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Standard molar enthalpies of formation and transition at 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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Short title: THERMODYNAMIC PROPERTIES OF As_2Se_3

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Fluorine-combustion calorimetry was used to determine the standard molar enthalpies of formation (at 298.15 K and $p^{\circ} = 101.325$ kPa) of the crystalline and vitreous forms of arsenic sesquiselenide. The following results were obtained: $\Delta_f H^{\circ}_m(\mathrm{As_2Se_3, cr}) = -(86.1 \pm 4.1)$ $\mathrm{kJ \cdot mol^{-1}}$ and $\Delta_f H^{\circ}_m(\mathrm{As_2Se_3, vit}) = -(58.1 \pm 4.2)$ $\mathrm{kJ \cdot mol^{-1}}$. The enthalpy of the transition from the vitreous to the crystalline forms of $\mathrm{As_2Se_3}$, $-(28.0 \pm 3.9)$ $\mathrm{kJ \cdot mol^{-1}}$ at 298.15 K, supports 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 recalculated from the literature to give, for $\mathrm{As_2Se_3(cr)}$ 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 $\mathrm{As_4Se_3(g)}$ and $\mathrm{As_4Se_4(g)}$ 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 $\mathrm{As_2Se_2(g)}$. Bond dissociation enthalpies $D^{\circ}_m(\mathrm{As{-}X})$ are given, where X = O, S, Se, and Te.

1. Introduction

Noncrystalline As_2Se_3 is an important material in several modern technologies. It has a highly-transparent region in the infrared, and fibers can be made from it that 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 important. 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. The need to understand the transformation of glass to crystal (the thermodynamic reference state) in As_2Se_3 has been an important driving force behind the present calorimetric study.

There is already a significant amount of thermodynamic information concerning As_2Se_3 in the literature. 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) High-temperature vaporization studies of As_2Se_3 have been described by Pelevin et al.,(8) Orlov et al.,(9) Kinoshita,(10) and Steblevskii et al.(11) Enthalpies of solution in base were measured calorimetrically by Hattori et al.,(12) and enthalpies of melting by Rasulov and Medzhidov,(7) Blachnik and Schneider,(13) and Myers and Felty.(14) Standard molar enthalpies of formation at 298.15 K have been reported by Blachnik and Schneider,(13) and have been deduced from high-temperature vaporization studies by Steblevskii et al.,(11) but both sets of results 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,(15) GeS_2,(16) $MoSe_2$ and Mo_6Se_6,(17) WSe_2,(18) and $MoTe_2$(19) and we have reviewed(20) 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 were 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:

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

have been determined, and the corresponding enthalpies of combustion have been combined with our previously reported results for $\Delta_f H_m^\circ(\mathrm{AsF_5})$(21) and $\Delta_f H_m^\circ(\mathrm{SeF_6})$(22) to deduce $\Delta_f H_m^\circ(\mathrm{As_2Se_3})$.

2. Experimental

As_2Se_3 is one member of an important family of i.r.-transmitting chalcogenide glasses.(23) 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.(23–25) This body of literature serves 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 materials 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. Fused silica tubes were etched in 25 mass per cent of HF(aq) and outgassed at 1273 K and p ≈0.1 mPa prior to use.

High-purity selenium (Asarco, 99.9995 mass per cent with respect to metal contaminants) was melted for 1 to 3 h in an evacuated (p ≈7 mPa) 25-mm i.d. fused-silica tube at 573 K. In this way, it is believed that hydrogen and oxygen were effectively removed 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 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, about 15 g total mass, were charged into 10-mm i.d. fused-silica tubes which were sealed off under a helium atmosphere ($p \approx 5 \times 10^{-3}$ Pa), loaded into a rocking furnace, brought slowly up 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 ≈ 273 K. The vitreous boules did not adhere to the ampoule walls, and when they were 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 ($CuK_{k\alpha}$, 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 0.5-mm thick slice of vitreous As_2Se_3, measured with a Brücker FTIR-98. The bands at 2800 to 3000 cm^{-1} arise from

C–H stretching and the weak band at 745 cm^{-1} from C–H_2 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 $\rangle$As—O—As species, i.e. oxygen substitutionally incorporated for selenium in the network.(25) The absorption coefficient is consistent with a mass fraction of oxygen contaminant of 6×10^{-6} in the glass. There is obviously 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 to 3×10^{-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 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 spectroscopic examination of As_2Se_3 showed evidence for just As–O bonds.

The fluorine-bomb calorimetric technique and equipment have been described in detail.(18) 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 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 present in the crucible after most combustions. This residue, according to SEM analysis, was composed mostly of nickel and arsenic, but insufficient quantities could be isolated for X-ray analysis. Therefore, 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) according to the reaction

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

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

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

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. All the symbols in the table have been explained previously,(16) with the exception of $\Delta U(\mathrm{NiAs})$. This quantity denotes the thermochemical correction for the formation, or fluorination, of the the NiAs residue in the crucible, according to reactions (2) or (3). 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 $\Delta U(\mathrm{blank})$ 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 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 $\Delta_f H_m^\circ$ of the compounds, as well as the impurity corrections and $\Delta U(NiAs)$, we have used $\Delta_f H_m^\circ$ of SeF_6(22) and AsF_5.(21) Both values were originally reported by us but, due to a new, more accurate, method we have recently introduced(26) for calculating ΔU(blank), the published result for $\Delta_f H_m^\circ(AsF_5)$ has to be changed in much the same way(22) that we earlier revised $\Delta_f H_m^\circ(SeF_6)$. In our original report(21) 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, $\Delta_f H_m^\circ(AsF_5, g)$ is changed from $-(1236.7\pm0.8)$ $kJ\cdot mol^{-1}$ to $-(1237.0\pm0.8)$ $kJ\cdot mol^{-1}$, and this value has been used in the present paper. In addition, our calculation of $\Delta U(NiAs)$ incorporated $\Delta_f H_m^\circ(NiAs) = -(72.0\pm3.8)$ $kJ\cdot mol^{-1}$(27) and $\Delta_f H_m^\circ(NiF_2) = -(657.7\pm1.7)$ $kJ\cdot mol^{-1}$.(28)

The standard molar energies and enthalpies of combustion of the arsenic selenides are given in table 2, and are based on a molar mass of 386.7 $g\cdot mol^{-1}$ 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 $S_m^\circ(As_2Se_3$, cr, 298.15 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(29) 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(30) which reproduced quite accurately the experimental heat capacities between 50 and 200 K. From Nemilov's procedure, we obtain for As_2Se_3(cr): $\{S_m^\circ(53\ K)-S_m^\circ(0)\} = 46.1\ J\cdot K^{-1}\cdot mol^{-1}$ and, from Zhdanov and Mal'tsev, by graphical integration, $\{S_m^\circ(298.15\ K)-S_m^\circ(53\ K)\} = 160.3\ J\cdot K^{-1}\cdot mol^{-1}$. Therefore, $\{S_m^\circ(298.15\ K)-S_m^\circ(0)\} = (206\pm3)\ J\cdot K^{-1}\cdot mol^{-1}$, where the uncertainty has been estimated. This result, combined with S_m°s for As(cr), 35.7 $J\cdot K^{-1}\cdot mol^{-1}$,(31) and Se(cr), 42.27 $J\cdot K^{-1}\cdot mol^{-1}$(32) yields the $\Delta_f S_m^\circ$ and, thus, $\Delta_f G_m^\circ$ given for As_2Se_3(cr) in table 2.

4. Discussion

STANDARD MOLAR ENTHALPIES OF FORMATION AT 298.15 K

Two previous determinations of $\Delta_f H_m^\circ(As_2Se_3)$, one direct and the other indirect, have been described. Blachnik and Schneider(13) 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 $\Delta_f H_m^\circ = -(103 \pm 21)\ kJ \cdot mol^{-1}$. 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 $\Delta_f H_m^\circ$ for crystalline and vitreous As_2Se_3 from the equilibrium pressures of the reactions summarized in table 3. In that 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 significantly more uncertain than, but nevertheless agree with, the present values. Reactions (1) and (6) 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.(12) 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.

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 between 273.15 K and the melting temperature, which Rasulov and Medzhidov took to be 634 K, were reported in polynomial form. We have recalculated those results to refer to 298.15 K as the base temperature, and for that purpose have used $\{H^{\circ}_{m}(273.15\ K) - H^{\circ}_{m}(298.15\ K)\} = -3021\ J{\cdot}mol^{-1}$ given by Zhdanov and Malt'sev.(4) We have added the further constraint that $C^{\circ}_{p,m} = 121.42\ J{\cdot}K^{-1}{\cdot}mol^{-1}$(4) at 298.15 K. The following expression has been obtained:

$$\{H^{\circ}_{m}(T) - H^{\circ}_{m}(298.15\ K)\}/(J \cdot mol^{-1}) = 121.23(T/K)$$

$$-1.9085 \times 10^{-2}(T/K)^2 + 4.3403 \times 10^{-5}(T/K)^3 - 35597. \qquad (4)$$

By differentiation:

$$C^{\circ}_{p,m}(T)/(J \cdot K^{-1} \cdot mol^{-1}) = 121.23 - 3.8170 \times 10^{-2}(T/K) + 1.3021 \times 10^{-4}(T/K)^2. \qquad (5)$$

The enthalpy increments of vitreous As_2Se_3 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 equations are as follows:

$$\{H^{\circ}_{m}(T) - H^{\circ}_{m}(298.15\ K)\}/(J \cdot mol^{-1}) = -26740 + 42.9300(T/K) + 0.2041(T/K)^2$$

$$-1.5851 \times 10^{-4}(T/K)^3,\ T < 460\ K; \qquad (6)$$

$$\{H^{\circ}_{m}(T) - H^{\circ}_{m}(298.15\ K)\}/(J \cdot mol^{-1}) = -55633 + 338.92(T/K) - 0.8683(T/K)^2$$

$$+1.4064 \times 10^{-3}(T/K)^3 - 6.9673 \times 10^{-7}(T/K)^4, T < 803\ K. \qquad (7)$$

THERMODYNAMIC PROPERTIES OF CRYSTALLINE ARSENIC SESQUISELENIDE

The conventional thermodynamic properties of As_2Se_3(cr) to the melting temperature are given in table 4. The enthalpy increments and heat capacities are calculated from equations (4) and (5), and the standard molar entropy of As_2Se_3(cr) has been given earlier. As auxiliary quantities, we have used the enthalpy increments and standard molar entropies of As$^{(31)}$ and Se.$^{(32)}$

ENTHALPIES OF TRANSITION AND FUSION

For the transition:

$$As_2Se_3(\mathrm{vit}, T') = As_2Se_3(\mathrm{cr}, T') \qquad (8)$$

at $T' = 298.15$ K, the difference between our enthalpy of combustion results gives $\Delta_{trs}H^{\circ}_{m} = -(28.0\pm3.9)$ kJ·mol^{-1}, which is significantly more positive than the $-(40\pm7)$ kJ·mol^{-1} calculated from the weighted $\Delta_f H^{\circ}_{m}$s from the Steblevskii et al.$^{(11)}$ study (see table 3). If, instead, we take the results for reactions (1) and (6) from table 3, then $\Delta_{trs}H^{\circ}_{m} = -(32\pm12)$ kJ·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):

$$As_2Se_3(\mathrm{vit},\ T') = As_2Se_3(\mathrm{l},\ 633\ \mathrm{K}), \qquad (9)$$

$$As_2Se_3(\mathrm{l}, 633\ \mathrm{K}) = As_2Se_3(\mathrm{cr}, 633\ \mathrm{K}), \qquad (10)$$

$$As_2Se_3(\mathrm{cr}, 633\ \mathrm{K}) = As_2Se_3(\mathrm{cr}, T'). \qquad (11)$$

Summation of the above equations gives:

$$\Delta_{trs}H^{\circ}_{m}(T') = \Delta H^{\circ}_{m}(8) = \Delta H^{\circ}_{m}(9) + \Delta H^{\circ}_{m}(10) + \Delta H^{\circ}_{m}(11). \qquad (12)$$

From equation (7), $\Delta H^{\circ}_{m}(9) = (55.8\pm3.4)$ kJ·mol^{-1}; $\Delta H^{\circ}_{m}(10) = -\Delta_{fus}H^{\circ}_{m}(As_2Se_3)$; and $\Delta H^{\circ}_{m}(11) = -(44.5\pm2.7)$ kJ·mol^{-1} from equation (4). In summary,

$$\Delta_{trs}H^{\circ}_{m}(298.15\ \mathrm{K})/(\mathrm{kJ\cdot mol^{-1}}) = -(44.5 \pm 2.7) + (55.8 \pm 3.4) - \Delta_{fus}H^{\circ}_{m}. \qquad (13)$$

Unfortunately, there are at least four disparate values for $\Delta_{\text{fus}}H^{\circ}_{\text{m}}$ in the literature. Rasulov and Medzhidov$^{(7)}$ reported 12.6 kJ·mol^{-1}, which, from equation (13), implies an unlikely $\Delta_{\text{trs}}H^{\circ}_{\text{m}} \approx 0$. Blachnik and Schneider's$^{(13)}$ result, (29.3±6.3) kJ·mol^{-1}, yields $\Delta_{\text{trs}}H^{\circ}_{\text{m}}$ = −(18±8) kJ·mol^{-1}. From Meyers and Felty's$^{(14)}$ determination, (40.8±1.3) kJ·mol^{-1}, we deduce $\Delta_{\text{trs}}H^{\circ}_{\text{m}}$ = −(29±5) kJ·mol^{-1}, in excellent accord with the present investigation. Finally, Thornberg and Johnson$^{(34)}$ have reported an enthalpy of crystallization of −34.7 kJ·mol^{-1}($\Delta_{\text{fus}}H^{\circ}_{\text{m}}$ = 34.7 kJ·mol^{-1}) which, from equation (13), leads to $\Delta_{\text{trs}}H^{\circ}_{\text{m}}$ = −(23±4) kJ·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 Thornberg and Johnson result.

BOND ENTHALPIES OF ARSENIC SELENIDES

There is very little information about the strengths of As–Se bonds 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 available to deduce mean bond enthalpies $< D_{\text{m}} >$ 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 $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (298.15 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:

$$\mathrm{As_2Se_3(vit)} = \frac{1}{2}\mathrm{As_4Se_3(g)} + \frac{3}{4}\mathrm{Se_2(g)}, \quad \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}} = (222.8 \pm 8.0)\ \mathrm{kJ\cdot mol^{-1}}; \tag{14}$$

and

$$\mathrm{As_2Se_3(cr)} = \frac{1}{2}\mathrm{As_4Se_4(g)} + \frac{1}{2}\mathrm{Se_2(g)}, \quad \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}} = (219.7 \pm 7.0)\ \mathrm{kJ\cdot mol^{-1}}. \tag{15}$$

We take $\Delta_f H^\circ_m$ values of $-(58.1\pm4.2)$ and $-(86.1\pm4.1)$ $\mathrm{kJ\cdot mol^{-1}}$ from the present study for As_2Se_3(vit) and As_2Se_3(cr), respectively, and (144.1 ± 0.6) $\mathrm{kJ\cdot mol^{-1}}$(32) for Se_2(g), and calculate from equations (14) and (15): $\Delta_f H^\circ_m(As_4Se_3, g) = (113\pm18)$ $\mathrm{kJ\cdot mol^{-1}}$ and $\Delta_f H^\circ_m(As_4Se_4, g) = (123\pm16)$ $\mathrm{kJ\cdot mol^{-1}}$. (In this section, all $\Delta_f H^\circ_m$s refer to 298.15 K).

It is well established that solid As_4Se_3(35,36) and As_4Se_4(37) have cage structures. In the absence of experimental evidence, we assume that the gaseous forms of those molecules have similar molecular geometries. This assumption is indirectly supported by Lu and Donohue's(38) finding that the cage form persisted when (solid) realgar was vaporized to As_4S_4(g). The structural information on the selenides also suggests that the As–As bonds are single and similar to those in As_4(g). We shall therefore assume that the As–As bond 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 equation:

$$\Delta_{at} H^\circ_m(As_4Se_3) = 4\Delta_f H^\circ_m(As,\ g) + 3\Delta_f H^\circ_m(Se,\ g)\ - \Delta_f H^\circ_m(As_4Se_3,\ g), \qquad (16)$$

in which the $\Delta_f H^\circ_m$s of As(g)(33) and Se(g)(32) are taken to be (287.3 ± 1.7) and (237.6 ± 0.7) $\mathrm{kJ\cdot mol^{-1}}$, respectively. Thus, $\Delta_{at} H^\circ_m(As_4Se_3) = (1749\pm19)$ $\mathrm{kJ\cdot mol^{-1}}$. This quantity, by definition, is also the sum of the mean bond dissociation enthalpies (sometimes called "bond-energy terms"):

$$\Delta_{at} H^\circ_m(As_4Se_3) = 3 < D_m(As - As) > +6 < D_m(As - Se) >, \qquad (17)$$

since As_4Se_3 has three As–As and six As–Se bonds. Our derivation of $< D_m(As-As)>$ is based on the following equation:

$$< D_m(As - As) >= \frac{1}{6}\{4\Delta_f H^\circ_m(As,\ g) - \Delta_f H^\circ_m(As_4,\ g)\}. \qquad (18)$$

With $\Delta_f H^\circ_m(As, g)$ given previously, and $\Delta_f H^\circ_m(As_4, g) = (158.2\pm2.5)$ $\mathrm{kJ\cdot mol^{-1}}$,(33) it follows that $< D_m(As - As) > = (165\pm1)$ $\mathrm{kJ\cdot mol^{-1}}$. Thus, from equation (17), $< D_m(As - Se) > = (209\pm3)$ $\mathrm{kJ\cdot mol^{-1}}$.

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

$$\Delta_{\mathrm{at}}\mathrm{H}^{\circ}_{\mathrm{m}}(\mathrm{As_4Se_4}) = 2 < \mathrm{D_m}(\mathrm{As-As}) > +8 < \mathrm{D_m}(\mathrm{As-Se}) > . \tag{19}$$

With $< \mathrm{D_m}(\mathrm{As-As}) >$ = (165±1) kJ·mol^{-1} given previously, $< \mathrm{D_m}(\mathrm{As-Se}) >$ = (206±2) kJ·mol^{-1}.

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

Two other (arsenic + selenium) molecules have been observed in the gas phase: $\mathrm{As_2Se_2}$ and AsSe. Gospodinov et al.(39) studied the vaporization of AsSe(cr) by mass spectrometry and detected $\mathrm{As_2Se_2^+}$, $\mathrm{AsSe_2^+}$, and $\mathrm{As_2Se^+}$. They concluded that sublimation of AsSe yielded $\mathrm{As_2Se_2}$ as the principal molecule in the gas phase:

$$2\mathrm{AsSe(cr)} = \mathrm{As_2Se_2(g)}. \tag{20}$$

Steblevskii et al.(11) also detected $\mathrm{As_2Se_2}$ and AsSe and reported the following thermodynamic values:

$$\mathrm{As_2Se_2(g)} = \frac{1}{2}\mathrm{As_4Se_4(g)}, \quad \Delta_{\mathrm{r}}\mathrm{H}^{\circ}_{\mathrm{m}} = -(104 \pm 3)\ \mathrm{kJ \cdot mol^{-1}}, \tag{21}$$

and

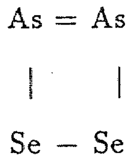
$$2\mathrm{AsSe(g)} = \frac{1}{2}\mathrm{As_4Se_4(g)},\ \Delta_{\mathrm{r}}\mathrm{H}^{\circ}_{\mathrm{m}} = -(285 \pm 12)\ \mathrm{kJ \cdot mol^{-1}}. \tag{22}$$

Therefore, for the reverse of the dimerization reaction:

$$\mathrm{As_2Se_2(g)} = 2\mathrm{AsSe(g)}, \tag{23}$$

$\Delta_{\mathrm{r}}\mathrm{H}^{\circ}_{\mathrm{m}}$ = (181±12) kJ·mol^{-1}, from equations (21) and (22).

There is little information on $As_2Se_2(g)$ in the literature, but a likely structure for it may be rationalized from $\Delta_r H^\circ_m$ of reaction (23). 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 to be reasonable:



I

$$\mathrm{Se = As - As = Se} \;.$$

II

Decomposition of I to 2AsSe(g), i.e., the rupture of the As=As bond and one Se–Se bond, requires an amount of energy approximately equivalent to $\{< D_m(\mathrm{As = As}) > + < D_m(\mathrm{Se - Se}) >\}$. We estimate $< D_m(\mathrm{As = As}) > \approx D^\circ_m(\mathrm{As_2, g}) = 383$ kJ·mol^{-1},(31) and $< D_m(\mathrm{Se - Se}) > = 216$ kJ·mol^{-1}, from the enthalpies of atomization(31) of $Se_6(g)$ and $Se_8(g)$. Thus, for the dissociation of structure I to 2AsSe(g), $\Delta_r H^\circ_m \approx 600$ kJ·mol^{-1}, very much larger than the $\Delta_r H^\circ_m = (181 \pm 12)$ kJ·mol^{-1} calculated for reaction (23).

On the other hand, decomposition of structure II to 2AsSe(g) involves only the rupture of the central As-As bond which, earlier, we have calculated to require about 165 kJ·mol^{-1}, fairly close to the value for $\Delta_r H^\circ_m$ of reaction (23). Thus, it is clear that the thermochemical evidence is consistent with a linear, rather than a cyclic, structure for As_2Se_2.

If structure II is indeed correct, we should obtain comparable values for $< D_m(\mathrm{As - As}) >$ 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(40) attributed some bands in the high-temperature Raman spectra of (arsenic + sulfur) vapors to As_2S_2, and Pashinkin et al.(41) reported the presence of significant quantities of As_2S_2 in the high-temperature vapor phase over As_2S_3 and gave $\Delta_r H^\circ_m = -138$ kJ·mol^{-1} for the dimerization of AsS(g). On the other hand, Steblevskii et al.,(42) 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.$^{(43)}$ have studied the vapor phase over arsenic telluride and reported the following values at 298.15 K:

$$As_2Te_2(g) = 2As(s) + 2Te(s),\ \Delta_r H^\circ_m = -(196.2 \pm 4.5)\ kJ \cdot mol^{-1}, \qquad (24)$$

and

$$2As(s) + 2Te(s) = 2AsTe(g),\ \Delta_r H^\circ_m = (370 \pm 16.0)\ kJ \cdot mol^{-1}. \qquad (25)$$

Combination of reactions (24) and (25) yields:

$$As_2Te_2(g) = 2AsTe(g),\ \Delta_r H^\circ_m = (174 \pm 17)\ kJ \cdot mol^{-1}. \qquad (26)$$

This bond-dissociation enthalpy is very close to the value of 165 $kJ \cdot mol^{-1}$ which we have assigned to the As–As single bond, and to $\Delta_r H^\circ_m$ for reaction (23), 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) had not yet been reported, but this value can now be deduced. Equation (22), combined with our previously calculated $\Delta_f H^\circ_m(As_4Se_4,\ g)$ yields $\Delta_f H^\circ_m(AsSe,\ g) = (173 \pm 10)\ kJ \cdot mol^{-1}$. This result, along with $\Delta_f H^\circ_m$s for As(g)$^{(33)}$ and Se(g),$^{(32)}$ leads to $D^\circ_m(As\text{–}Se) = (352 \pm 10)\ kJ \cdot mol^{-1}$ for the dissociation reaction:

$$AsSe(g) = As(g) + Se(g). \qquad (27)$$

It is not surprising that the As–Se bond in the diatomic molecule ("bond-order" = 2.5) is approximately 140 $kJ \cdot mol^{-1}$ stronger 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, but a more precise D°_m(As–S) would clearly be very helpful in further rationalizing this trend.

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 point of view, it is the bond enthalpies of the solid compounds that appear to be of most significance for practical applications, and we shall now describe how they may be calculated.

Renninger and Averbach(47) have given perspective 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 As_2Se_3 unit, there are five arsenic-to-selenium bonds. Accordingly, the mean bond enthalpy <u>in the crystal</u> is given by:

$$< \mathrm{D_m(As-Se,cr)} >= \frac{1}{5}\{2\Delta_f H^\circ_m(\mathrm{As,g}) + 3\Delta_f H^\circ_m(\mathrm{Se,g}) - \Delta_f H^\circ_m(\mathrm{As_2Se_3,cr})\}, \qquad (28)$$

and refers to the atomization reaction:

$$\mathrm{As_2Se_3(cr) = 2As(g) + 3Se(g).} \qquad (29)$$

Earlier in the present paper, values were given for $\Delta_f H^\circ_m$(As, g)(33) and $\Delta_f H^\circ_m$(Se, g),(32) and $\Delta_f H^\circ_m(As_2Se_3$, cr) is in table 2. Thus, from equation (28), $<$ D_m(As–Se, cr)$>$ = (275±1) kJ·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 similar to equation (28) yields $<$ D_m(As–Se, vit)$>$ = (269±1) kJ·mol^{-1}.

These bond enthalpies are approximately 40 kJ·mol^{-1} larger than the values we reported(16) for $<$ D_m(Ge–Se, s)$>$ in $GeSe_2$(s). In <u>gaseous</u> 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. Unfortunately, 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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FIGURE CAPTION

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

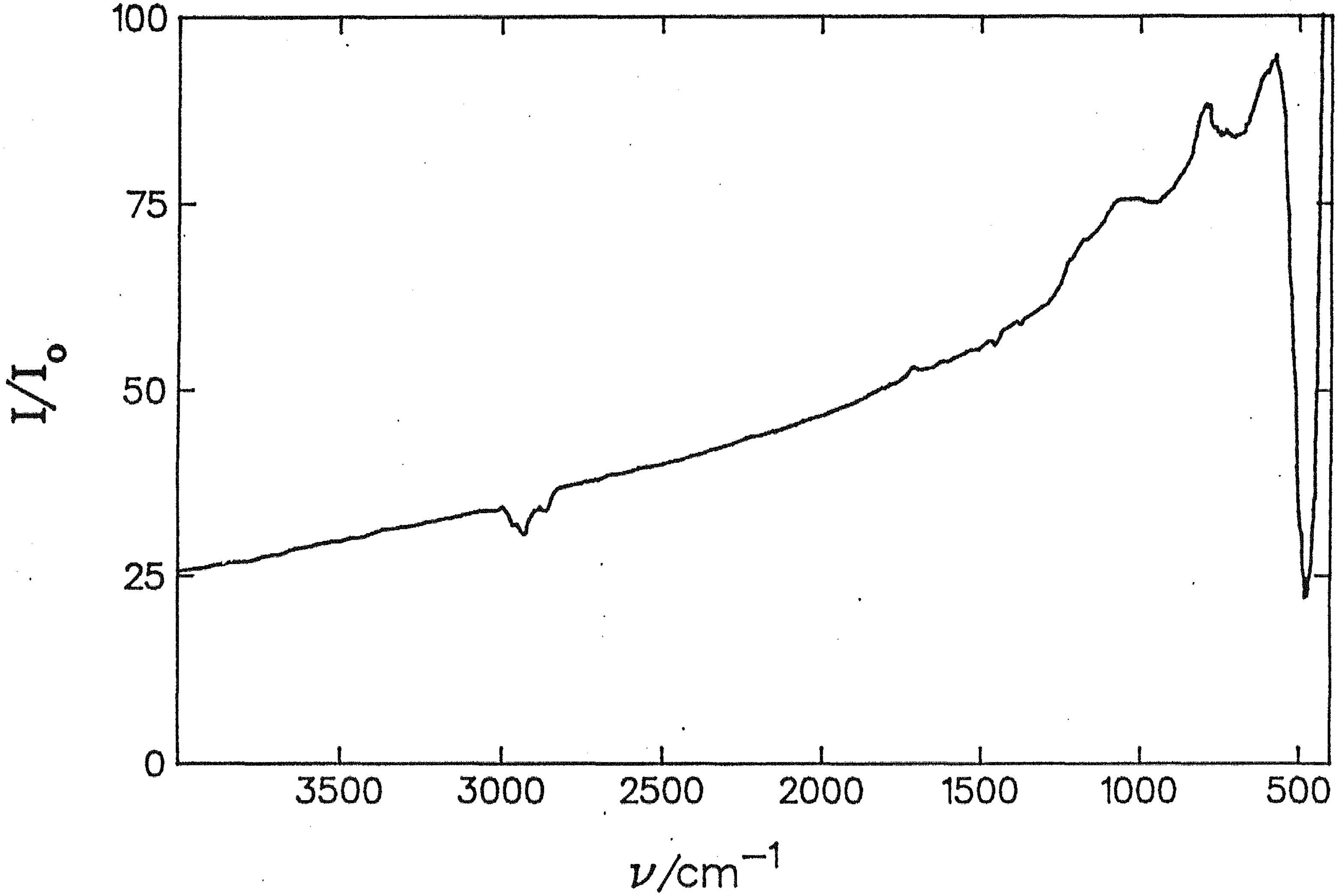
100
75
50
25
0
I/I_o
3500
3000
2500
2000
1500
1000
500
ν/cm^{-1}

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)					As_2Se_3(vit)				
Expt. no.	2	3	4	5	6	1	2	3	5	7
m/g	0.53700	0.51450	0.58217	0.52377	0.50476	0.56085	0.49749	0.49476	0.49160	0.54519
$\Delta\theta_c$/K	0.57034	0.54572	0.61681	0.55584	0.53545	0.59774	0.53008	0.52776	0.52314	0.58093
ϵ(calor)$(-\Delta\theta_c)$/J [a]	−7931.0	−7588.7	−8577.2	−7729.4	−7445.9	−8311.7	−7370.9	−7338.6	−7274.4	−8078.3
ΔU(cont)/J	−6.9	−6.6	−7.4	−6.7	−6.4	−7.2	−6.4	−6.3	−6.3	−7.0
ΔU(gas)/J	−0.3	−0.3	−0.3	−0.3	−0.3	−0.3	−0.3	−0.3	−0.3	−0.3
ΔU(blank)/J	−7.4	−7.4	−7.4	0.3	−7.4	−4.0	−4.0	−4.0	−4.0	−4.0
ΔU(NiAs)/J	1.2	0.4	−9.6	−10.9	−6.1	−11.4	−7.9	0.0	−9.9	−13.9
$\dfrac{\Delta_c U^\circ_m/M(\text{sample})}{J \cdot g^{-1}}$	−14794.0	−14776.7	−14775.6	−14790.8	−14791.4	−14860.7	−14853.6	−14854.1	−14839.1	−14863.6

$< \Delta_c U^\circ_m/M(\text{sample}) > = -(14785.7 \pm 3.9)\ J \cdot g^{-1}$ [b]

Impurity correction $= -(4.3 \pm 0.5)\ J \cdot g^{-1}$ [b]

$< \Delta_c U^\circ_m/M(As_2Se_3, \text{cr}) > = -(14790.0 \pm 3.9)\ J \cdot g^{-1}$ [b]

$< \Delta_c U^\circ_m/M(\text{sample}) > = -(14854.2 \pm 4.2)\ J \cdot g^{-1}$ [b]

Impurity correction $= -(8.1 \pm 0.9)\ J \cdot g^{-1}$ [b]

$< \Delta_c U^\circ_m/M(As_2Se_3, \text{vit}) > = -(14862.3 \pm 4.3)\ J \cdot g^{-1}$ [b]

---

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

[b] Uncertainties are standard deviations of the mean.

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

	$\Delta_c U^\circ_m / \mathrm{kJ \cdot mol^{-1}}$ [b]	$\Delta_c H^\circ_m / \mathrm{kJ \cdot mol^{-1}}$ [b]	$\Delta_f H^\circ_m / \mathrm{kJ \cdot mol^{-1}}$ [c]	$\Delta_f S^\circ_m / \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [c]	$\Delta_f G^\circ_m / \mathrm{kJ \cdot mol^{-1}}$ [c]
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 g·mol^{-1}.

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

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

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] / $kJ \cdot mol^{-1}$	$\Delta_f H_m^\circ(As_2Se_3)$ / $kJ \cdot mol^{-1}$
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: $\Delta_f H_m^\circ(As_4, g) = (158.2 \pm 2.5)\ kJ \cdot mol^{-1}$ (33) and $\Delta_f H_m^\circ(Se_2, g) = (144.1 \pm 0.6)\ kJ \cdot mol^{-1}$.(32)

[b] From reference 11.

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

$\frac{T}{K}$	$\frac{C^\circ_{p,m}}{R}$	$\frac{\Delta^T_{T'} H^\circ_m}{R \cdot K}$	$\frac{\Delta^T_0 S^\circ_m}{R}$	$\frac{\Delta_f H^\circ_m}{kJ \cdot mol^{-1}}$ [a]	$\frac{\Delta_f G^\circ_m}{kJ \cdot mol^{-1}}$ [a]
298.15	14.603	0	24.78	−86.1	−88.4
300	14.612	27.02	24.87	−86.1	−88.4
400	15.249	1517	29.15	−86.5	−88.5
500	16.200	3087	32.65	−105.3	−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: $2As(cr) + 3Se(cr) = As_2Se_3(cr)$; uncertainties are approximately ±5 $kJ \cdot mol^{-1}$.

[b] Melting temperature of As_2Se_3(cr).

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

X	O	S	Se	Te
$\frac{D_m^\circ}{\mathrm{kJ \cdot mol^{-1}}}$	481±10 [a]	375±38 [b]	352±10 [c]	312±10 [d]

[a] References 44 and 45.

[b] Reference 46.

[c] This paper.

[d] Calculated from reference 43 and $\Delta_f H_m^\circ$s for As(g) and Te(g) from references 33 and 32, respectively.