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Standard molar enthalpies of formation and transition at the temperature 298.15 K and other thermodynamic properties of the crystalline and vitreous forms of arsenic sesquiselenide (As_2Se_3). Dissociation enthalpies of As–Se bonds[a]

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Fluorine-combustion calorimetry was used to determine the standard molar enthalpies of formation (at the temperature 298.15 K and with standard pressure $p^{\circ} = 101.325$ kPa) of the crystalline and vitreous forms of arsenic sesquiselenide. The following results were obtained: $\Delta_f H^{\circ}_m(As_2Se_3, cr) = -(86.1 \pm 4.1)\ kJ \cdot mol^{-1}$ and $\Delta_f H^{\circ}_m(As_2Se_3, vit) = -(58.1 \pm 4.2)\ kJ \cdot mol^{-1}$. The enthalpy of the transition from the vitreous to the crystalline forms of As_2Se_3, $-(28.0 \pm 3.9)\ kJ \cdot mol^{-1}$ at 298.15 K, is consistent with two of several published values for the enthalpy of fusion of the crystalline sesquiselenide. The present results have been combined with enthalpy increments and the standard entropy has been recalculated from the literature to give, for As_2Se_3(cr) only, $\Delta_f H^{\circ}_m$ and the standard molar Gibbs energy of formation $\Delta_f G^{\circ}_m$ as functions of temperature. Mean bond enthalpies have been deduced for As_4Se_3(g) and As_4Se_4(g) on the basis of the new $\Delta_f H^{\circ}_m$ values, and the thermodynamic results are shown to be consistent with a linear structure for As_2Se_2(g) with a central As–As bond. Bond dissociation enthalpies D°_m(As–X) are given, where X = O, S, Se, and Te.

1. Introduction

Noncrystalline As_2Se_3 is an important substance in several modern technologies. It has a highly-transparent region in the infrared, and fibers can be made from it that

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exhibit very low optical losses in the 10.2 μm (CO_2-laser) region. Such fibers are important in medical applications where small bending radius and durability are desirable. This material is also a semiconducting glass used in xerography, the most prominent form of electrophotography or electrostatic imaging. Glassy As_2Se_3 is formed as a large-area thin-film photoconductor with a bandgap of approximately 200 kJ. Of even greater significance is its property of photo-induced crystallization with obvious application as a computer-memory material. This work was undertaken in order to provide precise and reliable enthalpy of formation $\Delta_f H_m^\circ(As_2Se_3)$ values for use in modelling studies of the amorphous state and for the elucidation of the glass-to-crystal (the thermodynamic reference state) transformation.

There is already in the literature a significant amount of thermodynamic information concerning As_2Se_3. Several low-temperature heat-capacity studies of the vitreous and crystalline forms have been reported: by Easteal *et al.*,(1) Orlova and Borisova,(2) Zigel' and Orlova,(3) and Zhdanov and Mal'tsev.(4) High-temperature heat capacities have been determined by Zigel' *et al.*,(5) and by Orlova and Muromtsev,(6) and high-temperature enthalpy increments by Rasulov and Medzhidov.(7) Vaporization of As_2Se_3 at high temperatures has been studied by Pelevin *et al.*,(8) Orlov *et al.*,(9) Kinoshita,(10) Steblevskii *et al.*,(11) and, very recently, by Vande Gucht and Drowart.(12) Enthalpies of solution in base were measured calorimetrically by Hattori *et al.*(13) and Neverov *et al.*,(14) and enthalpies of melting by Rasulov and Medzhidov,(7) Blachnik and Schneider,(15) and Myers and Felty.(16) Standard molar enthalpies of formation at 298.15 K have been reported by Blachnik and Schneider(15) and Neverov *et al.*,(14) and have been deduced from high-temperature vaporization studies by Steblevskii *et al.*,(11) but those results all have rather large uncertainties, and this also contributed to the motivation for the present investigation.

At this laboratory, we have been performing calorimetric measurements on chalcogenides of technological importance. Among the materials we have studied of late are VS,(17) GeS_2,(18) $MoSe_2$ and Mo_6Se_6,(19) WSe_2,(20) $MoTe_2$,(21) and GeSe,(22) and we have reviewed(23) the thermodynamic properties of other selected chalcogenides. Our determinations of the standard molar enthalpies of formation $\Delta_f H_m^\circ$ at 298.15 K have been based on measurements of the energies of combustion of the subject materials in high-pressure fluorine. The same technique has been used in the present investigation. The standard molar energies at 298.15 K of the combustion reactions:

$$As_2Se_3(\text{cr or vit}) + 14F_2(g) = 2AsF_5(g) + 3SeF_6(g), \qquad (1)$$

have been determined, and the corresponding enthalpies of combustion have been combined with our previously reported results for $\Delta_f H_m^\circ(AsF_5)$,(24) and $\Delta_f H_m^\circ(SeF_6)$,(25) to deduce $\Delta_f H_m^\circ(As_2Se_3)$.

2. Experimental

As_2Se_3 is one member of an important family of i.r.-transmitting chalcogenide glasses.(26) The principal source of undesired extrinsic i.r. absorption is light-atom impurities (oxygen and hydrogen). Therefore, the transmission characteristics of As_2Se_3(vit) have been extensively investigated in the infrared region to characterize the As–O, Se–O, and H–Se absorption bands.[26–28] This body of literature served as a convenient basis for monitoring our various purification procedures.

Elemental As and Se are commercially available as "high-purity" materials, at least with respect to cation contaminants. Unfortunately, all such specimens that we have surveyed have varying amounts of anion contamination. Hydrogen and oxygen are present in elemental selenium shot both as a surface contaminant (surface –OH) and as a bulk impurity (substitutional –O–, nonbridging H–Se–, and dissolved H_2Se). Oxygen appears as an As_2O_3 impurity both on the surface and in the bulk of as-received "high-purity" arsenic.

Additional sources of contamination are air and the fused-silica containers used for glass synthesis and crystal growth. Therefore, all manipulations connected with the syntheses have been carried out in a glovebox purged with recirculating helium with a volume fraction of $H_2O < 1 \times 10^{-6}$ and $p(O_2) < 1 \times 10^{-4}$ Pa, and fused silica tubes were etched in 25 mass per cent of HF(aq) and outgassed at 1273 K and $p \approx 0.1$ mPa prior to use.

High-purity selenium (Asarco, 99.9995 mass per cent with respect to metal contaminants) was melted for 1 h to 3 h in an evacuated ($p \approx 7$ mPa) 25 mm i.d. fused-silica tube at 573 K. It is believed that hydrogen and oxygen were effectively removed in this way as volatile H_2Se and SeO_2 because there was no detectable H–Se absorption at 2320 cm^{-1} or Se–O absorption at 892 cm^{-1} (room temperature, 1 mm to 2 mm pathlength) in the material thus purified. High-purity arsenic (Cominco Electronic Materials, 99.9999 mass per cent with respect to metal contaminants) was purified in a similar manner below its melting temperature, effectively removing the highly volatile As_2O_3 from the surface and the bulk of the brilliantly shiny ingots.

Stoichiometric amounts of the purified arsenic and selenium reactants, having approximately 15 g of total mass, were transferred into 10 mm i.d. fused-silica tubes which were sealed under a helium atmosphere ($p \approx 5 \times 10^{-3}$ Pa), loaded into a rocking furnace, brought slowly to 873 K (melting temperature, 633 K) and rocked gently for 18 h. The melts were equilibrated at 673 K for 1 h and, to make a glass, some tubes were quenched at approximately 100 $K \cdot s^{-1}$ into an ice bath with $T \approx 273$ K. The vitreous boules did not adhere to the walls and, when broken up inside the sealed ampoules, they fractured conchoidally. The glasses were relaxed in the unopened ampoules for 1 h at 456 K (the glass transition temperature is 451 K) where neither phase separation nor crystallization occur. Debye–Scherrer X-ray patterns (Cu Kα, 40 kV, 20 mA, 20 h) indicated no crystalline contamination.

Crystalline As_2Se_3 was prepared by cooling a melt to 593 K, equilibrating it for 18 h at that temperature (the crystallization temperature is 560 K), and then slowly cooling it to room temperature. The polycrystalline ingot was also annealed at 456 K for 1 h in the unopened tube.

Figure 1 presents the infrared absorption spectrum of a 0.4 mm thick slice of vitreous As_2Se_3, measured with a Brücker FTIR-98. The bands at 2800 cm^{-1} to 3000 cm^{-1} arise from C–H stretching and the weak band at 745 cm^{-1} from $C–H_2$

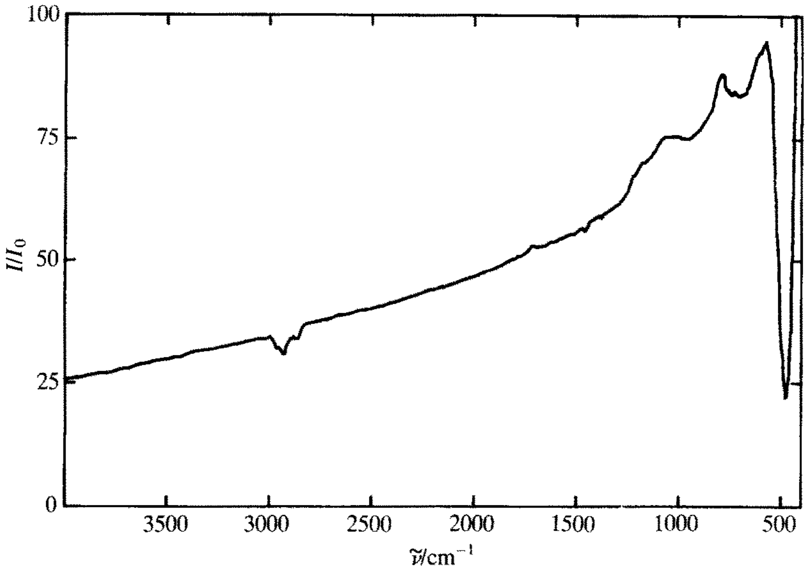


FIGURE 1. F.t.i.r. spectrum of calorimetric specimen of vitreous As_2Se_3.

rocking and are due to a thin protective kerosene layer on the polished specimen. The weak band at 650 cm^{-1} riding as a shoulder on the multiphonon absorption at 690 cm^{-1} is due to the $>$As–O–As species, *i.e.* oxygen substitutionally incorporated for selenium in the network.(28) The absorption coefficient is consistent with a mass fraction of oxygen contaminant of 6×10^{-6} in the glass. There is clearly no As_4O_6 band at 785 cm^{-1} (which appears only for mass fraction of oxygen $> 3 \times 10^{-5}$).

The arsenic selenides were reduced to powder and small (≈ 1 mm) pieces by crushing the as-prepared ingots in an agate mortar. First, however, the surfaces of the ingots, which, during preparation, had been in contact with the quartz tubes, were scraped with a clean razor blade to remove possible oxide contamination. Calorimetric and analytical specimens were weighed with an accuracy of $(2\ \text{to}\ 3) \times 10^{-5}$ g on an analytical balance (Sartorius, model R160P) in our helium-filled glovebox.

Traditionally, our calorimetric samples have been analyzed for O, H, and N by the inert-gas fusion technique. The following results (mass fraction $\times 10^{-6}$) have been obtained: H, (9 ± 3); N, (19 ± 5); O, (187 ± 45) for As_2Se_3(cr), and H, (0 ± 5); N, (3 ± 2); O, (344 ± 80) for As_2Se_3(vit). Clearly, the oxygen content of As_2Se_3(vit) is in substantial disagreement with the spectroscopic value, and we are unable to explain this discrepancy. Fortunately, however, because of the relatively low level of oxygen, the impurity correction is not excessive and is, in fact, comparable in magnitude with the final uncertainty of the $\Delta_f H_m^\circ$ value. We have assumed that the oxygen was present as As_2O_3, because the spectroscopic examination of As_2Se_3 showed evidence for just As–O bonds. No significant metallic contaminants were detected by emission spectroscopy.

The fluorine-bomb calorimetric technique and equipment have been described in detail.(20) The storage tank was charged to a pressure of 1.824 MPa at 297 K with high-purity (>99.99 mass per cent) redistilled fluorine. A combustion pressure of approximately 0.80 MPa resulted upon expansion of the fluorine into the bomb. As_2Se_3, supported on a prefluorinated nickel crucible of approximate mass 10.5 g, ignited spontaneously in the fluorine and, after the calorimetric experiments, the only i.r.-active gaseous products detected were AsF_5 and SeF_6, consistent with equation (1). In addition, a small black residue was observed in the crucible after most combustions. This residue, according to SEM analysis, was composed of nickel and arsenic, but insufficient quantities could be isolated for identification by X-ray analysis. Singleton and Nash(29) have recently listed four distinct compositions in the (arsenic + nickel) phase diagram: Ni_5As_2, $Ni_{11}As_8$, NiAs, and $NiAs_2(\alpha, \beta)$. On the basis of the SEM result, the residue was assumed to be NiAs which, during the combustion, either formed (increase in mass of crucible and contents) according to the reaction:

$$\mathrm{Ni(s) + As(s) = NiAs(s)}, \tag{2}$$

or was consumed (decrease in mass of crucible and contents) according to

$$\mathrm{NiAs(s) + (7/2)F_2(g) = NiF_2(cr) + AsF_5(g)}. \tag{3}$$

As usual, the specimens and nickel crucible were not exposed to the air between experiments and the reaction vessel only when substantive repairs to the bomb or tank were necessary.

3. Results

Detailed calorimetric results for reaction (1) are given in table 1. Most of the symbols in the table have been explained previously.(18)

The nickel arsenide formed in each of our experiments was assumed to be the 1-1 intermetallic, as we have just stated, and ΔU(NiAs) is the correction for reactions (2) and (3). This is the only assumption open to us, because $\Delta_f H_m^\circ$ is available for just NiAs.(30) We estimated $\Delta_f H_m^\circ(\pm 20$ per cent) values for the other compounds ($-252\ \mathrm{kJ \cdot mol^{-1}}$ for Ni_5As_2, $-684\ \mathrm{kJ \cdot mol^{-1}}$ for $Ni_{11}As_8$, and $-216\ \mathrm{kJ \cdot mol^{-1}}$ for $NiAs_2$), and found the spread in the corrections for the reactions corresponding to (2) and (3) to be approximately 0.5 J. Accordingly, in our calculations of the specific energies of combustion of As_2Se_3, we have assumed each entry for ΔU(NiAs) in table 1 to be uncertain by ±10 per cent. If $\Delta_f H_m^\circ$s become available in the future for the other nickel arsenides, a more exact correction should be calculable because, for each experiment in table 1, we have included Δm(crucible), the change in mass of the (crucible + residue) from the previous experiment.

After experiment no. 4 with As_2Se_3(cr), we had to expose the interior of the reaction vessel to the atmosphere in order to repair a leak in the bomb. Thus, as shown in table 1, the ΔU(blank) value measured immediately after this experiment was large, but it subsequently returned to its normal value.

The impurity corrections were based upon the assumption that As_2O_3 reacted with F_2(g) to form $2AsF_5$(g) and $\frac{3}{2}O_2$(g). Coincidentally, these corrections are

TABLE 1. Energies of combustion in fluorine of crystalline and vitreous As_2Se_3 ($T = 298.15$ K, $p^\circ = 101.325$ kPa)

			$As_2Se_3(cr)$		
Expt. no.	2	3	4	5	6
m/g	0.53700	0.51450	0.58217	0.52377	0.50476
Δm(crucible)/g	−0.00009	−0.00003	0.00071	0.00080	0.00045
$\Delta\theta_c$/K	0.57034	0.54572	0.61681	0.55584	0.53545
ε(calor)$(-\Delta\theta_c)$/J [a]	−7931.0	−7588.7	−8577.2	−7729.4	−7445.9
ΔU(cont)/J	−6.9	−6.6	−7.4	−6.7	−6.4
ΔU(gas)/J	−0.3	−0.3	−0.3	−0.3	−0.3
ΔU(blank)/J	−7.4	−7.4	−7.4	0.3	−7.4
ΔU(NiAs)/J	1.2	0.4	−9.6	−10.9	−6.1
$\{\Delta_c U^\circ_m/M(\text{sample})\}/(\text{J}\cdot\text{g}^{-1})$	−14794.0	−14776.7	−14775.6	−14790.8	−14791.4

$\langle\Delta_c U^\circ_m/M(\text{sample})\rangle = -(14785.7 \pm 3.9)\ \text{J}\cdot\text{g}^{-1}$ [b]
Impurity correction $= -(4.3 \pm 0.5)\ \text{J}\cdot\text{g}^{-1}$ [b]
$\langle\Delta_c U^\circ_m/M(As_2Se_3, \text{cr})\rangle = -(14790.0 \pm 3.9)\ \text{J}\cdot\text{g}^{-1}$ [b]

			$As_2Se_3(vit)$		
Expt. no.	1	2	3	5	7
m/g	0.56085	0.49749	0.49476	0.49160	0.54519
Δm(crucible)/g	0.00084	0.00056	0.00000	0.00073	0.00102
$\Delta\theta_c$/K	0.59774	0.53008	0.52776	0.52314	0.58093
ε(calor)$(-\Delta\theta_c)$/J [a]	−8311.7	−7370.9	−7338.6	−7274.4	−8078.3
ΔU(cont)/J	−7.2	−6.4	−6.3	−6.3	−7.0
ΔU(gas)/J	−0.3	−0.3	−0.3	−0.3	−0.3
ΔU(blank)/J	−4.0	−4.0	−4.0	−4.0	−4.0
ΔU(NiAs)/J	−11.4	−7.9	0.0	−9.9	−13.9
$\{\Delta_c U^\circ_m/M(\text{sample})\}/(\text{J}\cdot\text{g}^{-1})$	−14860.7	−14853.6	−14854.1	−14839.1	−14863.6

$\langle\Delta_c U^\circ_m/M(\text{sample})\rangle = -(14854.2 \pm 4.2)\ \text{J}\cdot\text{g}^{-1}$ [b]
Impurity correction $= -(8.1 \pm 0.9)\ \text{J}\cdot\text{g}^{-1}$ [b]
$\langle\Delta_c U^\circ_m/M(As_2Se_3, \text{vit})\rangle = -(14862.3 \pm 4.3)\ \text{J}\cdot\text{g}^{-1}$ [b]

[a] For experiments 1, 2, 3, and 5 with As_2Se_3(vit), ε(calor) $= (13905.2 \pm 0.7)\ \text{J}\cdot\text{K}^{-1}$; for all other experiments, ε(calor) $= (13905.8 \pm 0.7)\ \text{J}\cdot\text{K}^{-1}$.

[b] Uncertainties are standard deviations of the mean.

essentially the same whether oxygen is taken to be present as As_2O_3, SeO_2, or a mixture of both.

In order to calculate $\Delta_f H^\circ_m$ of the compounds, as well as the impurity corrections and ΔU(NiAs), we have used $\Delta_f H^\circ_m$ of SeF_6,(25) and of AsF_5.(24) Both values were originally reported by us but, due to a new more accurate method we have recently introduced(31) for calculating ΔU(blank), the published result for $\Delta_f H^\circ_m(AsF_5)$ has to be changed in much the same way(25) that we earlier revised $\Delta_f H^\circ_m(SeF_6)$. In our original report(24) on the energy of combustion of arsenic in fluorine, the mean value of ΔU(blank) was given as 6.2 J; the recalculation using our new method gives 3.0 J. Accordingly, $\Delta_f H^\circ_m(AsF_5, \text{g})$ is changed from $-(1236.7 \pm 0.8)\ \text{kJ}\cdot\text{mol}^{-1}$ to $-(1237.0 \pm 0.8)\ \text{kJ}\cdot\text{mol}^{-1}$, and this value has been used in the present paper. In addition, our calculation of ΔU(NiAs) incorporated $\Delta_f H^\circ_m(\text{NiAs}) = -(72.0 \pm 3.8)\ \text{kJ}\cdot\text{mol}^{-1}$,(30) and $\Delta_f H^\circ_m(NiF_2) = -(657.7 \pm 1.7)\ \text{kJ}\cdot\text{mol}^{-1}$.(32)

TABLE 2. Standard molar thermodynamic properties of arsenic sesquiselenides at 298.15 K and $p^\circ = 101.325\ \mathrm{kPa}$[a]

	$\Delta_c U^\circ_m$ [b] / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_c H^\circ_m$ [b] / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_f H^\circ_m$ [c] / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_f S^\circ_m$ [c] / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta_f G^\circ_m$ [c] / $\mathrm{kJ \cdot mol^{-1}}$
As_2Se_3(cr)	-5719.3 ± 3.5	-5741.6 ± 3.5	-86.1 ± 4.1	7.8 ± 3.2	-88.4 ± 4.2
As_2Se_3(vit)	-5747.3 ± 3.6	-5769.6 ± 3.6	-58.1 ± 4.2		

[a] The molar mass of As_2Se_3 was taken to be 386.7 $\mathrm{g \cdot mol^{-1}}$.

[b] Energies and enthalpies of combustion for reaction (1); $\Delta n RT = -22.3\ \mathrm{kJ \cdot mol^{-1}}$.

[c] For the formation reaction: $2As(cr) + 3Se(cr) = As_2Se_3(s)$.

The standard molar energies and enthalpies of combustion of the arsenic selenides, reaction (1), are given in table 2, and are based on a molar mass of 386.7 $\mathrm{g \cdot mol^{-1}}$ for As_2Se_3.

Zhdanov and Mal'tsev(4) determined the molar heat capacities of crystalline and vitreous As_2Se_3 by low-temperature adiabatic calorimetry to 53 K. Their value for the standard entropy $S^\circ_m(As_2Se_3, \mathrm{cr}, 298.15\ \mathrm{K})$ was obtained by extrapolation from 53 K to $T \rightarrow 0$ by means of the relation $C_{p,m} = AT^n$, and the dependence of n on T was estimated from the heat capacities of analogous compounds. Nemilov(33) rejected this method of extrapolation because it did not reproduce the experimental results at $T > 53$ K and used instead a quantum-theory based function developed by Deltour and Kartheuser(34) which reproduced quite accurately the experimental heat capacities between 50 K and 200 K. From Nemilov's procedure, we obtain for As_2Se_3(cr): $\{S^\circ_m(53\ \mathrm{K}) - S^\circ_m(0)\} = 46.1\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and, from Zhdanov and Mal'tsev, by graphical integration, $\{S^\circ_m(298.15\ \mathrm{K}) - S^\circ_m(53\ \mathrm{K})\} = 160.3\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. Therefore, $\{S^\circ_m(298.15\ \mathrm{K}) - S^\circ_m(0)\} = (206 \pm 3)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, where the uncertainty has been estimated. This result, combined with S°_ms for As(cr), 35.7 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$,(35) and Se(cr), 42.27 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$,(36) yields the $\Delta_f S^\circ_m$ and, thus, $\Delta_f G^\circ_m$ given for As_2Se_3(cr) in table 2.

4. Discussion

STANDARD MOLAR ENTHALPIES OF FORMATION AT 298.15 K

There have been several other determinations of $\Delta_f H^\circ_m(As_2Se_3)$. Blachnik and Schneider(15) used a modified "Kubaschewski–Dench" calorimeter to measure the enthalpy of combination of appropriate stoichiometric amounts of arsenic and selenium; for As_2Se_3, presumably the crystalline form at 298.15 K, they reported $\Delta_f H^\circ_m = -(103 \pm 21)\ \mathrm{kJ \cdot mol^{-1}}$. Few experimental details and no calorimetric information were given. This result overlaps ours, but only because of the very large uncertainty, the source of which has not been documented by the authors.

Steblevskii and coworkers(11) have studied the high-temperature vaporization of crystalline and amorphous (arsenic + selenium) by a Knudsen-effusion mass-spectrometric technique. They deduced values of $\Delta_f H^\circ_m$ for crystalline and vitreous As_2Se_3 from the equilibrium pressures of the reactions summarized in table 3. In that

TABLE 3. Enthalpies of the high-temperature decomposition of As_2Se_3 and the derived $\Delta_f H_m^\circ$ values at 298.15 K[a]

Reaction	$\Delta_r H_m^\circ$[b] / $kJ \cdot mol^{-1}$	$\Delta_f H_m^\circ(As_2Se_3, s)$ / $kJ \cdot mol^{-1}$
1. $As_2Se_3(vit) = \frac{1}{2}As_4Se_3(g) + \frac{3}{4}Se_2(g)$	222.8 ± 8.0	-59 ± 9
2. $\frac{1}{2}As_4(g) + \frac{3}{4}Se_2(g) = \frac{1}{2}As_4Se_3(g)$	-131.3 ± 3.0	
3. $As_2Se_3(vit) = \frac{1}{2}As_4Se_4(g) + \frac{1}{2}Se_2(g)$	177.8 ± 7.0	-49 ± 8
4. $\frac{1}{2}As_4(g) + Se_2(g) = \frac{1}{2}As_4Se_4(g)$	-166.5 ± 3.0	
5. $As_2Se_3(cr) = \frac{1}{2}As_4Se_3(g) + \frac{3}{4}Se_2(g)$	259.4 ± 8.0	-95 ± 9
6. $As_2Se_3(cr) = \frac{1}{2}As_4Se_4(g) + \frac{1}{2}Se_2(g)$	219.7 ± 7.0	-91 ± 8

[a] For the derivation of $\Delta_f H_m^\circ$, the following auxiliary values at 298.15 K have been used: $\Delta_f H_m^\circ(As_4, g) = (158.2 \pm 2.5)\ kJ \cdot mol^{-1}$,(41) and $\Delta_f H_m^\circ(Se_2, g) = (144.1 \pm 0.6)\ kJ \cdot mol^{-1}$.(36)

[b] From reference 11.

table, we have updated the derived $\Delta_f H_m^\circ$s. It is clear from table 3 that the $\Delta_f H_m^\circ$s are more uncertain than, but nevertheless agree with, the present values. Reactions (1) and (6) in table 3 give $\Delta_f H_m^\circ$ values that are close to ours and that we shall use later in the present paper.

Hattori *et al.*(13) measured calorimetrically the enthalpy of reaction of As_2Se_3(vit) with NaOH(aq) at 313 K. However, the solution-reaction scheme is complicated, the results are given only graphically, and such key auxiliary information as enthalpies of formation and heat capacities of the product ionic species are not available in the literature. Thus, we are unable to deduce $\Delta_f H_m^\circ(As_2Se_3, vit)$ from this work.

In a similar study, Neverov *et al.*(14) measured the enthalpies of solution of several compositions of $AsSe_n$ in "bromine-saturated alkali". If, as a guideline, we use the scheme they give for AsSe, we may conclude that the following was the calorimetric reaction of As_2Se_3:

$$\begin{aligned} As_2Se_3(s) &+ (11/4)Br_2(aq) + (11/4)BrO_3^-(aq) + (35/2)OH^-(aq) \\ &= 2AsO_4^{3-}(aq) + 3SeO_3^{2-}(aq) + (33/4)Br^-(aq) + (35/4)H_2O(aq). \end{aligned} \tag{4}$$

The experimental enthalpy of the reaction of As_2Se_3(cr) was given as $-(2496 \pm 2)\ kJ \cdot mol^{-1}$ at 298.15 K. These authors used auxiliary thermochemical values that had been assessed 20 to 40 years ago to derive $\Delta_f H_m^\circ(As_2Se_3, cr) = -(122 \pm 10)\ kJ \cdot mol^{-1}$ from equation (4). When, instead, the most recently selected auxiliary quantities(37) are used, we obtain $\Delta_f H_m^\circ(As_2Se_3, cr, 298.15\ K) = -(94 \pm 10)\ kJ \cdot mol^{-1}$, in fair agreement with our result and those quoted earlier.

Neverov *et al.* have also reported a value of $-(2716 \pm 2)\ kJ \cdot mol^{-1}$ for the enthalpy of reaction (4) with As_2Se_3(vit). This result would imply an unlikely enthalpy of transition of $-(2716 + 2496) = -220\ kJ \cdot mol^{-1}$. We conjecture that the enthalpy of reaction has been misprinted as $-2716\ kJ \cdot mol^{-1}$ instead of $-2516\ kJ \cdot mol^{-1}$, which would lead to an enthalpy of transition of $-20\ kJ \cdot mol^{-1}$, close to the value of $-18\ kJ \cdot mol^{-1}$ implied by the summary tabulated results of Neverov *et al.*

We have been informed by Drowart(38) of the results of a recent study of the high-temperature vaporization of As_2Se_3 (part of the crystalline sample used in our fluorine-bomb measurements) performed in his laboratory. His result, $\Delta_f H^\circ_m(As_2Se_3, cr, 298.15\ K) = -(56.7 \pm 6)\ kJ \cdot mol^{-1}$, disagrees with ours but, despite a lengthy correspondence and several discussions we have been unable to locate the source of the discrepancy.

HIGH-TEMPERATURE ENTHALPY INCREMENTS

High-temperature heat capacities of crystalline and vitreous arsenic sesquiselenides have been determined by Zigel' *et al.*(5) and by Rasulov and Medzhidov;(7) the results of the latter investigation better suit our purposes, and we shall therefore use them in subsequent calculations.

Enthalpy increments of As_2Se_3(cr) between 273.15 K and the melting temperature, which Rasulov and Medzhidov took to be 634 K, were reported in polynomial form only. Experimental enthalpy increments were not given. We have recalculated those results to refer to 298.15 K as the base temperature, and for that purpose have used $\{H^\circ_m(273.15\ K) - H^\circ_m(298.15\ K)\} = -3021\ J \cdot mol^{-1}$ obtained by Zhdanov and Malt'sev.(4) We have added the further constraint that $C^\circ_{p,m}(298.15\ K) = 121.42\ J \cdot K^{-1} \cdot mol^{-1}$.(4) The following expression has been obtained:

$$\{H^\circ_m(T) - H^\circ_m(298.15\ K)\}/(J \cdot mol^{-1}) = 121.23(T/K) - 1.9085 \times 10^{-2}(T/K)^2 + 4.3403 \times 10^{-5}(T/K)^3 - 35597. \qquad (5)$$

By differentiation:

$$C^\circ_{p,m}(T)/(J \cdot K^{-1} \cdot mol^{-1}) = 121.23 - 3.8170 \times 10^{-2}(T/K) + 1.3021 \times 10^{-4}(T/K)^2. \qquad (6)$$

Adiabatic calorimetric studies of As_2Se_3(vit) by Zhdanov and Malt'sev,(4) Zigel' *et al.*,(5) and Orlova and Muromtsev,(6) covered the temperature range from 53 K to 600 K and gave results for $C_{p,m}$ that were in reasonable accord with each other. Both Zigel' *et al.* and Orlova and Muromtsev showed that the heat capacity was by no means an uneventful function of temperature; at $T \approx 450\ K$, $C_{p,m}$ rose steeply through the softening region as As_2Se_3 changed from a brittle to a viscous substance. This steep rise was followed by a sharp fall, after which $C_{p,m}$ was almost linear with T. Thus, it is to be expected that an accurate description of the variation of $C_{p,m}$ across a wide range of temperature would require several equations.

The enthalpy increments of As_2Se_3(vit) were expressed by Rasulov and Medzhidov(7) as two polynomials—one below the softening temperature of 460 K, and the other to 803 K, well into the liquid region. Once again, we have referred the equations to 298.15 K and take, for that purpose, $\{H^\circ_m(273.15\ K) - H^\circ_m(298.15\ K)\} = -3033\ J \cdot mol^{-1}$.(4) The revised relations are as follows:

$$\{H^\circ_m(T) - H^\circ_m(298.15\ K)\}/(J \cdot mol^{-1}) = -26740 + 42.9300(T/K) + 0.2041(T/K)^2 - 1.5851 \times 10^{-4}(T/K)^3, \quad T < 460\ K; \qquad (7)$$

$$\{H^\circ_m(T) - H^\circ_m(298.15\ K)\}/(J \cdot mol^{-1}) = -55633 + 338.92(T/K) - 0.8683(T/K)^2 + 1.4064 \times 10^{-3}(T/K)^3 - 6.9673 \times 10^{-7}(T/K)^4, \quad T < 803\ K. \qquad (8)$$

Rasulov and Medzhidov[7] have given two equations for the heat capacity. One is for $T \leqslant 460$ K, and the other for $460 \leqslant (T/\mathrm{K}) \leqslant 803$; they are the first derivatives with respect to temperature of the polynomials used to represent the experimental enthalpy increments. The $C_{p,\mathrm{m}}$s so calculated differ significantly, often by more than 10 per cent, from the adiabatic calorimetric results[5,6] at high temperatures; the disagreement is smaller, about 2 per cent, at $T \approx 300$ K. A further difficulty with the derivatives of equations (7) and (8) is that values of $\partial C_{p,\mathrm{m}}/\partial T$ become negative at the upper reaches of their respective temperature ranges. This additional problem was introduced by our imposed condition that $\partial\{H^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(298.15\ \mathrm{K})\}/\partial T$ should correspond to the experimental result[4] for $C_{p,\mathrm{m}}(298.15\ \mathrm{K})$. Although the Rasulov and Medzhidov equations for the enthalpy increments are more than likely reliable, those derived from them to represent the heat capacity appear not to be so.

THERMODYNAMIC PROPERTIES OF CRYSTALLINE ARSENIC SESQUISELENIDE

The conventional thermodynamic properties of $\mathrm{As_2Se_3(cr)}$ to the melting temperature are given in table 4. The enthalpy increments and heat capacities were calculated from equations (5) and (6), and the standard molar entropy of $\mathrm{As_2Se_3(cr)}$ has been given earlier. As auxiliary quantities, we have used the enthalpy increments and standard molar entropies of As[35] and Se.[36] Similar calculations for $\mathrm{As_2Se_3(vit)}$ cannot be reliably performed for reasons we have discussed earlier.

ENTHALPIES OF TRANSITION AND FUSION

For the transition:

$$\mathrm{As_2Se_3}(\mathrm{vit}, T') = \mathrm{As_2Se_3}(\mathrm{cr}, T'), \qquad (9)$$

at $T' = 298.15$ K, the difference between our enthalpy of combustion results for the two forms of $\mathrm{As_2Se_3}$ gives $\Delta_\mathrm{trs}H^\circ_\mathrm{m} = -(28.0 \pm 3.9)\ \mathrm{kJ \cdot mol^{-1}}$, which is significantly more positive than the $-(40 \pm 7)\ \mathrm{kJ \cdot mol^{-1}}$ calculated from the weighted $\Delta_\mathrm{f}H^\circ_\mathrm{m}$s of

TABLE 4. Thermodynamic properties of $\mathrm{As_2Se_3(cr)}$
($T' = 298.15$ K, $R = 8.31451\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, $p^\circ = 101.325$ kPa)

$\frac{T}{\mathrm{K}}$	$\frac{C^\circ_{p,\mathrm{m}}}{R}$	$\frac{\Delta^T_{T'}H^\circ_\mathrm{m}}{R \cdot \mathrm{K}}$	$\frac{\Delta^T_0 S^\circ_\mathrm{m}}{R}$	$\frac{\Delta_\mathrm{f}H^\circ_\mathrm{m}}{\mathrm{kJ \cdot mol^{-1}}}$ [a]	$\frac{\Delta_\mathrm{f}G^\circ_\mathrm{m}}{\mathrm{kJ \cdot mol^{-1}}}$ [a]
298.15	14.603	0	24.78	−86.1	−88.4
300	14.612	27	24.87	−86.1	−88.4
400	15.249	1517	29.15	−86.5	−88.5
500	16.200	3087	32.65	−105.3[c]	−96.0
600	17.463	4768	35.71	−107.1	−96.8
633[b]	17.950	5352	36.66	−107.3	−97.0

[a] For the reaction: $\mathrm{2As(cr) + 3Se(cr) = As_2Se_3(cr)}$; uncertainties are approximately $\pm 5\ \mathrm{kJ \cdot mol^{-1}}$.

[b] Melting temperature of $\mathrm{As_2Se_3(cr)}$.

[c] The discontinuity is due to the Se(cr) = Se(l) transition at $T = 494$ K.

the Steblevskii *et al.*(11) study (see table 3). If, instead, we take the results for reactions (1) and (6) from table 3, then $\Delta_{trs}H^\circ_m = -(32 \pm 12)\ \mathrm{kJ \cdot mol^{-1}}$.

There is another route to $\Delta_{trs}H^\circ_m$. It comprises the following steps (in which the melting temperature is taken to be 633 K):(39)

$$As_2Se_3(\mathrm{vit}, T') = As_2Se_3(\mathrm{l}, 633\ \mathrm{K}), \tag{10}$$

$$As_2Se_3(\mathrm{l}, 633\ \mathrm{K}) = As_2Se_3(\mathrm{cr}, 633\ \mathrm{K}), \tag{11}$$

$$As_2Se_3(\mathrm{cr}, 633\ \mathrm{K}) = As_2Se_3(\mathrm{cr}, T'). \tag{12}$$

Summation of the above equations gives:

$$\Delta_{trs}H^\circ_m(T') = \Delta H^\circ_m(9) = \Delta H^\circ_m(10) + \Delta H^\circ_m(11) + \Delta H^\circ_m(12). \tag{13}$$

From equation (8), $\Delta H^\circ_m(10) = (55.8 \pm 3.4)\ \mathrm{kJ \cdot mol^{-1}}$; $\Delta H^\circ_m(11) = -\Delta_{fus}H^\circ_m(As_2Se_3)$; and $\Delta H^\circ_m(12) = -(44.5 \pm 2.7)\ \mathrm{kJ \cdot mol^{-1}}$ from equation (5). In summary,

$$\Delta_{trs}H^\circ_m(298.15\ \mathrm{K})/(\mathrm{kJ \cdot mol^{-1}}) = -(44.5 \pm 2.7) + (55.8 \pm 3.4) - \Delta_{fus}H^\circ_m. \tag{14}$$

Unfortunately, there are at least four disparate values for $\Delta_{fus}H^\circ_m$ in the literature. Rasulov and Medzhidov(7) reported $12.6\ \mathrm{kJ \cdot mol^{-1}}$, which, from equation (14), implies an unlikely $\Delta_{trs}H^\circ_m \approx 0$. Blachnik and Schneider's(15) result, $(29.3 \pm 6.3)\ \mathrm{kJ \cdot mol^{-1}}$, yields $\Delta_{trs}H^\circ_m = -(18 \pm 8)\ \mathrm{kJ \cdot mol^{-1}}$. From Meyers and Felty's(16) determination, $(40.8 \pm 1.3)\ \mathrm{kJ \cdot mol^{-1}}$, we deduce $\Delta_{trs}H^\circ_m = -(29 \pm 5)\ \mathrm{kJ \cdot mol^{-1}}$, in excellent accord with the present investigation. Finally, Thornburg and Johnson(40) have reported an enthalpy of crystallization of $-34.7\ \mathrm{kJ \cdot mol^{-1}}$ ($\Delta_{fus}H^\circ_m = 34.7\ \mathrm{kJ \cdot mol^{-1}}$) which, from equation (14), leads to $\Delta_{trs}H^\circ_m = -(23 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$. Indirectly, therefore, our study strongly supports the Meyers and Felty value for the enthalpy of fusion of As_2Se_3, but it is also consistent, within the combined uncertainty limits, with the Thornburg and Johnson result.

BOND ENTHALPIES OF ARSENIC SELENIDES

A number of technological applications of arsenic selenides involve processing at high temperatures, evaporation, or deposition from the vapor phase. Thus, it is important to understand the thermodynamics of gaseous (arsenic + selenium) molecules. Very little information of this kind is available in the literature. This situation can be ameliorated somewhat by taking the present results for the arsenic sesquiselenides and combining them with the most reliable auxiliary thermochemical values to deduce mean bond enthalpies $\langle D_m \rangle$ as for As–Se bonds in different molecular environments.

As we have mentioned earlier, Steblevskii *et al.*(11) studied in detail the high-temperature vaporization of As_2Se_3. One of their $\Delta_f H^\circ_m(298.15\ \mathrm{K})$ results for As_2Se_3(vit) and one for As_2Se_3(cr) are consistent with ours, as we have shown (see table 3), and we select from their work:

$$As_2Se_3(\mathrm{vit}) = \tfrac{1}{2}As_4Se_3(\mathrm{g}) + \tfrac{3}{4}Se_2(\mathrm{g}), \quad \Delta_r H^\circ_m = (222.8 \pm 8.0)\ \mathrm{kJ \cdot mol^{-1}}; \tag{15}$$

and

$$As_2Se_3(\mathrm{cr}) = \tfrac{1}{2}As_4Se_4(\mathrm{g}) + \tfrac{1}{2}Se_2(\mathrm{g}), \quad \Delta_r H^\circ_m = (219.7 \pm 7.0)\ \mathrm{kJ \cdot mol^{-1}}. \tag{16}$$

We take $\Delta_f H_m^\circ$ values of $-(58.1 \pm 4.2)\ \mathrm{kJ \cdot mol^{-1}}$ and $-(86.1 \pm 4.1)\ \mathrm{kJ \cdot mol^{-1}}$ from the present study for As_2Se_3(vit) and As_2Se_3(cr), respectively, and $(144.1 \pm 0.6)\ \mathrm{kJ \cdot mol^{-1}}$ for Se_2(g),(36) and calculate from equations (15) and (16): $\Delta_f H_m^\circ(As_4Se_3, g) = (113 \pm 18)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_f H_m^\circ(As_4Se_4, g) = (123 \pm 16)\ \mathrm{kJ \cdot mol^{-1}}$. (In this section, all $\Delta_f H_m^\circ$s refer to 298.15 K.)

It is well established that solid As_4Se_3,(42,43) and As_4Se_4,(44) have cage structures. In the absence of firm experimental evidence, we shall assume that the gaseous forms of those molecules have similar molecular geometries. This assumption is indirectly supported by Lu and Donohue's(45) finding that the cage form persisted when (solid) realgar was vaporized to As_4S_4(g). The structural information on the arsenic selenides also suggests that the As–As bonds are single and similar to those in As_4(g). It seems reasonable, therefore, to assume that the As–As mean bond dissociation enthalpy in As_4(g) is transferable to the arsenic selenides.

For the calculation of the enthalpy of atomization of As_4Se_3, we use the following:

$$\Delta_{at} H_m^\circ(As_4Se_3) = 4\Delta_f H_m^\circ(As, g) + 3\Delta_f H_m^\circ(Se, g) - \Delta_f H_m^\circ(As_4Se_3, g), \tag{17}$$

in which the $\Delta_f H_m^\circ$s of As(g),(41) and Se(g),(36) are taken to be $(287.3 \pm 1.7)\ \mathrm{kJ \cdot mol^{-1}}$ and $(237.6 \pm 0.7)\ \mathrm{kJ \cdot mol^{-1}}$, respectively. Thus, $\Delta_{at} H_m^\circ(As_4Se_3) = (1749 \pm 19)\ \mathrm{kJ \cdot mol^{-1}}$. This quantity, by definition, is also the sum of the mean bond dissociation enthalpies (sometimes called "bond-energy terms"):

$$\Delta_{at} H_m^\circ(As_4Se_3) = 3\langle D_m(\text{As–As})\rangle + 6\langle D_m(\text{As–Se})\rangle, \tag{18}$$

since As_4Se_3 has three As–As and six As–Se bonds. Our derivation of $\langle D_m(\text{As–As})\rangle$ is based on the equation:

$$\langle D_m(\text{As–As})\rangle = \tfrac{1}{6}\{4\Delta_f H_m^\circ(As, g) - \Delta_f H_m^\circ(As_4, g)\}. \tag{19}$$

With $\Delta_f H_m^\circ(As, g)$(41) given previously, and $\Delta_f H_m^\circ(As_4, g) = (158.2 \pm 2.5)\ \mathrm{kJ \cdot mol^{-1}}$,(41) it follows that $\langle D_m(\text{As–As})\rangle = (165 \pm 1)\ \mathrm{kJ \cdot mol^{-1}}$. Thus, from equation (18), $\langle D_m(\text{As–Se})\rangle = (209 \pm 3)\ \mathrm{kJ \cdot mol^{-1}}$.

A similar calculation gives $\Delta_{at} H_m^\circ(As_4Se_4) = (1977 \pm 18)\ \mathrm{kJ \cdot mol^{-1}}$. In this molecule, there are two As–As and eight As–Se bonds. Therefore,

$$\Delta_{at} H_m^\circ(As_4Se_4) = 2\langle D_m(\text{As–As})\rangle + 8\langle D_m(\text{As–Se})\rangle. \tag{20}$$

With $\langle D_m(\text{As–As})\rangle = (165 \pm 1)\ \mathrm{kJ \cdot mol^{-1}}$, $\langle D_m(\text{As–Se})\rangle = (206 \pm 2)\ \mathrm{kJ \cdot mol^{-1}}$.

It is clear, therefore, that the mean enthalpies of the As–Se bonds in the two caged molecules are almost identical and this indicates that there is little or no significant ring strain in gaseous As_4Se_3 and As_4Se_4. The suggested mean energy of the As–Se single bond is $(208 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$. To the best of our knowledge, this result has not been published previously.

Two other gaseous (arsenic + selenium) molecules have been reported: As_2Se_2 and AsSe. Gospodinov *et al.*(46) studied the vaporization of AsSe(cr) by mass spectrometry and detected $As_2Se_2^+$, $AsSe_2^+$, and As_2Se^+. They concluded that, in the sublimation of AsSe, As_2Se_2 was the principal molecule in the gas phase:

$$2AsSe(cr) = As_2Se_2(g). \tag{21}$$

Steblevskii *et al.*(11) also observed $As_2Se_2(g)$ and AsSe(g) and deduced the following thermodynamic values from their mass-spectrometric studies:

$$As_2Se_2(g) = \tfrac{1}{2}As_4Se_4(g), \quad \Delta_r H_m^\circ = -(104 \pm 3)\ kJ \cdot mol^{-1}, \tag{22}$$

and

$$2AsSe(g) = \tfrac{1}{2}As_4Se_4(g), \quad \Delta_r H_m^\circ = -(285 \pm 12)\ kJ \cdot mol^{-1}. \tag{23}$$

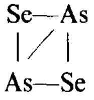
Therefore, for the reverse of the dimerization reaction:

$$As_2Se_2(g) = 2AsSe(g), \tag{24}$$

$\Delta_r H_m^\circ = (181 \pm 12)\ kJ \cdot mol^{-1}$, from the combination of equations (22) and (23).

There is very little information on $As_2Se_2(g)$ in the literature, but a likely structure for it may be rationalized from $\Delta_r H_m^\circ$ of reaction (24). In most arsenic chalcogenides, the arsenic and the chalcogen atoms exhibit valencies of 3 and 2, respectively. Bearing that in mind, and also that many such compounds have cyclic structures, the following possible arrangements for As_2Se_2 appear *a priori* to be reasonable:

I



II

Se=As—As=Se.

III

Decomposition of I to 2AsSe(g), *i.e.* the rupture of the As=As and Se—Se bonds, requires an amount of energy approximately equivalent to $\{\langle D_m(As{=}As)\rangle + \langle D_m(Se{-}Se)\rangle\}$. We estimate $\langle D_m(As{=}As)\rangle \approx D_m^\circ(As_2, g) = 383\ kJ \cdot mol^{-1}$,(35) and $\langle D_m(Se{-}Se)\rangle = 216\ kJ \cdot mol^{-1}$, from the enthalpies of atomization(35) of $Se_6(g)$ and $Se_8(g)$. Thus, for the dissociation of structure I to 2AsSe(g), $\Delta_r H_m^\circ \approx 600\ kJ \cdot mol^{-1}$, very much larger than the $\Delta_r H_m^\circ = (181 \pm 12)\ kJ \cdot mol^{-1}$ calculated for reaction (24).

Clearly, the breakdown of structures I (dissociation of an As–As double bond and a Se–Se single bond) and II (dissociation of an As–As single bond and two As–Se single bonds) would require energies greatly in excess of the $(181 \pm 12)\ kJ \cdot mol^{-1}$ for reaction (24). On the other hand, decomposition of structure III to 2AsSe(g) involves only the rupture of the central As–As bond which, earlier, we have calculated to require about $165\ kJ \cdot mol^{-1}$, fairly close to the value for $\Delta_r H_m^\circ$ of reaction (24). Simple chemical logic would also tend to preclude structures I and II, both of which would be highly strained. Thus, it is clear that the thermochemical evidence is consistent with a linear, rather than a cyclic, structure for As_2Se_2.

If structure III is indeed correct, we should obtain comparable values for $\langle D_m(As{-}As)\rangle$ in the analogous As_2S_2 and As_2Te_2. Unfortunately, $As_2S_2(g)$ has not been positively identified in the gas phase. Rogstad(47) attributed some bands in the high-temperature Raman spectra of (arsenic + sulfur) vapors to As_2S_2, and Pashinkin *et al.*(48) reported the presence of significant quantities of As_2S_2 in the high-temperature vapor phase over As_2S_3 and gave $\Delta_r H_m^\circ = -138\ kJ \cdot mol^{-1}$ for the dimerization of AsS(g). On the other hand, Steblevskii *et al.*,(49) in a recent high-temperature study, found no As_2S_2 in vapors over As_2S_3 and β-As_4S_4. Thus, there is as yet little convincing evidence for the existence of $As_2S_2(g)$.

The situation with $As_2Te_2(g)$ is much more conclusive. Alikhanyan *et al.*⁽⁵⁰⁾ have studied the vapor phase over arsenic telluride and reported the following values at 298.15 K:

$$As_2Te_2(g) = 2As(s) + 2Te(s), \quad \Delta_r H_m^\circ = -(196.2 \pm 4.5)\ kJ \cdot mol^{-1}, \qquad (25)$$

and

$$2As(s) + 2Te(s) = 2AsTe(g), \quad \Delta_r H_m^\circ = (370 \pm 16.0)\ kJ \cdot mol^{-1}. \qquad (26)$$

Combination of reactions (25) and (26) yields:

$$As_2Te_2(g) = 2AsTe(g), \quad \Delta_r H_m^\circ = (174 \pm 17)\ kJ \cdot mol^{-1}. \qquad (27)$$

This enthalpy value is very close to the 165 $kJ \cdot mol^{-1}$ which we have assigned to the As–As single bond, and to $\Delta_r H_m^\circ$ for reaction (24), and lends further support to our conclusion that, for X = S, Se, and Te, the structure of $As_2X_2(g)$ is linear.

A search of the current literature revealed that D_m°(As–Se) in AsSe(g) had not yet been reported, but this value can now be deduced. Equation (23), combined with our previously calculated $\Delta_f H_m^\circ(As_4Se_4, g)$ yields $\Delta_f H_m^\circ(AsSe, g) = (173 \pm 10)\ kJ \cdot mol^{-1}$. This result, along with $\Delta_f H_m^\circ$s for As(g),⁽⁴¹⁾ and for Se(g),⁽³⁶⁾ leads to D_m°(As–Se) $= (352 \pm 10)\ kJ \cdot mol^{-1}$ for the dissociation reaction:

$$AsSe(g) = As(g) + Se(g). \qquad (28)$$

It is not surprising that the As–Se bond in the diatomic molecule ("bond-order" = 2.5) is significantly stronger, by approximately 140 $kJ \cdot mol^{-1}$, than that in As_4Se_4 and As_4Se_3 ("bond-order" = 1).

In table 5, we have summarized the "best" values for D_m° of the gaseous arsenic monochalcogenides. The relative magnitudes of D_m°(As–X) from X = O through X = Te are not unexpected, with D_m°(As–O) much greater than the other bond-dissociation enthalpies, and a monotonic decrease in D_m° from X = S through X = Te.

BOND ENTHALPIES IN SOLID As_2Se_3

Although the mean bond enthalpies of gaseous arsenic selenides, which we have just discussed, are important from a general chemical and technological point of view, the bond enthalpies of the solid compounds are also of great significance for practical applications, and we shall now describe how they may be calculated.

Renninger and Averbach⁽⁵⁴⁾ gave prespective plots of crystalline As_2Se_3 molecules in which it was shown that each arsenic atom was tetrahedrally bonded to three selenium atoms which, in turn, were each bonded to an arsenic atom. Thus, in the

TABLE 5. Bond dissociation enthalpies D_m°(As–X) of the gaseous diatomic arsenic chalcogenides

X:	O	S	Se	Te
$D_m^\circ/(kJ \cdot mol^{-1})$:	481 ± 10^a	389 ± 3^b	352 ± 10^c	312 ± 10^d

[a] References 51 and 52. [b] Reference 53. [c] This paper. [d] Calculated from reference 50 and $\Delta_f H_m^\circ$s for As(g) and Te(g) from references 41 and 36, respectively.

As_2Se_3 unit,(5) there are five arsenic-to-selenium bonds. Accordingly, the mean bond enthalpy *in the crystal* is given by:

$$\langle D_m(\text{As–Se, cr})\rangle = \tfrac{1}{5}\{2\Delta_f H_m^\circ(\text{As, g}) + 3\Delta_f H_m^\circ(\text{Se, g}) - \Delta_f H_m^\circ(\text{As}_2\text{Se}_3\text{, cr})\}, \qquad (29)$$

and refers to the atomization reaction:

$$\text{As}_2\text{Se}_3(\text{cr}) = 2\text{As(g)} + 3\text{Se(g)}. \qquad (30)$$

Earlier in the present paper, values were given for $\Delta_f H_m^\circ(\text{As, g})$,(41) and $\Delta_f H_m^\circ(\text{Se, g})$,(36) and $\Delta_f H_m^\circ(\text{As}_2\text{Se}_3\text{, cr})$ is in table 2. Thus, from equation (29), $\langle D_m(\text{As–Se, cr})\rangle = (275 \pm 1)\,\text{kJ}\cdot\text{mol}^{-1}$. If it is assumed that, qualitatively, the bonding in As_2Se_3(vit) is the same as in the crystal (and there is no convincing evidence to the contrary), then a calculation based on equation (29) yields $\langle D_m(\text{As–Se, vit})\rangle = (269 \pm 1)\,\text{kJ}\cdot\text{mol}^{-1}$.

These bond enthalpies are approximately $40\,\text{kJ}\cdot\text{mol}^{-1}$ larger than the values we reported(18) for $\langle D_m(\text{Ge–Se, s})\rangle$ in $GeSe_2$(s). In *gaseous* compounds, bonds between elements of groups 14 and 16 tend to be stronger than those between groups 15 and 16. That tendency is reversed in the present case, and may be due to crystal-field stabilization of As_2Se_3 over $GeSe_2$. Such stabilization would, presumably, be reflected in the enthalpies of sublimation, but all the experimental evidence to date indicates that As_2Se_3 (see reference 11, for example) does not sublime without decomposition.

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