

Inorganic chalcogenides: high-tech materials, low-tech thermodynamics

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1. Introduction

At a three-day symposium of the American Chemical Society held in Chicago in late 1985,⁽¹⁾ speakers told of a multitude of newly synthesized inorganic materials. An entire recent issue⁽²⁾ of *Scientific American* was devoted to advanced materials, with emphasis on their use in new technologies and their impact on the economy of the United States. These two examples illustrate the importance that has now been assumed in science and industry by the so-called "high-tech" materials. Largely ignored, or unappreciated to date, apparently, are the thermodynamic properties of such compounds, both new and well known, and how they can be used advantageously, for example, to predict chemical behavior at extremes of temperature and pressure or in aggressive surroundings, or to design efficient methods of synthesis. That the relevant basic thermodynamic information has, in general, not been determined or, if it has, is still in many instances not known with any degree of reliability, should, therefore, not be surprising. Thus, the title of my lecture was chosen so as to have a rather pejorative flavor.

For a number of years, our group at Argonne National Laboratory has been using fluorine-combustion calorimetry to determine standard molar enthalpies of formation $\Delta_f H_m^\circ$ of high-temperature and refractory materials. In the past few years, our studies have tended to concentrate on chalcogenides—compounds of metals and non-metals with S, Se, or Te, many of which are important in the new technologies. It is therefore not surprising that our interests have intersected with the field of

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"high-tech" materials. The chalcogenides among those materials have many applications, including the following:

- tribology (high-temperature lubricants)
- semiconductors, thin films, glasses, photoresists, photomicrography (electronics)
- intercalation of alkali and other metals (battery technology)
- catalysis (dehydrosulfurization)
- solar-energy conversion
- manufacture of ceramics (Si_3N_4 , for example)
- extractive metallurgy (desulfurization as practiced in the steel industry)
- corrosion in sulfur-containing atmospheres (e.g. H_2S).

In a recent publication⁽³⁾ from this laboratory, an up-to-date list was given of the chalcogenides we have studied by fluorine-combustion calorimetry. Perusal of the corresponding papers shows that this technique is uniquely suited to the determination of $\Delta_f H_m^\circ$ of chalcogenides and why, in general, it yields results superior to other methods.

When I was informed that the Calorimetry Conference had selected me as the Huffman Award winner for 1986, it occurred to me that a useful purpose might be served by discussing in my award address some of the unsatisfactory thermodynamic properties available for a number of the technologically interesting chalcogenides and, in that way, perhaps, inspire some of the attendees and other thermodynamicists to provide more accurate and reliable results. As I searched the literature, it soon became apparent that, in order to keep my talk to a bearable length, I should have to pick and choose carefully the compounds to be discussed and also restrict the thermodynamic properties to just one, $\Delta_f H_m^\circ$ at 298.15 K.

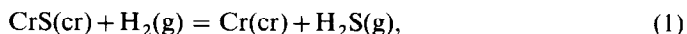
The material to be presented in this talk is based on a computer search of *Chemical Abstracts* up to July 1986 (in certain instances, more recent information has been added) and will embrace the solid chalcogenides of Cr, Mo, W, Si, and Ge.

2. (Chromium + sulfur)

CHROMIUM MONOSULFIDE

Several compounds of chromium with sulfur have been identified by Jellinek⁽⁴⁾ and others and listed and reviewed by Rau.⁽⁵⁾ There is strong evidence for the existence of CrS , Cr_7S_8 , Cr_5S_6 , Cr_3S_4 , and two modifications of Cr_2S_3 . Notwithstanding the great technological importance of (chromium + sulfur), particularly in connection with the sulfidation of (nickel + chromium) alloys, the quantity of thermodynamic information on chromium sulfides is very sparse indeed.

The earliest work, a high-temperature study of the reaction:

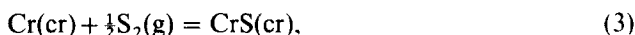


was reported by Hager and Elliott⁽⁶⁾ who found, for reaction (1) between 1375 and

1570 K,

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 112.1 - 6.7 \times 10^{-3} (T/\text{K}). \quad (2)$$

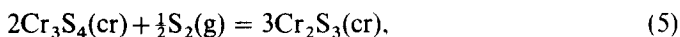
Young *et al.*⁽⁷⁾ measured directly, at one temperature only (973 K), the equilibrium $\text{S}_2(\text{g})$ pressure necessary to form a particular chromium sulfide. For the formation of CrS ,



they deduced $\Delta_r G_m^\circ = -(140 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$, which just overlaps the result of $-(148 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$ obtained by extrapolating equation (1) and combining it with $\Delta_r G_m^\circ$ for the reaction:⁽⁸⁾



Igaki *et al.*⁽⁹⁾ reported equilibrium $\text{S}_2(\text{g})$ pressures over a variety of chromium sulfides. For the sulfidation of Cr_3S_4 :



they gave the expression ($1270 \text{ K} < T < 1370 \text{ K}$):

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = -246.9 + 0.162(T/\text{K}). \quad (6)$$

At 973 K, $\Delta_r G_m^\circ = -89 \text{ kJ} \cdot \text{mol}^{-1}$; for the same reaction and temperature, Young *et al.* gave $-(77 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$. Once again, the agreement is not very good.

We believe that equation (2) represents the most reliable thermodynamic values on CrS to date and use $\Phi_m^\circ(T, T')$ for CrS ,⁽¹⁰⁾ H_2 ,⁽¹¹⁾ Cr ,⁽¹¹⁾ and H_2S ⁽¹¹⁾ to deduce by means of a third-law calculation, $\Delta_r H_m^\circ(\text{CrS, cr, } 298.15 \text{ K}) = -(154 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$.† Mills⁽¹⁰⁾ performed a second-law analysis of the same results and recommended $\Delta_r H_m^\circ(\text{CrS, cr, } 298.15 \text{ K}) = -(145 \pm 17) \text{ kJ} \cdot \text{mol}^{-1}$. The true result is probably in the vicinity of $-(150 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$. A redetermination of this value is clearly needed in order to reduce the large uncertainty.

3. (Molybdenum + sulfur)

MOLYBDENUM DISULFIDE

Unlike the chromium sulfides, there is a relatively large amount of thermodynamic information available for MoS_2 , less for Mo_2S_3 , and almost none at all for the other molybdenum sulfides.

The various investigations leading to $\Delta_r H_m^\circ(\text{MoS}_2)$ have been summarized in table 1. Historically, Parravano and Malquori⁽¹²⁾ appear to have been the first investigators to study this system. They measured the amounts of H_2S in a stream of H_2 that had been passed over (molybdenum + molybdenum disulfide) at 1078 to 1373 K. They believed that reduction almost certainly had proceeded to Mo :

† Throughout this paper, $\Phi_m^\circ(T, T') \stackrel{\text{def}}{=} \{\Delta_0^T S_m^\circ(T) - \Delta_T^T H_m^\circ(T)/T\}$, $\Delta_T^T H_m^\circ(T) = \{H_m^\circ(T) - H_m^\circ(T')\}$, $R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and $T' = 298.15 \text{ K}$. When the temperature for $\Delta_r H_m^\circ$ or $\Delta_r G_m^\circ$ is not specified, it is to be taken as 298.15 K.

TABLE 1. Reactions and $\Delta_r G_m^\circ(T)$ values that lead to $\Delta_r H_m^\circ(\text{MoS}_2, \text{cr}, 298.15 \text{ K})$, $p = 101.325 \text{ kPa}$

| | $\Delta_r G_m^\circ(\langle T \rangle)$ $\text{kJ} \cdot \text{mol}^{-1}$ | $\Delta_r H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ |
|--|--|---|
| 1. $\text{Mo}(\text{cr}) + 2\text{H}_2\text{S}(\text{g}) = \text{MoS}_2(\text{cr}) + 2\text{H}_2(\text{g})^a$ | -159 ± 10 | -235 ± 10 |
| 2. $\text{MoS}_2(\text{cr}) + 3\text{O}_2(\text{g}) = \text{MoO}_3(\text{cr}) + 2\text{SO}_2(\text{g})^b$ | -741.2 ± 1.2 | -275.3 ± 3.0 |
| 3. $\frac{2}{3}\text{Mo}(\text{cr}) + \text{H}_2\text{S}(\text{g}) = \frac{1}{3}\text{Mo}_2\text{S}_3(\text{cr}) + \text{H}_2(\text{g})^c$ | -54.2 ± 2.0 | |
| 4. $\text{Mo}_2\text{S}_3 + \text{H}_2\text{S}(\text{g}) = 2\text{MoS}_2(\text{cr}) + \text{H}_2(\text{g})^d$ | -42.2 ± 2.0 | -272.5 ± 5.9 |
| 5. $\text{MoS}_2(\text{cr}) + 3\text{O}_2(\text{g}) = \text{MoO}_3(\text{cr}) + 2\text{SO}_2(\text{g})^e$ | | -278.1 ± 3.0^e |
| 6. $\frac{4}{3}\text{Mo}(\text{cr}) + 2\text{H}_2\text{S}(\text{g}) = \frac{2}{3}\text{Mo}_2\text{S}_3(\text{cr}) + 2\text{H}_2(\text{g})^{f,g}$ | -125.2 ± 2.0 | |
| 7. $2\text{Mo}_2\text{S}_3(\text{cr}) + 2\text{H}_2\text{S}(\text{g}) = 4\text{MoS}_2(\text{cr}) + 2\text{H}_2(\text{g})^{f,h}$ | -124.1 ± 2.0 | -269.5 ± 2.8 |
| 8. $\text{MoS}_2(\text{cr}) + 9\text{F}_2(\text{g}) = \text{MoF}_6(\text{g}) + 2\text{SF}_6(\text{g})^i$ | | -276.5 ± 4.9 |

^a Makolkin;⁽¹⁵⁾ e.m.f. measurements; $T = 298.15 \text{ K}$; $E_m^\circ(T) = 0.4119 \text{ V}$.

^b Larson and Elliott;⁽¹⁸⁾ e.m.f. measurements; $1120 \text{ K} < T < 1370 \text{ K}$; $\langle T \rangle = 1200 \text{ K}$;

$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -899.2 + 0.1317(T/\text{K})$.

^c Stubbles and Richardson;⁽¹⁴⁾ $p(\text{H}_2\text{S})$ measurements; $1120 \text{ K} < T < 1470 \text{ K}$; $\langle T \rangle = 1300 \text{ K}$;

$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -89.0 + 2.68 \times 10^{-2}(T/\text{K})$.

^d Stubbles and Richardson;⁽¹⁴⁾ $p(\text{H}_2\text{S})$ measurements; $1270 \text{ K} < T < 1470 \text{ K}$; $\langle T \rangle = 1400 \text{ K}$;

$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -90.4 + 3.44 \times 10^{-2}(T/\text{K})$.

^e Schaefer and Gokcen;⁽¹⁹⁾ e.m.f. measurements; $867 \text{ K} < T < 1209 \text{ K}$; $\langle T \rangle = 1000 \text{ K}$; mean of 34 determinations.

^f Pouillard and Perrot;⁽²⁰⁾ controlled chemical potentials of sulfur; $930 \text{ K} < T < 1280 \text{ K}$; $\langle T \rangle = 1000 \text{ K}$.

^g $\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -169.3 + 4.41 \times 10^{-2}(T/\text{K})$.

^h $\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -187.0 + 6.29 \times 10^{-2}(T/\text{K})$.

ⁱ O'Hare *et al.*;⁽²¹⁾ fluorine-combustion calorimetry.

however, McCabe⁽¹³⁾ and Stubbles and Richardson⁽¹⁴⁾ subsequently established that Mo_2S_3 and not MoS_2 was the lowest sulfide in equilibrium with Mo. The results of Parravano and Malquori are, therefore, not considered further. Makolkin's⁽¹⁵⁾ e.m.f. measurements give a $\Delta_r H_m^\circ$ about $40 \text{ kJ} \cdot \text{mol}^{-1}$ less negative than the others shown in table 1. A possible reason for this large discrepancy could be formation of Mo_2S_3 in addition to MoS_2 . All the other measurements give reasonably consistent results, but that deduced from the Pouillard and Perrot study is somewhat low. The results from the fluorine-bomb study have been recalculated to take into account the most recent molar masses of the elements and the consequent changes in $\Delta_r H_m^\circ(\text{MoF}_6, \text{g})$,⁽¹⁶⁾ and $\Delta_r H_m^\circ(\text{SF}_6, \text{g})$.⁽¹⁷⁾ The selected value, $\Delta_r H_m^\circ(\text{MoS}_2, \text{cr}, 298.15 \text{ K}) = -(274.1 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$, is the weighted mean of the results in table 1 derived from the work of Larson and Elliott,⁽¹⁸⁾ Stubbles and Richardson,⁽¹⁴⁾ Schaefer and Gokcen,⁽¹⁹⁾ Pouillard and Perrot,⁽²⁰⁾ and O'Hare *et al.*⁽²¹⁾

Several years ago, Mills⁽¹⁰⁾ reviewed the thermodynamic properties of MoS_2 and recommended $\Delta_r H_m^\circ = -(275.3 \pm 5.0) \text{ kJ} \cdot \text{mol}^{-1}$, the fluorine-bomb calorimetric result as originally published. He also included a second-law analysis of the measurements of Larson and Elliott⁽¹⁸⁾ and deduced $\Delta_r H_m^\circ = -(281 \pm 13) \text{ kJ} \cdot \text{mol}^{-1}$, which is much less precise than the $\Delta_r H_m^\circ$ s in table 1 and, for that reason, has not been included in the present analysis.

MOLYBDENUM SESQUISULFIDE

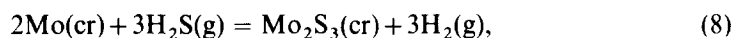
In 1970, our publication⁽²¹⁾ on $\Delta_f H_m^\circ(\text{MoS}_2)$ included a review of the literature related to $\Delta_f H_m^\circ(\text{Mo}_2\text{S}_3)$. Since that time, one new investigation of Mo_2S_3 , by Pouillard and Perrot,⁽²⁰⁾ has been described. Mills⁽¹⁰⁾ showed that analyses based on second-law calculations did not give consistent results for Mo_2S_3 ; thus, in our approach, we have used the third-law method exclusively.

For reaction (3) in table 1, Stubbles and Richardson⁽¹⁴⁾ gave

$$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -88.99 + 2.68 \times 10^{-2}(T/\text{K}), \quad (7)$$

over the temperature range 1123 to 1473 K. At the mean temperature of the measurements, 1300 K, $\Delta_r G_m^\circ = -(54.1 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$ which, combined appropriately with $\Phi_m^\circ(T, T')^{(10,11)}$ and $\Delta_f H_m^\circ(\text{H}_2\text{S}, \text{g})^{(11)}$ leads to $\Delta_f H_m^\circ(\text{Mo}_2\text{S}_3, \text{cr}, 298.15 \text{ K}) = -(399.9 \pm 14.4) \text{ kJ} \cdot \text{mol}^{-1}$.

For the sulfidation of Mo to form Mo_2S_3 :



Pouillard and Perrot's results may be summarized as follows ($\langle T \rangle = 1000 \text{ K}$):

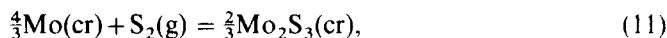
$$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -254.0 + 6.61 \times 10^{-2}(T/\text{K}). \quad (9)$$

Hager and Elliott's⁽⁶⁾ study yields a similar expression ($\langle T \rangle = 1500 \text{ K}$):

$$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -252.3 + 6.90 \times 10^{-2}(T/\text{K}). \quad (10)$$

With the appropriate auxiliary quantities mentioned earlier, we deduce $\Delta_f H_m^\circ(\text{Mo}_2\text{S}_3) = -(393.7 \pm 4.0)$ and $-(407.1 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$ from Pouillard and Perrot and Hager and Elliott, respectively.

McCabe's⁽¹³⁾ Knudsen-effusion measurements of the equilibrium

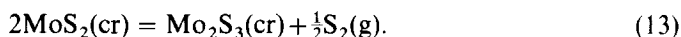


yield the expression ($\langle T \rangle = 1360 \text{ K}$):

$$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -405.9 + 0.1748(T/\text{K}). \quad (12)$$

By means of a third-law analysis, including $\Delta_f H_m^\circ(\text{S}_2, \text{g})^{(11)}$ $\Delta_f H_m^\circ(\text{Mo}_2\text{S}_3)$ is found to be $-(427 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$.

Isakova⁽²²⁾ studied the thermal decomposition of MoS_2 :



According to Brewer and Lamoreaux,⁽²³⁾ the results of this work are summarized by:

$$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = 159.1 - 5.67 \times 10^{-2}(T/\text{K}). \quad (14)$$

We use our selected value for $\Delta_f H_m^\circ(\text{MoS}_2)$ and $\Delta_f H_m^\circ(\text{S}_2, \text{g})$ from reference 11 to deduce $\Delta_f H_m^\circ(\text{Mo}_2\text{S}_3) = -(379 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$.

The recalculated results are summarized in table 2. The agreement among the five values is not very good. The selected $\Delta_f H_m^\circ$ is $-(400 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$, taken to

TABLE 2. Recalculated values for $\Delta_f H_m^\circ(\text{Mo}_2\text{S}_3, \text{cr}, 298.15 \text{ K})$; $p^\circ = 101.325 \text{ kPa}$

| | $\Delta_f H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ | | $\Delta_f H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ |
|---|---|--------------------------------------|---|
| McCabe ^(1,3) | -427 ± 7 | Hager and Elliott ⁽⁶⁾ | -407 ± 5 |
| Stubbles and Richardson ⁽¹⁴⁾ | -400 ± 14 | Pouillard and Perrot ⁽²⁰⁾ | -394 ± 5 |
| Isakova ⁽²²⁾ | -379 ± 10 | Selected value: | -400 ± 10 |

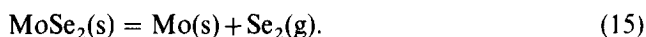
embrace all but the extreme values of McCabe and Isakova. Clearly, there is need for an unequivocal determination of $\Delta_f H_m^\circ(\text{Mo}_2\text{S}_3)$.

4. (Molybdenum + selenium)

The (molybdenum + selenium) phase diagram was explored by Spiesser *et al.*,⁽²⁴⁾ who reported that, at $T < 1473 \text{ K}$, only the diselenide was formed by heating the elements together in various proportions. The lower compositional limit of this phase was found to be $\text{MoSe}_{1.9}$. At 1523 K , a second phase " Mo_3Se_4 " was observed with limiting compositions of $\text{MoSe}_{1.45}$ and $\text{MoSe}_{1.27}$. Brewer and Lamoreaux⁽²³⁾ have supplemented this information with phase-diagram calculations. Other molybdenum selenides, *e.g.* Mo_6Se_6 and $\text{Mo}_{15}\text{Se}_{19}$, have been synthesized,⁽²⁵⁾ but not by direct combination of just molybdenum and selenium.

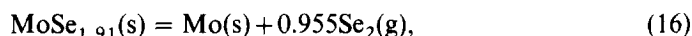
MOLYBDENUM DISELENIDE

The first thermodynamic study of MoSe_2 was reported by Glazunov *et al.*⁽²⁶⁾ They used a mass-spectrometric Knudsen-effusion method to analyze the composition of the vapor phase over MoSe_2 and determined the vapor pressures from 973 to 1473 K ; they deduced a value of $(213 \pm 13) \text{ kJ} \cdot \text{mol}^{-1}$ for the enthalpy of vaporization of MoSe_2 , which they attributed to the reaction:



This result, combined with $\Delta_f H_m^\circ(\text{Se}_2, \text{g})$,⁽²⁷⁾ implies $\Delta_f H_m^\circ(\text{MoSe}_2, \text{s}) = -(69 \pm 13) \text{ kJ} \cdot \text{mol}^{-1}$. However, Brewer and Lamoreaux⁽²³⁾ have shown that Mo and MoSe_2 cannot coexist and suggest that the measured dissociation pressures were really for $(\text{Mo} + \text{Mo}_3\text{Se}_{4-x})$ since the Knudsen-effusion cell was coated with TaC . We shall show, also, that the magnitude of this $\Delta_f H_m^\circ$ value is unreasonable for MoSe_2 .

Viksman *et al.*⁽²⁸⁾ have recently described a mass-spectrometric Knudsen-effusion study of the vaporization of hypostoichiometric diselenide. For the dissociation of the selenide:



they report $\Delta_f H_m^\circ = (404.4 \pm 30.0) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K , and this corresponds to $\Delta_f H_m^\circ(\text{MoSe}_{1.91}) = -(267 \pm 30) \text{ kJ} \cdot \text{mol}^{-1}$, which is significantly more negative and reasonable than the result of Glazunov *et al.*

Our own fluorine-combustion calorimetric study of MoSe_2 ⁽²⁹⁾ yielded $\Delta_f H_m^\circ = -(234.2 \pm 3.3) \text{ kJ} \cdot \text{mol}^{-1}$, which is much more precise than, and barely in agreement with, the result of Viksman *et al.* This value corresponds to $\Delta_f H_m^\circ(\text{MoSe}_{1.91}) \approx -227 \text{ kJ} \cdot \text{mol}^{-1}$. Clearly, the calorimetric result is superior to the earlier determinations.

It is interesting to compare the experimental vapor pressures with $p(\text{Se}_2)$ derived by combining the calorimetric result and appropriate thermodynamic values. At 1460 K, $p(\text{Se}_2)$ is calculated to be $(17 \pm 11) \text{ Pa}$, while Viksman *et al.* report 1.07 Pa; at 1570 K the calculated result is $(115^{+70}_{-43}) \text{ Pa}$ and the experimental value is 3.43 Pa.

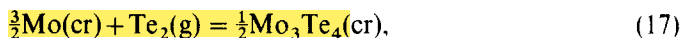
HEXAMOLYBDENUM HEXASELENIDE

Our determination⁽²⁹⁾ of the energy of combustion of Mo_6Se_6 in fluorine yielded $\Delta_f H_m^\circ(\text{Mo}_6\text{Se}_6, \text{cr}, 298.15 \text{ K}) = -(477.8 \pm 10.0) \text{ kJ} \cdot \text{mol}^{-1}$. There are no other $\Delta_f H_m^\circ$ values for the so-called Chevrel phases. Such information would clearly be valuable, for instance in connection with intercalation reactions of Li with host layered lattices.

5. (Molybdenum + tellurium)

The only stoichiometric phases in (molybdenum + tellurium) for which thermodynamic information is available are MoTe_2 and Mo_3Te_4 . Brewer and Lamoreaux⁽²³⁾ cite phase-diagram studies on MoTe_{2-x} and $\text{Mo}_3\text{Te}_{2\pm x}$ which show rather wide variations of x ; however, Krabbes and Oppermann⁽³⁰⁾ contend that neither phase shows a wide homogeneity range, and they found $x = (0.01 \pm 0.01)$ for MoTe_{2-x} and $x = -(0.07 \pm 0.06)$ for $\text{Mo}_3\text{Te}_{4\pm x}$.

Krabbes and Oppermann have measured manometrically the equilibrium $\text{Te}_2(\text{g})$ pressure over (molybdenum tellurides + tellurium + molybdenum) at temperatures between 1100 and 1330 K. For the reaction:



they gave the relation:

$$\log_{10}(p/p^\circ) = 5.56 - 9879(\text{K}/T), \quad (18)$$

where p denotes the $\text{Te}_2(\text{g})$ equilibrium pressure and, in their work, $p^\circ = 1 \times 10^5 \text{ Pa}$; it follows that

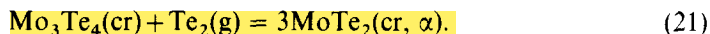
$$\Delta_f G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -189.2 + 0.1065(T/\text{K}). \quad (19)$$

We have used a third-law calculation with auxiliary thermodynamic values from references 11, 23, and 27, and $\Delta_f H_m^\circ(\text{Te}_2, \text{g})$,⁽²⁷⁾ to deduce, from equation (19), $\Delta_f H_m^\circ(\text{Mo}_3\text{Te}_4) = -(177 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$, where the uncertainty has been estimated.

As part of the same investigation, Krabbes and Oppermann reported

$$\log_{10}(p/p^\circ) = 8.398 - 11790(\text{K}/T), \quad (20)$$

for the reaction:



Equation (20) implies that

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = -225.8 + 0.1608(T/\text{K}), \quad (22)$$

and, by means of a third-law treatment with the value of $\Delta_f H_m^\circ(\text{Mo}_3\text{Te}_4)$ calculated above, $\Delta_f H_m^\circ(\text{MoTe}_2, \text{cr}, \alpha, 298.15 \text{ K}) = -(83 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$.

In their paper, Krabbes and Oppermann state that the equilibrium pressures as a function of T for reaction (21) are in good agreement with those reported by Opalovskii *et al.*⁽³¹⁾ Neither group gives those pressures explicitly; however, the Krabbes and Oppermann value for $\Delta_r H_m^\circ$ of reaction (21), which they reported to be $-226 \text{ kJ} \cdot \text{mol}^{-1}$, is seriously at variance with the $-55 \text{ kJ} \cdot \text{mol}^{-1}$ from the Opalovskii *et al.* study.

Krabbes and Oppermann stated that $\beta\text{-MoTe}_2$ was the stable ditelluride at $T \geq 1173 \text{ K}$ with $\Delta_{\text{tr}} H_m^\circ = 4.9 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K . This enthalpy of the α -to- β transition gives $\Delta_f H_m^\circ(\text{MoTe}_2, \text{cr}, \beta, 298.15 \text{ K}) = -(78 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$.

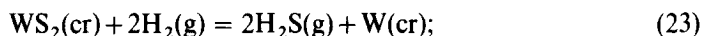
It is clear that (molybdenum + tellurium) requires additional study; in the meantime, the results deduced from Krabbes and Oppermann are recommended.

6. (Tungsten + sulfur)

According to Wildervanck and Jellinek,⁽³²⁾ only WS_2 and WS_3 were identified in the (tungsten + sulfur) phase diagram. No thermodynamic information is available for WS_3 .

TUNGSTEN DISULFIDE

In a recent publication,⁽³³⁾ we discussed the rather chaotic state of the literature values for $\Delta_f H_m^\circ(\text{WS}_2)$. Three general techniques have been used in efforts to establish this quantity, namely, high-temperature equilibrium measurements on the reaction:



e.m.f. studies of essentially the same reaction and of oxidation of WS_2 to WO_3 and 2SO_2 ; and combustion calorimetry in oxygen and in fluorine.

According to Richardson and Jeffes,⁽⁸⁾ the results of the pioneering measurements by Parravano and Malquori⁽¹²⁾ have to be adjusted to allow for thermal segregation. Indeed, the original vapor pressures given in Parravano and Malquori's paper imply an unreasonable $\Delta_r H_m^\circ$. Accordingly, for the reaction:



Richardson and Jeffes recommended

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = -260.9 + 9.62 \times 10^{-2}(T/\text{K}). \quad (25)$$

Addition of the expression⁽⁸⁾ for $\Delta_f G_m^\circ(T)$ of H_2S gives for reaction (23):

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 80.3 + 2.6 \times 10^{-3}(T/\text{K}). \quad (26)$$

Use of the appropriate $\Phi_m^\circ(T, T')$ values for $W,^{(11)} S_2,^{(11)}$ and $WS_2,^{(33)}$ and $\Delta_f H_m^\circ(H_2S, g)^{(11)}$ yields $\Delta_f H_m^\circ(WS_2) = -(240 \pm 40) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K, where the uncertainty is that assessed by Richardson and Jeffes.

Thirty years elapsed before a thermodynamic study of reaction (23) was again reported in the literature. Černý *et al.*⁽³⁴⁾ used a flow apparatus to deduce the equilibrium constant K as a function of temperature ($660 \text{ K} \leq T \leq 778 \text{ K}$); the results for reaction (23) are given by

$$\log_{10} K^\circ = 0.524 - 8334(K/T). \quad (27)$$

This equation, in turn, yields

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 159.6 - 1.003 \times 10^{-2}(T/\text{K}). \quad (28)$$

There is an error in this paper: the equilibrium constants given by Černý *et al.* in their table I apply to their equation (3), not equation (2) as stated. We use the appropriate auxiliary thermodynamic values^(11,33) to obtain $\Delta_f H_m^\circ(WS_2) = -(270 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$.

Several years later, authors from the same laboratory used an improved flow apparatus to study the reduction of WS_2 . Bartovská *et al.*⁽³⁵⁾ cited evidence from their studies for the existence of low- and high-temperature modifications of WS_2 ; the conversion temperature was stated to be spread over about 300 K. No other authors have mentioned such a transition; indeed, our recent drop-calorimetric measurements⁽³³⁾ on WS_2 showed a smooth continuous heat-capacity from 350 to 1500 K. For temperatures from 573 to 773 K, the results of Bartovská *et al.* for reaction (23) are summarized by

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 201.6 - 5.74 \times 10^{-2}(T/\text{K}). \quad (29)$$

When combined with the appropriate auxiliary thermodynamic quantities, this equation yields $\Delta_f H_m^\circ(WS_2) = -(277 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$.

We have referred earlier to Hager and Elliott's⁽⁶⁾ work on CrS and Mo_2S_3 ; as part of the same investigation, they also examined the reduction of WS_2 and, for reaction (23), gave

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 155.6 - 5.78 \times 10^{-2}(T/\text{K}). \quad (30)$$

We derive $\Delta_f H_m^\circ(WS_2) = -(249 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ from the above equation.

Degroise and Oudar⁽³⁶⁾ studied the reduction of WS_2 prepared from powdered tungsten and H_2S doped with ^{35}S ; the quantities of $H_2^{35}S$ produced were measured with a Geiger-Müller counter. The standard molar Gibbs energy change for the reaction is given by:

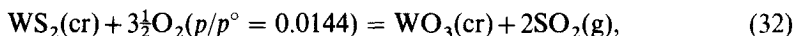
$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 157.4 - 5.06 \times 10^{-2}(T/\text{K}). \quad (31)$$

The temperatures of the measurements ranged from 1023 to 1273 K; $\Delta_f H_m^\circ(WS_2) = -(251 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K is deduced from this work.

So far, therefore, $\Delta_f H_m^\circ$ recalculated from the high-temperature vapor-pressure experiments: -240 , -270 , -277 , -249 , and -251 $\text{kJ} \cdot \text{mol}^{-1}$, does not exhibit outstanding consistency. Let us now proceed to the e.m.f. studies.

The determinations of Černý *et al.*⁽³⁴⁾ and of Leitner and Černý⁽³⁷⁾ are based on electrochemical measurements of the reduction of WS_2 , as shown in equation (23). At 298.15 K, the Černý *et al.* value for the cell potential: $E_m^\circ = 0.8632$ V, implies $\Delta_r G_m^\circ = 166.6$ $\text{kJ} \cdot \text{mol}^{-1}$; combination of that result with $\Delta_r G_m^\circ(\text{H}_2\text{S})$,⁽¹¹⁾ and standard entropies S_m° for WS_2 ,⁽³³⁾ W,⁽¹¹⁾ and S(cr, rh),⁽¹¹⁾ yields $\Delta_f H_m^\circ(\text{WS}_2) = -(242 \pm 5)$ $\text{kJ} \cdot \text{mol}^{-1}$ at 298.15 K. Leitner and Černý gave $E_m^\circ = 0.9614$ V for reaction (23) at 293.15 K; this result implies $\Delta_r G_m^\circ = (185.5 \pm 5)$ $\text{kJ} \cdot \text{mol}^{-1}$ at 293.15 K, from which we deduce $\Delta_f H_m^\circ(\text{WS}_2) = -(260 \pm 5)$ $\text{kJ} \cdot \text{mol}^{-1}$ at 298.15 K.

Schaefer⁽³⁸⁾ has reported e.m.f. measurements of the oxidation of WS_2 at 872 to 1210 K according to the reaction:



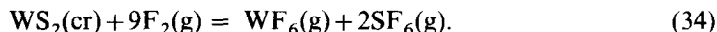
for which

$$\Delta_r G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = -1163.8 + 0.332(T/\text{K}). \quad (33)$$

Use of the appropriate values for $\Phi_m^\circ(T, T')^{(11,33)}$ and $\Delta_f H_m^\circ$ of WO_3 ,⁽¹¹⁾ and SO_2 ,⁽¹¹⁾ yields $\Delta_f H_m^\circ(\text{WS}_2) = -(260 \pm 3)$ $\text{kJ} \cdot \text{mol}^{-1}$.

Two combustion calorimetric studies of WS_2 have been quoted by Mills;⁽¹⁰⁾ Hartmann and Wagner's⁽³⁹⁾ result, $\Delta_f H_m^\circ(\text{WS}_2) \approx -200$ $\text{kJ} \cdot \text{mol}^{-1}$ at 298.15 K appears to be seriously in error as is the value of ≈ -300 $\text{kJ} \cdot \text{mol}^{-1}$ attributed to this laboratory. Efforts were made at Argonne, about 25 years ago, to determine $\Delta_f H_m^\circ$ of MoS_2 and WS_2 by oxygen bomb calorimetry; however, severe analytical problems with the products of combustion yielded unreliable $\Delta_f H_m^\circ$ s for the sulfides which, nevertheless, are quoted from time to time. These values should be disregarded. The Hartmann and Wagner study employed a high-temperature differential calorimeter; multiple S-containing combustion products were obtained. This research apparently suffered from analytical problems similar to those encountered in the earlier Argonne work.

Finally, we refer to our own determination⁽³³⁾ of the energy of combustion of WS_2 in $\text{F}_2(\text{g})$:



Due to an intervening change in $\Delta_f H_m^\circ(\text{SF}_6, \text{g})$,⁽¹⁷⁾ our published $\Delta_f H_m^\circ(\text{WS}_2)$ has to be adjusted slightly, to $-(241.6 \pm 2.5)$ $\text{kJ} \cdot \text{mol}^{-1}$. This result is in good agreement with those of Černý *et al.*, and Parravano and Malquori, and is close to that of Hager and Elliott. All the recalculated values are summarized in table 3. Because of the large scatter in the other results, even for identical reactions, it is felt that the fluorine-bomb value is the most reliable and is therefore recommended.

Why is there such wide disagreement among the results for WS_2 ? We do not have a convincing answer to that question but suggest that instability of H_2S may have contributed. Thus, for example, Fukuda *et al.*⁽⁴⁰⁾ and Chivers *et al.*⁽⁴¹⁾ have demonstrated the catalytic efficacy of MoS_2 and WS_2 in the decomposition of H_2S , even at temperatures as low as 870 K.

TABLE 3. Recalculated results for $\Delta_f H_m^\circ(\text{WSe}_2, \text{cr}, 298.15 \text{ K})$; $p^\circ = 101.325 \text{ kPa}$

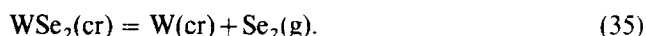
| | $\Delta_f H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ | | $\Delta_f H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ |
|--|---|---|---|
| Parravano and Malquori ^(12, a) | -240 ± 40 | Černý <i>et al.</i> ^(34, b) | -242 ± 5 |
| Černý <i>et al.</i> ^(34, a) | -270 ± 10 | Leitner and Černý ^(37, b) | -260 ± 5 |
| Bartovská <i>et al.</i> ^(35, a) | -277 ± 10 | Schaefer ^(38, b) | -260 ± 3 |
| Hager and Elliott ^(6, a) | -249 ± 5 | Hartmann and Wagner ^(39, c) | ≈ -200 |
| Degroise and Oudar ^(36, a) | -251 ± 5 | O'Hare <i>et al.</i> ^(33, c) | -241.6 ± 2.5 |

^a High-temperature equilibrium measurements. ^b High-temperature e.m.f. study. ^c Combustion calorimetry.

7. (Tungsten + selenium)

TUNGSTEN DISELENIDE

The only tungsten selenide on which thermodynamic measurements have been made is WSe_2 . The first such investigation was described in the literature in 1977. Mikhailov *et al.*⁽⁴²⁾ reported a Knudsen-effusion mass-spectrometric determination of the vapor pressure over WSe_2 and used the intensities of the mass-spectral lines as a function of temperature ($973 \text{ K} \leq T \leq 1523 \text{ K}$) as a basis on which they performed a second-law calculation of the enthalpy of sublimation. They assumed that sublimation occurred as follows:



From their result, $\Delta_{\text{sub}} H_m^\circ = (259 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_f H_m^\circ(\text{Se}_2, \text{g}) = (144.1 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$,⁽²⁷⁾ we calculate $\Delta_f H_m^\circ(\text{WSe}_2) = -(115 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K.

Thermogravimetric studies of the vaporization of WSe_2 were reported by Piskarev *et al.*⁽⁴³⁾ Those authors also assumed that vaporization took place according to equation (35), and they found for the equilibrium pressure over WSe_2 :

$$\log_{10}\{p(\text{Se}_2)/p^\circ\} = 13.550 - 19850(\text{K}/T). \quad (36)$$

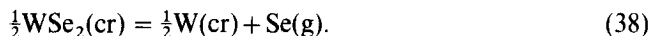
(There is an error in the original paper; the first term on the right-hand side of the equation is given as 13550.) Piskarev *et al.* took $\Delta_f H_m^\circ(\langle T \rangle) = 380 \text{ kJ} \cdot \text{mol}^{-1}$, as implied by equation (36), with $\langle T \rangle = 1200 \text{ K}$. With enthalpy increments for W ,⁽¹¹⁾ $\text{Se}_2(\text{g})$,⁽²⁷⁾ and WSe_2 (estimated), we deduce $\Delta_f H_m^\circ \approx (387 \pm 20) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K and $\Delta_f H_m^\circ(\text{WSe}_2) \approx -(243 \pm 20) \text{ kJ} \cdot \text{mol}^{-1}$. This result is approximately $130 \text{ kJ} \cdot \text{mol}^{-1}$ more negative than that of Mihailov *et al.* If, on the other hand, a third-law calculation is performed, a significantly different result emerges. From equation (36), we derive

$$\Delta_f G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = 380.1 - 0.2595(T/\text{K}), \quad (37)$$

and, with an estimated $\Phi_m^\circ(T, T')$ for WSe_2 and literature values for W ,⁽¹¹⁾ and $\text{Se}_2(\text{g})$,⁽²⁷⁾ we obtain $\Delta_f H_m^\circ = (278 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (35). This result, combined with $\Delta_f H_m^\circ(\text{Se}_2, \text{g})$,⁽²⁷⁾ yields $\Delta_f H_m^\circ(\text{WSe}_2) = -(134 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K.

The most comprehensive study of the vaporization of WSe_2 has been reported by Schiffman *et al.*⁽⁴⁴⁾ One of the significant findings in their work was that WSe_2 did not vaporize exclusively according to equation (35). Mikhailov *et al.* and Piskarev *et al.* had assumed that Se(g) observed during their measurements arose solely from dissociative ionization within the mass spectrometer; however, Schiffman *et al.* showed that WSe_2 vaporized not only to $\text{Se}_2(\text{g})$ but to Se(g) as well and concluded that the results from the two earlier studies were not valid.

Second-law calculations by Schiffman *et al.* on the basis of pressures and ion intensities gave $\Delta_r H_m^\circ = (311 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K for the reaction:



For the same reaction, and using their relation:

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 317 - 0.159(T/\text{K}), \quad (39)$$

we deduce, by means of a third-law treatment, $\Delta_r H_m^\circ = (287 \pm 11) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K. For this calculation we estimated $\Phi_m^\circ(T, T') = 164.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for WSe_2 at $T = 1500 \text{ K}$. The $\Delta_r H_m^\circ$ values of (311 ± 8) and $(287 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K yield $\Delta_r H_m^\circ(\text{WSe}_2) = -(147 \pm 8)$ and $-(99 \pm 22) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. Schiffman *et al.* express a clear preference for the more negative value. A second-law calculation by the same authors for the dissociation to $\text{Se}_2(\text{g})$, reaction (35), gave $\Delta_r H_m^\circ = (327 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K, which corresponds to $\Delta_r H_m^\circ(\text{WSe}_2) = -(183 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$.

Zelikman *et al.*⁽⁴⁵⁾ obtained $\Delta_r H_m^\circ$ by two methods: measurement of the dissociation pressure of WSe_2 , and a calorimetric determination of its enthalpy of synthesis from the elements. Calorimetric enthalpies of synthesis are usually reliable, and $\Delta_r H_m^\circ$ s so obtained are the values of choice. However, in this instance, the reaction between W and Se in the calorimeter was far from complete; about 10 to 15 mass per cent of the Se failed to react, traces of unreacted W also remained, and the X-ray diffraction lines of the WSe_2 formed showed it to have a *c*-axis lattice parameter that differed from the standard hexagonal form. On the basis of this work, Zelikman *et al.* gave $\Delta_r H_m^\circ = -154.2 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K, with an uncertainty of $\pm 2 \text{ kJ} \cdot \text{mol}^{-1}$. We believe, in view of the analytical problems, that the uncertainty should be at least $\pm 5 \text{ kJ} \cdot \text{mol}^{-1}$.

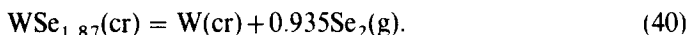
Where comparison is possible, the equilibrium vapor pressures reported by Zelikman *et al.* are close to those given by Mikhailov *et al.* Unlike Schiffman *et al.*, Zelikman *et al.* found no evidence for gaseous selenium molecules other than $\text{Se}_2(\text{g})$. There is a contradiction here, because the temperature regions of the measurements overlap. We are unable to resolve this discrepancy, but Schiffman *et al.* argue that the absence of Se(g) is unexpected and contrary to what one would predict on the basis of thermodynamic values for $\text{Se}_2(\text{g})$ and Se(g) in the literature.

Zelikman *et al.* report $\Delta_r H_m^\circ$ for dissociation of WSe_2 to $\text{Se}_2(\text{g})$, equation (35), to be $(259.6 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$ at 1100 to 1423 K; they used the temperature dependence of $C_{p,m}^\circ(\text{MoSe}_2)$,⁽⁴⁶⁾ to estimate the hitherto undetermined $C_{p,m}^\circ(\text{WSe}_2)$, and deduced $\Delta_r H_m^\circ$ of reaction (35) to be $284.7 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K. A similar result, about $(282 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$, is obtained with the enthalpy increments for WSe_2

approximated by Viksman *et al.*⁽²⁸⁾ Those authors state that their estimates are uncertain by at least 5 per cent and, even though $C_{p,m}^\circ$ at 298.15 K is lower than the experimental result of Kiwia and Westrum⁽⁴⁷⁾ by less than 2 per cent, their value for S_m° at 298.15 K is too low by about 6 per cent. This indicates that their temperature dependence of $C_{p,m}^\circ(T)$ is erroneous.

We believe that the Viksman *et al.* estimate of $\Delta_f^\circ H_m^\circ(T)$ is too high. This conclusion is based on an examination of such values tabulated for chalcogenides by Mills⁽¹⁰⁾ and on our own experimental values for MoS_2 ,⁽⁴⁸⁾ and WS_2 .⁽³³⁾ We have observed that substitution of W for Mo (MoS_2 , WS_2) and of Se for S (*e.g.* SnS , SnSe ; Cu_2S , Cu_2Se) has only a small effect ($\approx \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$) on the relative values of $\Delta_f^\circ H_m^\circ(T)$. Thus, for WSe_2 at $T = 1200 \text{ K}$, we estimate $\Delta_f^\circ H_m^\circ(T) = (67 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ (we earlier used this estimate without elaboration in our analysis of the results of Piskarev *et al.*) and, with corresponding values of 23.9 and $36.0 \text{ kJ} \cdot \text{mol}^{-1}$ for W ,⁽¹¹⁾ and $\text{Se}_2(\text{g})$,⁽²⁷⁾ recalculate the $\Delta_f^\circ H_m^\circ$ result of Zelikman *et al.* to be $(267 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K, close to that of Mikhailov *et al.*⁽⁴²⁾ $(259 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$. This agreement is not unexpected, since the vapor pressures reported by both investigators appear to overlap. This recalculated result from Zelikman *et al.* leads to $\Delta_f^\circ H_m^\circ(\text{WSe}_2) = -(123 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K, about $31 \text{ kJ} \cdot \text{mol}^{-1}$ less negative than their calorimetric value.

We come finally to the recent study by Viksman *et al.*⁽²⁸⁾ of the vaporization of $\text{WSe}_{1.87}$. They report $\Delta_f^\circ H_m^\circ = (392 \pm 30) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K for the reaction:



The large error should take into account our aforementioned misgivings about the estimated high-temperature thermodynamic properties of WSe_2 . The enthalpy of dissociation corresponds to $\Delta_f^\circ H_m^\circ(\text{WSe}_{1.87}) = -(257 \pm 30) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K from which, for stoichiometric WSe_2 , we estimate $\Delta_f^\circ H_m^\circ \approx -(269 \pm 30) \text{ kJ} \cdot \text{mol}^{-1}$.

In table 4, we have summarized the values derived for $\Delta_f^\circ H_m^\circ(\text{WSe}_2)$. It is clearly impossible to recommend a value, although the preponderance of the evidence suggests $\Delta_f^\circ H_m^\circ \approx -150 \text{ kJ} \cdot \text{mol}^{-1}$. Much additional work on (tungsten + selenium) is required.

TABLE 4. Derived standard molar enthalpies of formation of WSe_2 at 298.15 K ($p^\circ = 101.325 \text{ kPa}$)

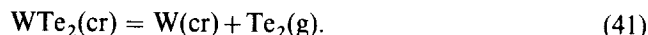
| Investigators | $\Delta_f^\circ H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ | Investigators | $\Delta_f^\circ H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ |
|---|---|---|---|
| Mikhailov <i>et al.</i> ⁽⁴²⁾ | -115 ± 8^a | Schiffman <i>et al.</i> ⁽⁴⁴⁾ | -147 ± 8^d |
| Piskarev <i>et al.</i> ⁽⁴³⁾ | -243 ± 20^a | | -99 ± 22^e |
| | -134 ± 10^b | | -183 ± 8^a |
| Viksman <i>et al.</i> ⁽²⁸⁾ | -269 ± 30^c | Zelikman <i>et al.</i> ⁽⁴⁵⁾ | -154 ± 5^f |
| | | | $-123 \pm 6^{a,c}$ |

^a Second-law treatment of the reaction: $\text{WSe}_2 = \text{W} + \text{Se}_2(\text{g})$. ^b Third-law treatment of the reaction: $\text{WSe}_2 = \text{W} + \text{Se}_2(\text{g})$. ^c Recalculated as outlined in text. ^d Schiffman *et al.* express a preference for this result based on a second-law treatment of the reaction: $\text{WSe}_2 = \text{W} + 2\text{Se}(\text{g})$. ^e Third-law treatment of the reaction: $\text{WSe}_2 = \text{W} + 2\text{Se}(\text{g})$. ^f Result from synthesis calorimetry.

8. (Tungsten + tellurium)

TUNGSTEN DITELLURIDE

We are aware of only two investigations which lead to $\Delta_f H_m^\circ(\text{WTe}_2)$: both Obolonchik and Nesterovskaya⁽⁴⁹⁾ and Opalovskii *et al.*⁽³¹⁾ measured the dissociation pressure corresponding to the reaction:



Obolonchik and Nesterovskaya studied the dissociation of WTe_2 in a current of argon; their results for reaction (41) may be summarized as follows ($973 \text{ K} \leq T \leq 1223 \text{ K}$):

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 124.5 - 0.145(T/\text{K}). \quad (42)$$

From $\Delta_r G_m^\circ$ at 1000, 1100, and 1200 K, we have calculated values of 156, 156, and 155 $\text{kJ} \cdot \text{mol}^{-1}$ ($\pm 10 \text{ kJ} \cdot \text{mol}^{-1}$) for $\Delta_r H_m^\circ$ at 298.15 K, using $\Phi_m^\circ(T, T')$ for W ,⁽¹¹⁾ and $\text{Te}_2(\text{g})$,⁽²⁷⁾ and for WTe_2 estimated by analogy with WS_2 .⁽³³⁾ The mean $\Delta_r H_m^\circ$ at 298.15 K, $(156 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$, leads to $\Delta_f H_m^\circ(\text{WTe}_2) = (7 \pm 12) \text{ kJ} \cdot \text{mol}^{-1}$ when $\Delta_f H_m^\circ(\text{Te}_2, \text{g})$ from reference 27 is used. We note in passing that the equation given in that paper for the molar mass M is, in fact, for $\log_{10}\{M/(\text{g} \cdot \text{mol}^{-1})\}$.

Opalovskii *et al.* employed a quartz-membrane manometer to measure the dissociation pressure directly. No pressures are tabulated; instead, $\Delta_r H_m^\circ(T) = (196.6 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$ is given for reaction (41), where $1080 \text{ K} \leq T \leq 1162 \text{ K}$. We take, for a convenient intermediate temperature of 1100 K, literature values for $\Delta_f H_m^\circ(T)$ of W ,⁽¹¹⁾ and $\text{Te}_2(\text{g})$,⁽²⁷⁾ and an estimated $(59.3 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ for WTe_2 , and calculate $\Delta_r H_m^\circ = (202 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (41) at 298.15 K. This $\Delta_r H_m^\circ$ combined with $\Delta_f H_m^\circ(\text{Te}_2, \text{g})$,⁽²⁷⁾ yields $\Delta_f H_m^\circ(\text{WTe}_2) = -(39 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$.

There is a great disparity between the two results for $\Delta_f H_m^\circ(\text{WTe}_2, \text{cr}, 298.15 \text{ K})$ and neither can be confidently recommended at this time.

9. (Silicon + sulfur)

This section deals with the selection of $\Delta_f H_m^\circ$ values for SiS and SiS_2 , apparently the only two solid compounds in (silicon + sulfur).

SILICON MONOSULFIDE

Although the present paper is concerned, almost exclusively, with solid-state chalcogenides, it is necessary at this junction to discuss briefly, and select, $\Delta_f H_m^\circ(\text{SiS}, \text{g}, 298.15 \text{ K})$ for use in subsequent calculations.

Mills⁽¹⁰⁾ assessed the literature related to the derivation of the dissociation enthalpy $D_m^\circ(\text{SiS})$ at $T \rightarrow 0$ and included in his survey equilibrium studies by Rosenqvist and Tunesvik,⁽⁵⁰⁾ and spectroscopic analyses by Gaydon,⁽⁵¹⁾ Lagerqvist *et al.*,⁽⁵²⁾ and Robinson and Barrow.⁽⁵³⁾ He recommended $D_m^\circ(\text{SiS}) = (613 \pm 13) \text{ kJ} \cdot \text{mol}^{-1}$ at $T \rightarrow 0$. Later, Huber and Herzberg⁽⁵⁴⁾ selected a

similar value, $619.4 \text{ kJ} \cdot \text{mol}^{-1}$ (no uncertainty given), as did Glushko *et al.*,⁽¹¹⁾ $(613.7 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1}$, which we accept. D_m° at $T \rightarrow 0$ is adjusted to 298.15 K by means of enthalpy increments⁽¹¹⁾ for SiS(g), Si(g), and S(g); in this way, we obtain $D_m^\circ(\text{SiS}) = (619.0 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K which, when combined with $\Delta_f H_m^\circ(\text{S, g})$,⁽¹¹⁾ and $\Delta_f H_m^\circ(\text{Si, g})$,⁽¹¹⁾ yields $\Delta_f H_m^\circ(\text{SiS, g, 298.15 K}) = (108.0 \pm 4.8) \text{ kJ} \cdot \text{mol}^{-1}$.

Although crystalline SiS has been prepared recently⁽⁵⁵⁾ at Argonne National Laboratory, it is reasonable to conclude that most or all earlier samples of SiS, variously described in the literature as being yellow, black, or red in colour, were amorphous. Byerley and Teo⁽⁵⁶⁾ quenched SiS(g) and showed that the product was amorphous SiS and not (silicon disulfide + silicon) as some authors had proposed. Efforts to quench SiS(cr) from the gas phase were not successful.

Byerley and Teo measured, by Knudsen effusion, the equilibrium vapor pressure ($857 \text{ K} \leq T \leq 1017 \text{ K}$) of SiS(g) in the reaction:



They based the enthalpy of sublimation on results for unannealed yellow SiS. We do likewise, but use, instead of their estimated $\Phi_m^\circ(T, T')$ values, those given by Glushko *et al.*⁽¹¹⁾ For reaction (43), we calculate $\Delta_r H_m^\circ = (215 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K. There is an obvious trend with T , approximately $55 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, in the individual $\Delta_r H_m^\circ$ values. Nevertheless, we combine the mean $\Delta_r H_m^\circ$ with our selected $\Delta_f H_m^\circ(\text{SiS, g})$ to deduce $\Delta_f H_m^\circ(\text{SiS, am, 298.15 K}) = -(107 \pm 15) \text{ kJ} \cdot \text{mol}^{-1}$.

SILICON DISULFIDE

$\Delta_f H_m^\circ(\text{SiS}_2)$ has been determined both by solution-reaction calorimetry and high-temperature Knudsen-effusion techniques. We shall deal with the calorimetric studies first.

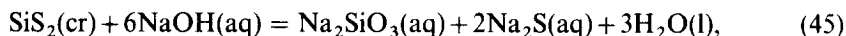
Sabatier's⁽⁵⁷⁾ measurements, dating from 1881, are now probably of only historical interest, although the result obtained from his work does not differ greatly from some of those reported in the more recent literature. Sabatier measured the enthalpy change for hydrolysis of SiS₂ which, he assumed, proceeded as follows:



He appears to have regarded the SiO₂ as being essentially suspended in the calorimetric solvent and made no correction for the interaction of SiO₂ with the solution. Gabriel and Alvarez-Tostado⁽⁵⁸⁾ suggested that silicic acids had formed, and Rocquet and Ancy-Moret⁽⁵⁹⁾ corrected Sabatier's result on the assumption that the SiO₂ had been hydrated. Another problem with this study is the likelihood that not all the H₂S was released as a gas and that a significant quantity of it remained in solution. This determination suggests a value of about $-200 \text{ kJ} \cdot \text{mol}^{-1}$ with a large uncertainty for $\Delta_f H_m^\circ(\text{SiS}_2)$.

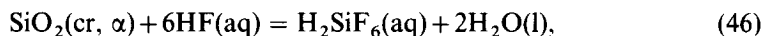
Gabriel and Alvarez-Tostado⁽⁵⁸⁾ used NaOH(aq) as a reactant in order to avoid the uncertainty associated with the disposition of the SiO₂. Hydrolysis of SiS₂ in the

calorimeter was assumed to have taken place as follows:

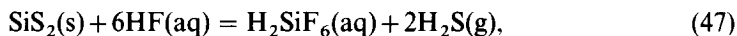


and $\Delta_f H_m^\circ$, presumably at about 298.15 K, was reported to be $-193 \text{ kJ} \cdot \text{mol}^{-1}$. Literature values⁽⁶⁰⁾ for $\Delta_f H_m^\circ$ of $\text{NaOH}(\text{aq})$, $\text{Na}_2\text{SiO}_3(\text{aq})$, $\text{Na}_2\text{S}(\text{aq})$, and $\text{H}_2\text{O}(\text{l})$, combined with $\Delta_f H_m^\circ$, yield $\Delta_f H_m^\circ(\text{SiS}_2) = -(329 \pm 20) \text{ kJ} \cdot \text{mol}^{-1}$, where the uncertainty has been estimated. This result should be regarded with scepticism because of the method of synthesis and manipulation of the extremely hygroscopic and air-sensitive SiS_2 .

Solution calorimetry in $\text{HF}(\text{aq})$ was used by Rocquet and Ancey-Moret.⁽⁵⁸⁾ Their analytical results for SiS_2 tend to be disturbingly low for both the silicon and sulfur contents, and this suggests the presence of a considerable amount of impurity, probably mostly oxygen which, it is now suspected,⁽⁵⁵⁾ may be inevitable in SiS_2 synthesized by heating (sulfur + silicon) in silica tubes. The calorimetric part of this study consisted of measurements of the enthalpies of two reactions in 18.7 mass per cent $\text{HF}(\text{aq})$:



with $\Delta_f H_m^\circ = -136.9 \text{ kJ} \cdot \text{mol}^{-1}$ and



with $\Delta_f H_m^\circ = -304.6 \text{ kJ} \cdot \text{mol}^{-1}$. The enthalpy of reaction of SiO_2 with $\text{HF}(\text{aq})$ is not unreasonable when compared with modern determinations.⁽⁶¹⁾ We estimate $\Delta_f H_m^\circ$ of reaction (47) to be uncertain by at least $9 \text{ kJ} \cdot \text{mol}^{-1}$. Values of $\Delta_f H_m^\circ$ of $\text{SiO}_2(\alpha)$,^(60,62) $\text{HF}(\text{aq})$,^(60,62) $\text{H}_2\text{O}(\text{l})$,⁽⁶⁰⁾ and $\text{H}_2\text{S}(\text{g})$,⁽¹¹⁾ were used to estimate $\Delta_f H_m^\circ(\text{SiS}_2) = -(213 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$, close to Sabatier's result.

We have found a very brief report by Ivanovna⁽⁶³⁾ of measurements of the enthalpies of reaction and solution in $3 \text{ mol} \cdot \text{dm}^{-3} \text{ NaOH}(\text{aq})$ of SiS_2 , Na_2S , and Na_2SiO_3 , from which $\Delta_f H_m^\circ(\text{SiS}_2) = -300 \text{ kJ} \cdot \text{mol}^{-1}$ was derived. No details are given of the individual enthalpies of reaction or solution and little more can be stated about this work.

The most recent calorimetric study of SiS_2 has been described by Matskevich and Gorsh⁽⁶⁴⁾ as part of the proceedings of the 1977 All-Union Conference held in Moscow. This investigation is similar in method to that of Ivanovna, but considerably more details are given. When the components of the Hess cycle outlined by Matskevich and Gorsh are combined, the following relation (at 298.15 K) is obtained:

$$\Delta_f H_m^\circ(\text{SiS}_2) = 2\Delta_f H_m^\circ(\text{Na}_2\text{S}, \text{cr}) + \Delta_f H_m^\circ(\text{Na}_2\text{SiO}_3, \text{cr}) + 3\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) - 6\Delta_f H_m^\circ(\text{NaOH}, \text{aq}) + 280.5 \text{ kJ} \cdot \text{mol}^{-1}. \quad (48)$$

We use auxiliary $\Delta_f H_m^\circ$ values from the National Bureau of Standards compilation⁽⁶⁰⁾ and recalculate Matskevich and Gorsh's result to be: $\Delta_f H_m^\circ(\text{SiS}_2) = -(308 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$.

In summary, the reaction-calorimetric studies point to two distinct groups of results for $\Delta_f H_m^\circ$, one of approximately $-200 \text{ kJ} \cdot \text{mol}^{-1}$ and the other, perhaps

more plausible because of the modernity of the work, in the vicinity of $-300 \text{ kJ} \cdot \text{mol}^{-1}$. Earlier assessments of the investigations we have just discussed usually accepted the Rocquet and Ancy-Moret study as being the most authoritative, thus lending some support to the less negative value of $\Delta_f H_m^\circ(\text{SiS}_2)$.

High-temperature vaporization studies of SiS_2 have been described by Drowart and Colin,⁽⁶⁵⁾ Fruehan and Turkdogan,⁽⁶⁶⁾ Emons and Theisen,⁽⁶⁷⁾ and Byerley and Teo.⁽⁶⁸⁾ Mills⁽¹⁰⁾ has quoted an unpublished report by Drowart and Colin of the decomposition of SiS_2 :



We back-calculate $\Delta_f H_m^\circ = (421 \pm 25) \text{ kJ} \cdot \text{mol}^{-1}$ for the above reaction, and combine with it $\Delta_f H_m^\circ$ values for $\text{SiS}(\text{g})$ and $\text{S}_2(\text{g})$,⁽¹¹⁾ to obtain $\Delta_f H_m^\circ(\text{SiS}_2) = -(249 \pm 25) \text{ kJ} \cdot \text{mol}^{-1}$.

Of papers in the more accessible literature that deal with the high-temperature thermodynamics of SiS_2 , the first to appear was that of Fruehan and Turkdogan. Those authors used a Knudsen-effusion mass-spectrometric arrangement to study the reduction of disulfide:



at $1000 \text{ K} \leq T \leq 1686 \text{ K}$. Individual vapor pressures were not given, but the authors used the second-law method to derive $\Delta_f H_m^\circ = 428 \text{ kJ} \cdot \text{mol}^{-1}$ at $\langle T \rangle = 1100 \text{ K}$. With enthalpy increments for $\text{SiS}(\text{g})$, Si , and SiS_2 taken from Glushko *et al.*,⁽¹¹⁾ we calculate $\Delta_f H_m^\circ = (449 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (50) at 298.15 K ; this value, combined with our selected $\Delta_f H_m^\circ(\text{SiS}, \text{g})$, leads to $\Delta_f H_m^\circ(\text{SiS}_2) = -(233 \pm 14) \text{ kJ} \cdot \text{mol}^{-1}$.

The same reaction was studied by Emons and Theisen who used a combined Knudsen-effusion mass-loss technique. They gave equations to represent the equilibrium vapor pressure {note that in their table 1 the heading " p " should be " $\log_{10}(p/p^\circ)$ "}. For reaction (50)

$$\log_{10}(p/p^\circ) = 13.82 - 20642(\text{K}/T), \quad (51)$$

from which may be derived

$$\Delta_f G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = 395.2 - 0.2646(T/\text{K}). \quad (52)$$

Combination of this equation with auxiliary thermodynamic quantities⁽¹¹⁾ gives $\Delta_f H_m^\circ(\text{SiS}_2) = -(255 \pm 22) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K . From the $\log_{10}(p/p^\circ)$ against T^{-1} slope read from the Emons and Theisen plot of the vapor pressure, we estimate $\Delta_f H_m^\circ = (408 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ at 1000 K and, with the appropriate enthalpy increments,⁽¹¹⁾ $\Delta_f H_m^\circ(\text{SiS}_2) = -(210 \pm 14) \text{ kJ} \cdot \text{mol}^{-1}$.

Emons and Theisen also investigated the decomposition of SiS_2 according to reaction (49). From their equation for the combined partial pressures of $\text{SiS}(\text{g})$ and $\frac{1}{2}\text{S}_2(\text{g})$,

$$\log_{10}(p/p^\circ) = 8.196 - 13500(\text{K}/T), \quad (53)$$

it follows that

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 387.7 - 0.2354(T/\text{K}), \quad (54)$$

at $990 \text{ K} \leq T \leq 1180 \text{ K}$. A third-law calculation, using $\Phi_m^\circ(T, T')$ from Glushko *et al.*⁽¹¹⁾ gives $\Delta_r H_m^\circ = (406 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K , and the corresponding $\Delta_r H_m^\circ(\text{SiS}_2)$ is $-(234 \pm 11) \text{ kJ} \cdot \text{mol}^{-1}$. A second-law calculation from equation (54) gives $\Delta_r H_m^\circ(\text{SiS}_2) = -(231 \pm 11) \text{ kJ} \cdot \text{mol}^{-1}$.

We come finally to two studies by Byerley and Teo, both of which yield $\Delta_r H_m^\circ(\text{SiS}_2)$. In the first paper,⁽⁶⁸⁾ they described an investigation of reaction (50). A recalculation of their results by the third-law method using the $\Phi_m^\circ(T, T')$ values of Glushko *et al.*⁽¹¹⁾ gives a remarkably consistent set of $\Delta_r H_m^\circ(298.15 \text{ K})$ results with no discernible trend with temperature. We take $\Delta_r H_m^\circ = (474 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$, from which it follows that $\Delta_r H_m^\circ(\text{SiS}_2) = -(258 \pm 11) \text{ kJ} \cdot \text{mol}^{-1}$. From the plot of $\ln(p/p^\circ)$ against T^{-1} for the same reaction, we estimate $\Delta_r H_m^\circ(298.15 \text{ K}) = (472 \pm 15) \text{ kJ} \cdot \text{mol}^{-1}$ and, therefore, $\Delta_r H_m^\circ(\text{SiS}_2) = -(256 \pm 31) \text{ kJ} \cdot \text{mol}^{-1}$.

In their other publication,⁽⁵⁶⁾ the authors studied the disproportionation of SiS_2 to gaseous SiS and S_2 , as Drowart and Colin had done earlier. A recalculation of their results gives $\Delta_r H_m^\circ(298.15 \text{ K}) = -(241 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$ by the third-law method and $-(243 \pm 21) \text{ kJ} \cdot \text{mol}^{-1}$ by the second-law method.

The recalculated results for $\Delta_r H_m^\circ(\text{SiS}_2)$ gathered together in table 5 exhibit a very large scatter. Those from solution calorimetry extend from -200 to $-329 \text{ kJ} \cdot \text{mol}^{-1}$, and those from the high-temperature studies show a spread that is smaller, from about -210 to $-258 \text{ kJ} \cdot \text{mol}^{-1}$, but that is, nevertheless, disturbing. There is some evidence, as we have mentioned, that synthesis of SiS_2 by heating silicon and sulfur together in a silica tube can bring about significant oxygen contamination from the silica. Such contamination is expected to have a much more profound effect on the calorimetric experiments and leads one to put greater credence in the less negative $\Delta_r H_m^\circ$ values obtained by that technique. We note that in none of the calorimetric studies was the SiS_2 analyzed for impurities. The effect of less volatile impurities such as SiO_2 should not be as significant in the high-

TABLE 5. Recalculated results for $\Delta_r H_m^\circ(\text{SiS}_2, \text{cr}, 298.15 \text{ K})$, $p^\circ = 101.325 \text{ kPa}$

| Investigators | $\Delta_r H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ | Investigators | $\Delta_r H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ |
|---|---|-----------------------------------|---|
| Sabatier ⁽⁵⁷⁾ | $\approx -200^a$ | Emons and Theisen ⁽⁶⁷⁾ | $-255 \pm 22^{b, d, e}$ |
| Gabriel and Alvarez-Tostado ⁽⁵⁸⁾ | -329 ± 20^a | | $-210 \pm 14^{b, d, f}$ |
| Rocquet and Ancy-Moret ⁽⁵⁹⁾ | -213 ± 10^a | | $-234 \pm 11^{b, c, e}$ |
| Ivanovna ⁽⁶³⁾ | -300^a | | $-231 \pm 11^{b, c, f}$ |
| Matskevich and Gorsch ⁽⁶⁴⁾ | -308 ± 10^a | Byerley and Teo ⁽⁶⁸⁾ | $-258 \pm 11^{b, d, e}$ |
| Colin and Drowart ⁽⁶⁵⁾ | $-249 \pm 25^{b, c, e}$ | | $-256 \pm 31^{b, d, f}$ |
| Fruehan and Turkdogan ⁽⁶⁶⁾ | $-233 \pm 14^{b, d, f}$ | Byerley and Teo ⁽⁵⁶⁾ | $-241 \pm 6^{b, c, e}$ |
| | | | $-243 \pm 21^{b, c, f}$ |

^a From solution-reaction calorimetry. ^b High-temperature equilibrium study. ^c Reaction studied: $\text{SiS}_2(\text{s}) = \text{SiS}(\text{g}) + \frac{1}{2}\text{S}_2(\text{g})$. ^d Reaction studied: $\text{SiS}_2(\text{s}) + \text{Si}(\text{s}) = 2\text{SiS}(\text{g})$. ^e Third-law calculation.

^f Second-law calculation.

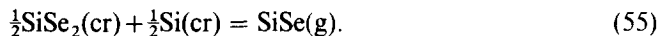
temperature studies; from this consideration alone, it is surprising that there is also such a wide disagreement among those results. It is clearly impossible at present to select $\Delta_f H_m^\circ(\text{SiS}_2)$ without a very large uncertainty.

10. (Silicon + selenium)

SILICON DISELENIDE

There appears to be no precise thermodynamic information in the literature for SiSe_2 . A recalculated solution-calorimetric determination by Gabriel and Alvarez-Tostado⁽⁵⁸⁾ gives an unlikely and uncertain $\Delta_f H_m^\circ$ of approximately $-(20 \pm 40) \text{ kJ} \cdot \text{mol}^{-1}$ which Mills⁽¹⁰⁾ considered unreasonable and adjusted to $-(146 \pm 42) \text{ kJ} \cdot \text{mol}^{-1}$.

Emons and Theisen⁽⁶⁷⁾ used Knudsen effusion to study the reduction of SiSe_2 according to



From their expression for the equilibrium vapor pressure, we obtain for reaction (55):

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 235.2 - 0.167(T/\text{K}). \quad (56)$$

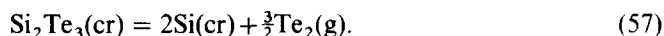
There are no $\Phi_m^\circ(T, T')$ values for SiSe_2 ; therefore, we assume $\Delta\Phi_m^\circ(T, T')$ at $T = 1000 \text{ K}$ to be the same as for SiS_2 . In that way, we estimate $\Delta_r H_m^\circ(298.15 \text{ K}) = (239 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ and, with $\Delta_f H_m^\circ(\text{SiSe}, \text{g}) = (199 \pm 21) \text{ kJ} \cdot \text{mol}^{-1}$ calculated from Mills's⁽¹⁰⁾ selection for $D_m^\circ(\text{SiSe})$ and $\Delta_f H_m^\circ(\text{Se}, \text{g})$,⁽²⁷⁾ we obtain $\Delta_f H_m^\circ(\text{SiSe}_2) = -(80 \pm 42) \text{ kJ} \cdot \text{mol}^{-1}$. A second-law analysis of the same experimental information gives $\Delta_f H_m^\circ = -(84 \pm 48) \text{ kJ} \cdot \text{mol}^{-1}$. Until such time as $\Delta_f H_m^\circ(\text{SiSe}, \text{g})$ is established more precisely, the above values will be of only very limited utility.

11. (Silicon + tellurium)

SILICON SESQUITELLURIDE

There is strong evidence in the literature⁽⁶⁹⁻⁷²⁾ that only one solid compound, Si_2Te_3 , forms in (silicon + tellurium). For that reason, we disregard the determinations by Bousquet *et al.*^(73, 74) of $\Delta_f H_m^\circ$ of "SiTe" and "SiTe₂". Brebrick⁽⁷⁰⁾ has shown that the homogeneity field of $\text{Si}_2\text{Te}_{3-x}$ lies within the range $x = (0.000 \pm 0.065)$.

Brebrick⁽⁷⁰⁾ has used optical-density measurements to deduce the equilibrium vapor pressure of $\text{Te}_2(\text{g})$ in the decomposition of Si_2Te_3 :



The partial pressure of $\text{Te}_2(\text{g})$ is given by

$$\log_{10}(p/p^\circ) = -10152(\text{K}/T) + 7.5634, \quad (58)$$

from which we derive the relation:

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 291.6 - 0.217(T/\text{K}). \quad (59)$$

A third-law calculation using $\Phi_m^\circ(T, T')$ for $\text{Si}^{(11)}$, $\text{Te}_2(\text{g})^{(27)}$ and $\text{Si}_2\text{Te}_3(\text{cr})^{(10)}$ and $\Delta_f H_m^\circ(\text{Te}_2, \text{g})^{(27)}$ gives $\Delta_f H_m^\circ(\text{Si}_2\text{Te}_3) = -(71 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$. The corresponding second-law calculation with $\Delta_T^\circ H_m^\circ(T)$ from the same sources yields $\Delta_f H_m^\circ = -(69 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$.

The Knudsen-effusion mass-spectrometric experiments of Exsteen *et al.*⁽⁷¹⁾ resulted in the equation for the equilibrium vapor pressure of $\text{Te}_2(\text{g})$:

$$\log_{10}(p/p^\circ) = -11100(\text{K}/T) + 7.9. \quad (60)$$

For reaction (57), we deduce

$$\Delta_r G_m^\circ / (\text{kJ} \cdot \text{mol}^{-1}) = 318.8 - 0.227(T/\text{K}). \quad (61)$$

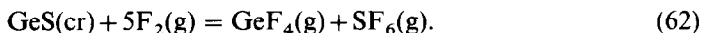
A third-law calculation, using the same sources of auxiliary thermodynamic information as for Brebrick's work, yields $\Delta_f H_m^\circ(\text{Si}_2\text{Te}_3) = -(89 \pm 17) \text{ kJ} \cdot \text{mol}^{-1}$, where the uncertainty is taken from the original paper. A second-law calculation gives $\Delta_f H_m^\circ = -(93 \pm 17) \text{ kJ} \cdot \text{mol}^{-1}$.

All four results agree within their combined uncertainties. We conclude that the best value for $\Delta_f H_m^\circ(\text{Si}_2\text{Te}_3, \text{cr}, 298.15 \text{ K})$ lies in the vicinity of $-(80 \pm 15) \text{ kJ} \cdot \text{mol}^{-1}$. Compared with other systems discussed earlier, these derived values are in reasonable accord, but it should be pointed out that, at 900 K for example, (p/p°) from Brebrick is 1.92×10^{-4} whereas it is 3.69×10^{-5} according to Exsteen *et al.* Thus, Si_2Te_3 should also be regarded as another candidate for future thermodynamic studies, in order, at least, to reduce the large uncertainty in $\Delta_f H_m^\circ$.

12. (Germanium + sulfur)

GERMANIUM MONOSULFIDE

We are aware of just two investigations which have a bearing on $\Delta_f H_m^\circ(\text{GeS}, \text{cr})$. Adams *et al.*⁽⁷⁵⁾ measured the energy of combustion of GeS in a fluorine-bomb calorimeter:



A recalculation that allows for changes in molar mass and in $\Delta_f H_m^\circ$ of $\text{SF}_6^{(17)}$ and $\text{GeF}_4^{(76)}$ gives $\Delta_f H_m^\circ(\text{GeS}) = -(77.7 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$.

Ono and Sudo⁽⁷⁷⁾ used a flow system to study the reduction of GeS at elevated temperatures:



They summarized their results as follows {where $K^\circ = p(\text{H}_2\text{S})/p(\text{H}_2)$ }:

$$\log_{10} K^\circ = -2113(\text{K}/T) + 0.773. \quad (64)$$

TABLE 6. Values of constants in the equations $\log_{10}(p/p^\circ) = A - B(K/T)$ and $\Delta_r G_m^\circ/(kJ \cdot mol^{-1}) = C - D(T/K)$ for reactions of $GeS_2(cr)$ at $\langle T \rangle$

| $\langle T \rangle / K$ | A | B | C | D | Reference |
|-------------------------|--------|-------|-------|-------|-----------|
| 700 ^a | 4.951 | 4876 | 93.4 | 0.095 | 77 |
| 900 ^b | 10.033 | 11823 | 679.1 | 0.576 | 80 |
| 800 ^b | 9.56 | 10970 | 630.2 | 0.549 | 78 |
| 700 ^b | 10.542 | 11822 | 679.1 | 0.606 | 79 |
| 900 ^b | 8.52 | 10680 | 613.5 | 0.489 | 81 |
| 700 ^b | 9.36 | 10700 | 614.7 | 0.538 | 84 |
| 950 ^b | 14.40 | 16878 | 484.8 | 0.414 | 83 |

^a For the reaction: $GeS_2(cr) + H_2(g) = GeS(cr) + H_2S(g)$.^b For the reaction: $2GeS_2(cr) = 2GeS(g) + S_2(g)$.

We deduce for reaction (63):

$$\Delta_r G_m^\circ/(kJ \cdot mol^{-1}) = 40.5 - 1.48 \times 10^{-2}(T/K). \quad (65)$$

With appropriate $\Phi_m^\circ(T, T')$ values and $\Delta_f H_m^\circ(H_2S) = -20.6 kJ \cdot mol^{-1}$ from Glushko *et al.*,⁽¹¹⁾ we calculate by the third-law method $\Delta_f H_m^\circ(GeS) = -(74.8 \pm 10) kJ \cdot mol^{-1}$. A second-law calculation with $\Delta_f^\circ H_m^\circ(T)$ from the same source yielded $\Delta_f H_m^\circ(GeS) = -(68.7 \pm 10) kJ \cdot mol^{-1}$.

There is good agreement between all three results; because the calorimetric determination is more precise, we recommend $\Delta_f H_m^\circ(GeS, cr, 298.15 K) = -(78 \pm 4) kJ \cdot mol^{-1}$.

GERMANIUM DISULFIDE

In an earlier publication,⁽³⁾ we discussed briefly the literature related to $\Delta_f H_m^\circ(GeS_2)$. It consisted of, exclusively, high-temperature equilibrium studies of the reduction by $H_2(g)$ of GeS_2 to GeS or of the decomposition of GeS_2 to $GeS(g)$ and $\frac{1}{2}S_2(g)$. In table 6, we have summarized the equations from which $\Delta_f H_m^\circ$ is derived and, in table 7, the recalculated $\Delta_f H_m^\circ$ values are given along with our own result⁽³⁾

TABLE 7. Recalculated $\Delta_f H_m^\circ$ values for $GeS_2(cr)$ at 298.15 K and $p^\circ = 101.325 kPa$

| Investigators | $\Delta_f H_m^\circ$ $kJ \cdot mol^{-1}$ | Investigators | $\Delta_f H_m^\circ$ $kJ \cdot mol^{-1}$ |
|---|---|--|---|
| Ono and Sudo ⁽⁷⁷⁾ | -196 ± 12^a -157 ± 7^b | Sosnovskii and Abdeev ⁽⁸¹⁾ | -156 ± 15^a -150 ± 8^b |
| Diev and Davidov ⁽⁷⁸⁾ | -163 ± 25^a -135 ± 10^b | Karbanov <i>et al.</i> ⁽⁸²⁾ Karbanov <i>et al.</i> ⁽⁸³⁾ | -103 ± 15^b -92 ± 14^a |
| Shimazaki and Matsumoto ⁽⁷⁹⁾ | -185 ± 15^a -143 ± 10^b | Seta <i>et al.</i> ⁽⁸⁴⁾ | -121 ± 18^b -153 ± 15^a |
| Pogorelyi and Morozova ⁽⁸⁰⁾ | -189 ± 15^a -143 ± 10^b | O'Hare and Murray ⁽³⁾ | -134 ± 8^b -126.0 ± 1.7^c |

^a Second-law calculation. ^b Third-law calculation. ^c Fluorine-combustion calorimetry.

which has been revised to take into account the most recent relative atomic masses and $\Delta_f H_m^\circ$ of $\text{GeF}_4(\text{g})$,⁽⁷⁶⁾ and $\text{SF}_6(\text{g})$.⁽¹⁷⁾

Table 7 shows a large spread in $\Delta_f H_m^\circ$ with, almost invariably, the second-law value being significantly more negative than the third-law result. These large discrepancies suggest that the high-temperature behavior of GeS_2 is not as well understood as the literature might indicate, and we conclude that the fluorine-bomb result, $-(126.0 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$, is the most reliable. It agrees with the third-law values of Diev and Davidov,⁽⁷⁸⁾ Karbanov *et al.*,⁽⁸³⁾ and Seta *et al.*,⁽⁸⁴⁾ but only because of their large uncertainties.

13. (Germanium + selenium)

We have found no evidence in the literature for the existence of any selenides of germanium other than GeSe and GeSe_2 .

CRYSTALLINE GERMANIUM DISELENIDE

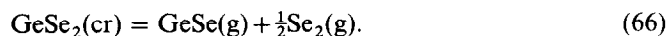
In a recent publication,⁽⁷⁶⁾ we described a determination of $\Delta_f H_m^\circ(\text{GeSe}_2)$ by fluorine-bomb calorimetry, and mentioned that earlier values for this quantity had been deduced, with concomitant large uncertainties, from studies of the high-temperature sublimation of GeSe_2 . The fluorine-bomb result, $\Delta_f H_m^\circ(\text{GeSe}_2, \text{cr}, 298.15 \text{ K}) = -(102.2 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$, is clearly superior to all others.

VITREOUS GERMANIUM DISELENIDE

Although our determination of $\Delta_f H_m^\circ(\text{GeSe}_2, \text{cr})$ had been undertaken because of the importance of GeSe_2 in electronic devices and in solid-state science in general, it subsequently turned out that there was even greater interest in the amorphous diselenide: $\text{GeSe}_2(\text{vit})$. Because of that interest, we measured⁽⁸⁵⁾ the energies of combustion in fluorine of vitreous GeSe_2 and of a specimen of GeSe_2 recrystallized from the vitreous material. The enthalpy of transition between the two forms was found to be $-(12.1 \pm 4.2) \text{ kJ} \cdot \text{mol}^{-1}$; $\Delta_f H_m^\circ(\text{GeSe}_2, \text{cr}) = -(103.7 \pm 3.1) \text{ kJ} \cdot \text{mol}^{-1}$ was also determined, and agrees very well with our selected value of $-(102.2 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$.

GERMANIUM MONOSELENIDE

There has, as yet, been no direct determination of $\Delta_f H_m^\circ(\text{GeSe}, \text{cr})$. It is possible, however, to deduce this value reliably by combining our selected result for $\Delta_f H_m^\circ(\text{GeSe}_2, \text{cr})$ with the enthalpy of sublimation of $\text{GeSe}(\text{cr})$ and our previously selected enthalpy change for the reaction:



The enthalpy of sublimation of $\text{GeSe}(\text{cr})$ to $\text{GeSe}(\text{g})$ has been reported by a

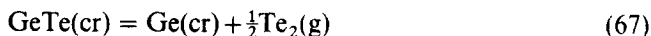
number of authors with generally harmonious results. The vapor-pressure equations are summarized in table 8 along with our derived $\Delta_{\text{sub}}H_m^\circ$ s. Apart from the results from Ch'ün-hua *et al.*,⁽⁸⁶⁾ there is quite good agreement not only between second- and third-law values, but also between individual investigations. We feel confident that $\Delta_{\text{sub}}H_m^\circ(\text{GeSe}) = (173 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ is a reliable selection.

The thermodynamic studies of reaction (66) have been discussed at length in our earlier publication,⁽⁷⁶⁾ and the reader is referred to that source for details. At that time, we selected $\Delta_f H_m^\circ = (290 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ for reaction (66), and see no reason to change that choice. Thus, inserting into equation (66) our selected value for $\Delta_f H_m^\circ(\text{GeSe}_2)$, along with $\frac{1}{2}\Delta_f H_m^\circ(\text{Se}_2, \text{g}) = (72.1 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$,⁽²⁷⁾ and $\Delta_f H_m^\circ(\text{GeSe}, \text{g}) = \Delta_f H_m^\circ(\text{GeSe}, \text{cr}) + (173 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$, we obtain $\Delta_f H_m^\circ(\text{GeSe}, \text{cr}, 298.15 \text{ K}) = -(57 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}$.

14. (Germanium + tellurium)

There is no evidence in the literature for any solid (germanium + tellurium) compound other than GeTe.

We have found four publications that describe work from which $\Delta_f H_m^\circ(\text{GeTe}, \text{cr})$ may be deduced. In 1964, Colin and Drowart⁽⁹²⁾ used a Knudsen-effusion mass-spectrometric technique to study the vaporization of GeTe. They reported that GeTe(cr) vaporized mostly to GeTe(g), but also detected Te₂(g) and GeTe₂(g) in the vapor over GeTe. The Te₂(g) was formed by the reaction:



between 788 and 870 K, and they gave the partial pressures of Te₂(g) at four temperatures. We have used those pressures, in conjunction with $\Phi_m^\circ(T, T')$ for Ge(cr),⁽¹¹⁾ Te₂(g),⁽²⁷⁾ and GeTe(cr),⁽¹⁰⁾ to deduce, by the third-law method, $\Delta_f H_m^\circ = (96 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K. With $\Delta_f H_m^\circ(\text{Te}_2, \text{g})$ from the literature,⁽²⁷⁾ we then obtain $\Delta_f H_m^\circ(\text{GeTe}, \text{cr}, 298.15 \text{ K}) = -(14 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$.

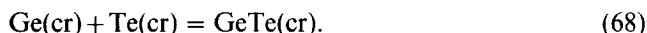
Sadykov and Semenkovich⁽⁹³⁾ studied the formation of GeTe in an

TABLE 8. Sublimation of GeSe(cr): values of the constants *A*, *B*, *C*, and *D* in the equations $\log_{10}(p/p^\circ) = A - B(K/T)$ and $\Delta_f G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = C - D(T/K)$, and $\Delta_{\text{sub}}H_m^\circ$ at 298.15 K and $p^\circ = 101.325 \text{ kPa}$ ^{a, b}

| Investigators | <i>A</i> | <i>B</i> | <i>C</i> | <i>D</i> | $\frac{\Delta_{\text{sub}}H_m^\circ}{\text{kJ} \cdot \text{mol}^{-1}}$ | |
|---|----------|----------|----------|----------|--|-----------|
| | | | | | Second law | Third law |
| Ch'ün-hua <i>et al.</i> ⁽⁸⁶⁾ | 7.847 | 9384 | 179.7 | 0.150 | 188 ± 12 | 191 ± 12 |
| Karbanov <i>et al.</i> ⁽⁸⁷⁾ | 7.329 | 8090 | 154.9 | 0.140 | 166 ± 8 | 175 ± 6 |
| Pashinkin <i>et al.</i> ⁽⁸⁸⁾ | 8.787 | 8680 | 166.2 | 0.168 | 172 ± 8 | 165 ± 6 |
| Wiedemeier and Irene ⁽⁸⁹⁾ | 8.23 | 8640 | 165.4 | 0.158 | 172 ± 15 | 170 ± 6 |
| Zlomanov <i>et al.</i> ⁽⁹⁰⁾ | 7.924 | 8540 | 163.5 | 0.152 | 170 ± 10 | 173 ± 3 |
| Ferro <i>et al.</i> ⁽⁹¹⁾ | 7.94 | 8730 | 167.2 | 0.152 | 175 ± 4 | 176 ± 4 |

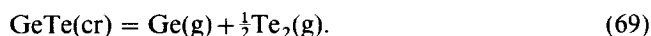
^a The sublimation reaction is: $\text{GeSe}(\text{cr}) = \text{GeSe}(\text{g})$. ^b Auxiliary $\Phi_m^\circ(T, T')$ and $\Delta_f H_m^\circ(T)$ values were taken from Mills.⁽¹⁰⁾

electrochemical cell at $553\text{ K} < T < 653\text{ K}$. They gave an expression for the cell potential as a function of T from which, at $\langle T \rangle = 600\text{ K}$, we calculate $\Delta_f G_m^\circ = -(53.8 \pm 4)\text{ kJ} \cdot \text{mol}^{-1}$ for the formation reaction:



With the appropriate $\Phi_m^\circ(T, T')$ values for Ge ,⁽¹¹⁾ Te ,⁽²⁷⁾ and GeTe ,⁽¹⁰⁾ we deduce $\Delta_f H_m^\circ = -(48 \pm 4)\text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K . A second-law calculation with $\Delta_f^\circ H_m(T)$ from the same sources gave $\Delta_f H_m^\circ = -(58 \pm 5)\text{ kJ} \cdot \text{mol}^{-1}$.

Brebrick,^(94, 95) as he did for (silicon + tellurium), used an optical-density method to deduce the equilibrium pressure of $\text{Te}_2(\text{g})$ formed in the reaction:



The expression:

$$\Delta_f G_m^\circ/(\text{kJ} \cdot \text{mol}^{-1}) = (492.9 \pm 12.6) - 0.228(T/\text{K}), \quad (70)$$

has been used along with $\Phi_m^\circ(T, T')$ for $\text{GeTe}(\text{cr})$, $\text{Ge}(\text{g})$, and $\text{Te}_2(\text{g})$ from references 10, 11, and 27 to derive $\Delta_f H_m^\circ = (473.5 \pm 12.6)\text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K . Combination of this result with $\Delta_f H_m^\circ(\text{Ge}, \text{g})$,⁽¹¹⁾ and $\Delta_f H_m^\circ(\text{Te}_2, \text{g})$,⁽²⁷⁾ gives $\Delta_f H_m^\circ(\text{GeTe}, \text{cr}) = -(43 \pm 13)\text{ kJ} \cdot \text{mol}^{-1}$. A second-law calculation using $\Delta_f^\circ H_m(T)$ from the same compilations gives $\Delta_f H_m^\circ(\text{GeTe}, \text{cr}) = -(67 \pm 13)\text{ kJ} \cdot \text{mol}^{-1}$. Both values are in fair agreement with those from Sadykov and Semenkovich.

Finally, we refer to a study by Shamsuddin.⁽⁹⁶⁾ He determined $\Delta_f H_m^\circ(\text{GeTe})$ by two techniques: d.t.a. and dissolution in molten tin in a calorimeter. From the d.t.a. study, $\Delta_f H_m^\circ = -(32 \pm 7)\text{ kJ} \cdot \text{mol}^{-1}$, and from the solution calorimetry, $\Delta_f H_m^\circ = -(35 \pm 2)\text{ kJ} \cdot \text{mol}^{-1}$, both at 298.15 K . Shamsuddin expresses a preference for the more negative value.

In summary, we have derived $\Delta_f H_m^\circ(\text{GeTe})$ values that range all the way from -14 to $-67\text{ kJ} \cdot \text{mol}^{-1}$. As with so many of the other chalcogenides that we have discussed in this paper, it is not possible to recommend a value for $\Delta_f H_m^\circ(\text{GeTe})$.

SELECTED $\Delta_f H_m^\circ$ VALUES

It is clear that $\Delta_f H_m^\circ$ of very few of the chalcogenides surveyed in this lecture appear to be well established. Those that are have been collected together in table 9.

TABLE 9. Recommended $\Delta_f H_m^\circ$ values at 298.15 K and 101.325 kPa for chalcogenides

| $\Delta_f H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ | | $\Delta_f H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ | | $\Delta_f H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$ | |
|---|-------------------|---|------------------|---|------------------|
| $\text{CrS}(\text{cr})$ | -150 ± 10 | $\text{Mo}_3\text{Te}_4(\text{cr})$ | -177 ± 5 | $\text{Si}_2\text{Te}_3(\text{cr})$ | -80 ± 15 |
| $\text{MoS}_2(\text{cr})$ | -274.1 ± 1.5 | $\text{MoTe}_2(\text{cr}, \alpha)$ | -83 ± 4 | $\text{GeS}(\text{cr})$ | -78 ± 4 |
| $\text{Mo}_3\text{S}_3(\text{cr})$ | -400 ± 10 | $\text{MoTe}_2(\text{cr}, \beta)$ | -78 ± 4 | $\text{GeS}_2(\text{cr})$ | -126.0 ± 1.7 |
| $\text{MoSe}_2(\text{cr})$ | -234.2 ± 3.3 | $\text{WS}_2(\text{cr})$ | -241.6 ± 2.5 | $\text{GeSe}(\text{cr})$ | -57 ± 8 |
| $\text{Mo}_6\text{Se}_6(\text{cr})$ | -477.8 ± 10.0 | $\text{SiS}(\text{am})$ | -107 ± 15 | $\text{GeSe}_2(\text{cr})$ | -102.2 ± 2.6 |
| | | | | $\text{GeSe}_2(\text{vit})$ | -90.1 ± 3.2 |

Although his subject matter was clearly otherwise, the poet Rilke⁽⁹⁷⁾ could have had the contents of my talk in mind when he wrote:

Strange
to see things
that seemed to
belong together
floating in every
direction.

My survey has been limited, of necessity, to the chalcogenides of just five elements. However, even a casual search of the literature shows clearly that the deficiencies which dominated my lecture are not confined to only those elements. It is my hope that this survey will bring to the notice of the appropriate scientific communities the grave distress that afflicts the thermodynamic properties, particularly $\Delta_f H_m^\circ$ s, of the chalcogenides. The realization that there is valuable work to be done, combined with the current and potential technological importance of these materials will lead, I trust, to experimental studies designed to eliminate at least part of the chaos through which this lecturer has just been wandering.

I should like to thank: the Calorimetry Conference for this marvelous award; Henry Mackle and Ward Hubbard (who learned calorimetry from Hugh Huffman himself) for all they taught me about calorimetry; management and scientific colleagues at Argonne National Laboratory, including Gerald Johnson, Ian Tasker, Howard Flotow, and Kathleen Shields for their help, moral support, and many beneficial discussions; and the U.S. Department of Energy for supporting the fluorine-bomb combustion work described in this lecture.

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