Thermochemistry of (germanium+sulfur)

IV. Critical evaluation of the thermodynamic properties of solid and gaseous germanium(II) sulfide GeS and germanium(IV) disulfide GeS$_2$, and digermanium disulfide Ge$_2$S$_2$(g). Enthalpies of dissociation of bonds in GeS(g), GeS$_2$(g), and Ge$_2$S$_2$(g)

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This is a critical evaluation of the thermodynamic properties of the known solid and gaseous compounds of (germanium+sulfur): GeS(cr), GeS(g), GeS$_2$(cr), GeS$_2$(g), and Ge$_2$S$_2$(g). The heat capacity of GeS(cr) at low and moderate temperatures was evaluated from all the information available in the literature, and the properties: $C_{p,m}^\circ(T)$, $\{H_m^\circ(T)-H_m^\circ(T')\}$, $S_m^\circ(T)$, and $\Phi_m^\circ(T)=(\Delta_0^T S_m^\circ-\Delta_{T'}^T H_m^\circ/T)$, where $T'=298.15$ K, were computed to $T=930$ K, close to the melting temperature, above which decomposition to a (germanium+sulfur) eutectic and uncombined germanium is believed to occur. On the basis of our recent value for $\Delta_f H_m^\circ$(GeS, cr, 298.15 K) (*J. Chem. Thermodynamics* **1994,** 26, 727), $\Delta_f H_m^\circ(T)$ and $\Delta_f G_m^\circ(T)$ were also calculated over the same temperature range. A critical assessment of the enthalpy of sublimation $\Delta_{sub} H_m^\circ$ yielded $\Delta_f H_m^\circ$(GeS, g, T). In another part of the present series (*J. Chem. Thermodynamics* **1995,** 27, 99), we determined $\Delta_f H_m^\circ$(GeS$_2$, cr, 298.15 K); the corresponding $\Delta_f H_m^\circ$(GeS$_2$, cr, T) is tabulated in the present paper to $T=1000$ K. *Ab initio* molecular-orbital calculations showed the cyclic (C$_{2v}$) arrangement to be the most stable for Ge$_2$S$_2$(g), and the predicted structure and vibrational wavenumbers were used in calculations of its thermodynamic properties as a function of temperature by means of statistical mechanics. A similar treatment of the linear GeS$_2$(g) is described. The assessed $\Delta_f H_m^\circ$(GeS, g, $T\to0$) is in harmony with our reinterpreted molar enthalpy of dissociation D_m°(GeS) from spectroscopy; and the enthalpies of dissociation of the bonds in GeS$_2$(g) and Ge$_2$S$_2$(g) are also discussed. In summary, the molar enthalpy of dissociation of the (triple) bond in GeS, 535 kJ·mol^{-1}, is the largest for any Ge-to-S linkage, and the mean molar enthalpy of dissociation of the (double) bonds in GeS$_2$, 404 kJ·mol^{-1}, is greater by 110 kJ·mol^{-1} than $\langle D_m^\circ$(Ge$_2$S$_2$)$\rangle$ because, presumably, Ge$_2$S$_2$(g) has essentially single Ge–S bonds only. The molar enthalpy of dissociation of the "primary" bond D_m°(S–GeS) is of comparable magnitude to the mean molar dissociation enthalpy of the Ge–S bonds in Ge$_2$S$_2$(g).

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1. Introduction

Recent calorimetric research[1–3] on solid compounds of (germanium + sulfur) was performed because those materials play important roles in a variety of modern technologies (as exemplified by studies of their crystal-growth behavior in the microgravity environments of the Skylab and Apollo-Soyuz missions, and their use in information-recording media, in optical tracking devices, and as photoreceptors, to cite just a few applications). Industrial processing of the germanium sulfides frequently involves operations at elevated temperatures. Therefore, the thermodynamic properties are important not only of the parent condensed phases GeS and GeS_2, but also of the derived gas-phase species, of which there are three: GeS(g), GeS_2(g), and Ge_2S_2(g). In the present paper, we detail calculations of the thermodynamic properties of GeS(cr) that incorporate the most up-to-date heat-capacity and enthalpy-increment information; and revise the standard molar enthalpy of formation of $\Delta_f H_m^\circ(T)$ and the standard molar Gibbs free energy of formation $\Delta_f G_m^\circ(T)$ of GeS(cr) and GeS(g) in light of our new result[2] for $\Delta_f H_m^\circ$(GeS, cr, 298.15 K). We tabulate the same quantities for GeS_2(cr). New calculations are described of the thermodynamic properties of GeS_2(g) and Ge_2S_2(g). Those were performed on the basis of geometries and vibrational wavenumbers computed, in the absence of experimental information, by means of *ab initio* molecular-orbital procedures.

Most previous discussions of the chemical bonding of germanium sulfides have been essentially semiquantitative, and were of necessity limited to intercomparisons of such properties as internuclear distances and stretching force constants. Now, however, sufficient reliable thermodynamic information is available to derive the much more definitive standard molar enthalpies of dissociation D_m° of the bonds in those compounds. Briefly, we show that a reassignment of the spectroscopic designations of the atomic products of the dissociation of GeS gives D_m° that agrees with results from combined thermochemical and high-temperature vaporization measurements, and that the mean molar enthalpy of dissociation $\langle D_m^\circ \rangle$ of a Ge-to-S nominal double bond in GeS_2(g) is significantly larger than that of the (presumably single) Ge–S bonds in the Ge_2S_2(g) ring.

2. Calculations

The scarcity of experimental information on the structures and vibrational wavenumbers of the gaseous molecules to be discussed in this paper poses an immediate problem with respect to calculation of their thermodynamic properties by means of the conventional formulae of statistical mechanics. Previous authors, faced with this difficulty, resorted to estimates made by analogy with comparable molecules. However, *ab initio* molecular-orbital computations have reached an advanced stage of sophistication and rely less on empirical estimates, for example of the correlation energy to deduce enthalpies of dissociation.[4] Consequently, the requisite properties for the statistical calculations can be obtained from molecular-orbital computations with a good degree of reliability. Accordingly, we used *ab initio* molecular-orbital

theory[5, 6] to obtain structural and spectroscopic information on GeS(g), GeS$_2$(g), and Ge$_2$S$_2$(g).

All calculations were done at the Hartree-Fock level of theory. The 6-31G* and 641(d) basis sets were used for S,[7] and Ge,[8] respectively. These are split-valence basis sets with d-polarization functions (six d-type Gaussians) added. Three structures were considered for Ge$_2$S$_2$(g): linear Ge–S–S–Ge and S–Ge–Ge–S, and a cyclic arrangement; and, for GeS$_2$(g), just the linear. Full geometry optimization was carried out, with the linear structures constrained to $D_{\infty h}$ symmetry, and the cyclic to C_{2v}. Harmonic vibrational wavenumbers ω were calculated for the structures to determine whether they were local minima on the potential energy surface. Values of ω computed by means of molecular-orbital treatments at the present level usually tend to be too large by an average of $0.1 \cdot \omega$,[8, 9] and were adjusted accordingly for all three molecules. Within the probable uncertainties, ω and the vibrational wavenumber $\tilde{\nu}$ are believed to be indistinguishable, so the latter designation is used throughout this manuscript. Results from the molecular-orbital study are summarized in table 1.

Thermodynamic properties of the gaseous molecules were calculated by means of the formulae of statistical mechanics and procedures as delineated, for example, in the introduction to the JANAF tables.[10] Details of the molecular dimensions, vibrational wavenumbers, and other information used in the statistical calculations are to be found in table 1 and elsewhere in this paper. Fundamental constants were those recommended by CODATA.[11] Although experimental vibrational wavenumbers usually refer to mono-isotopic molecules, and the statistical-mechanical calculations described have treated normal isotopic compositions, uncertainties assigned to the thermodynamic functions are believed to account adequately for the effects of such differences.

TABLE 1. Properties of GeS(g), GeS$_2$(g), and Ge$_2$S$_2$(g) calculated by molecular-orbital methods. Equilibrium internuclear distance is denoted by r_e, vibrational wavenumbers by $\tilde{\nu}$, principal moments of inertia by I_A, I_B, and I_C, and molar mass by M

	GeS [a]	GeS$_2$ ($D_{\infty h}$) [b]	Ge$_2$S$_2$ (C_{2v}) [b]
r_e(Ge–S)/pm	199.6	198.8	227.1
r_e(Ge–Ge)/pm			308.3
r_e(S–S)/pm		397.6	327.4
$\tilde{\nu}$/cm^{-1}	570	655, 465, 126, 126	62, 184, 221, 386.7,[c] 361.3,[c] 368
I_A/(10^{-39}·g·cm^2)	14.72	42.09	29.271
I_B/(10^{-39}·g·cm^2)			58.033
I_C/(10^{-39}·g·cm^2)			85.824
M/(g·mol^{-1})	104.68	136.74	209.35

[a] Calculations on GeS are included as an energy reference for reaction (7). Note that both ω_e and r_e are close to the experimental results of 574.3 cm^{-1},[20] and 201.2 pm.[41]

[b] Rotational symmetry number and electronic ground-state degeneracy taken to be 2 and 1, respectively.

[c] Experimental results.[42]

Second- and third-law analyses of high-temperature equilibrium vapor pressures also followed JANAF prescriptions.[10]

3. Results and discussion

Five molecular entities will be discussed, namely, GeS(cr), GeS(g), GeS$_2$(cr), GeS$_2$(g), and Ge$_2$S$_2$(g).

THERMODYNAMIC PROPERTIES OF GeS(cr,orthorhombic)

In the course of their assessments of the thermodynamic properties of GeS(cr), Gurvich et al.[12] and Mills[13] used the low-temperature heat capacities $C_{p,\mathrm{m}}^{\circ}$ from Weller and Kelley's[14] adiabatic calorimetric measurements over the temperature range from 52 K to 296.4 K as the sole experimental basis of the estimated thermodynamic properties at $T > 300$ K. Wiedemeier et al.[15] determined $C_{p,\mathrm{m}}^{\circ}$ by d.s.c. at $220 \leqslant (T/\mathrm{K}) \leqslant 610$, but Gurvich et al. did not refer to this work, and it appeared in print after Mills had completed his compilation. In turn, Wiedemeier et al. made no mention of the Weller and Kelley study with which they could, presumably, have blended their results. Recently, Medzhidov[16] determined enthalpy increments $\{H_{\mathrm{m}}^{\circ}(T) - H_{\mathrm{m}}^{\circ}(T')\}$, where $T' = 298.15$ K, of GeS as a function of T between 298.15 K and 970 K by drop calorimetry. This author appeared to be unaware of the measurements of either Weller and Kelley or Wiedemeier et al. and, in his analysis, used an estimate of $S_{\mathrm{m}}^{\circ}(T')$ by Hirayama[17] as a reference for the quantity $(\Delta_0^T S_{\mathrm{m}}^{\circ} - \Delta_{T'}^T H_{\mathrm{m}}^{\circ}/T)$. Unfortunately, Medzhidov did not report $\{H_{\mathrm{m}}^{\circ}(T) - H_{\mathrm{m}}^{\circ}(T')\}$ at the individual experimental temperatures. Instead, he summarized the results in a figure (the scale of which is insufficiently fine to interpolate the experimental information reliably) and as polynomials in T, one of which implies an impossible $\{H_{\mathrm{m}}^{\circ}(T) - H_{\mathrm{m}}^{\circ}(T')\} = -145$ J·mol^{-1} at $T = T'$.

In light of the foregoing discussion, we considered it essential to recalculate the thermodynamic properties of GeS(s) on the basis of all the information now available on heat capacities, enthalpy increments, and the standard molar enthalpy of formation.[2]

We judge the results of Weller and Kelley to be the more accurate. In our extrapolation of those heat capacities from $T = 50$ K to $T \rightarrow 0$ in order to delineate the $C_{p,\mathrm{m}}^{\circ}(T)$ against T curve for the integration leading to the standard molar entropy increments $\{S_{\mathrm{m}}^{\circ}(T) - S_{\mathrm{m}}^{\circ}(0)\}$ and the other properties, we made the assumptions: that $C_{p,\mathrm{m}}^{\circ} = C_{V,\mathrm{m}}^{\circ}$ within the probable error of the procedure; that GeS obeyed the Debye model; and that the Debye temperature $\Theta_{\mathrm{D}} = 177.3$ K, with 3 degrees of freedom, on the basis of the experimental $C_{p,\mathrm{m}}^{\circ}$s at $50 < (T/\mathrm{K}) < 75$. At $T < 10$ K, we used the formula: $C_{V,\mathrm{m}}^{\circ} = 233.78 \cdot R \cdot (T/\Theta_{\mathrm{D}})^3$ to calculate $C_{p,\mathrm{m}}^{\circ}(T)$ at 1 K temperature intervals. Estimated uncertainties of extrapolated $C_{p,\mathrm{m}}^{\circ}$s increase from $2 \cdot 10^{-2} \cdot C_{p,\mathrm{m}}^{\circ}(T)$ at $T = 50$ K to $1.2 \cdot 10^{-1} \cdot C_{p,\mathrm{m}}^{\circ}(T)$ at $T \leqslant 10$ K.

Wiedemeier et al. did not give experimental values of the heat capacities at individual temperatures. Instead, they summarized their results in the form of a polynomial. It

gives $C_{p,\mathrm{m}}^{\circ}$s that differ from the Weller and Kelley values by approximately $2 \cdot 10^{-2} \cdot C_{p,\mathrm{m}}^{\circ}(T)$ in the region of overlap between $T = 220$ K and $T = 296.4$ K. Therefore, we have arbitrarily multiplied the parameters of the Wiedemeier *et al.* polynomial by 0.9815 to obtain:

$$C_{p,\mathrm{m}}^{\circ}(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 45.6 + 1.46 \cdot 10^{-2} \cdot (T/\mathrm{K}) - 1.97 \cdot 10^{5} \cdot (T/\mathrm{K})^{-2}. \qquad (1)$$

In an earlier analysis of the heat capacity of GeSe,[18] we resorted to a similar adjustment, by a factor of 0.98, of the results of Wiedemeier *et al.* in order to bring them into harmony with values from low-temperature adiabatic calorimetry. Expression (1) should be valid to $T = 510$ K, in accordance with the statements of Wiedemeier *et al.*, and it merges smoothly with the Weller and Kelley curve of $C_{p,\mathrm{m}}^{\circ}(T)$ against T. For example, at $T \approx 286$ K, $\mathrm{d}C_{p,\mathrm{m}}^{\circ}/\mathrm{d}T$ from equation (1) is $0.031 \; \mathrm{J \cdot K^{-2} \cdot mol^{-1}}$, and from Weller and Kelley's study it is approximately $0.032 \; \mathrm{J \cdot K^{-2} \cdot mol^{-1}}$. Wiedemeier *et al.* presented evidence for a transition at $T \approx 520$ K, but this observation is not supported by other authors. Indeed, Viaene and Moh[19] explicitly state that there is no solid-to-solid phase transition below the melting temperature (932 K) of GeS, and assert that the "thermal event" attributed to a transition is, in fact, due to prior decomposition of GeS(l) to the eutectic $\mathrm{Ge}_{1-x}\mathrm{S}$ and uncombined $x\mathrm{Ge}$ as separate phases. (Indirectly, our combustion calorimetric measurements[2] support the latter conclusion.) We have, accordingly, chosen to extrapolate equation (1) to $T = 930$ K, just below the melting temperature but, recognizing the risk of doing so, assign a conservative error of $\pm 5 \cdot 10^{-2} \cdot C_{p,\mathrm{m}}^{\circ}(T)$ at $T \geqslant 500$ K.

A spline function was used to fit the complete set of heat capacities of GeS, that is, those measured by Weller and Kelley; those estimated by the Debye-theta procedure between $T = 50$ K and $T \rightarrow 0$; and those calculated from equation (1) at 25 K intervals from $T = 300$ K to $T = 930$ K. Properties of GeS(cr) derived from the spline fit by means of the standard thermodynamic relations are listed in table 2, with estimated uncertainties summarized in the footnotes. Throughout this paper, uncertainties correspond to the uncertainty interval.

Weller and Kelley used combined Debye and Einstein functions to extrapolate $C_{p,\mathrm{m}}^{\circ}$s to $T \leqslant 51$ K. The disparity between their value of the estimated entropy difference $\{S_{\mathrm{m}}^{\circ}(51 \; \mathrm{K}) - S_{\mathrm{m}}^{\circ}(0)\} = 7.4 \; \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and ours, $8.1 \; \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, presumably due to two different methods of approximation, is covered by the uncertainty limits; within the likely errors, our recalculated $C_{p,\mathrm{m}}^{\circ}(T)$ at $T < 286$ K agrees with the Weller and Kelley values.

The first derivative of a polynomial representation of the experimental $\{H_{\mathrm{m}}^{\circ}(T) - H_{\mathrm{m}}^{\circ}(T')\}$ against T often fails to give a realistic description of the variation of heat capacity with T. In Medzhidov's[16] paper, for example, $C_{p,\mathrm{m}}^{\circ}(T')$ derived in that way is almost 5 per cent smaller than the result given in table 2.

There is no substitute for the actual experimental values, but lacking alternatives, we used Medzhidov's analytical expression to calculate $\{H_{\mathrm{m}}^{\circ}(T) - H_{\mathrm{m}}^{\circ}(T')\}$ at temperature intervals of 100 K, then fitted various polynomials to those values with the constraint that $\{H_{\mathrm{m}}^{\circ}(T) - H_{\mathrm{m}}^{\circ}(T')\} = 0$ at $T = T'$. Reasonably good fits were obtained with polynomials in T^n, where $n = 3$ or 4. At $T = T'$,

TABLE 2. Selected thermodynamic properties of GeS(cr) ($p^\circ = 101.325$ kPa, $R = 8.31451$ J·K^{-1}·mol^{-1}, and $T' = 298.15$) [a, b]

$\dfrac{T}{\text{K}}$	$\dfrac{C^\circ_{p,m}}{R}$	$\dfrac{\Delta^T_{T'} H^\circ_m}{10^3 \cdot R \cdot \text{K}}$	$\dfrac{\Delta^T_0 S^\circ_m - \Delta^T_{T'} H^\circ_m/T}{R}$	$\dfrac{\Delta^T_0 S_m}{R}$	$\dfrac{\Delta_f H^\circ_m}{10^3 \cdot R \cdot \text{K}}$	$\dfrac{\Delta_f G^\circ_m}{10^3 \cdot R \cdot \text{K}}$
0	0	-1.164	∞	0	-7.43	-7.43
100	3.549	-0.996	12.730	2.769	-7.42	-7.43
200	5.203	-0.541	8.562	5.856	-7.38	-7.46
298.15	5.745	0	8.050	8.050	-7.36	-7.49
300	5.748	0.011	8.050	8.086	-7.36	-7.49
400	6.039	0.600	8.280	9.781	-7.61	-7.54
500	6.267	1.216	8.721	11.15	-7.77	-7.50
600	6.472	1.853	9.226	12.31	-7.87	-7.44
700	6.665	2.510	9.741	13.33	-7.91	-7.36
800	6.852	3.186	10.247	14.23	-7.94	-7.28
900	7.036	3.881	10.735	15.05	-7.95	-7.20
930 [c]	7.090	4.093	10.879	15.28	-7.95	-7.18

[a] Both $\Delta_f H^\circ_m(T)$ and $\Delta_f G^\circ_m(T)$ refer to the formation reaction: Ge(cr, cubic) + S(cr, rhombohedral) = GeS(cr, orthorhombic) and their numerical values are therefore subject to discontinuities as the elements pass from one reference state to another.

[b] Estimated uncertainties are: $\pm 10^{-2} \cdot C^\circ_{p,m}$ ($T < 298.15$ K); $\pm 5 \cdot 10^{-3} \cdot C^\circ_{p,m}$ $\{100 \leqslant (T/\text{K}) \leqslant 300\}$; $\pm 10^{-2} \cdot C^\circ_{p,m}$ $\{300 \leqslant (T/\text{K}) \leqslant 500\}$; $\pm 5 \cdot 10^{-2} \cdot C^\circ_{p,m}$ ($T > 500$ K); $\pm 10^{-2} \cdot S^\circ_m$ ($T \leqslant 500$ K); $\pm 2.10^{-2} \cdot S^\circ_m$ ($T > 500$ K). For the enthalpy increments, the uncertainty increases progressively from $\pm 2 \cdot 10^{-2} \cdot \{H^\circ_m(T) - H^\circ_m(298.15 \text{ K})\}$ at the lower temperatures to $\pm 4 \cdot 10^{-2} \cdot \{H^\circ_m(T) - H^\circ_m(298.15 \text{ K})\}$ at $T \geqslant 800$ K. For $(\Delta^T_0 S^\circ_m - \Delta^T_{T'} H^\circ_m/T)$, where $T' = 298.15$ K, the uncertainty rises almost linearly from $\pm 1.5 \cdot 10^2 \cdot (\Delta^T_0 S^\circ_m - \Delta^T_{T'} H^\circ_m/T)$ at T' to $\pm 2.8 \cdot 10^{-2} \cdot (\Delta^T_0 S^\circ_m - \Delta^T_{T'} H^\circ_m/T)$ at $T = 930$ K. Both $\Delta_f H^\circ_m(T)$ and $\Delta_f G^\circ_m(T)$ are uncertain by ± 1.2 kJ·mol^{-1} at $T \leqslant 600$ K, and that increases almost monotonically to ± 1.8 kJ·mol^{-1} at $T = 930$ K.

[c] Melting temperature of GeS(cr).

the polynomial in T^3 gives $C^\circ_{p,m} = 43.8$ J·K^{-1}·mol^{-1}, more than 8 per cent lower than experiment, and $\mathrm{d}C^\circ_{p,m}/\mathrm{d}T = 0.018$ J·K^{-2}·mol^{-1}, in serious disagreement with the low-temperature result of 0.032 J·K^{-2}·mol^{-1}. Although $\mathrm{d}C^\circ_{p,m}/\mathrm{d}T = 0.036$ J·K^{-2}·mol^{-1} at $T = T'$ derived from the polynomial in T^4 is reasonable, the calculated $C^\circ_{p,m} = 42.9$ J·K^{-1}·mol^{-1} is more than 10 per cent lower than experiment. Thus, we are unable constructively to use Medzhidov's results in this assessment. Nevertheless, the recommended enthalpy increments in table 2 differ from his by less than 1 kJ·mol^{-1} at any given temperature and, within the uncertainty limits, $\Phi^\circ_m(T)$ agrees with Gurvich et al.'s tabulation and Medzhidov's equation, but with the latter now referred to $S^\circ_m(T') = 66.93$ J·K^{-1}·mol^{-1} from table 2.

Values of $\Delta_f H^\circ_m(T)$ and $\Delta_f G^\circ_m(T)$, calculated on the basis of $\Delta_f H^\circ_m$(GeS, cr, 298.15 K) $= -(61.2 \pm 1.2)$ kJ·mol^{-1},[2] are also listed in table 2. Auxiliary quantities $\{H^\circ_m(T) - H^\circ_m(T')\}$ and $S^\circ_m(T)$ for Ge(s) and S(s) were taken from Gurvich et al.[12]

THERMODYNAMIC PROPERTIES OF GeS(g)

Precise spectroscopic constants for GeS(g) recently determined by Uehara et al.[20] for the $^1\Sigma$ ground state, and an up-to-date molar mass[21] lead to calculated thermodynamic

quantities somewhat different than those reported by Gurvich *et al*. Results were given by Uehara *et al*. for ^{74}GeS, and we have adjusted them to refer to Ge of normal isotopic composition (see the footnote in table 3) by the method recommended by Herzberg.[22] Constants for the lowest-lying excited state $^{3}\Sigma$ were taken from Linton.[23] Statistical-mechanical calculations were performed on the basis of the approximation that GeS(g) is an anharmonic oscillator, semirigid rotor with centrifugal distortion. Both $\Delta_f H_m^\circ(T)$ and $\Delta_f G_m^\circ(T)$ were revised because of our new value for $\Delta_f H_m^\circ(\text{GeS, cr, } T')$,[2] and the standard molar enthalpy of sublimation discussed in the following section. Complete results for the thermodynamic properties of GeS(g) are given in table 3.

STANDARD MOLAR ENTHALPY OF SUBLIMATION OF GeS(cr)

Over the past 35 years, at least 11 thermodynamic studies of the high-temperature sublimation of GeS have been reported, of which some were too recent to have been considered by Gurvich *et al*.[12] Because of the adjustments in thermodynamic properties of GeS(cr and g) discussed in previous sections and their bearing on the standard molar enthalpy of sublimation $\Delta_{sub} H_m^\circ$ and the standard molar enthalpy of dissociation $D_m^\circ(\text{GeS})$, we now examine in detail results for the reaction:

$$\text{GeS(cr)} = \text{GeS(g)}. \tag{2}$$

TABLE 3. Standard thermodynamic properties of GeS(g) in the ideal-gas state ($p^\circ = 101.325$ kPa, $R = 8.31451$ J·K^{-1} mol^{-1}, and $T' = 298.15$ K) [a]

$\dfrac{T}{\text{K}}$	$\dfrac{C_{p,m}^\circ}{R}$ [b]	$\dfrac{\Delta_T^T H_m^\circ}{10^3 \cdot R \cdot \text{K}}$ [b]	$\dfrac{\Delta_0^T S_m^\circ - \Delta_T^T H_m^\circ / T}{R}$ [b]	$\dfrac{\Delta_0^T S_m^\circ}{R}$ [b]	$\dfrac{\Delta_f H_m^\circ}{10^3 \cdot R \cdot \text{K}}$ [c]	$\dfrac{\Delta_f G_m^\circ}{10^3 \cdot R \cdot \text{K}}$ [c]
0	0	−1.099	∞	0	12.75	12.75
100	3.518	−0.749	31.723	24.238	12.94	10.78
200	3.783	−0.385	28.671	26.745	12.89	8.64
298.15	4.047	0	28.309	28.309	12.76	6.58
300	4.051	0.007	28.309	28.334	12.76	6.54
400	4.209	0.421	28.470	29.523	12.33	4.50
500	4.301	0.847	28.778	30.473	11.99	2.58
600	4.356	1.280	29.128	31.262	11.69	0.73
700	4.392	1.718	29.483	31.936	11.42	−1.08
800	4.416	2.158	29.827	32.525	11.16	−2.85
900	4.433	2.601	30.156	33.046	10.90	−4.59
1000	4.445	3.044	30.469	33.513	10.65	−6.28
1100	4.454	3.489	30.765	33.937	10.37	−7.95
1200	4.461	3.935	31.046	34.325	10.10	−9.60
1300	4.467	4.382	31.312	34.683	5.38	−10.90
1400	4.471	4.829	31.565	35.014		
1500	4.475	5.276	31.805	35.323		

[a] The following spectroscopic values for GeS of normal isotopic composition were recalculated (see text) from the Uehara *et al*. results[20] for Ge^{74}S: $\omega_e = 577.41$ cm^{-1}; $\omega_e x_e = 1.657$ cm^{-1}; $B_e = 0.18866$ cm^{-1}; $\alpha_e = 7.578 \cdot 10^{-4}$ cm^{-1}; $D_e = 8.06 \cdot 10^{-8}$ cm^{-1}. Linton's results[23] for the first excited state $^3\Sigma$ were also used: $T_e = 21986$ cm^{-1}; $\omega_e = 388.9$ cm^{-1}; and $\omega_e x_e = 1.35$ cm^{-1}. Missing spectroscopic values were assumed to be the same as those for the ground state.

[b] Maximum uncertainty in this property is estimated as ≈ 0.1 per cent.

[c] Uncertainty is $\approx \pm 0.35$.

TABLE 4. Standard molar enthalpies of sublimation $\Delta_{sub}H_m^\circ$ of GeS(cr) at $T = 298.15$ K calculated by the second- and third-law methods [a]

	$\dfrac{\Delta_{sub}H_m^\circ}{kJ \cdot mol^{-1}}$		$\dfrac{\delta S_m}{J \cdot K^{-1} \cdot mol^{-1}}$ [b]	$\dfrac{T}{K}$
	Third law	Second law		
GeS(cr) = GeS(g)				
Barrow et al.[27]				
(torsion)	168.8 ± 0.3	161.8 ± 3.6	4 ± 3	579 to 609
(torsion effusion)	166.7 ± 0.7	160.7 ± 8.4	1 ± 7	621 to 649
Shimazaki, Wada[30]	173.0 ± 2.2	183.3 ± 7.8	-24 ± 6	611 to 672
Davydov, Diyev[28]	168.2 ± 2.8	149.4 ± 6.3		574 to 776
Sudo[31]	167.8 ± 10.6	133 ± 16	35 ± 10	706 to 869
Kenworthy et al.[32]	159.0 ± 11.5	124 ± 5	36 ± 3	673 to 873
Spandau, Klanberg[33]	166.2 ± 1.2	151.3 ± 5.1	7 ± 3	798 to 885
Sosnovskii, Abdeyev[29]	167.3 ± 2.0	149		673 to 823
Karbanov et al.[37]	166.3 ± 0.8	155 ± 4	1 ± 2	563 to 652
Nakamura, Fuwa[25]	169.9 ± 4.0	140 ± 14		700 to 900
Kogai, Rolinski[26]	164.6 ± 3.3	115		567 to 657

[a] Thermodynamic functions used in the calculations were taken from tables 2 and 3.
[b] For defintion of δS_m°, see equation (3).

Recalculated second- and third-law enthalpies of sublimation at T' are given in table 4. In addition to the investigations considered by Gurvich et al. (Galimov and Okunov's[24] work is omitted because we were unable to obtain a copy of their paper), those described recently by Nakamura and Fuwa[25] and Kogai and Rolinski[26] were also surveyed. It is clear from table 4 that the second-law values are erratic and, in general, cannot be relied upon to yield a credible $\Delta_{sub}H_m^\circ(\text{GeS}, 298.15 \text{ K})$. Such inconsistencies suggest inaccurate measurements of the experimental temperatures or, in the case of effusion studies, possible thermal gradients in the cell. Thus, only third-law evaluations will be considered here.

Barrow et al.[27] were concerned that the two techniques they employed, torsion and torsion-effusion, gave significantly different values for the equilibrium pressure $p(\text{GeS}, T)$. They concluded that the GeS sample used in the torsion apparatus had been partially hydrolyzed, resulting in the formation of GeO_2, and that pressures obtained by means of the torsion-effusion technique were therefore more reliable.

First of all, we found a typographical error: $p(\text{GeS})$ tabulated for the torsion-effusion study is a factor of 10 too large. The summary in table 4 shows that the second- and third-law results for torsion and torsion-effusion are close, unlike the majority of the other determinations. Both have a small δS_m°, defined according to JANAF as:[10]

$$\delta S_m^\circ = \Delta_r S_m^\circ(\text{second law}, T') - \Delta_r S_m^\circ(\text{third law}, T'). \qquad (3)$$

(In general, studies for which δS_m° is large are regarded as inferior to those for which it is small.) Davydov and Diyev[28] described four series of measurements, each with a

Knudsen-effusion-cell orifice of different size. Three of those give concordant results (series A, B, and D), one with a small δS_m°, but $p(\text{GeS})$ is clearly inconsistent in the fourth set (series C), so we calculated $\Delta_{\text{sub}} H_m^{\circ}$ only from series A, B, and D, and give the average value in table 4. Sosnovskii and Abdeyev,[29] Nakamura and Fuwa,[25] and Kogai and Rolinski,[26] did not report $p(\text{GeS})$ as a function of T but, instead, summarized their results as $\lg(p/p^{\circ})$ against T^{-1}. Incidentally, δS_m° cannot be evaluated from such a representation.

The third-law $\Delta_{\text{sub}} H_m^{\circ}$s are remarkably consistent and, most weight being given to those with small δS_m°, we recommend $\Delta_{\text{sub}} H_m^{\circ}(\text{GeS, cr, 298.15 K}) = (167.3 \pm 2.8) \text{ kJ} \cdot \text{mol}^{-1}$. The corresponding $\Delta_{\text{sub}} H_m^{\circ}(\text{GeS, cr, 0}) = (167.8 \pm 2.8) \text{ kJ} \cdot \text{mol}^{-1}$ was obtained by combining $\{H_m^{\circ}(0) - H_m^{\circ}(T')\}$ values of $-9.68 \text{ kJ} \cdot \text{mol}^{-1}$ for GeS(cr) (table 2) and $-9.14 \text{ kJ} \cdot \text{mol}^{-1}$ for GeS(g) (table 3). Gurvich et $al.$[12] selected $\Delta_{\text{sub}} H_m^{\circ} = (168.4 \pm 3) \text{ kJ} \cdot \text{mol}^{-1}$ at $T \rightarrow 0$. We note that the assessed results[12] of Galimov and Okunov[24] fit comfortably within the error limits of the present selection

THERMODYNAMIC PROPERTIES OF GeS$_2$(cr)

In Part III[3] of this series, we concluded that the "best" value of $\Delta_f H_m^{\circ}(\text{GeS}_2, \text{cr}, 298.15 \text{ K})$ was $-(127.8 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$, and use it here as the basis of the recommended $\Delta_f H_m^{\circ}(T)$ and $\Delta_f(G_m^{\circ}(T))$. In the construction of table 5, $\{H_m^{\circ}(T) - H_m^{\circ}(T')\}$ and $\Delta_0^T S_m^{\circ}$ for Ge(cr), S(cr), and GeS$_2$(cr) were taken from reference 12.

THERMODYNAMIC PROPERTIES OF GeS$_2$(g)

Only two, unfortunately nondefinitive, studies of the high-temperature behavior of GeS$_2$ lead to $\Delta_f H_m^{\circ}(\text{GeS}_2, \text{g})$. Karbanov et $al.$[34] showed by mass spectrometry that GeS$_2$ sublimed mostly by dissociation to GeS(g) and $(1/2) S_2$(g), but that GeS$_2$(g) also formed, albeit in much smaller quantities, with $\{p(\text{GeS, g})/p(\text{GeS}_2, \text{g})\} \approx 1.4 \cdot 10^3$. The same research group[35] subsequently measured the total vapor pressure of the gases in equilibrium with GeS$_2$ at elevated temperatures by quartz-membrane manometry.

TABLE 5. Standard molar enthalpies $\Delta_f H_m^{\circ}$ and Gibbs free energies $\Delta_f G_m^{\circ}$ of formation of GeS$_2$(cr) as a function of temperature ($p^{\circ} = 101.325 \text{ kPa}$, $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) [a]

$\dfrac{T}{\text{K}}$	$\dfrac{\Delta_f H_m^{\circ}(T)}{10^3 \cdot R \cdot \text{K}}$	$\dfrac{\Delta_f G_m^{\circ}(T)}{10^3 \cdot R \cdot \text{K}}$	$\dfrac{T}{\text{K}}$	$\dfrac{\Delta_f H_m^{\circ}(T)}{10^3 \cdot R \cdot \text{K}}$	$\dfrac{\Delta_f G_m^{\circ}(T)}{10^3 \cdot R \cdot \text{K}}$
		Ge(cr) + 2S(cr) = GeS$_2$(cr)			
0	−15.29	−15.29	600	−16.69	−14.75
298.15	−15.37	−15.31	700	−16.93	−14.40
300	−15.37	−15.31	800	−17.15	−14.05
400	−15.96	−15.27	900	−17.33	−13.63
500	−16.37	−15.04	1000	−17.51	−13.21

[a] Values of the tabulated quantities X are estimated to be uncertain by $\pm 10^{-2} \cdot X$.

Schäfer and Trenkel[36] studied the reaction:

$$Ge(cr) + GeS_2(g) = 2GeS(g), \qquad (4)$$
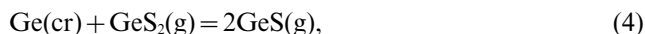
by mass-transport, mass-spectrometric, and thermogravimetric techniques, and concluded that $\Delta_r H_m^\circ(4) = (138 \pm 8)$ kJ·mol^{-1}. The latter result, combined with the values of $\Delta_f H_m^\circ$ for GeS$_2$(cr) and GeS(g) given in the present paper, lead to $\Delta_{sub} H_m^\circ(GeS_2) = (203 \pm 10)$ kJ·mol^{-1} which, in turn, requires $p(GeS_2, g) \approx p(GeS, g)$, contrary to the mass-spectrometric observations.[34] Gurvich *et al.* rejected Schäfer and Trenkel's study for that reason, and recommended $\Delta_{sub} H_m^\circ(GeS_2) = (240 \pm 20)$ kJ·mol^{-1} on the basis of the Karbanov *et al.* studies.[34, 35] Thus, $\Delta_f H_m^\circ(GeS_2, g, 298.15 \text{ K}) = (112 \pm 20)$ kJ·mol^{-1}. Because of the large uncertainty, we believe it not worthwhile to tabulate $\Delta_f H_m^\circ(GeS_2, g, T)$ here.

Little additional experimental information is available concerning GeS$_2$(g). There is a consensus, however, that its structure is linear (D$_{\infty h}$), similar to dioxides of Group 14. Hassanzadeh and Andrews[38] gave values of the $\tilde{v}_3$ absorption bands of germanium sulfides, oxides, and sulfide-oxides observed by i.r. spectroscopy in an argon matrix. For ^{32}S^{73}Ge^{32}S, the isotopic composition closest to the normal mixture, they reported $\tilde{v}_3 = 655.4$ cm^{-1} and also predicted the Raman-active $\tilde{v}_1 = (500 \pm 20)$ cm^{-1}. Köppe and Schnöckel,[39] by means of self-consistent-field computations, determined $\tilde{v}_3 = 655.6$ cm^{-1} for the same isotopic composition, in excellent agreement with the findings of Hassanzadeh and Andrews and, also, $r_e(\text{S–GeS}) = 201$ pm. There is no value in the literature for the doubly degenerate $\tilde{v}_2$, whose intensity is expected to be low. Gurvich *et al.*[12] estimated the vibrational wavenumbers ($\pm 0.1 \cdot \tilde{v}$) to be 475 cm^{-1}, 155 cm^{-1}, and 600 cm^{-1} by analogy with the experimental quantities for SiS$_2$(g), and $r_e(\text{S–GeS}) \approx (205 \pm 5)$ pm.

Molecular-orbital calculations, procedural details of which are given earlier in this paper, yielded the values of $\tilde{v}$ and r_e shown in table 1 and used, as previously outlined, to calculate the thermodynamic properties of GeS$_2$(g) listed in table 6. Taking our values of the wavenumbers $\tilde{v}$ to be uncertain by $\pm 5 \cdot 10^{-2} \cdot \tilde{v}$, and $r_e(\text{S–GeS}) = (199 \pm 2)$ pm, the thermodynamic properties of GeS$_2$(g) are assigned the uncertainties given at the bottom of table 6.

THERMOCHEMISTRY OF Ge$_2$S$_2$(g)

To complete the survey of the (germanium + sulfur)(g) species, we now deal with Ge$_2$S$_2$(g), a relatively minor component of the vapor found in equilibrium with germanium sulfides at high temperatures by Schäfer and Trenkel[36] and, more recently, by Balducci *et al.*,[40] who studied its dissociation reaction:

$$Ge_2S_2(g) = 2GeS(g). \qquad (5)$$
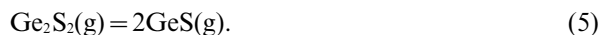
As in the case of GeS$_2$(g), very little structural or spectroscopic information is available on Ge$_2$S$_2$(g). In the general absence of experimental results, we used the molecular-orbital procedures outlined at the beginning of this paper to deduce the most stable structure of Ge$_2$S$_2$ and to estimate its vibrational wavenumbers and moments of inertia.

TABLE 6. Standard thermodynamic properties of GeS$_2$ in the ideal-gas state ($p^\circ = 101.325$ kPa, $R = 8.31451$ J·K^{-1}·mol^{-1}, $T' = 298.15$ K) [a]

$\dfrac{T}{\text{K}}$	$\dfrac{C_{p,\text{m}}^\circ}{R}$ [a]	$\dfrac{\Delta_{T'}^T H_\text{m}^\circ}{10^3 \cdot R \cdot \text{K}}$ [a]	$\dfrac{\Delta_0^T S_\text{m}^\circ - \Delta_{T'}^T H_\text{m}^\circ / T}{R}$ [a]	$\dfrac{\Delta_0^T S_\text{m}^\circ}{R}$ [a]
0	0	−1.598	∞	0
100.00	5.095	−1.176	37.820	26.058
200.00	5.996	−0.619	32.979	29.883
298.15	6.569	0	32.394	32.394
300.00	6.578	0.012	32.395	32.435
400.00	6.904	0.688	32.657	34.377
500.00	7.091	1.388	33.162	35.939
600.00	7.205	2.104	33.737	37.243
700.00	7.278	2.828	34.319	38.359
800.00	7.327	3.558	34.887	39.335
900.00	7.362	4.293	35.430	40.200
1000.00	7.387	5.031	35.946	40.977
1100.00	7.406	5.771	36.436	41.682
1200.00	7.421	6.511	36.901	42.327
1300.00	7.432	7.254	37.341	42.921
1400.00	7.441	7.998	37.760	43.473
1500.00	7.449	8.742	38.158	43.986

[a] Estimated uncertainties are as follows: $\pm 6 \cdot 10^{-2} \cdot C_{p,\text{m}}^\circ(T)$ and $\pm 5 \cdot 10^{-2} \cdot X$, where X denotes the other functions.

Total energies were obtained for three optimized configurations, two linear and one cyclic, described in section 2 of this paper. The cyclic structure was found to be the most stable, with a total energy of $-4941.62252 \cdot E_{\text{h,m}}$, where $E_{\text{h,m}} = 2.6255$ MJ·mol^{-1}. This structure has all positive wavenumbers, indicating that it is a local minimum. One linear arrangement (Ge–S–S–Ge) is unstable with respect to 2GeS(g); the other (S–Ge–Ge–S) is a saddlepoint in the potential-energy surface, has one imaginary wavenumber, and is 380 kJ·mol^{-1} less stable than the cyclic array, to which it optimizes if the linear constraint is relaxed. The plane D$_{2\text{h}}$ structure assumed by Balducci *et al*. is a saddlepoint on the potential-energy surface, and is just 1 kJ·mol^{-1} less stable than the nonplanar C$_{2\text{v}}$.

Figure 1 shows mutually perpendicular views of the calculated structure of Ge$_2$S$_2$(g). It has $r_\text{e}(\text{Ge–S}) = 227.1$ pm, and is slightly nonplanar ("butterfly shaped") with a dihedral angle of $0.879 \cdot \pi$. The Ge–S internuclear distance in the dimer is thus substantially longer than in GeS(g), $r_\text{e} = 201.2$ pm,[41] and GeS$_2$(g), $r_\text{e} = (199 \pm 2)$ pm.

Vibrational wavenumbers of Ge$_2$S$_2$(g) are given in table 1. Marino *et al*.[42] assumed Ge$_2$S$_2$(g) to be a planar molecule and, on that basis reported two wavenumbers: 386.7 cm^{-1} and 361.3 cm^{-1}, assigned as the B$_{2\text{u}}$ and B$_{3\text{u}}$ modes, respectively, measured by matrix-isolation i.r. spectroscopy. These values, which we have used unchanged in the calculations of thermodynamic properties, are close to the theoretical predictions of 352 cm^{-1} (B$_2$) and 341 cm^{-1} (B$_1$) for the non-planar structure. The vibrational wavenumber for the out-of-plane bend of the dimer is 62 cm^{-1}, consistent with both a very "floppy" structure and the small difference in energy between it and the planar configuration. Experimentally, it is likely that Ge$_2$S$_2$(g) would be observed as a planar
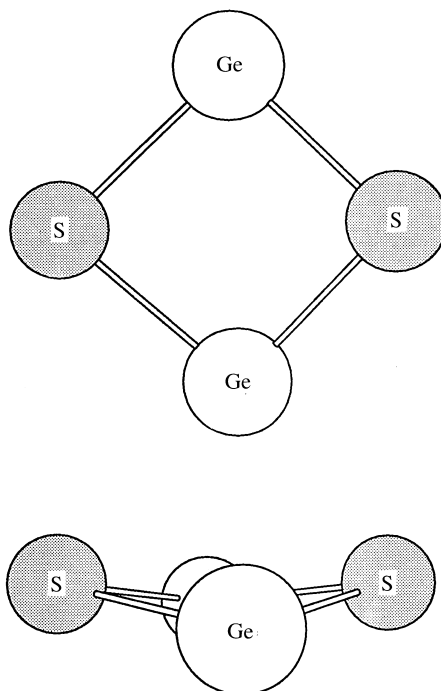
FIGURE 1. Vertical and horizontal views of molecular structure of $Ge_2S_2(g)$. (a), Internuclear separations are as follows: $r_e(Ge–S) = 227.1$ pm; $r_e(S–S) = 327.4$ pm; $r_e(Ge–Ge) = 308.3$ pm. (b), The dihedral angle is $0.879 \cdot \pi$.

molecule. Thermodynamic properties of $Ge_2S_2(g)$ are given in table 7. We assumed the empirically adjusted vibrational wavenumbers to be uncertain by $\pm 5 \cdot 10^{-2} \cdot \tilde{\nu}$ which, in turn, implies a maximum error in a thermodynamic property X of $\pm 4 \cdot 10^{-3} \cdot X$, especially at high temperatures.

Balducci et al.[40] used a combination of Knudsen-effusion and mass spectrometry to deduce the equilibrium vapor pressure of $Ge_2S_2(g)$ over $2GeS(cr)$ as a function of temperature, and recommended $\Delta_r H_m^\circ(5) = (106.5 \pm 2.1)$ kJ·mol^{-1} at $T \to 0$ from closely agreeing second- and third-law values. They calculated the auxiliary thermodynamic functions from vibrational wavenumbers obtained by the Wilson FG method, estimated force constants, a structure assumed to be planar, and a Ge–S internuclear distance taken to be 221 pm. At $T = 700$ K and $T' \to 0$, for example, there is a difference of approximately 1 J·K^{-1}·mol^{-1} between our result for $\Phi_m^\circ(T)$ and theirs. Our third-law derivation of $\Delta_r H_m^\circ(5)$, (107.8 ± 2) kJ·mol^{-1} at $T \to 0$, hardly differs from theirs: (107.9 ± 0.7) kJ·mol^{-1}. The Balducci et al. value of (105.0 ± 2.1) kJ·mol^{-1} for $\Delta_r H_m^\circ(5)$ from a second-law treatment is close to our recalculated (104.9 ± 2.1) kJ·mol^{-1}. An estimate of $\Delta_r H_m^\circ(5) = (105 \pm 3)$ kJ·mol^{-1} at $T \to 0$ seems to be reasonable. Thus, with $\Delta_f H_m^\circ(GeS, g, T \to 0) = (106.0 \pm 3.1)$ kJ·mol^{-1} given previously, it follows that $\Delta_f H_m^\circ(Ge_2S_2, g, T \to 0) =$

TABLE 7. Standard thermodynamic properties of Ge₂S₂ in the ideal-gas state ($p° = 101.325$ kPa, $R = 8.31451$ J·K⁻¹·mol⁻¹, $T' = 298.15$ K) [a]

$\dfrac{T}{\text{K}}$	$\dfrac{C_{p,m}°}{R}$ [a]	$\dfrac{\Delta_{T'}^{T}H_m°}{10^3 \cdot R \cdot \text{K}}$ [a]	$\dfrac{\Delta_0^T S_m° - \Delta_{T'}^T H_m°/T}{R}$ [a]	$\dfrac{\Delta_0^T S_m°}{R}$ [a]
0	0	−2.120	∞	0
100.00	6.377	−1.616	48.358	32.197
200.00	8.366	−0.865	41.648	37.322
298.15	9.147	0	40.831	40.831
300.00	9.156	0.017	40.831	40.888
400.00	9.498	0.952	41.195	43.575
500.00	9.670	1.911	41.892	45.714
600.00	9.767	2.884	42.681	47.487
700.00	9.827	3.863	43.478	48.997
800.00	9.867	4.848	44.252	50.312
900.00	9.894	5.836	44.992	51.476
1000.00	9.914	6.827	45.693	52.520
1100.00	9.929	7.819	46.357	53.465
1200.00	9.940	8.813	46.986	54.330
1300.00	9.949	9.807	47.582	55.126
1400.00	9.956	10.801	48.148	55.863
1500.00	9.962	11.799	48.685	56.551

[a] Maximum error is estimated to be $\pm 4 \cdot 10^{-3} \cdot X$, where X denotes a thermodynamic property of Ge₂S₂(g).

(107 ± 7) kJ·mol⁻¹. Because of the rather large uncertainty in the latter value, we have not tabulated the corresponding values of $\Delta_f H_m°(T)$ or $\Delta_f G_m°(T)$.

4. Enthalpies of dissociation of germanium-to-sulfur bonds

As we mentioned earlier, derivation of thermochemical enthalpies of dissociation of germanium-to-sulfur bonds is one of the principal objectives of this study. We now discuss the bonding in GeS(g), GeS₂(g), and Ge₂S₂(g).

There is general agreement that GeS has a triple bond, and that the bonds in GeS₂(g) are formally double. We have found few statements in the literature about the bonding in Ge₂S₂(g). Marino et al.[42] showed the stretching-force constant of the Ge–S bond in the dimer to be approximately half that for the monomer, from which it may be inferred that the mean standard molar enthalpy of dissociation $\langle D_m° \rangle(\text{Ge}_2\text{S}_2)$ is significantly less than $D_m°(\text{GeS})$.
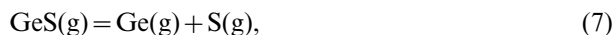
ENTHALPY OF DISSOCIATION OF GeS(g)

Drummond and Barrow[43] deduced the molar enthalpy of dissociation of the (excited) E-state of GeS to be 95.52 kJ·mol⁻¹, by an extrapolation (of approximately 1.20 kJ·mol⁻¹) of the vibrational intervals. Combination of that result with the GeS($X^1\Sigma$)-to-GeS($E^1\Sigma$) molar excitation energy: 463.58 kJ·mol⁻¹,[43] yields $D_m = (559.10 \pm 0.48)$ kJ·mol⁻¹, very close to the directly observed dissociation limit of 559.00 kJ·mol⁻¹, for

$$\text{GeS}(X^1\Sigma) = \text{Ge}(^3P) + \text{S}(^3P), \qquad (6)$$

where $X^1\Sigma$ denotes the ground state. Gurvich $et\ al.$[12] used this information, together with the assumption that the dissociation products of the E-state were $Ge(^3P_1)$ and $S(^3P_1)$, to deduce $D_m(GeS, X^1\Sigma)$. They then adjusted that result to refer to the ground states of the product atoms: $Ge(^3P_0)$ and $S(^3P_2)$, and thus selected $D_m^\circ(GeS) = (547.53 \pm 0.48)\ kJ\cdot mol^{-1}$.

Thermochemical quantities can also be used to derive $D_m^\circ(GeS)$, as follows. Our result for $\Delta_f H_m^\circ(GeS, cr, T\to 0) = -(61.8 \pm 1.3)\ kJ\cdot mol^{-1}$ (table 2), combined with the recommended $\Delta_{sub} H_m^\circ(GeS, cr, T\to 0) = (167.8 \pm 2.8)\ kJ\cdot mol^{-1}$, gives $\Delta_f H_m^\circ(GeS, g, T\to 0) = (106.0 \pm 3.1)\ kJ\cdot mol^{-1}$. Therefore, for the dissociation reaction:

$$GeS(g) = Ge(g) + S(g), \tag{7}$$

at $T\to 0$ and with values[12] of $(365.0 \pm 1.0)\ kJ\cdot mol^{-1}$ and $(274.9 \pm 0.2)\ kJ\cdot mol^{-1}$ for $\Delta_f H_m^\circ(T\to 0)$ of $Ge(g)$ and $S(g)$, we calculate $D_m^\circ(GeS) = (533.9 \pm 3.3)\ kJ\cdot mol^{-1}$, where Ge and S are in their previously specified spectroscopic ground states. This molar enthalpy of dissociation differs from the Gurvich $et\ al.$ choice by about $14\ kJ\cdot mol^{-1}$, and lies well outside the combined uncertainty limits of the two values. We accordingly sought reasons for the discrepancy between these two carefully determined D_m°s.

Differences between the atomic energy levels of multiplets of the lowest-lying ^3P states of Ge and S are not trivial, especially for the heavier atom,[44] so the choice of those levels affects significantly the derived enthalpy of dissociation of the E-state and, thus, $D_m^\circ(GeS)$. In concluding the description of their study of GeS, Drummond and Barrow[43] were reluctant to speculate as to the precise spectroscopic designations of the products of dissociation of the E-states of germanium monochalcogenides, GeX. "It is reasonable" they wrote "to suppose that the ground states dissociate into $Ge(^3P_0) + X(^3P_2)$, but is is hardly possible to be certain about the E-states". Consequently, they increased the experimental uncertainty of their results to encompass all the possible lowest-lying states ($^3P_0$, $^3P_1$, and $^3P_2$) of the dissociation products and, accordingly, recommended $D_m^\circ(GeS) = (548 \pm 13)\ kJ\cdot mol^{-1}$. In a "note added in proof," Drummond and Barrow referred to their just-completed work on SnO (formed, like GeS, from elements of Groups 14 and 16) as indirect evidence that the E-state of GeS dissociated to $Ge(^3P_2)$ because, by assuming that $SnO(g)$ dissociated to $Sn(^3P_2)$ and $O(^3P_2)$, the $D_m^\circ(SnO)$s from thermochemistry and spectroscopy could be brought into agreement. Over the intervening years, however, the selected values of $\Delta_f H_m^\circ$ for $SnO(g)$, $Sn(g)$, and $O(g)$ have changed in such a way as to render Barrow and Drummond's hypothesis probably no longer valid. Modern thermochemical information appears to be reasonably consistent with the dissociation of the E-state of SnO to $Sn(^3P_1)$ and $O(^3P_1)$, although the extrapolation from the highest observed vibrational molar energy of the E-state to the dissociation limit is uncomfortably large at almost $24\ kJ\cdot mol^{-1}$.

In an earlier publication,[18] we discussed the chemical bonding of the analogous $GeSe(g)$. Two thermochemical cycles led to harmonious values for $D_m^\circ(Ge-Se)$, and a weighted mean of $(483.05 \pm 4.07)\ kJ\cdot mol^{-1}$ was selected. Gaydon[45] assessed Drummond and Barrow's[43] spectroscopic studies of GeSe. On the basis of the convergence limit of the E-state, and the assumption that dissociation took place to

Ge($^3P_1$) and Se($^3P_1$), he recommended $D_m(\text{Ge–Se}) = 504.6$ kJ·mol^{-1}, recalculated here to 504.1 kJ·mol^{-1}, a value greater by 21 kJ·mol^{-1} than that derived from thermochemistry. However, if the products of dissociation of the E-state are assumed, instead, to be Ge($^3P_2$) and Se($^3P_2$), then, taking the molar energy difference between Ge($^3P_2$) and Ge($^3P_0$) as 16.9 kJ·mol^{-1},[44] $D_m^\circ(\text{Ge–Se})$ from spectroscopy becomes (487.2 ± 2.4) kJ·mol^{-1}, in agreement, within the combined errors, with the thermomechanical result.

A similar analysis of GeTe could be enlightening, but values of $\Delta_f H_m^\circ(\text{GeTe, cr, 298.15 K})$ deduced[46] from reports in the literature range from -14 kJ·mol^{-1} to -67 kJ·mol^{-1}, and make such an appraisal unpromising. It is expected that calorimetric studies of the monotelluride now underway at this Laboratory will help to resolve these discrepancies.

We also found recently[47] that the spectroscopic D_m° of SiSe(g), isoelectronic with GeS, agreed best with the thermochemical result when it was assumed that the dissociation products of the E-state were Si($^3P_2$) and Se($^3P_2$).

If, by analogy, the E-state of GeS is taken to dissociate according to:

$$\text{GeS(g)} = \text{Ge}(^3P_2) + \text{S}(^3P_2), \tag{8}$$

Gurvich *et al.*'s selection would have to be adjusted to $D_m^\circ(\text{GeS}) = (542.2 \pm 1.2)$ kJ·mol^{-1}, which still does not agree with the result (533.9 ± 3.3) kJ·mol^{-1} from thermochemistry. On the other hand, if it is assumed that S($^3P_0$) is formed, or even S($^3P_1$), the agreement becomes very much better, as shown by the italicized values of the molar enthalpies of dissociation in table 8. The most satisfactory choice of products is Ge($^3P_2$) and S($^3P_0$) and, consequently, $D_m^\circ(\text{GeS}) = (535 \pm 1)$ kJ·mol^{-1}.

Although definite rules (Wigner-Witmer) correlate specific spectroscopic states of diatomic molecules with their atomic products of dissociation, no similar guidance is available from spectroscopy *per se* with regard to the choice of J (the total angular momentum quantum number, with possible values 0, 1, and 2 for the ^3P states of Ge and S), and thermochemical evidence has frequently been invoked to help resolve such ambiguities. Indeed, Gaydon (reference 45, p. 248) has discussed this very problem in

TABLE 8. Molar enthalpy of dissociation of the ground state (X$^1\Sigma$) of GeS, and its dependence on the assumed atomic dissociation products of the (E$^2\Sigma$)-state. Uncertainties in the spectroscopic values correspond to the standard deviation of the mean ^{a}

	$D_m^\circ(\text{GeS, X}^1\Sigma)/(\text{kJ·mol}^{-1})$ ^{b}
Thermochemistry:	533.9 ± 3.3
Spectroscopy, assumed dissociation products:	
GeS(E$^1\Sigma$) = Ge($^3P_1$) + S($^3P_1$)	547.7 ± 0.6
GeS(E$^1\Sigma$) = Ge($^3P_2$) + S($^3P_0$)	*535.4 ± 0.6* ^{c}
GeS(E$^1\Sigma$) = Ge($^3P_2$) + S($^3P_2$)	542.2 ± 0.6
GeS(E$^1\Sigma$) = Ge($^3P_2$) + S($^3P_1$)	*537.5 ± 0.6*

^{a} By extrapolation: GeS(E$^1\Sigma$) = Ge(^3P) + S(^3P), $D_m = (95.5 \pm 0.5)$ kJ·mol^{-1}.[43] For GeS(X$^1\Sigma$) = GeS(E$^1\Sigma$), $\Delta_r U_m = 463.6$ kJ·mol^{-1}.[43] Thus, for GeS(X$^1\Sigma$) = Ge(^3P) + S(^3P), $D_m = (559.1 \pm 0.5)$ kJ·mol^{-1}.

^{b} For GeS(X$^1\Sigma$) = Ge($^3P_0$) + S($^3P_2$).

^{c} Preferred value: $D_m^\circ(\text{GeS}) = (535 \pm 1)$ kJ·mol^{-1}.

detail with respect to the diatomic molecules formed between elements of Groups 14 and 16 of the periodic table of the elements. He cites, as an example, how the original assumption by spectroscopists that the E-state of lead chalcogenides dissociated to $Pb(^3P_0)$ had to be changed and the $Pb(^3P_1)$ state adopted to force agreement with mass-spectroscopic results for $D_m^\circ(PbO)$ and $D_m^\circ(PbS)$. The present analysis indicates that, even for related diatomic molecules (here, the chalcogenides of Group 14), the spectroscopic products of dissociation evidently do not follow predictable patterns. Thermochemistry-based D_m°s do not suffer from that particular handicap.

   Gurvich $et\ al.$ discussed only the spectroscopic result in connection with $D_m^\circ(GeS)$ and made no mention of other measurements, notably by Drowart and his colleagues, who used combined mass-spectrometric, Knudsen effusion,[48] and photoionization[49] techniques. In the first of those, the equilibrium constant K for the reaction:

$$GeS(g) + Sn(g) = Ge(g) + SnS(g), \qquad (9)$$
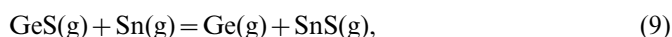
was reported for the temperature range 1420 K to 1730 K:

$$\lg K = -(4160 \pm 250)(K/T) + (0.25 \pm 0.09), \qquad (10)$$

from which it follows that:

$$\Delta_r H_m^\circ(9) = D_m^\circ(GeS) - D_m^\circ(SnS). \qquad (11)$$

Taking values of $\Phi_m^\circ(T)$ at $\langle T \rangle = 1575$ K and $T' \rightarrow 0$ from Gurvich $et\ al.$,[12] we obtain by means of a third-law evaluation $\Delta_r H_m^\circ(9) = (86 \pm 6)$ kJ·mol^{-1} and, with $D_m^\circ(SnS) = (463.7 \pm 4.7)$ kJ·mol^{-1},[12] $D_m^\circ(GeS) = (551 \pm 7)$ kJ·mol^{-1}. A second-law calculation gives $D_m^\circ(GeS) = (546 \pm 8)$ kJ·mol^{-1}. The mean result, weighted as the inverse of the squares of the uncertainties, is (549 ± 5) kJ·mol^{-1}. Note that $D_m^\circ(SnS)$ stems from the molar dissociation limit of (488.7 ± 2.4) kJ·mol^{-1} found by Barrow $et\ al.$[50] for the E-state and taken by Gurvich $et\ al.$ to yield the $^3P_1$ states of both Sn and S. If, rather, the E-state of SnS were assumed to dissociate to $Sn(^3P_2)$ and $S(^3P_2)$ and, correspondingly, $D_m^\circ(SnS) = (449 \pm 7)$ kJ·mol^{-1}, then $D_m^\circ(GeS) = (535 \pm 9)$ kJ·mol^{-1} would be in agreement with thermochemistry. However, this lower $D_m^\circ(SnS)$ would then be inconsistent with the apparently well established values of $\Delta_f H_m^\circ$ and $\Delta_{sub} H_m^\circ$ of SnS(cr).[12] We do not regard $\Delta_f H_m^\circ(SnS, cr, 298.15$ K$)$ as firmly established, however, and are planning to redetermine this value in our laboratory.

   In their photoionization study of GeS, Drowart $et\ al.$[49] reported a molar threshold of $\leqslant(1303.5 \pm 2.9)$ kJ·mol^{-1} for the reaction:

$$GeS(g) = Ge^+(g) + S(g) + e^-, \qquad (12)$$
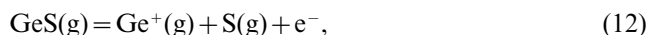
at $T = 800$ K. In a personal communication,[51] Drowart informed us that this molar threshold energy was then corrected by (6.9 ± 6.8) kJ·mol^{-1} to allow for internal energy transfer. Combined with the molar ionization energy of Ge: (762.1 ± 0.1) kJ·mol^{-1},[52] the adjusted molar threshold energy yields $D_m^\circ(GeS) \leqslant (548 \pm 7)$ kJ·mol^{-1}. Drowart adds: "our conclusion is that otherwise determined values for $D_m^\circ(GeS)$ are confirmed in general terms and especially that Ge^+ is formed at or close to the expected threshold, not that a new value for $D_m^\circ(GeS)$ was determined."

We mention here the result of a recent calculation[53] of $D_m^\circ(\text{GeS}) = (544 \pm 12)$ kJ·mol^{-1} performed on the basis of G2 theory[54] extended to third-row non-transition-metal elements, with spin-orbit corrections included. Similar treatments[53] of smaller Group-14 chalcogenide molecules for which there are accurate experimental D_m°s gave results that were too high, by 8 kJ·mol^{-1} for CO and 4 kJ·mol^{-1} for CS, and too low, by 8 kJ·mol^{-1}, for SiO. Thus, we have no guidance as to whether $D_m^\circ(\text{GeS}) = (544 \pm 12)$ kJ·mol^{-1} is likely to be too large or too small, and it is not possible to decide whether it favors either the (547.5 ± 0.5) kJ·mol^{-1} proposed by Gurvich *et al.* or the ≈ 535 kJ·mol^{-1} supported by the present study.

In summary, the agreement between the values of $D_m^\circ(\text{GeS})$: (534 ± 3) kJ·mol^{-1} from thermochemistry, and (535 ± 1) kJ·mol^{-1} from spectroscopy, is very good, and we recommend $D_m^\circ(\text{GeS}) = (534 \pm 3)$ kJ·mol^{-1}. If, for whatever reason, our arguments for the formation of Ge(^{3}P$_2$) and S(^{3}P$_0$) from GeS(E$^1\Sigma$) turned out to be untenable, then D_m°s from spectroscopy, as interpreted by Gurvich *et al.*, and from the high-temperature study of Drowart *et al.*, would be in agreement. That would then imply an unlikely error of about 14 kJ·mol^{-1} in the thermochemical cycle derived from equation (7), either in the apparently well established $\Delta_{sub}H_m^\circ(\text{GeS, cr}, T \to 0)$, or in $\Delta_f H_m^\circ(\text{GeS, cr, 298.15 K})$ just reported by us,[2] or in a combination of the two and, in turn, would lead to significant discrepancies between the now-harmonious[3] results from calorimetric and high-temperature investigations of the reaction:

$$\text{GeS}_2(\text{cr}) = \text{GeS}(\text{g}) + (1/2)\text{S}_2(\text{g}). \tag{13}$$
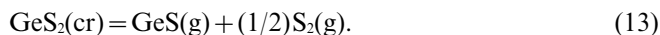
ENTHALPIES OF DISSOCIATION OF BONDS IN Ge$_2$S$_2$(g) AND GeS$_2$(g)

The standard molar enthalpy change for atomization of Ge$_2$S$_2$(g) at $T \to 0$:

$$\text{Ge}_2\text{S}_2(\text{g}) = 2\text{Ge}(\text{g}) + 2\text{S}(\text{g}), \tag{14}$$

is given by:

$$\Delta_{at}H_m^\circ(\text{Ge}_2\text{S}_2) = 2 \cdot \Delta_f H_m^\circ(\text{Ge, g}) + 2 \cdot \Delta_f H_m^\circ(\text{S, g}) - \Delta_f H_m^\circ(\text{Ge}_2\text{S}_2, \text{g}), \tag{15}$$

where $\Delta_f H_m^\circ(\text{Ge, g}) = (365.0 \pm 1)$ kJ·mol^{-1},[12] and $\Delta_f H_m^\circ(\text{S, g}) = (274.9 \pm 0.2)$ kJ·mol^{-1}.[12] Thus, $\Delta_{at}H_m^\circ(\text{Ge}_2\text{S}_2) = (1173 \pm 7)$ kJ·mol^{-1}. There are four equivalent bonds in the molecule, and the mean enthalpy of dissociation of the Ge–S linkage $\langle D_m^\circ(\text{Ge}_2\text{S}_2) \rangle = 0.25 \cdot \Delta_{at}H_m^\circ(\text{Ge}_2\text{S}_2) = (293 \pm 2)$ kJ·mol^{-1}.

The enthalpy of dissociation of the "first" bond in GeS$_2$(g) is $\Delta_r H_m^\circ$ for the reaction:

$$\text{GeS}_2(\text{g}) = \text{GeS}(\text{g}) + \text{S}(\text{g}), \tag{16}$$

and we calculate $D_m^\circ(\text{S–GeS}) = (269 \pm 20)$ kJ·mol^{-1} from values of $\Delta_f H_m^\circ$ quoted elsewhere in this paper. Thus, $D_m^\circ(\text{S–GeS})/D_m^\circ(\text{GeS}) \approx 0.5$, an empirical relation we previously have found[18] valid for the other germanium dichalcogenides, but for which we have no explanation.

TABLE 9. Calculated lengths r_e, experimental stretching force constants f, and mean molar enthalpies of dissociation $\langle D_m^\circ \rangle$ of Ge–S bonds

	r_e/pm	$f/(\text{J} \cdot \text{m}^{-2})$ [a]	$\langle D_m^\circ \rangle/(\text{kJ} \cdot \text{mol}^{-1})$
$Ge_2S_2(g)$	277	184	293 ± 2
$GeS_2(g)$	199	450	401 ± 3
$GeS(g)$	200 [b]	422	534 ± 3

[a] References 38 and 42.
[b] The experimental r_e is 201 pm.[41]

The mean molar enthalpy of dissociation $\langle D_m^\circ(\text{GeS}_2) \rangle = (401 \pm 3)$ kJ·mol^{-1} refers to $0.5 \cdot \Delta_r H_m^\circ(17)$:

$$\text{GeS}_2(g) = \text{Ge}(g) + 2\text{S}(g). \tag{17}$$

The average molar enthalpy of dissociation of the Ge–S bond in the nominally double-bonded GeS_2 is approximately 110 kJ·mol^{-1} greater than in $Ge_2S_2(g)$.

Mean molar enthalpies of dissociation of Ge–S bonds, internuclear separations r_e, and stretching force constants f, are summarized in table 9 for the three gaseous molecules discussed in this paper. Not surprisingly, the triple-bonded GeS has the largest D_m°. The ratio $\langle D_m^\circ(\text{GeS}_2) \rangle / \langle D_m^\circ(\text{Ge}_2\text{S}_2) \rangle = 1.36$, f, and r_e, all suggest a Ge–S bond order $\ll 2$ in $Ge_2S_2(g)$, and are consistent with the presence of just nominal single bonds in the tetra-atomic molecule.

Liebman[55] has suggested a method by which the enthalpy of dissociation can be approximated for the "pure" Ge–S single bond. In the disulfide, Ge is tetrahedrally joined by single bonds to four neighboring S atoms; therefore, the mean molar dissociation enthalpy of Ge–S in the crystal is $0.25 \cdot \Delta_{at} H_m^\circ(\text{GeS}_2)$, calculated for:

$$\text{GeS}_2(cr) = \text{Ge}(g) + 2\text{S}(g), \tag{18}$$

where $\Delta_{at} H_m^\circ = (1042.6 \pm 1.5)$ kJ·mol^{-1} from values of $\Delta_f H_m^\circ$ given elsewhere in this paper. Therefore, $\langle D_m^\circ(\text{GeS}_2, \text{cr}) \rangle = (261 \pm 1)$ kJ·mol^{-1}. In order to refer this result to gaseous "polymeric" GeS_2, we estimate $\Delta_{sub} H_m^\circ \approx 40$ kJ·mol^{-1},[56] for the hypothetical conversion of the solid to the corresponding "polymeric" gas of identical molecular architecture, that is, with Ge tetrahedrally bonded to S. The average correction for each bond is ≈ 10 kJ·mol^{-1}, and the mean molar dissociation enthalpy of a Ge–S single bond is estimated to be 251 kJ·mol^{-1}. Note that $\langle D_m^\circ(\text{Ge}_2\text{S}_2) \rangle$ is about 40 kJ·mol^{-1} larger, which is consistent with the presence in the ring of essentially single Ge–S bonds with, perhaps, some double-bond character.

Several investigators[39, 40, 57] have drawn attention to the somewhat surprising experimental observations that $r_e(\text{S–Ge–S}) < r_e(\text{GeS})$ and $f(\text{S–Ge–S}) > f(\text{GeS})$, as shown in table 9, whereas the opposite is true for the (carbon + sulfur) and (carbon + oxygen) analogs. Köppe and Schnöckel's[39] electron-population analysis showed GeS(g) to be completely nonpolar (although the experimental dipole moment of $4.2 \cdot 10^{-30}$ C·m,[58] suggests otherwise), and that the bonds in GeS_2 were shortened due to their partial ionic character, with both sulfur atoms bearing significant negative

charges. The molar enthalpies of dissociation show clearly, although r_e and f may point to a contrary conclusion, that the bonding is much stronger in GeS(g) than in GeS$_2$(g). In summary, thermodynamic and other evidence is consistent with the Ge–S bonds being triple in GeS, double in GeS$_2$, and essentially single in Ge$_2$S$_2$(g).

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