A fluorine-combustion calorimetric study of two molybdenum selenides: $MoSe_2$ and $Mo_6Se_6^a$

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Combustion calorimetric measurements of the energies of fluorination of molybdenum selenides have yielded the following standard molar enthalpies of formation at 298.15 K and $p^{-} = 101.325 \text{ kPa}$: $\Delta_{f} H_{m}^{\circ} (\text{MoSe}_{2}, \text{cr}) = -(234.2 \pm 3.3) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{f} H_{m}^{\circ} (\text{Mos}_{6}\text{Se}_{6}, \text{cr}) = -(477.8 \pm 10.0) \text{ kJ} \cdot \text{mol}^{-1}$. The dissociation enthalpy for the reaction: $\text{MoSe}_{2}(\text{cr}) = \text{Mo}(\text{cr}) + \text{Se}_{2}(\text{g})$, is $(378.3 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K. A brief discussion is included of the thermodynamics of dissociation of the molybdenum dichalcogenides.

1. Introduction

Molybdenum selenides, the best known of which is the diselenide (nominally $MoSe_2$), are increasingly being used in a number of high technologies, for example, as solid lubricants,⁽¹⁾ electrode materials,^(2,3) and in solar-energy conversion.^(4,5) The (molybdenum + selenium) phase behavior was explored by Spiesser *et al.*⁽⁶⁾ who reported that, up to 1473 K, only the diselenide was formed by heating the elements together in various proportions; the lower compositional limit of this phase was found to be $MoSe_{1.9}$. However, at 1523 K, a second phase was observed with limiting compositions of $MoSe_{1.45}$ and $MoSe_{1.27}$. Since that work was published, other molybdenum selenides, *e.g.* Mo_6Se_6 and $Mo_{15}Se_{19}$, have been synthesized, but not by direct combination of just molybdenum and selenium. These Chevrel phases are being explored^(3,7) as electrodes for secondary lithium batteries.

Few thermodynamic studies of (molybdenum + selenium) have been described.

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The molar heat capacities of Mo_6Se_8 below 30 K^(8,9) and of $MoSe_2$ to 350 K⁽¹⁰⁾ have been reported. Studies of the vaporization of the molybdenum diselenide phase have been described by Glazunov *et al.*⁽¹¹⁾ and by Viksman and Gordienko.⁽¹²⁾ Mills⁽¹³⁾ has estimated the standard molar enthalpy of formation $\Delta_f H_m^{\circ}$ and standard molar entropy S_m° of MoSe₂ at 298.15 K.

As an additional step toward firmly establishing the thermodynamic properties of the molybdenum selenides, the present research was undertaken to determine $\Delta_f H_m^\circ$ of MoSe₂ and Mo₆Se₆ at 298.15 K. As with recent studies of inorganic chalcogenides at this laboratory (see reference 14, for example), the experimental approach used fluorine-combustion calorimetric measurements on carefully characterized materials.

2. Experimental

Molybdenum diselenide, $MoSe_2$, a gift from Professor H. C. Gerischer, Fritz-Haber-Institut der Max-Planck-Gesellschaft, West Berlin, was synthesized by heating a mixture of molybdenum of 99.9 mass per cent purity and selenium of 99.9999 mass per cent purity in a sealed quartz ampoule at 873 K. The specimen consisted of shiny flakes and was shipped to Argonne in a sealed evacuated ampoule. Upon receipt, the ampoule was opened and the sample stored under a high-purity helium atmosphere. The following impurities (in mass per cent) were found: (0.078 ± 0.020) of O, (0.005 ± 0.002) of H, (0.005 ± 0.003) of N, (0.004 ± 0.001) of Fe, (0.003 ± 0.001) of Mg, and (0.030 ± 0.003) of Sn. Our specimen was also characterized by X-ray diffraction and energy-dispersive X-ray analysis. The diffraction pattern corresponded closely to that of the hexagonal form of MoSe₂ reported by James and Lavik.⁽¹⁵⁾

 Mo_6Se_6 was prepared at Bell Communications Research; the detailed synthesis has been described by Tarascon.⁽³⁾ Briefly, $In_2Mo_6Se_6$ was formed by direct combination of the elements in an evacuated silica tube at 1373 K and was then oxidized under a stream of HCl(g) at 693 K. By-product InCl₃ condensed on the colder part of the tube and Mo_6Se_6 remained:

$$In_2Mo_6Se_6(cr) + 6HCl(g) = Mo_6Se_6(cr) + 2InCl_3(cr) + 3H_2(g).$$
(1)

The reaction was complete after 24 h. The sample was shipped to Argonne in a sealed ampoule; it was opened, and the Mo_6Se_6 stored, in a helium-atmosphere glovebox. The X-ray powder pattern of Mo_6Se_6 has been reported by Tarascon.⁽³⁾ The following impurities (in mass per cent) were found: (0.050 ± 0.010) of Si, (0.010 ± 0.001) of Ca, (0.010 ± 0.001) of Fe, (0.005 ± 0.001) of Mg, (0.18 ± 0.01) of In, and (0.148 ± 0.007) of O. Both H and N were below the limits of detection (0.0005 mass per cent). Particular care was taken with the analysis for In: the result was determined by Zeeman graphite-furnace atomic-absorption spectrophotometry using both standard additions and direct calibrations. This value was confirmed by flame atomic-absorption spectrometry using an aliquot of the prepared sample. The specimen of Mo_6Se_6 was prepared for analysis by dissolution in 15 mol \cdot cm⁻³ HNO₃(aq) in a Carius tube.

Fluorine of ≥ 99.99 moles per cent purity was obtained by distillation of the commercial gas in a low-temperature still.⁽¹⁶⁾

In preliminary experiments, both $MoSe_2$ and Mo_6Se_6 were found to ignite spontaneously in high-pressure fluorine. Thus, the calorimetric measurements had to be performed in our (bomb + tank) reaction vessel in order to isolate the selenium compounds from F₂ until reaction was desired. The prototypes of the bomb calorimeter⁽¹⁷⁾ (laboratory designation ANL-R-2) and tank⁽¹⁸⁾ have been described previously. Satisfactory reactions with high-pressure F₂ ($p \approx 650$ kPa) were obtained when 0.5 g samples of selenide were supported on a 26.5 g nickel crucible which, in turn, rested on a thin 7 g nickel ring. This arrangement provided a modicum of thermal insulation which helped to raise the temperature of the crucible during the combustion and promote complete fluorination of the samples. The selenides reacted as follows:

$$MoSe_2(cr) + 9F_2(g) = MoF_6(g) + 2SeF_6(g),$$
 (2)

$$Mo_6Se_6(cr) + 36F_2(g) = 6MoF_6(g) + 6SeF_6(g).$$
 (3)

The sample masses chosen were such that no condensed-phase MoF_6 was formed in any of the experiments. Calorimetric temperatures were measured with a quartzcrystal thermometer (Hewlett-Packard Model 2804-A). The calorimetric system was calibrated by combustion in oxygen of National Bureau of Standards sample 39i of benzoic acid, and the energy equivalent obtained is given as footnotes in tables 1 and 2.

Calorimetric specimens were weighed in the nickel crucible which was then placed on the support ring and sealed in the bomb. (The crucible, ring, and bomb interior had all been prefluorinated by the combustion of several 1 g samples of selenium in fluorine.) The tank was charged to a pressure of 1.48 MPa of fluorine and attached to the bomb. All the above operations, apart from charging the tank, were performed in a helium-atmosphere glovebox. At no time during the experiments were the crucible or bomb interior exposed to the air.

Upon completion of each measurement, the excess fluorine and the gaseous fluorides were removed by pumping through an activated-Al₂O₃ trap, and the crucible and bomb interior were inspected. After Mo₆Se₆ combustions, the crucible invariably contained a fluffy residue, of mass usually < 1 mg, that could be dislodged by a gentle jet of He. This residue was analyzed by X-ray diffraction and energy-dispersive X-ray fluorescence and identified as InF₃ (major) with minor amounts of CaF2, FeF3, and MgF2. Traces of the same fluorides were found on the bomb walls and lid. After some MoSe₂ combustions, the crucible mass increased by 0.08 to 0.23 mg. Because this residue was too minute to be recovered for analysis, we were constrained to assume that it was composed of FeF_3 , MgF_2 , and SnF_4 from combustion of the metallic impurities. Of course, it could be argued that formation of NiF₂ caused the increase in mass. However, this possibility was dismissed because, as mentioned earlier, care was taken to prefluorinate the crucible thoroughly. For those combustions of MoSe₂ in which the mass of the crucible remained constant, it was assumed that the solid fluorides had been deposited exclusively outside the crucible, on the bomb walls and lid.

3. Results

Detailed calorimetric results for the combustion experiments are given in tables 1 and 2; the symbols in those tables have been used in our earlier publications. The blank correction, as explained previously,⁽¹⁹⁾ is assumed to account for the combined effect of endothermic expansion of F_2 and its exothermic reaction with recalcitrant traces of moisture adhering to the bomb walls and trapped in interstices. Standard-state corrections were calculated as detailed by Hubbard;⁽²⁰⁾ for the computation of $\Delta U(\text{gas})$, intermolecular-force constants for $F_2(g)$, $MoF_6(g)$, and $SeF_6(g)$ were taken from references 21, 22, and 23, respectively.

A rationalization of the disposition of the impurities in our samples is not

Expt no.	1	2	3	4	5	6	7	8
m(sample)/g	0.50877	0.51900	0.51462	0.51572	0.50960	0.52031	0.49680	0.50136
$\Delta \theta_{\rm c}/{\rm K}$	0.50962	0.51943	0.51560	0.51613	0.51091	0.52090	0.49806	0.50184
$\varepsilon(\text{calor})(-\Delta\theta_c)/J^a$	- 7089.0	-7225.5	-7172.2	-7179.6	-7107.0	-7245.9	-6928.2	-6982.3
$\Delta U(\text{contents})/J$	-9.3	-9.5	-9.4	-9.4	-9.4	-9.5	-9.1	-9.2
$\Delta U(\text{gas})/\text{J}$	-0.2	~0.2	-0.2	-0.2	-0.2	-0.2	-0.2	-0.2
$\Delta U(\text{blank})/J$	-4.6	~4.6	-4.6	-4.6	-4.6	-4.6	-4.6	-4.6
$\frac{\Delta_{\rm c} U_{\rm m}^{\circ}/M({\rm sample})}{{\rm J} \cdot {\rm g}^{-1}}$	- 13961.3	-13949.5	- 13964.5	-13949.0	- 13974.1	- 13953.6	-13973.6	-13954.6
		$\langle \Delta_{ m c} U_{ m m}^{ m o}/M$	(sample) > ≈		\pm 3.6) J · g ⁻	1 6		
		Impurity	correction ≈	$= -(3 \pm 9) J$	$\cdot g^{-1c}$			
	$\langle \Delta_{\rm c} U_{\rm m}^{\circ} / M({\rm MoSe}_2) \rangle = -(13963.0 \pm 12.0) {\rm J} \cdot {\rm g}^{-1} {\rm c}. d$							

TABLE 1. Energy of combustion of $MoSe_2$ (p = 101.325 kPa, T = 298.15 K)

^a ε (calor) = (13910.4±0.6) J · K⁻¹ except in experiment no. 8 for which ε (calor) = 13913.4 J · K⁻¹.

^b Uncertainty is the standard deviation of the mean.

^c Uncertainty corresponds to twice the standard deviation of the mean.

^d Uncertainty includes contributions from ε (calor), ΔU (blank), the impurity correction, and $\langle \Delta_c U_{\omega}^{*}/M(\text{sample}) \rangle$.

Expt no.	1	2	3	4	5		
m(sample)/g	0.51395	0.49250	0.51398	0.51271	0.51389		
$\Delta \theta_c/K$	0.54423	0.52158	0.54426	0.54288	0.54391		
$\varepsilon(\text{calor})(-\Delta\theta_c)/J^a$	-7570.5	-7255.4	7570.9	-7551.7	7566.0		
ΔU (contents)/J	- 10.0	-9.5	-10.0	-9.9	-10.0		
$\Delta U(\text{gas})/\text{J}$	-0.2	-0.2	-0.2	-0.2	-0.2		
$\Delta U(\text{blank})/J$	-3.3	-3.3	-3.3	-3.3	- 3.3		
$\{\Delta_{c} U_{m}^{\circ}/M(\text{sample})\}/(\mathbf{J}\cdot\mathbf{g}^{-1})$	-14756.3	- 14758.2	-14756.2	-14755.1	- 14749.3		
	$\langle \Delta_{\rm c} U_{\rm m}^{\circ} / M({ m sample})$	$ e\rangle\rangle = -(14755)$	$.0 \pm 1.5$) J · g ^{-1 i}	6			
Impurity correction = $-(32.0 \pm 7.0) \mathbf{J} \cdot \mathbf{g}^{-1} \cdot \mathbf{g}^{-1}$							
	$\langle \Delta_{\rm c} U_{\rm m}^{\circ} / M({ m Mo}_6{ m Se})$	$_{6})\rangle = -(14787)$	$.0 \pm 7.6$) J · g ⁻¹	z, d			

TABLE 2. Energy of combustion of Mo_6Se_6 ($p^{\circ} = 101.325$ kPa, T = 298.15 K)

^{*a*} ε (calor) = (13910.4 ± 0.6) J · K⁻¹.

^b Uncertainty is the standard deviation of the mean.

^c Uncertainty corresponds to twice the standard deviation of the mean.

^d Uncertainty includes contributions from ϵ (calor), ΔU (blank), the impurity correction, and $\langle \Delta_c U_m^{\circ}/M(\text{sample}) \rangle$.

uncomplicated. The nature of the selenides themselves introduces the possibility of intercalated as well as chemically-bound impurities involving hydrogen, nitrogen, and oxygen. However, we believe that the metallic impurities can safely be assumed to have been present as selenides which reacted to give $SeF_6(g)$ and the most stable metallic fluorides.

IMPURITY CORRECTION FOR MoSe₂

The metallic impurities in our MoSe₂ were Fe, Mg, and Sn: the $\Delta_{\rm f} H_{\rm m}^{\circ}$ values for FeSe, MgSe, and SnSe have been taken from Mills's⁽¹³⁾ compilation and for FeF₃, MgF₂, SnF₄, and SeF₆(g) from references 24, 25, 26, and 14, respectively. Thus, that part of the impurity correction due to the metals was calculated to be $-(0.7\pm0.2) \, \rm J \cdot g^{-1}$.

Our first assumption regarding hydrogen, nitrogen, and oxygen was that they were present in their entirety as intercalated $H_2(g)$, $O_2(g)$, and $N_2(g)$; that the energy of intercalation was negligible; that O_2 and N_2 did not react with $F_2(g)$; and that the H_2 produced 2HF(g). The standard molar enthalpy (and, therefore, energy) of combustion of $H_2(g)$ was taken to be $-(273.3\pm0.7)$ kJ·mol⁻¹,⁽²⁵⁾ and the total correction, including metals, was calculated to be (0.6 ± 6.0) J·g⁻¹.

Our second assumption was that hydrogen was present entirely as intercalated $H_2O(g)$ and that the remaining oxygen and nitrogen were intercalated as $O_2(g)$ and $N_2(g)$, the energy of intercalation again being taken as negligible. The specific energy of combustion of $H_2O(g)$ to $\{2HF(g) + \frac{1}{2}O_2(g)\}$ is $-(16986 \pm 78) \text{ J} \cdot \text{g}^{-1}$, on the basis of literature $\Delta_f H_m^{\circ}$ values⁽²⁵⁾ for $H_2O(g)$ and HF(g). The total impurity correction calculated in this way was $-(5.3 \pm 1.5) \text{ J} \cdot \text{g}^{-1}$.

The third method used to calculate the impurity correction had as its basis the assumption that one-half of the oxygen was present as MoO_2 which reacted to give $MoF_6(g)$ and $O_2(g)$, the other half as SeO_2 which reacted to give $MoF_6(g)$ and $O_2(g)$, and that N_2 and H_2 were intercalated. Taking $\Delta_f H_m^\circ$ values from the literature⁽²⁷⁾ for MoO_2 and SeO_2 , the total impurity correction was calculated to be $-(5.8 \pm 6.1) \, J \cdot g^{-1}$.

In order to encompass the three values and their uncertainties, we estimate the impurity correction for $MoSe_2$ to be $-(3\pm9) J \cdot g^{-1}$.

IMPURITY CORRECTION FOR Mo₆Se₆

Corrections for impurities in Mo_6Se_6 were somewhat more easily made because of the absence of hydrogen and nitrogen. Part of the oxygen impurity was known to be present as SiO₂ which had been detached from the quartz tube during the synthesis. Emission spectrochemical analysis revealed (0.05 ± 0.01) mass per cent of Si, which corresponded to 0.057 mass per cent of O combined as SiO₂. The other metallic impurities were assumed to be present as CaSe, FeSe, MgSe, and In₂Se₃. Of course, In was almost certainly combined as In₂Mo₆Se₆, but there is no $\Delta_f H_m^\circ$ value for this compound; for calculations of the impurity correction, however, we believe our assumption introduces little error. The $\Delta_f H_m^\circ$ values for the binary selenides were taken from Mills⁽¹³⁾ and from other literature sources for SiO₂,⁽²⁵⁾ SiF₄,⁽²⁸⁾ CaF_{2} ,⁽²⁷⁾ FeF₃,⁽²⁴⁾ MgF₂,⁽²⁵⁾ InF₃,⁽²⁹⁾ and SeF₆.⁽¹⁴⁾ The contribution of the trace metals to the impurity correction was $-(13.7\pm1.2) J \cdot g^{-1}$.

The correction for that part of the oxygen not combined as SiO₂, 0.091 mass per cent, was calculated in two ways. One approach assumed it to be present as intercalated O₂ and gave an impurity correction of $-(13.4\pm1.0)$ J \cdot g⁻¹; the other assumed 0.0455 mass per cent of oxygen to be combined as MoO₂ and an equal amount as SeO₂ and gave an impurity correction of $-(23.7\pm2.0)$ J \cdot g⁻¹. A mean of those two values, $-(18.6 \pm 7.0) \, \mathrm{J} \cdot \mathrm{g}^{-1}$, was taken and, thus, the total impurity correction, including that for the metals, was $-(32\pm7) J \cdot g^{-1}$.

4. Discussion

A summary of the thermodynamic values for MoSe₂ and Mo₆Se₆ is given in table 3. There have been no previous thermochemical studies of Mo_6Se_6 , and our $\Delta_{\rm f} H_{\rm m}^{\circ}$ results at 298.15 K, $-(234.2\pm3.3) \,\rm kJ\cdot mol^{-1}$ for MoSe₂ and $-(477.8 \pm 10.0) \text{ kJ} \cdot \text{mol}^{-1}$ for Mo₆Se₆, are the first direct determinations to appear in the literature. Mills's⁽¹³⁾ estimate, $\Delta_{f} H_{m}^{\circ}(MoSe_{2}) = -(197 \pm 42) \text{ kJ} \cdot \text{mol}^{-1}$, overlaps the present result.

Of the four molybdenum dichalcogenides $MoCh_2$ (Ch = O, S, Se, Te), only the oxide is known to vaporize to the gaseous triatomic molecule MoO₂(g). Therefore, we are unable, with the exception of the oxide, to calculate $\langle D_m^{\circ} \rangle$ for dissociation of $MoCh_2(g)$ to Mo(g) and 2Ch(g), and instead base our calculations on the reaction:

$$MoCh_2(cr) = Mo(cr) + Ch_2(g),$$
(4)

 -24.0 ± 0.9 °

 -3 ± 20^{f}

 -227.0 ± 3.3

 -477 ± 12

which is known to take place at elevated temperatures.

In the case of Ch = O, $\Delta_r H_m^\circ$ of reaction (4) is simply $-\Delta_f H_m^\circ(MoO_2, cr)$ $= (589 \pm 3) \text{ kJ} \cdot \text{mol}^{-1}.^{(27)}$

Our earlier result⁽³¹⁾ for $\Delta_f H^{\circ}_m(MoS_2, cr. 298.15 \text{ K})$ is revised to $-(276.5 \pm 4.9)$ kJ·mol⁻¹ because of recent small changes in $\Delta_f H_m^{\circ}(SF_6, g)^{(19)}$ and the relative atomic masses of the elements; this value, combined with $\Delta_{\rm f} H_{\rm m}^{\circ}(S_2, {\rm g}, 298.15 {\rm K}) =$

 $\Delta_{\rm c} U_{\rm m}^{\rm o} = b$ $\Delta_{\rm c} H_{\rm m}^{\circ} = {}^{b}$ c,d $\Delta_{\rm f} H_{\rm m}^{\rm o}$ $\Delta_f S_m^{\circ}$ $\Delta_{\rm f} G_{\rm m}^{\rm c}$ $kJ \cdot mol^{-1}$ $J \cdot K^{-1} \cdot mol^{-1}$ kJ · mol^{−1} $kJ \cdot mol^{-1}$ $kJ \cdot mol^{-1}$

 -234.2 ± 3.3

 -477.8 ± 10.0

 -3559.5 ± 3.0

TABLE 3.	Molar	thermod	ynamic	quantities	for 1	MoSe ₂	and	Mo ₆ Se ₆
	1	(T = 298)	15 K, p	$^{\circ} = 101.323$	5 kPa	a)"		

^a Molar masses of MoSe ₂	and Mo ₆ Se ₆ taken to be	253.86 and 1049.4 g	$(\cdot mol^{-1}, respectively; s)$	pecific
energies of combustion from	tables 1 and 2.	-		•

^b For reactions (2) or (3).

MoSe₂(cr)

 $Mo_6Se_6(cr)$

^c For the formation of the compounds from Mo(cr) and Se(cr).

 $-15517.5 \pm 7.9 - 15577.0 \pm 7.9$

 -3544.6 ± 3.0

 ${}^{d}\Delta_{f}H_{m}^{*}$ calculated from $\Delta_{f}H_{m}^{*}(MoF_{6}, g, 298.15 \text{ K}) = -(1557.9 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1(30)}$ and $\Delta_{f}H_{m}^{*}(SeF_{6}, g, 298.15 \text{ K}) = -(1117.9 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}(^{14)}$ ${}^{c}\Delta_{f}S_{m}^{*}$ calculated from values of $S_{m}^{*}/(J \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$ of (28.57 ± 0.2) for Mo, (42.26 ± 0.42) for Se, and

(89.08 ±0.18) for MoSe₂ from references 29, 13, and 10, respectively. ${}^{f}\Delta_{f}S_{m}^{\circ}$ calculated from an estimated S_{m}° of (422 ± 20) J·K⁻¹·mol⁻¹ for Mo₆Se₆ and S_{m}° for Mo and Se

given in footnote e.

 $(128.5 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1},^{(25)} \text{ yields } \Delta_r H_m^{\circ} = (405.0 \pm 4.9) \text{ kJ} \cdot \text{mol}^{-1} \text{ for reaction (4)}$ with Ch = S.

The high-temperature dissociation of $MoSe_2$ has been investigated by Glazunov *et al.*⁽¹¹⁾ and, more recently, by Viksman and Gordienko.⁽¹²⁾ The former authors studied the evaporation of $MoSe_2$ from an effusion cell and deduced $\Delta_{vap}H_m^{\circ} = 213 \text{ kJ} \cdot \text{mol}^{-1}$, which they attributed to the reaction:

$$MoSe_2(cr) = Mo(cr) + Se_2(g).$$
(5)

Viksman and Gordienko observed mass spectrometrically the dissociation of hypostoichiometric diselenide:

$$MoSe_{1.92}(cr) = Mo(cr) + 0.96Se_2(g),$$
 (6)

and reported $\Delta_r H_m^{\circ} = (378.1 \pm 25) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K. Our result for $\Delta_f H_m^{\circ}(\text{MoSe}_2)$, combined with $\Delta_f H_m^{\circ}(\text{Se}_2, g) = (144.1 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1},^{(32)}$ gives $\Delta_r H_m^{\circ} = (378.3 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (5). This enthalpy of vaporization is very different from that given by Glazunov *et al.*, but probably agrees with Viksman and Gordienko's determination, since the effect of nonstoichiometry on their value is likely to lie within the quoted $\pm 25 \text{ kJ} \cdot \text{mol}^{-1}$ uncertainty.

Only two recent studies with a bearing on $\Delta_f H^{\circ}_m(MoTe_2)$ have been found in the literature. Krabbes and Oppermann⁽³³⁾ determined the vapor pressure at 1100 and 1330 K of Te₂(g) over Mo₃Te₄, MoTe₂, and mixtures of those tellurides with one another and with the elements. For MoTe₂(cr), they reported $\Delta_f H^{\circ}_m = -91.1 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K; using that result and $\Delta_f H^{\circ}_m(Te_2, g) = (163.2 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$,⁽³²⁾ we deduce $\Delta_r H^{\circ}_m = (254.3 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (4) with Ch = Te. The other study, by Opalovskii *et al.*,⁽³⁴⁾ does not yield $\Delta_f H^{\circ}_m(MoTe_2)$ uniquely, but gives, instead, $\Delta_r H^{\circ}_m = -55.2 \text{ kJ} \cdot \text{mol}^{-1}$ for the reaction:

$$Mo_3Te_4(cr) + Te_2(g) = 3MoTe_2(cr).$$
 (7)

There is an enormous difference between that value and the $-243.5 \text{ kJ} \cdot \text{mol}^{-1}$ which may be deduced from the Krabbes and Opperman study. We have been unable to procure complete manuscripts of the work described in references 33 and 34, and are therefore not in a position to suggest possible reasons for the discrepancy. However, Krabbes and Oppermann derived $S_m^{\circ}(MoTe_2) = 115.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, at 298.15 K, very close to Kiwia and Westrum's⁽¹⁰⁾ $115.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ determination of by low-temperature calorimetry, and this agreement suggests that the work of Opalovskii et al. may be seriously in error.

As expected, the enthalpy changes for reaction (4) are in the sequence O > S > Se > Te. That the value for Ch = O is very much larger than the others is due to the significant ionic character of the Mo–O bonds; the largely covalent bonds in MoS₂, MoSe₂, and MoTe₂ decrease monotonically in strength, in parallel with the Mo–Ch interatomic separations.^(15, 35, 36)

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Note added in proof

Just recently, the work reported by Viksman and Gordienko⁽¹²⁾ has been published⁽³⁷⁾ in greater detail and in somewhat revised form. The enthalpy of dissociation at 298.15 K of $MoSe_{1.91}$ to Mo and $0.955Se_2(g)$ is given as $(404.4 \pm 30.0) \text{ kJ} \cdot \text{mol}^{-1}$, which agrees with our value of $(378.3 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$ for the dissociation of $MoSe_2$ to Mo and $Se_2(g)$.

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