{-1} \cdot mol^{-1}$, and $281.4\ J \cdot K^{-1} \cdot mol^{-1}$, for W,(28) and $Te_2(g)$,(29) respectively. By means of a third-law calculation: $\Delta_r H^\circ_m(298.15\ K) = -(200.8 \pm 11)\ kJ \cdot mol^{-1}$ for reaction (6) and, thence, with $\Delta_f H^\circ_m(Te_2, g, 298.15\ K) = (163.2 \pm 0.5)\ kJ \cdot mol^{-1}$,(29) we obtain $\Delta_f H^\circ_m(WTe_2, cr, 298.15\ K) = -(38 \pm 11)\ kJ \cdot mol^{-1}$. This result, just as that deduced from the work of Opalovskii *et al.*,(22) agrees quite well with our present determination.

It is clear that the uncertainties in the enthalpy-of-formation values calculated from the high-temperature studies would be significantly reduced if precise experimental enthalpy increments were to become available for WTe_2. We hope to be in a position to provide such information in the very near future.

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