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Chemical vapour transport of bismuth and antimony chalcogenides M_2Q_3 ($M = \text{Sb, Bi}$, $Q = \text{Se, Te}$)

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Dedicated to Prof. Dr. Bernd Harbrecht on the occasion of his 60th birthday

Keywords: antimony selenide; antimony telluride; bismuth selenide; bismuth telluride; chemical vapour transport; thermodynamic modelling

Abstract. Thermodynamic modelling of the ternary systems $M/Q/I$ ($M = \text{Sb, Bi}$, $Q = \text{Se, Te}$) indicated solid-gas equilibria suitable for chemical vapour transport of bismuth and antimony chalcogenides. The predictions of the modelling were confirmed by transport experiments on a transport balance. The optimum transport conditions using iodine as transport agent were determined for all systems to:

$\vartheta_{\text{source}} = 500\text{ °C}$ and $\vartheta_{\text{sink}} = 450\text{ °C}$. For $\Delta T > 50\text{ K}$ the sequential transport of chalcogenide iodides MQI followed by M_2Q_3 occurs. Thermodynamic standard data of the gas species SbI(g) were concluded from equilibrium calculations: $\Delta H_{f,298}^0(\text{SbI(g)}) = 106 \pm 3\text{ kJ}\cdot\text{mol}^{-1}$; $S_{298}^0(\text{SbI(g)}) = 255 \pm 3\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $C_p(\text{SbI(g)}) = 37 \pm 1\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

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Introduction

The vapour transport of selenides and tellurides is fairly well investigated. First reports on chemical transport of chalcogenides are related to the systematic development of this synthesis method [1 – 4]. To date a large number of chemical vapour transport experiments concerning transition metal chalcogenides as well as chalcogenides of main group elements have been described. Hence, chemical vapour transport of chalcogenides of elements of groups 13, and 14 are reported (Al [1], Ga [3, 5 – 7], In [8, 9], Si [10 – 12], Ge [13 – 15], Sn [3, 16 – 18], Pb [19 – 21]). Transport experiments for crystal growth of Sb_2Te_3 using iodine are described to produce multiphase mixtures of Sb_2Te_3 and unknown phases [22]. Apart from this report no attention has been given to the transport behaviour of compounds M_2Q_3 of group 15 elements, despite their importance as thermoelectric materials. The “closed space vapour transport” of M_2Q_3 as a kind of Physical Vapour Deposition (CVD) process has been investigated [23].

Recent investigations are demonstrating the possibility of detailed thermodynamic modelling of gas phase equilibria and the vapour transport behaviour even for chalcogenides of complex composition, such as phases with homogeneity range or solid solutions. Using these calculations prior to the experiment, meticulous prediction of experimental transport conditions becomes possible [24, 25].

Our investigation on antimony and bismuth chalcogenides proves the power of thermodynamic modelling for the prediction of chemical vapour transport properties. The calculations concerning the solid-gas equilibria are presented at different levels of complexity.

Results and Discussion

1 Thermodynamic modelling of the vapour transport

Prior to the experiments, various thermodynamic calculations concerning the vapour transport behaviour of binary compounds M_2Q_3 ($M = \text{Sb, Bi}$, $Q = \text{Se, Te}$) were performed. The transport behaviour of chalcogenides of antimony and bismuth is discussed for the system $\text{Bi}_2\text{Se}_3/\text{I}_2$ as example.

In a first step, calculation of equilibrium constants K_p of individual equilibria were utilised to estimate the conditions of chemical vapour transport of M_2Q_3 . The vapour transport appears possible, if the equilibrium constant is not extreme ($10^{-4} < K_p < 10^4$). The direction of transport depends on the heat of reaction ($T_2 \rightarrow T_1$ if $\Delta H_r^0 > 0$ and $T_1 \rightarrow T_2$ if $\Delta H_r^0 < 0$). The transport of bismuth selenide using iodine as transport agent was examined according the equilibria (1), (2).

In contrast, vapour transport using bromine or chlorine is unfavourable due to its extreme equilibrium constants $K_{p,800} > 10^4\text{ bar}$. These result from the higher stability of the involved chlorides and bromides (compare: $\Delta H_{800}^0(\text{BiI}) = 93.7\text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_{800}^0(\text{BiBr}) = 72.4\text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_{800}^0(\text{BiCl}) = 43.8\text{ kJ}\cdot\text{mol}^{-1}$; and $\Delta H_{800}^0(\text{BiI}_3) = +25.2\text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_{800}^0(\text{BiBr}_3) = -115.5\text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_{800}^0(\text{BiCl}_3) = -224.2\text{ kJ}\cdot\text{mol}^{-1}$ [37])

Relating to the equilibria (1) and (2) the transport is expected to occur from the higher temperature in the source to the lower temperature in the sink ($T_2 \rightarrow T_1$; $\Delta H_{R,800}^0 > 0$).

Second, to obtain more detailed predictions on the experimental transport conditions as well as to reveal more complex interactions of different solid-gas equilibria, thermodynamic modelling of the ternary systems was performed by using the program TRAGMIN [25]. For the system $\text{Bi}_2\text{Se}_3/\text{I}_2$ the condensed phases Bi(s) , $\text{BiI}_3(\text{s})$, $\text{Bi}_2\text{Se}_3(\text{s})$, BiSeI(s) , $\text{I}_2(\text{s})$ and Se(s,l) and the gaseous species Bi(g) , $\text{Bi}_2(\text{g})$, BiSe(g) , BiI(g) , $\text{BiI}_3(\text{g})$, I(g) , $\text{I}_2(\text{g})$, $\text{Se}_x(\text{g})$ ($1 \leq x \leq 8$) were taken into account. The calculations show, that apart from $\text{Se}_2(\text{g})$ all other species $\text{Se}_x(\text{g})$ can be neglected, because their pressures are just too low. For the formation of gaseous BiSeI(g) in minor quantity, mass spectrometric experiments provide evidence [27], see also [28]. Nevertheless, its partial pressure is at least two orders of magnitude lower than those of BiI(g) and $\text{BiI}_3(\text{g})$. Since thermodynamic data have not yet been determined, the species BiSeI(g) has been neglected in our calculations.

The calculated composition of the equilibrium gas phase of an initial solid $\text{BiSeI(s)}/\text{Bi}_2\text{Se}_3(\text{s})$ ($n(\text{Bi}_2\text{Se}_3) = 1 \text{ mmol}$; $n(\text{I}_2) = 0.1 \text{ mmol}$; $V = 20 \text{ ml}$) is shown in Fig. 1. The break of the pressure curves at 450°C is related to the existence of BiSeI under the given conditions. At $\vartheta < 450^\circ\text{C}$ BiSeI condenses, while the compound is completely evaporated at $\vartheta > 450^\circ\text{C}$. Since only species with partial pressures $p \geq 10^{-5}$ bar are regarded as relevant for chemical vapour transport, the selenium-containing species $\text{Se}_2(\text{g})$, and the bismuth-containing species $\text{BiI}_3(\text{g})$, BiI(g) can contribute to the transport. Accordingly, vapour transport of Bi_2Se_3 should be possible at temperatures above 375°C (650 K , respectively). Neither iodides of selenium nor gaseous species of elemental bismuth could be found with relevant partial pressures.

Figure 1. Composition of the gas phase over $\text{Bi}_2\text{Se}_3(\text{s})/\text{I}_2(\text{s})$ calculated using the program TRAGMIN [26] ($n(\text{Bi}_2\text{Se}_3) = 2 \text{ mmol}$; $n(\text{I}_2) = 1 \text{ mmol}$; $V = 20 \text{ ml}$). Grey marked area: transport relevant region.

Third, for the estimation of transport conditions the pressure behaviour of coexistent phases in the pertinent system has to be considered: Fig. 2 shows the barogram of the system $\text{Bi}_2\text{Se}_3(\text{s})/\text{I}_2(\text{g})$ with thermal decomposition pressures of BiSeI(s) according to (3), [29] and $\text{Bi}_2\text{Se}_3(\text{s})$ (4), [30].

The transport of Bi_2Se_3 in the above estimated temperature region follows schematically the arrows in Fig. 2. Depending on the temperature gradient and the amount of the transport agent iodine (or more specifically its partial pressure) different transport results can be predicted.

Case I:

Phase pure transport of Bi_2Se_3 is possible with $\vartheta_{\text{source}} = 500^\circ\text{C}$ and a transport gradient $\Delta T = 100 \text{ K}$. The equilibrium pressure of $\text{BiI}_3(\text{g})$ must not exceed 10^{-3} bar. For this reason the initial amount of iodine needs to be restricted to $m_{\text{iodine}}/V_{\text{ampoule}} \leq 0.5 \text{ mg/ml}$.

Case II:

Transport experiments with Bi_2Se_3 at $\vartheta_{\text{source}} = 500^\circ\text{C}$ as starting material and transport gradients $\Delta T \leq 100 \text{ K}$ will result in the deposition of various solids in the growth zone depending on the amount of added iodine. If the equilibrium pressure of $\text{BiI}_3(\text{g})$ reaches 10^{-2} bar, the existence condition of BiSeI is fulfilled and its condensation in the sink occurs. With proceeding deposition of BiSeI in the sink the total pressure of BiI_3 decreases until in a second step transport of Bi_2Se_3 can be predicted (case II*, Fig. 2).

Case III:

Keeping the equilibrium pressure of $\text{BiI}_3(\text{g})$ constant at $p(\text{BiI}_3(\text{g})) < 10^{-3}$ bar (initial amount of iodine $m_{\text{iodine}}/V_{\text{ampoule}} \leq 0.5 \text{ mg/ml}$ and the temperature gradient at $\Delta T = 100 \text{ K}$, the phase pure transport of Bi_2Se_3 is dependent on the source temperature: with decreasing $\vartheta_{\text{source}} \leq 450^\circ\text{C}$ the existence condition of BiSeI is fulfilled again and the condensation of BiSeI in the sink occurs.

Case IV:

In the special case of varying the source temperature by $\vartheta_{\text{source}} \leq 450^\circ\text{C}$ jointly with an increase of the temperature gradient by $\Delta T \geq 100 \text{ K}$ the transport can be expanded to the existence condition of selenium, resulting in a simultaneous condensation of BiSeI and Se in the sink.

The phase relations and equilibrium pressures for the analogous systems M_2Q_3/I_2 including the ternary phases BiTeI [29], SbSeI [31], and SbTeI [32] can be assumed to be similar. For this reason, the temperature conditions and the amount of transport agent (iodine) has to be restricted in the same way. With hindsight the former transport experiments of Sb_2Te_3 using iodine ($m_{\text{iodine}}/V_{\text{ampoule}} = 7.5 \text{ mg/ml}$; $\vartheta = 610 \dots 470^\circ\text{C}$ [22]), the sequential transport of SbTeI and Sb_2Te_3 can be supposed analogous to case II.

Figure 2. Transport regions depending on source temperature and the coexistence pressure of $\text{BiI}_3(\text{g})$ (in dependence of initial amount of iodine). I – phase pure transport of Bi_2Se_3 ; II + III sequential transport of BiSeI and Bi_2Se_3 ; IV simultaneous transport of BiSeI and selenium.

The described transport behaviour is finally to consider by discussion of the temperature dependent transport efficiency $\Delta(p_i/p_L)$ of gaseous components. The transport efficiency is defined as the difference of a compounds partial pressure in the source and its partial pressure in the sink normalized by the partial pressure of a solvent L at both temperatures (here inert nitrogen gas, see equation (5)). This is attributed to the fact, that transport effective species exhibit positive and the transport agent negative

transport efficiencies respectively, whereas transport efficiencies are zero for species that are not involved in the transport reaction [33].

$$\Delta(p_i/p_L^*) = \left(\frac{p_i}{p_L^*} \right)_{T_{\text{source}}} - \left(\frac{p_i}{p_L^*} \right)_{T_{\text{sink}}} \quad (5)$$

The detailed calculation of the solid-gas equilibria over solid Bi_2Se_3 in the temperature gradient $\vartheta_{\text{source}} = 500^\circ\text{C}$, $\Delta T = 10 \dots 50$ K only shows efficiencies for the species $\text{BiI}(\text{g})$, $\text{BiI}_3(\text{g})$, $\text{Se}_2(\text{g})$, $\text{I}(\text{g})$, and $\text{I}_2(\text{g})$ as already concluded from the Figure 1. The phase pure transport of Bi_2Se_3 proceeds according to the dominant equilibrium (1) by formation of $\text{BiI}(\text{g})$ and $\text{Se}_2(\text{g})$ as the transport efficient species ($\Delta(p_i/p_L^*) > 0$), while iodine acts as the transport agent ($\Delta(p_i/p_L^*) < 0$), Fig. 3. Beside the solid-gas-reaction additional homogenous gas phase equilibria exist (6 – 8).

As a result of our calculations, the formation of $\text{BiI}_3(\text{g})$ (2) does not show a significant temperature dependence. Hence, its transport efficiency, which is proportional to $\Delta(p(\text{BiI}_3)/p_L^*)$, is rather low. In contrast, the partial pressure of $\text{BiI}(\text{g})$ changes more distinctly and thus effects the transport reaction. According to the detailed modelling for all the investigated systems M_2Q_3 ($M = \text{Sb, Bi, Q} = \text{Se, Te}$), the chemical vapour transport can be described by the general equilibrium (9):

The decomposition sublimation reactions of all compounds M_2Q_3 according to equation (10) only have a petty contribution to the vapour transport in the considered temperature range ($K_{p, 800} \approx 10^{-6}$ bar; $\Delta(p(MQ)/p_L^*) = 0$, Figure 3).

Figure 3. Transport efficiency $\Delta(p_i/p_L^*)$ for the transport of Bi_2Se_3 at $\vartheta_{\text{source}} = 500^\circ\text{C}$, $\Delta T = 10 \dots 50$ K with low iodine quantity ($m_{\text{iodine}}/V_{\text{ampoule}} \leq 0.5$ mg/ml).

By increasing the amount of the transport agent iodine and varying the temperature gradient BiSeI can be deposited at the sink, as predicted from the barograms (Fig. 2). Figure 4 shows the transport efficiency of one of these calculations: With increasing temperature gradient $\Delta T = 10 \dots 50$ K a change in the slope of the transport efficiency curves of the iodine rich species appears, which indicates a change of the transport equilibrium. With a gradient $\Delta T \geq 50$ K the transport equilibrium (11) for the condensation of BiSeI occurs:

Further calculations with variation of the initial amount of iodine show a shift in the temperature gradient for phase pure transport of Bi_2Se_3 or condensation of BiSeI , respectively. Thus the detailed calculations of the transport efficiency substantiate the dependence of the transport on the initial iodine quantity, as stated from the barograms (Fig. 2).

Figure 4. Transport efficiency $\Delta(p_i/p_L^*)$ with higher iodine quantity ($m_{\text{iodine}}/V_{\text{ampoule}} \geq 0.5$ mg/ml): transport of Bi_2Se_3 at $\vartheta_{\text{source}} = 500^\circ\text{C}$, $\Delta T < 40$ K and transport of BiSeI at $\vartheta_{\text{source}} = 500^\circ\text{C}$, $\Delta T > 40$ K.

2 Transport experiments

All chemical vapour transport experiments were conducted with identical amounts of samples M_2Q_3 and iodine ($m_{\text{iodine}}/V_{\text{ampoule}} = 0.44$ mg/ml) in silica ampoules. In order to verify the calculations, chemical vapour transport was performed at various source temperatures and temperature gradients by using a transport balance [34], which permits in situ measurements of the mass flow by time.

Figure 5 shows the experimental mass flow for Sb_2Se_3 , Sb_2Te_3 , Bi_2Se_3 , and Bi_2Te_3 under similar transport conditions of $\vartheta_{\text{source}} = 500^\circ\text{C}$, and $\Delta T = 50$ K. Basically transports are feasible for all M_2Q_3 compounds ($M = \text{Sb, Bi, Q} = \text{Se, Te}$) with the sink temperature above 450°C . The maximum in temperature is limited by the respective melting points of the compounds. The ideal gradient is – dependent on the amount of iodine – $\Delta T = 20 - 100$ K. Large gradients result in a large amount of transported polycrystalline material. Smaller gradients allow the formation of well formed crystals (Figures 7 – 10). At an average gradient of $\Delta T = 50$ K mass flow rates of $0.9 \text{ mg}\cdot\text{h}^{-1}$ for Sb_2Te_3 , $0.6 \text{ mg}\cdot\text{h}^{-1}$ for Sb_2Se_3 , $0.3 \text{ mg}\cdot\text{h}^{-1}$ for Bi_2Te_3 , and $0.1 \text{ mg}\cdot\text{h}^{-1}$ for Bi_2Se_3 result. The higher rates of antimony chalcogenides are the consequence of slightly higher equilibrium constants (12) + (13). The calculated transport rates agree with the experimental ones in the order of magnitude: $4.9 \text{ mg}\cdot\text{h}^{-1}$ for Sb_2Te_3 , $3.7 \text{ mg}\cdot\text{h}^{-1}$ for Sb_2Se_3 , $3.7 \text{ mg}\cdot\text{h}^{-1}$ for Bi_2Te_3 , and $0.3 \text{ mg}\cdot\text{h}^{-1}$ for Bi_2Se_3 . More precise predictions are inappropriate for transport rates of about $1 \text{ mg}\cdot\text{h}^{-1}$.

Specific measurements have been devised regarding the predicted problem of condensation of compounds MQI ($M = \text{Sb, Bi}$, $Q = \text{Se, Te}$ [29]) by using sink temperatures below 450°C in combination with higher amounts of iodine ($m_{\text{iodine}}/V_{\text{ampoule}} \geq 0.5 \text{ mg/ml}$). For a representative transport experiment with Bi_2Se_3 at $\vartheta_{\text{source}} = 500^\circ\text{C}$, and $\Delta T = 75 \text{ K}$ two regions with different linear mass flow were detected, Fig. 6. In the first region BiSeI is deposited at the sink. As a result of the formation of BiSeI the iodine partial pressure in the systems decreases, entailing a change of the transport equilibrium by the lowered iodine pressure. Phase pure transport of Bi_2Se_3 results, which is indicated by the smaller slope of the curve in the second transport region of figure 6. The observed behaviour can be explained with the help of the barogram (Figure 2): The transport starts under conditions similar to case II. During condensation of BiSeI the pressure decrease and the transport drifts in chronological sequence to case I.

Figure 5. Mass flow for transports of M_2Q_3 with constant experimentally conditions: $\vartheta_{\text{source}} = 500^\circ\text{C}$, $\Delta T = 50 \text{ K}$.

Figure 6. Sequential transport of BiSeI and Bi_2Se_3 on the transport balance $\vartheta_{\text{source}} = 500^\circ\text{C}$, $\Delta T = 75 \text{ K}$.

Crystals of investigated compounds M_2Q_3 have been analysed by electron microscopy. For all examined samples the composition $M : Q = 40 : 60$ is confirmed. No incorporation of the transport agent iodine is found in the deposited crystals. Antimony selenide is obtained as needle shaped crystals with lengths of about 0.5 to 1 cm . Crystals of antimony telluride form irregular lumps with a size up to 2 cm (Fig. 8). The bismuth compounds crystallize in well formed hexagonal platelets roughly $0.5 \times 0.5 \text{ cm}$ in size. For examples of the obtained crystals see figures 7 – 10.

Conclusions

The present work shows the investigation of the vapour transport of M_2Q_3 chalcogenides ($M = \text{Sb, Bi}$, $Q = \text{Se, Te}$) on the basis of thermodynamic modelling and experimental data. The results of modelling of solid-gas equilibria have been examined and validated by experiments on a transport balance. It could be shown, that a phase pure transport of M_2Q_3 chalcogenides is possible in a temperature range above 450°C with gradients $\Delta T \leq 100 \text{ K}$. The optimum transport temperatures have been determined for all systems to be $\vartheta_{\text{source}} = 500^\circ\text{C}$ and $\vartheta_{\text{sink}} = 450^\circ\text{C}$.

The modelling of solid-gas equilibria also predicts a pressure- and temperature-dependent change of the transport equilibrium regarding M_2Q_3 and MQI . It could be demonstrated, that the quantity of iodine is the controlling parameter of this change in the transport equilibrium.

Figure 7. Crystals of Sb_2Se_3 grown at conditions: $\vartheta_{\text{source}} = 500^\circ\text{C}$, $\Delta T = 50 \text{ K}$, ($m_{\text{iodine}}/V_{\text{ampoule}} = 0.44 \text{ mg/ml}$).

Figure 8. Intergrown crystals of Sb_2Te_3 obtained at conditions: $\vartheta_{\text{source}} = 500^\circ\text{C}$, $\Delta T = 50 \text{ K}$, ($m_{\text{iodine}}/V_{\text{ampoule}} = 0.44 \text{ mg/ml}$).

Figure 9. Crystals of Bi_2Se_3 grown at conditions: $\vartheta_{\text{source}} = 500\text{ }^\circ\text{C}$, $\Delta T = 50\text{ K}$, $(m_{\text{iodine}}/V_{\text{ampoule}} = 0.44\text{ mg/ml})$.

Figure 10. Crystals of Bi_2Te_3 grown at conditions: $\vartheta_{\text{source}} = 500\text{ }^\circ\text{C}$, $\Delta T = 50\text{ K}$, $(m_{\text{iodine}}/V_{\text{ampoule}} = 0.44\text{ mg/ml})$.

Experimental Section

Starting materials used to produce the chalcogenides were antimony (Chempur, 99.999 %), bismuth (Chempur, 99.9999 %), selenium (Heraeus, 99.999 %) and tellurium (Sigma Aldrich, 99.999 %).

Pre-synthesis of the chalcogenides M_2Q_3 ($M = \text{Sb, Bi}$, $Q = \text{Se, Te}$) were performed by solid-state reaction of stoichiometric mixtures of the elements in a sealed, evacuated silica tube. The mixtures have been heated for 2 h up to $500\text{ }^\circ\text{C}$ and slowly cooled

down to room temperature. By this method single phase powder samples, identifiable by powder XRD, has been obtained.

For all attempts of chemical vapour transport, 300 mg of M_2Q_3 powder and 7 mg of iodine (Grüssing, 99.5%, double sublimated over BaO) were stacked in a large silica ampoule ($V = 16\text{ ml}$; $l = 12\text{ cm}$, $A = 1.2\text{ cm}^2$). In order to verify the calculations, chemical vapour transport was performed at various source temperatures and temperature gradients by using a transport balance [34], which permits in situ measurements of the mass flow over time.

Phase identification of products has been realised by powder XRD. Patterns of synthesised compounds and mixtures were collected with a STOE Stadi P diffractometer using $\text{CuK}\alpha$ -radiation (transmission mode, Ge-monochromator) with an acceleration voltage of 40 kV and a filament current of 30 mA. The diffractometric scans were obtained between 5 and $110^\circ 2\theta$; step width $0.03^\circ 2\theta$.

Thermodynamic modelling of phase equilibria were accomplished using Calphad-methods based on the Eriksson Gibbs energy minimizer implemented in the program Tragmin [26]. The solid-gas equilibria in the ternary system $M/Q/I$ ($M = \text{Sb, Bi}$, $Q = \text{Se, Te}$) have been calculated for different compositions isothermally in the temperature range of $400 - 900\text{ K}$ with $\Delta T = 20\text{ K}$. The thermodynamic data of condensed phases used are displayed in Table 3. Data sets of all gaseous species containing the components M , Q and I were adopted from [36] and [37]. Merely the formation of gaseous antimony monoiodide is borrowed from [38]. The enthalpy of formation results in evaluation of the function of equilibrium constant (14). The entropy is concluded from the gas phase equilibrium (15). The obtained value is well consistent with pertinent standard entropies of similar species: $S_{298}^0(\text{BiI(g)}) = 275.4$ [36]; $S_{298}^0(\text{InI(g)}) = 267.3$ [36]; $S_{298}^0(\text{TlI(g)}) = 274.8$ [36]; $S_{298}^0(\text{BiSe(g)}) = 269.0$; $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ [36]; $S_{298}^0(\text{BiTe(g)}) = 273.0$ [36]; $S_{298}^0(\text{SbSe(g)}) = 255.9$ [37]; $S_{298}^0(\text{SbTe(g)}) = 262.4$ [39]. The average molar heat capacity of SbI(g) is deduced in comparison with similar known species.

$$C_p(\text{SbI(g)}) = 37 \pm 1\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

Table 1: Thermodynamic data of condensed species used for modelling of the systems Sb/Se/I, Sb/Te/I, BiSe/I, and Bi/Te/I.

Species	$\Delta H_T^0 /$ $\text{kJ}\cdot\text{mol}^{-1}$	$S_T^0 /$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	T / K	$C_p / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ [a]			Reference
				A	b	c	
Bi(l)	17.956	93.607	545	23.359	3.138	1.661	[36]
BiI ₃ (l)	-69.895	370.769	682	150.725			[36]
Bi ₂ Se ₃ (s)	-140.164	239.743	298	118.533	19.246		[36]
BiSeI(s)	-97.971	162.029	298	52.754	43.124	1.005	[29]
Bi ₂ Te ₃ (s)	-78.659	261.082	298	107.989	55.229		[36]
BiTeI(s)	-127.279	151.562	298	64.058	37.179		[29]
I ₂ (s)	0	116.135	298	30.125	81.630		[36]
Sb(l)	11.288	68.073	493	35.169			[36]
SbI ₃ (s)	-100.416	218.907	298	71.793	85.998	0.059	[36]
Sb ₂ Se ₃ (s)	-127.612	212.129	298	118.742	20.920		[36]
Sb ₂ Te ₃ (s)	-56.484	246.438	298	112.884	53.137		[36]
Se(l)	11.278	68.029	493	35.146			[36]
Te(s)	0	49.706	298	19.121	22.092		[36]
Te(l)	294.92	98.957	723	37.656			[36]

[a] $C_p = (a + b \cdot 10^{-3} \text{ K}^{-1} \cdot T + c \cdot 10^6 \text{ K}^2 \cdot T^{-2}) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

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