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Thermochemical studies of inorganic chalcogenides by fluorine-combustion calorimetry: binary compounds of germanium and silicon with sulfur, selenium and tellurium[1]

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Abstract

A general outline is given of the technique of fluorine-bomb calorimetry, including equipment, experimental procedures, sample purity requirements, post-combustion analyses, and interpretation of the results. Some recent measurements are described on Si_2Te_3, $SiSe_2$, GeS, and GeS_2. How the thermochemistry-based results for the dissociation enthalpies D_m° of the gaseous diatomic molecules SiTe, SiSe, GeS, and GeSe correlate with the D_m°s derived from spectroscopy is also discussed.

Keywords: Chalcogenide; Fluorine-combustion calorimetry; Germanium; Silicon

1. Introduction

About 8 years ago, I reviewed [1] the status of thermodynamic properties, with emphasis on the standard molar enthalpy of formation $\Delta_f H_m^\circ$, of a selected group of chalcogenides (compounds formed by the elements of Group 16 of the periodic table) of technological importance, and pointed out where values were particularly deficient. The

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[1] This paper is dedicated to the memory of Dr. Henry Mackle (21 May 1921–30 July 1994) who, as my Ph.D. mentor at the Queen's University of Belfast, encouraged me to regard the careful measurement of thermodynamic properties not only as an end in itself, but also as a powerful probe with which to elucidate the nature of chemical bonding in molecules. Presented at the 30th Anniversary Conference of the Japan Society of Calorimetry and Thermal Analysis, Osaka, Japan, 31 October–2 November 1994.

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rather pejorative title, *Inorganic chalcogenides: high-tech materials, low-tech thermodynamics,* was chosen to highlight for the thermodynamics research community the significance of such materials in the new technologies and, at the same time, the deplorable state of the thermochemical information about them. Has the situation improved in the meantime? Somewhat. However, there has been a relative lack of activity in this field of experimental thermodynamics. That is not unique. Other areas of research in reaction calorimetry, indeed most, suffer from similar neglect (certainly in North America) brought about by closures of preeminent laboratories or abolition of research groups, the retirement of many leading experimentalists and lack of replacements from younger generations, ignorance or disregard of the power of thermodynamics on the part of those working in the industrial and technological milieu, and the gradual disappearance of thermodynamics from university curricula. All this is compounded by what seems to amount to an antipathy towards thermodynamics on the part of funding agencies. A colleague once confided that he would be ill-advised to include the word "thermodynamics" in a grant request; his planned research in that area had to be camouflaged (most certainly not highlighted) lest his proposal perish.

I have been told often, and know from firsthand experience, that many industrial chemists and engineers are far more inclined to use the "Edisonian" approach to their problems, that is, to try various chemical combinations in a particular process until a workable (not necessarily the best) solution is arrived at, rather than perform a "back-of-the-envelope" calculation of the Gibbs free energy changes to decide whether the putative processes are even feasible. To a non-economist, that approach seems rather wasteful, an anomaly in this age of "competitiveness". Of course, if your competitors are also Edisonians, why worry?

Thermodynamic information needed for such calculations is not always available, and it is impossible to make measurements on all substances of interest. That imposes an obligation on experimentalists such as the present author to select for study those materials that appear to have the greatest technological importance or potential. Measurements on pivotal compounds, that is, those likely to play a role in several processes or that provide a basis upon which thermodynamic properties of related substances can be estimated reliably, yield the greatest dividends.

Over the past couple of decades, fluorine-bomb calorimetry has provided reliable $\Delta_f H_m^\circ$s of numerous "high-tech" materials (nitrides, borides, sulfides, carbides, and silicides of metals, for example) that cannot be obtained with comparable accuracy by other methods. Such information provides the vital foundation on which rests the Gibbs free energy of formation $\Delta_f G_m^\circ(T)$, essential, as just mentioned, as a predictor of the feasibility of chemical reactions and the equilibrium vapor pressure as a function of temperature. Experimental details of the technique of fluorine-bomb calorimetry are discussed in the present article, and some of our recent research in that area, with special emphasis on chalcogenides (compounds of Group 16 of the periodic table), are reviewed.

Three authoritative surveys of fluorine-combustion calorimetry have been published. Hubbard, the father of this technique as we know it today, described [2] the method during its early stages of development. In their book, *Ftornaya Kalorimetriya,* Leonidov and Medvedev [3] gave a very detailed account of most aspects of the experimental procedures, including descriptions of individual determinations of $\Delta_f H_m^\circ$ that predated 1978.

The most recent review, by Hubbard et al. [4] in 1979, included an updated list of values of $\Delta_f H^\circ_m$ of elemental fluorides and other compounds determined by fluorine-bomb calorimetry.

2. Background

The raison d'être of fluorine-bomb calorimetry is, as a foundation for the derivation of $\Delta_f H^\circ_m$, the measurement of energies of combustion of substances that do not react completely in the oxygen atmosphere of a combustion calorimeter, or that are not susceptible to dissolution in the conventional mineral-acid reagents or oxidants used in classic solution-reaction calorimetry. Put simply, the technique takes advantage of the superior oxidizing power of molecular fluorine. Compare, for example, the reactions of molybdenum disulfide (molybdenite) with $O_2(g)$ and with $F_2(g)$:

$$MoS_2(cr) + nO_2(g) = MoO_x(cr) + SO_2(g) + SO_3(g) + (Mo + S + O) + \cdots \quad (1)$$

$$MoS_2(cr) + 9F_2(g) = MoF_6(g) + 2SF_6(g) \quad (2)$$

As shown in Eq. (1), the likely products are a complicated mixture of molybdenum oxides, the oxides of sulfur, or ternary compounds of molybdenum, sulfur, and oxygen. In order to deduce $\Delta_f H^\circ_m(MoS_2)$ from the enthalpy of reaction $\Delta_r H^\circ_m(1)$, the identities, and quantities, of all the oxides must be known accurately, in addition to the amount of any unreacted MoS_2, thus posing a formidable analytical challenge. On the other hand, reaction (2) yields just two well-defined fluorides, which reduces significantly the analytical effort needed to quantify the reaction [5].

3. An overview of experimental techniques

Use of high-pressure fluorine for calorimetric purposes is not without penalties. Apart from its physiologically hazardous nature, which, in itself, demands careful handling, fluorine, because it is corrosive and highly reactive, requires special materials of construction and stringently dry operating conditions when employed as a calorimetric reagent. Thus, at the National Institute of Standards and Technology (NIST), manifold lines, valves, and storage cylinders for the manipulation of fluorine are made of 316 grade stainless steel or Monel; the combustion bomb itself is constructed of nickel; and pressure gauges are of stainless steel specially treated for fluorine service. Threaded connections are sealed with Teflon tape, and fittings in the bomb are of gold, Teflon, lead, and nickel.

All operations with high-pressure fluorine are confined to a well-ventilated hood with heavy Perspex windows and doors, and the experimentalist wears a face shield, safety glasses, and leather gloves for protection.

When the bomb is first put in service its interior surfaces have to be fluorinated. This is usually done by heating the bomb charged with fluorine to a pressure of approximately

200 kPa in an oven at $T \approx 400$ K for 1 h, or by performing several non-calorimetric combustions, preferably with a material that produces a gaseous hygroscopic fluoride. Examples include the reaction of P to $PF_5(g)$ or W to $WF_6(g)$. After that treatment, the interior surfaces of the bomb are dry and a protective film of NiF_2 has been formed on them, which ensures that, during a calorimetric combustion, no extraneous reactions occur with the nickel, occluded water, or water adsorbed on the NiF_2 coating. Such can have a catastrophic effect on the measurements because, as a rule, they cannot be quantified or detected. Thus, when open, the bomb must not be exposed to the air, but should be handled in a glovebox or enclosure with a dry, inert gas. At NIST, our glovebox atmosphere of continually circulating nitrogen typically contains mass fractions $\leq 1 \times 10^{-6}$ of $H_2O(g)$ and 5×10^{-6} of $O_2(g)$ under normal operating conditions.

As with all variants of reaction calorimetry, a major objective of this work, implicit in Eq. (2), for example, is the formation of well-defined products devoid of residual starting material. That often requires creative arrangements of the sample, such as the one used by Johnson [6] for studies of the combustion of uranium metal in fluorine. Frequently, the sample reacts readily when simply placed on a nickel saucer or crucible on the head of the bomb. The support is chosen empirically, however. It must not be too massive and quench the reaction prematurely, nor too light, resulting in a meltdown or extensive corrosion of the crucible. In some of our recent investigations [7,8], we positioned the combustion specimens in a tungsten saucer atop a nickel crucible; under those conditions, the vigorous reaction of W with F_2 to form WF_6 helps to fluorinate even the most refractory of compounds. Of course, the massic energy of combustion of the W has to be determined in separate experiments. Occasionally, the F_2 has had to be diluted with an inert gas in order to moderate the reaction and so prevent its premature extinction by melting of the sample [9].

Most materials and fluorine combine spontaneously to some extent and, therefore, must be kept apart during the fore-rating period of a calorimetric experiment. For that reason, the majority of fluorine-bomb measurements have required two-compartment calorimetric vessels [10,11]. At this laboratory, we use an apparatus first described by Nuttall et al. [12] but in the somewhat modified form shown in Fig. 1. It essentially consists of a storage tank, charged with F_2 at a typical initial pressure of 1–1.5 MPa, connected to a combustion bomb. This entire assembly sits within the water-filled calorimeter can. An isolation valve on the side of the tank is opened remotely to admit the F_2 (the instantaneous expanded pressure is approximately 0.5–0.8 MPa) and initiate combustion.

After each measurement, the combustion products are collected and analyzed (at this laboratory usually by FTIR for gases, and X-ray diffraction for solids), and the surfaces of the bomb interior and the crucible are inspected to be sure that no solid or liquid side-reaction products have been formed. Only by following such procedures can one be certain that the reaction has indeed proceeded as written, for example, in Eq. (2).

3.1. Characterization of the calorimetric sample

As we have mentioned, qualitative and quantitative confirmation of the combustion products is a sine qua non of reliable calorimetry. Of equal importance is the characterization of the substance whose $\Delta_f H_m^\circ$ is to be determined. Although specimens with neg-

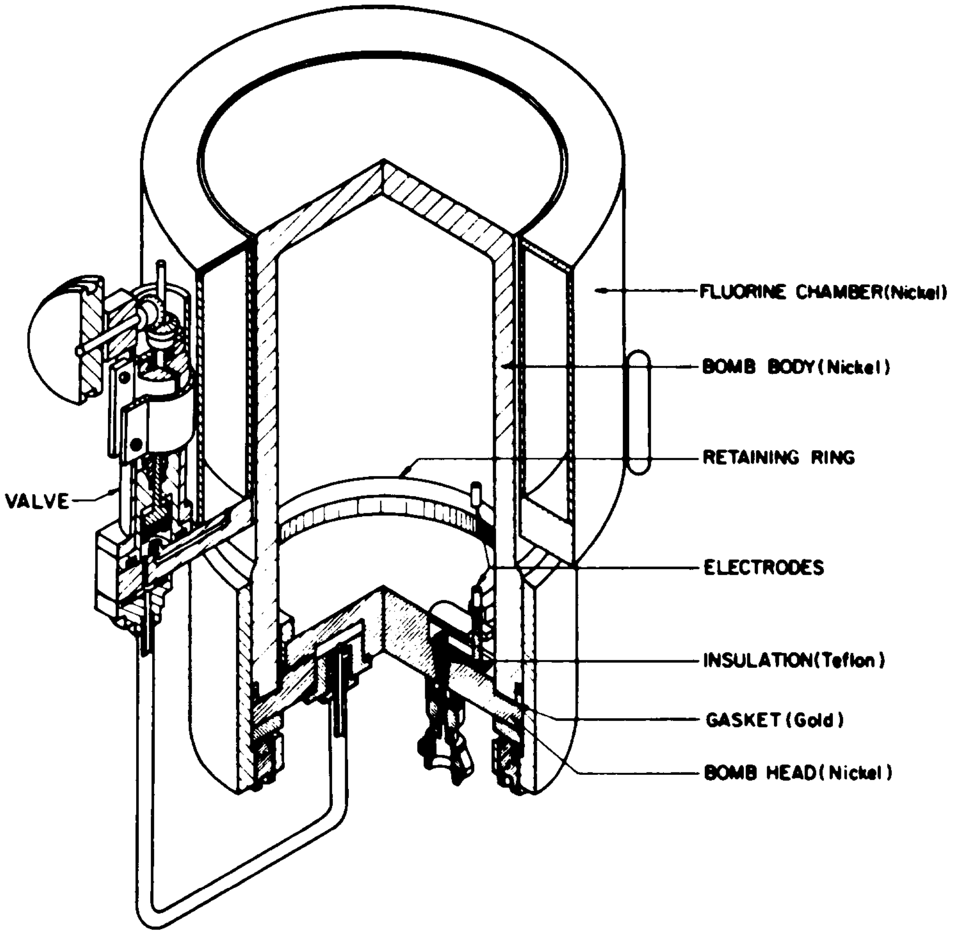

Fig. 1. Cross-section of fluorine-combustion reaction vessel consisting of the (interior) combustion chamber and the (exterior) fluorine chamber.

ligible impurity levels are clearly superior, such are rarely available, and extensive characterization by analytical chemistry is the norm in this work. For purposes of identification of the major (which may be the only) phase present, X-ray diffraction is the technique of choice; at the same time, significant contamination (at the several mass percent level) by minor phases may also be revealed by this method. Microscopic examination is also desirable. Levels of trace metals are determined by ICP or DCP, and C, H, O, and N by combustion and vacuum-fusion analysis. Because of their volatility, many inorganic substances, such as the germanium sulfides, cannot be analyzed by the latter technique, and we have used fast-neutron activation to ascertain their oxygen content. In those cases, one requires high-purity starting materials (Ge and S), in order to justify the (implicit) assumption that C, N, and H are absent to any significant extent.

Major-element analysis is necessary for compounds where there is a risk of non-stoichiometry, as indicated by the phase diagram. Thus, for example, it was essential that the value of ν be known for

$$Si_2Te_{3+\nu} + (13 + 3\nu)F_2(g) = 2SiF_4(g) + (3 + \nu)TeF_6(g) \tag{3}$$

because it determined not only the molar mass of the silicon sesquitelluride (used to convert the experimental massic energy of combustion to the corresponding molar quantity), but also the number by which $\Delta_f H^\circ_m(TeF_6,g)$ should be multiplied in order to derive $\Delta_f H^\circ_m(Si_2Te_{3+\nu})$ [17]. Calorimetric samples of such compounds should never be assumed to be stoichiometric; had we done so during our recent study of $W_5Si_{3+\nu}$ [13], a wildly erroneous result would have been obtained for $\Delta_f H^\circ_m$. In our experience, there is, in this phase of the sample characterization, no substitute for the classic methods of quantitative gravimetric analysis. Often, as in the case of $W_5Si_{3+\nu}$, to which we have just alluded, the conceptualization of a reliable analytical procedure can become a research project in its own right.

If accurately known amounts of high-purity elements are combined under strictly controlled conditions (in a sealed, evacuated tube, for example) in such a way that it is certain that complete reaction has taken place, then major-element appraisals of the resulting compound are superfluous, for they tell one nothing more than that the analytical technique is reliable, or that the correct masses of reactants were taken in the first instance, or both. Our work on the silicon selenides illustrates such a circumstance [14].

3.2. Purity of the fluorine

Impurities in the F_2 are of concern because of the possibility of side reactions with the substance under investigation. Commercial-grade fluorine is manufactured by electrolysis, with the major impurity being 1–2 mass percent of HF(g). As supplied to us, it has been distilled by the manufacturer and a middle fraction taken specifically for our use. At our laboratory, it is then passed through a Monel trap filled with NaF, where any HF present is removed by complexation:

$$NaF(s) + HF(g) = NaHF_2(s) \tag{4}$$

In separate experiments, we found the massic energy of combustion of sulfur with the resulting F_2 to be indistinguishable from results obtained with the high-purity gas prepared in a special still at Argonne National Laboratory. We have concluded that commercial fluorine, distilled and then treated with NaF as we have described, has a purity adequate for our work.

In order to obtain reliable results, meticulous characterization of the components of any reaction-calorimetric experiment is demanded by the first law of thermodynamics, and fluorine-bomb calorimetry is no exception to that rule. That species such as free radicals and ions may form fleetingly during the high-temperature fluorination reactions, although of great interest from other points of view, simply does not play a role in the thermodynamic calculations.

3.3. Calibration of the calorimetric system

Ideally, the calorimetric system should be calibrated by combustion of a well-characterized substance in fluorine but, for several reasons, that is not yet possible. Combustion of benzoic acid (NIST-SRM-39i) in pure $O_2(g)$ is used instead, after which the reaction vessel is thoroughly dried as described earlier. From time to time, the performance of the calorimetric system is checked by means of the reaction between high-purity rhombohedral sulfur and F_2 to form $SF_6(g)$, for which the enthalpy change is well known [15].

3.4. Measurement of the calorimetric temperature change

The calorimetric temperature is measured with a quartz-crystal thermometer at constant time intervals of approximately 10 s that are intrinsic to the thermometer, and the information is recorded and processed by computer. At the conclusion of the experiment, the corrected temperature change is calculated on the basis of the mathematical procedures outlined by Hubbard [16].

3.5. Standard-state corrections

Hubbard [2] treated in detail the corrections to standard states that must be applied to the experimental energy of reaction of substances with fluorine. Those calculations are straightforward and easily adapted to computer programming.

4. Results

In this section, we discuss some recent thermochemical results and their implications for compounds formed between elements of Groups 14 and 16.

4.1. Silicon sesquitelluride (Si_2Te_3) and silicon monotelluride (SiTe)

Although there are thermochemical quantities reported in the literature for the solid substances "SiTe" and "$SiTe_2$", it is now clear that neither exists, and that there is just one solid compound of (silicon + tellurium), namely, Si_2Te_{3+y}. The material used in our study [17] was purified by vapor transport and shown to be stoichiometric within the analytical uncertainty. On the basis of measurements of the massic energy of the reaction

$$Si_2Te_3(cr) + 13F_2(g) = 2SiF_4(g) + 3TeF_6(g), \qquad (5)$$

the standard molar enthalpy of formation $\Delta_f H_m^\circ$ was determined to be $-(71 \pm 6)$ kJ mol^{-1}, in satisfactory agreement with results from two other investigations [18,19], both at high temperatures.

In a related study [20], we surveyed the thermochemistry of SiTe(g). First, however, we offer some comments on diatomic molecules and one of their most useful and interesting properties, namely, the enthalpy of dissociation D_m°, usually derived from spectroscopic or thermochemical measurements, or both.

If $\Delta_f H_m^\circ(\mathrm{AB,g})$ is deduced, from high-temperature mass-spectrometric or Knudsen-effusion studies, for example, then

$$D_m^\circ(\mathrm{AB}) = \Delta_f H_m^\circ(\mathrm{A,g}) + \Delta_f H_m^\circ(\mathrm{B,g}) - \Delta_f H_m^\circ(\mathrm{AB,g}) \tag{6}$$

Since $\Delta_f H_m^\circ$ of A(g) and B(g) are usually well established [21], $D_m^\circ(\mathrm{AB})$ can be calculated. Note that the quantities in Eq. (6) generally refer to $T \rightarrow 0$.

Spectroscopic measurements can also yield D_m°. In the absence of information on any of the excited states of the molecule, the ground-state ($^1\Sigma$ for the chalcogenides being discussed here) vibrational levels can be extrapolated (linear Birge-Sponer extrapolation) to estimate D_m°. Results from this procedure are generally regarded as maximum values. Fortunately, spectroscopic measurements have been reported for the (excited) $\mathrm{E}^1\Sigma$ states of the molecules of interest here, and extrapolations to the dissociation limits are relatively short and accurate. That procedure leads to the enthalpy of dissociation of the E-state. However, the result for D_m° of the E-state depends upon the energy levels of the product atoms A and B. It is known from the Wigner-Witmer rules [22] that $\mathrm{AB}(^1\Sigma)$ dissociates to $\mathrm{A}(^3\mathrm{P})$ and $\mathrm{B}(^3\mathrm{P})$, but there is no guidance as to whether the states of A and B are $^3\mathrm{P}_0$, $^3\mathrm{P}_1$, or $^3\mathrm{P}_2$. When A and B have low molar masses (as in SiO, for example), such considerations are rarely of moment because the separations of the energy levels are less than, or comparable to, the experimental uncertainty of D_m°. However, when A or B are heavier atoms, belonging to the third row of the periodic table and beyond, the energy separations are significant and cannot be disregarded. Traditionally, as Drummond and Barrow [23] have done for SnO(g), dissociation products are assumed which bring about the best agreement with the thermochemical results for D_m°. In the absence of such adjuvant information, the disposition of atomic products is often assumed by analogy with similar molecules.

In the case of SiTe(g), we have shown [20] that $D_m^\circ = (37\,450 \pm 684)\ \mathrm{cm^{-1}}$ ($\mathrm{cm^{-1}} = 11.96266 \times 10^{-3}\ \mathrm{kJ\ mol^{-1}}$) from thermochemistry. The critically selected result from spectroscopy [24] is $37\,650\ \mathrm{cm^{-1}}$ for dissociation to $\mathrm{Si}(^3\mathrm{P}_2)$ and $\mathrm{Te}(^3\mathrm{P}_2)$, and the thermochemical and spectroscopic energies of dissociation are clearly in excellent agreement. Note that the dominant contribution to the uncertainty in the thermochemical value of $D_m^\circ(\mathrm{SiTe})$, $\pm 669\ \mathrm{cm^{-1}}$, stems from $\Delta_f H_m^\circ(\mathrm{Si,g})$ [21], is unusually large for the enthalpy of sublimation of an element, and pervades all thermochemically based D_m°s for silicon-containing diatomic molecules.

4.2. *Silicon diselenide ($SiSe_2$)*

There is little credible evidence for the existence of any solid compound of (silicon + selenium) other than the diselenide. Thermochemical measurements on $\mathrm{SiSe_2(cr)}$ are made difficult by its high reactivity toward air (formation of oxides) and H_2O (formation of H_2Se and SiO_2), and the concomitant challenge of keeping it pure. Values of $\Delta_f H_m^\circ(\mathrm{SiSe_2,cr})$ in the literature range from $5\ \mathrm{kJ\ mol^{-1}}$ [25] to $-145\ \mathrm{kJ\ mol^{-1}}$ [26]. Our recent measurements [14] of the massic energy of the reaction,

$$SiSe_2(cr) + 8F_2(g) = SiF_4(g) + 2SeF_6(g) \qquad (7)$$

yielded a quite different result: $\Delta_f H^\circ_m(SiSe_2,cr) = -(178.4 \pm 3.1)$ kJ mol^{-1}. Unlike the analogous GeS_2, which is discussed later, $SiSe_2$ does not decompose at high temperatures to SiSe(g) and ½Se_2(g) [14]. Emons and Theisen [27] reported that a mixture of Si and $SiSe_2$ heated in an effusion cell reacted as follows:

$$\tfrac{1}{2}SiSe_2(cr) + \tfrac{1}{2}Si(cr) = SiSe(g) \qquad (8)$$

and

$$SiSe_2(cr) = SiSe_2(g) \qquad (9)$$

Our new result for $\Delta_f H^\circ_m(SiSe_2,cr)$, combined with $\Delta_r H^\circ_m(8)$ and $\Delta_r H^\circ_m(9)$ deduced by means of a third-law calculation [14], gives for

$$SiSe_2(g) = SiSe(g) + Se(g) \qquad (10)$$

$\Delta_r H^\circ_m(10) = (312 \pm 18)$ kJ mol^{-1} and, for

$$SiSe(g) = Si(g) + Se(g) \qquad (11)$$

$\Delta_r H^\circ_m(11) - (534 \pm 13)$ kJ mol^{-1}. These quantities are, respectively, the enthalpies of dissociation of the "first" D°_m(Se–SiSe) and "second" D°_m(SiSe) bonds in $SiSe_2$(g).

This thermochemical $D^\circ_m(SiSe) = (44\,640 \pm 1100)$ cm^{-1} and the spectroscopic value 45 510 cm^{-1} selected on the assumption that the dissociation products of the E-state are $Si(^3P_2)$ and $Se(^3P_2)$ [14] are not in disagreement but, given a smaller error in the former, it could turn out to be so. Major contributions to this uncertainty come from the previously mentioned $\Delta_r H^\circ_m(Si,g)$ and the estimated high-temperature thermodynamic properties of $SiSe_2$(cr and g) used in the third-law calculations in the absence of experimental values.

4.3. Germanium sulfides (GeS and GeS$_2$)

There are two solid compounds of germanium and sulfur, germanium(II) sulfide (GeS) and germanium(IV) disulfide (GeS_2); and three gases GeS(g), GeS_2(g), and Ge_2S_2(g). Until recently, there were serious inconsistencies between the thermochemical properties of those substances. We discussed [1,28] the discrepant values of $\Delta_f H^\circ_m(GeS_2$, cr, 298.15 K) obtained by fluorine-combustion calorimetry and those deduced from several studies of the high temperature reaction:

$$GeS_2(cr) = GeS(g) + \tfrac{1}{2}S_2(g) \qquad (12)$$

Gurvich et al.'s evaluation [29] showed the "third-law" results to be compatible with $\Delta_r H^\circ_m(12) = (302 \pm 5)$ kJ mol^{-1} at $T = 298.15$ K. Their choice of $\Delta_f H^\circ_m$(GeS,g, 298.15 K) = (92.5 ± 1.2) kJ mol^{-1}, made on the basis of the spectroscopic result for the enthalpy of dissociation of $\text{GeS}(\text{E}^1\Sigma)$ to the assumed products $\text{Ge}(^3\text{P}_1)$ and $\text{S}(^3\text{P}_1)$, was supported by two values of $\Delta_f H_m^\circ$(GeS,cr): one determined by fluorine-combustion calorimetry [30], the other derived from a transpiration study [31] of the reduction of GeS by H_2(g) to Ge(cr) and H_2S(g). Each was combined with the mean of several congruent values of the enthalpy of sublimation $\Delta_{\text{sub}} H_m^\circ$(GeS,cr) to yield $\Delta_f H_m^\circ$(GeS,g). Those selections, along with the well-established $0.5\Delta_f H_m^\circ(\text{S}_2\text{,g})$ [21] and $\Delta_r H_m^\circ(12)$, gave $\Delta_f H_m^\circ(\text{GeS}_2\text{,cr}) \approx -(145 \pm 10)$ kJ mol^{-1}, far from the fluorine-bomb result of −(127.7 ± 1.6) kJ mol^{-1} [28]. Convinced of the validity of Gurvich et al.'s recommended $\Delta_f H_m^\circ$(GeS,g), and the consequent likelihood that our determination of $\Delta_f H_m^\circ(\text{GeS}_2\text{,cr})$ was in error, we used a new high-purity sample of the disulfide to remeasure the massic energy of the reaction:

$$\text{GeS}_2(\text{cr}) + 8\text{F}_2(\text{g}) = \text{GeF}_4(\text{g}) + 2\text{SF}_6(\text{g}) \qquad (13)$$

and, thus, $\Delta_f H_m^\circ(\text{GeS}_2\text{,cr})$. Our new result was virtually identical to the earlier one. This forced us to consider the possibility, unlikely as it seemed, that the recommended $\Delta_f H_m^\circ$(GeS,cr) was in error. On the basis of measurements of the massic enthalpy of the reaction (two specimens of GeS of completely different provenance were used):

$$\text{GeS}(\text{cr}) + 5\text{F}_2(\text{g}) = \text{GeF}_4(\text{g}) + \text{SF}_6(\text{g}) \qquad (14)$$

$\Delta_f H_m^\circ$(GeS,cr) was found to be −(61.2 ± 1.2) kJ mol^{-1} [32], almost 15 kJ mol^{-1} less negative than Gurvich et al.'s [29] choice. Consequently, the value of $\Delta_f H_m^\circ(\text{GeS}_2\text{,cr}$, 298.15 K) deduced from Eq. (12) on the basis of the high temperature measurements becomes approximately −(130 ± 10) kJ mol^{-1}, in satisfactory agreement with our fluorine-bomb results.

Of course, the question then arises as to how the Gurvich et al. selection of $\Delta_f H_m^\circ$(GeS,cr), based as it is on apparently solid experimental evidence from three sources, could be so much in error. First, we concluded [32] on the basis of Viaene and Moh's study [33] that the method used to synthesize GeS for the earlier fluorine-bomb study [30] was unlikely to produce pure GeS; that, because the sample had been melted, a mixture of a eutectic of composition Ge_{1-x}S and uncombined Ge had been formed. Second, we have shown [32] that results from the transpiration method of Ono and Sudo [31] are subject to systematic error. Third, it appears [34] that the E-state of GeS(g) does not dissociate to the $^3\text{P}_1$ states of Ge and S, and a more plausible hypothesis is that $\text{Ge}(^3\text{P}_2)$ and $\text{S}(^3\text{P}_0)$ are the products. With that assumption, the spectroscopic D_m°(GeS) is calculated to be (44 750 ± 50) cm^{-1}, in excellent agreement with the thermochemical value of (44 580 ± 280) cm^{-1}.

4.4. Germanium selenides (GeSe and GeSe$_2$)

Thermochemical cycles that have in common only the well-established $\Delta_f H_m^\circ$s of Ge(g), Se(g), and Se_2(g), lead to two semi-independent results for D_m°(GeSe) at T = 298.15 K, as shown in Tables 1 and 2, and the agreement between them is satisfac-

Table 1

First cycle used to calculate the enthalpy of dissociation of GeSe(g) from enthalpies of reaction $\Delta_f H^\circ_m$; all thermochemical quantities refer to $T = 298.15$ K

Reaction		$\Delta_f H^\circ_m$/(kJ mol^{-1})
1.	GeSe(g) = GeSe(cr)	-173 ± 5 [1]
2.	GeSe(cr) = Ge(cr) + Se(cr)	51.9 ± 1.5^a
3.	Ge(cr) = Ge(g)	367.9 ± 1.0 [29]
4.	Se(cr) = Se(g)	237.6 ± 0.7 [35]
5.	GeSe(g) = Ge(g) + Se(g)	484 ± 5^b

[a] $-\Delta_f H^\circ_m$(GeSe,cr) was slightly adjusted from the original value [10] to include $\Delta_f H^\circ_m$(GeF$_4$,g) = $-(1191.8 \pm 0.5)$ kJ mol^{-1}, which itself was revised [36] because of a change in the molar mass of Ge.

[b] D°_m(GeSe) at $T = 298.15$ K, where Ge and Se are in their respective ground states: $^3P_0$ and $^3P_2$.

tory. A mean value, calculated by weighting the D°_ms inversely as their uncertainties according to Rossini [37], gives D°_m(GeSe) = (487 ± 4) kJ mol^{-1}. Enthalpy increments $\{H^\circ_m(T) - H^\circ_m(0)\}$ for GeSe(g) [38], Ge(g) [29], and Se(g) [35] were used to adjust the latter result to D°_m(GeSe, $T \to 0$) = (483 ± 4) kJ mol^{-1}, or $(40\,380 \pm 340)$ cm^{-1}.

The most complete spectroscopic study of GeSe has been described by Drummond and Barrow [39]. On the basis of measurements of the ultraviolet absorption spectrum, they deduced the dissociation limit of the $E^1\Sigma$ state of GeSe to be 6775 cm^{-1} by extrapolation, where the products are Ge(^{3}P) and Se(^{3}P). We estimate the latter energy of dissociation to be uncertain by approximately ±200 cm^{-1}. In order to allow for all possible multiplets of the ^{3}P states of the atoms, which cover a range of 3940 cm^{-1} [29], Drummond and Barrow assumed a correction of (1970 ± 1970) cm^{-1} to the ground states of Ge and Se, and combined it with the excitation energy for $X \leftarrow E$, 35 367 cm^{-1}, to give D°_m(GeSe, $X^1\Sigma$) = $(40\,170 \pm 2000)$ cm^{-1} for dissociation to Ge($^3P_0$) and Se($^3P_2$). An identical value was chosen by Huber and Herzberg [40].

Unlike Drummond and Barrow, we have reliable thermochemical information at our disposal which, at the very least, helps eliminate from consideration several multiplets of

Table 2

Second cycle used to calculate the enthalpy of dissociation of GeSe(g) from enthalpies of reaction $\Delta_r H^\circ_m$; all thermochemical quantities refer to $T = 298.15$ K

Reaction		$\Delta_r H^\circ_m$/(kJ mol^{-1})
1.	GeSe(g) = ½Se$_2$(g) – GeSe$_2$(cr)	-290 ± 5 [36]
2.	GeSe$_2$ = Ge(cr) + 2Se(cr)	103.1 ± 1.9^a
3.	Ge(cr) = Ge(g)	367.9 ± 1.0 [29]
4.	Se(cr) = ½Se$_2$(g)	72.1 ± 1.3 [35]
5.	Se(cr) = Se(g)	237.6 ± 0.7 [35]
6.	GeSe(g) = Ge(g) + Se(g)	491 ± 5^b

[a] $-\Delta_f H^\circ_m$(GeSe$_2$) adjusted as described in footnote a of Table 1.

[b] See footnote b in Table 1.

Table 3

Comparison of enthalpies of dissociation D_m° of diatomic molecules of Group 14 obtained by thermochemistry and spectroscopy[a]

Molecule	$D_m^\circ/\mathrm{cm}^{-1}$	
	Thermochemistry	Spectroscopy
SiSe	44640 ± 1100	45510
SiTe	37450 ± 680	37650
GeS	44580 ± 280	44750
GeSe	40380 ± 340	40730 ± 200

[a] All spectroscopic values refer to the $^3P_2$ states of the product atoms with the exception of GeS, where $S(^3P_0)$ is assumed.

$Se(^3P_{0,1,2})$, only two give values of D_m°(GeSe) that overlap with the thermochemical result, (40 380 ± 340) cm^{-1}. Those are $Ge(^3P_0) + Se(^3P_1)$ to give D_m° = (40 150 ± 200) cm^{-1}; and $Ge(^3P_2) + Se(^3P_2)$ to give D_m° = (40 730 ± 200) cm^{-1}. Note that $SiS(E^1\Sigma)$ was assumed to dissociate to the $^3P_2$ states of Si(g) and S(g) [29] and, on that basis, D_m°(GeSe) = (40 730 ± 200) may well be the most reasonable choice.

In Table 3, we have summarized the enthalpies of dissociation of four diatomic chalcogenides for which a significant quantity of thermochemical and spectroscopic information is available. It is important to point out that the multiplicities of the atomic product states, chosen by us to constrain the spectroscopic values to conform as closely as possible to the thermochemical values of the enthalpy of dissociation, should be regarded at this time, and in the absence of other evidence, as no more than empirical fits.

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