Reviews

Selected Thermochemical Parameters for Tin(II) Halides, SnXX′ (X, X′ = Cl, Br, I)

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The tin(II) halides are important in a number of industrial processes and technological devices, for example, in the chemical vapor deposition of tin(IV) oxide films for the semiconductor industry, in the production of catalysts, and as a method of refining the spectral output of high intensity discharge lamps. Modeling of such processes requires databases of reliable, self-consistent thermochemical parameters. A survey of the physicochemical properties and appropriate standard thermochemical data has been made for the tin(II) halides, SnXX′ (X, X′ = Cl, Br, I), and a self-consistent set of thermochemical parameters are selected for the solid, liquid, and gas phases of these materials. In a few cases where data are simply unavailable, data are derived using a variety of estimation techniques. The benchmark employed to select the parameters in this work is that they accurately predict experimental vapor pressures where these are available. Finally, estimation techniques (Supporting Information) are used to provide supporting evidence as to the correctness of the magnitudes of data selected using the benchmark.

Introduction

This main text is intended to be read in close conjunction with the Supporting Information given for this paper.

Despite the fact that they are used in numerous important industrial applications, the tin(II) halides have been relatively understudied from a thermodynamic perspective when compared to many similarly important commercial materials. In the semiconductor industry, they find use as a precursor in the chemical vapor deposition of tin(IV) oxide films, in the production of catalysts, as reducing agents in the manufacture of dyes, and in tinning by electrochemical methods, and they are of considerable interest as sources of radiation in high intensity discharge (HID) lamps.

High intensity discharge lamps containing mixtures of sodium, thallium, and tin halides (Na, Sn, Tl, Br, I) are used in products,[1] with correlated color temperatures (CCT) of 3000 K, while color temperatures of 4000 K can be achieved by the addition of indium halides to the dose. In such lamps, the important radiating species derived from the tin(II) halides in the discharge are $SnX_2(g)$ and SnX(g). These molecular species give rise to continuum radiation in the visible region of the spectrum and promote high luminous efficiency and good color rendering properties.

The temperatures of the metal halide melts present in operating HID lamps lie in the range between (900 and 1300) K; the temperature of the envelope walls lie in the range (900 to 1500) K; and temperatures in the arc center lie in the range from (5000 to 7000) K. The metal halides in operating HID lamps are present in both the liquid (melt) and vapor phases, and the thermodynamic data are required to be self-consistent across these two phases. Consequently, the pragmatic acceptance criteria adopted for selection of the thermochemical parameters in this present work is that they should predict, in combination, experimentally measured vapor pressures when and if these are available.

The chemical equilibrium compositions of such HID lamp systems are often studied using Gibbs energy minimization software tools such as MTDATA,[2] an approach that requires an accurate set of thermochemical data for each of the chemical species present. The problems created by the data requirements are illustrated by noting that data for $SnCl_2(s)$, $SnBr_2(s)$, $SnI_2(s)$, $SnCl_2(g)$, $SnBr_2(g)$, and $SnI_2(g)$ are not included in either JANAF[3,4] or NIST[5] compilations of thermodynamic functions, thereby limiting the usefulness of what are otherwise powerful techniques.

The aim of this paper is to derive a selection of thermochemical data for the tin(II) halides, $SnCl_2$, $SnBr_2$, SnI_2, SnClBr, SnClI, and SnBrI, in both the condensed and gaseous phases for use in chemical equilibrium calculations. Fluorine-containing compounds are not employed in HID lamps due to their extreme reactivity with arctube materials and so are not included in this present study. Although thermodynamic functions for $SnCl_2$, $SnBr_2$, and SnI_2, in both the condensed and gaseous phases are available in the SGTE database,[6] these data are found *not* to predict accurately the experimentally determined vapor pressures.

Presentation of Data

The Scientific Group Thermodata Europe (SGTE)[7] format is employed for the thermochemical parameters derived in this study. This format requires the following values to be specified for each species: standard molar enthalpy of formation at 298.15 K; standard molar entropy at 298.15 K; transition temperatures

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and associated enthalpies; temperature variation of the molar heat capacity expressed using eq 1.

$$C^{o}_{p,m}(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = A + B(T/\mathrm{K}) + C(T/\mathrm{K})^2 + D(T/\mathrm{K})^{-2} \quad (1)$$

Values for thermochemical parameters are reported here to three decimal places, by convention, although this does not represent their precision. A standard pressure of 101325 Pa has been adopted throughout.

A complete set of thermochemical parameters for a pure component covers the solid, liquid, and gas phases. To illustrate the extent of the task of compiling these parameters, listed in the Supporting Information (Table S1) are the requirements for complete thermodynamic specification of three phases of a tin(II) halide compound, SnX_2.

To complete the derivation of a self-consistent set of thermochemical parameters, it is also necessary to know the species present in the gas phase and to have a description of the temperature variation of the relevant partial pressures.

Methods Used to Select Data

The selection of the thermochemical data for the tin(II) halide systems under investigation involved several stages.

Literature Data for Tin Halide Materials. First, a survey of the literature (up to August 2008) was made revealing the following $\Delta_f H^o/\mathrm{kJ \cdot mol^{-1}}$, $\Delta_f G^o/\mathrm{kJ \cdot mol^{-1}}$, $S^o/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and $C_p/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ values recorded for tin halide compounds in condensed and gaseous states (Supporting Information, Table S2). Those values, in Table S2, which the authors regard as being less reliable than the other entries, are contained within parentheses. Note that for completeness solvated halides are included. These may be utilized to make estimates in certain instances (see Supporting Information).

Protocol Followed to Select Data Consistent with Imposing the Requirement that $\Delta_f G^o = \Delta_f H^o - T\Delta_f S^o$. (a) Taking the values in Table S2 (Supporting Information), we assembled in a spreadsheet (EXCEL) every possible triplet combination of the individual values of $\Delta_f H^o/\mathrm{kJ \cdot mol^{-1}}$, $\Delta_f G^o/\mathrm{kJ \cdot mol^{-1}}$, and $S^o/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. Since for any compound, in any phase, accurate formation data are required to obey the relationship

$$\Delta_f G^o = \Delta_f H^o - T\Delta_f S^o \quad (2)$$

where $T = 298.15$ K and

$$\Delta_f S^o = S^o(\text{target compound}) - \Sigma S^o(\text{elements in standard states}) \quad (3)$$

(b) For each triplet of values, the term$\{(\Delta_f H^o - \Delta_f G^o)/T\ ] + S^o(\text{Sn, white, s}) + S^o(X_2, \text{ss})\}$ (being equal to $S^o(SnX_2$, ss, 298.15 K)) is calculated, for each data set, where ss is the standard state, and then is compared with the listed value of $S^o(SnX_2$, ss, 298.15 K) in Table S2, since from eq 2

$$\{[(\Delta_f H^o - \Delta_f G^o)/T] + S^o(\text{Sn, white, s}) + S^o(X_2, \text{ss})\} = S^o(SnX_2, \text{ss}, 298.15\ \text{K}) \quad (4)$$

The following standard NBS[8] values are adopted for the latter calculation: $S^o(\text{Sn, white, s}) = 51.5\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$; $S^o(Cl_2, g) = 222.94\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$; $S^o(Br_2, l) = 152.0\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and $S^o(I_2, s) = 116.0\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. If the value of $\{[(\Delta_f H^o - \Delta_f G^o)/T\ ] + S^o(\text{Sn, white, s}) + S^o(X_2, \text{ss})\}$ lies close to $S^o(SnX_2$, ss, 298.15 K) then that given combination of data can be deemed to satisfy eq 2. (c) This particular combination of $\Delta_f H^o/\mathrm{kJ \cdot mol^{-1}}$, $\Delta_f G^o/\mathrm{kJ \cdot mol^{-1}}$, and $S^o/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ is then considered to be "self-consistent" in respect to obeying eq 2. As such, it then becomes a candidate for further examination and refinement. This procedure leads to a number of potentially acceptable combinations of $\Delta_f H^o/\mathrm{kJ \cdot mol^{-1}}$, $\Delta_f G^o/\mathrm{kJ \cdot mol^{-1}}$, and $S^o/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. These are given in Table 1.

Statistical Mechanical Calculations

Gaseous Species. The standard molar entropies at 298.15 K and molar heat capacities in the range (298.15 to 6000) K have been calculated for the ground electronic states of the six species in the gas phase, using standard statistical thermodynamics relations,[9] and assuming the rigid rotator harmonic oscillator approximation. The molecular geometries and vibrational frequencies required for the calculation of $S^o_m(T)$ and $C^o_{p,m}(T)$ were computed in a parallel study.[10] The chosen molecular data from ref 10 are those calculated using the MP2 theory and the basis sets SDB-aug-cc-pVQZ and aug-cc-pVQZ. The calculated molar entropies and molar heat capacities at 298.15 K are listed in Table 2.

The calculated molar heat capacity, $C^o_{p,m}(T)$, data in the temperature range (298.15 to 6000) K were fitted to a temperature-dependent molar heat capacity polynomial, in the form of eq 1, using the "Fit and Plot" module of MTDATA.[2] The constants *A* to *D* are given in Table 3.

Refinement of Self-Consistent Data in Accordance with Vapor Pressure Studies

Where published vapor pressure data are available, the well-known second and third law methods (see below) were utilized

Table 1. Self-Consistent Combinations of $\Delta_f H^o$(298.15 K), $\Delta_f G^o$(298.15 K), and S^o(298.15 K) Data Which Obey Equation 2 for Binary Tin Halides, SnX_2(s), and SnX_2(g)[a]

	$\Delta_f H^o$	$\Delta_f G^o$	$\{[(\Delta_f H^o - \Delta_f G^o)/T] + S^o(\text{Sn, white, s}) + S^o(X_2, \text{ss})\} = S^o(298.15\ \text{K})$ (SnX_2, ss)
compound	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
$SnCl_2(s)^b$	−328.0	−286.2	134.1
$SnCl_2(s)^b$	−335.6 ± 3.9	−293.3	133.8 ± 1.3
$SnCl_2(g)$	−197.95	−207.35	305.9
$SnBr_2(s)^b$	−243.5	−228.5	153.0
$SnBr_2(s)^b$	−265.4 ± 0.8	−249.0 ± 0.5	148.1 ± 3.2
$SnBr_2(s)^b$	−252.9	−237.9	153.1
$SnBr_2(g)$	−118.7 ± 0.4	−156.4	330.0 ± 1.4
$SnI_2(s)^b$	−143.7 ± 0.2	−144.2 ± 0.2	168.9 ± 0.7
$SnI_2(s)^b$	−162.8	−163.6	170.1
$SnI_2(g)$	−3.1	−55.5	343.4

[a] X = Cl, Br, I. [b] In the above table, very closely similar self-consistent values have been grouped and an average then taken.

Table 2. Selected Thermochemical Parameters for Gaseous Binary Halide and Mixed Halide Species at 298.15 K Assigned in This Study

species	$\Delta_f H^\circ$ / $kJ \cdot mol^{-1}$	S° / $J \cdot K^{-1} \cdot mol^{-1}$	C_p / $J \cdot K^{-1} \cdot mol^{-1}$
$SnCl_2(g)$	−205.443	305.716	54.579[b]
$SnBr_2(g)$	−128.974	328.522	56.309[b]
$SnI_2(g)$	−14.600	344.429	56.986[b]
SnClBr(g)	(−167.2)[a]	322.900	55.451[b]
SnClI(g)	(−110.0)[a]	330.945	55.806[b]
SnBrI(g)	−71.787	342.287	56.652[b]

[a] These estimates are made for the binary halide data, on the basis that the value of $\Delta_f H^\circ(\text{SnBrI, g}) = -71.8\ kJ \cdot mol^{-1}$ in Table 1 is virtually identical to the average of the entries for $\Delta_f H^\circ(SnBr_2, g)$ and $\Delta_f H^\circ(SnI_2, g)$. [b] These entries correspond to the values obtained by substituting $T = 298.15$ K into the heat capacity functions as defined in Table 3 and discussed in the main text.

Table 3. Coefficients of Heat Capacity Function, $C_p(T) = A + BT + CT^2 + DT^{-2}/J \cdot K^{-1} \cdot mol^{-1}$, for Gaseous Species, SnXX′(g) (X, X’ = Cl, Br, I) in the Range $298.15 \leq T/K \leq 6000$ Calculated Using Statistical Mechanical and Quantum Chemistry Methods[a]

species	*A*	*B*	*C*	*D*
$SnCl_2(g)$	$5.8104 \cdot 10^{01}$	$4.5300 \cdot 10^{-05}$	$-4.9200 \cdot 10^{-09}$	$-3.1461 \cdot 10^{05}$
$SnBr_2(g)$	$5.8176 \cdot 10^{01}$	$1.1800 \cdot 10^{-05}$	$-1.2900 \cdot 10^{-09}$	$-1.6628 \cdot 10^{05}$
$SnI_2(g)$	$5.8191 \cdot 10^{01}$	$4.9000 \cdot 10^{-06}$	$-5.3000 \cdot 10^{-10}$	$-1.0728 \cdot 10^{05}$
SnClBr(g)	$5.8141 \cdot 10^{01}$	$2.8300 \cdot 10^{-05}$	$-3.0700 \cdot 10^{-09}$	$-2.3987 \cdot 10^{05}$
SnClI(g)	$5.8149 \cdot 10^{01}$	$2.4300 \cdot 10^{-05}$	$-2.6400 \cdot 10^{-09}$	$-2.0897 \cdot 10^{05}$
SnBrI(g)	$5.8184 \cdot 10^{01}$	$8.3000 \cdot 10^{-06}$	$-9.0000 \cdot 10^{-10}$	$-1.3640 \cdot 10^{05}$

[a] Constants are shown to four decimal places by convention and do not represent their precision.

to determine the enthalpies of vaporization, $\Delta_{vap}H^\circ_m$, and hence enthalpies of formation, $\Delta_f H^\circ_{298.15}$, of the gas phase species.

Calculation of Gas Phase $\Delta_f H^\circ_{298.15}$ from Vapor Pressure Measurements. From published vapor pressure measurements and assessed literature data for the condensed phases, the enthalpy, $\Delta_r H(298.15\ K)/kJ \cdot mol^{-1}$, and entropy, $\Delta_r S(298.15\ K)/J \cdot K^{-1} \cdot mol^{-1}$, of reaction for the evaporation (i.e., $SnX_2^l \rightarrow SnX_2(g)$) of $SnCl_2(g)$, $SnBr_2(g)$, and $SnI_2(g)$ and of reaction 5 were calculated. Second (6) and third law (7) methods were utilized

$$SnBr_2(g) + SnI_2(g) \rightarrow 2SnBrI(g) \tag{5}$$

$$\Delta_r H(T) = -R\{d \ln(K_p)/d(1/T)\} \tag{6}$$

$$\Delta_r H(298.15\ K) = -RT \ln K_p + T\Delta_r S(298.15) - \int_{298.15}^{T} \Delta_r C_p dT + T \int_{298.15}^{T} \Delta_r C_p/T dT \tag{7}$$

where $R/J \cdot K^{-1} \cdot mol^{-1}$, K_p, and $\Delta_r C_p/J \cdot K^{-1} \cdot mol^{-1}$ are the molar gas constant, equilibrium constant, and difference in molar heat capacities for the reaction r. From these molar enthalpies of reaction and the critically selected condensed phase data, the standard molar enthalpies of formation, $\Delta_f H^\circ_m(298.15\ K)/kJ \cdot mol^{-1}$ of gaseous halides and of SnBrI(g), were calculated. The standard molar entropies, $S^\circ_m(298.15\ K)/J \cdot K^{-1} \cdot mol^{-1}$, of the liquids were estimated as part of the intermediate calculations.

Detailed Considerations Involved in Selected Values

The gas phases above tin(II) halide condensed phases are known to contain monomers and dimers.[11−14] For the tin(II) chloride system, the temperature variation of the (monomer + dimer) equilibrium reported in ref 12 (where the study had been conducted over the same range as the vapor pressure measurements) was used. The mole fraction, *x*, of the dimer above the liquid decreased with increasing temperature.

Table 4. Selected Thermochemical Parameters for Solid Binary Halide and Mixed Halide Species at 298.15 K Assigned in This Study[a]

species	$\Delta_f H^\circ$ / $kJ \cdot mol^{-1}$	S° / $J \cdot K^{-1} \cdot mol^{-1}$	C_p / $J \cdot K^{-1} \cdot mol^{-1}$
$SnCl_2(s)$	−334.900	134.700	78.075[b]
$SnBr_2(s)$	−264.760	151.900	78.598[b]
$SnI_2(s)$	−152.088	180.000	77.749[b]
SnClBr(s)	−313.200	138.400	78.366[c]
SnClI(s)	−257.700	145.300	78.770[b]
SnBrI(s)	−207.300	168.000	78.609[b]

[a] N.B. Parameters (by convention) are shown to three decimal places from results of calculations but do not imply precision to this level. [b] These values are obtained by substituting $T = 298.15$ K into the corresponding heat capacity functions in refs 22 and 24. [c] This value is obtained by substituting $T = 298.15$ K into the corresponding heat capacity function in Table 6.

Although the tin(II) bromide system is known to contain both $SnBr_2$ and Sn_2Br_4 in the gas phase, there are contradictory reports about the temperature variation of the (monomer + dimer) equilibrium. The results from ref 13 predict that the mole fraction of the dimer above the liquid decreases with increasing temperature from $x = 0.016$ at 510 K to $x = 0.014$ at 573 K. However, the results from Karpenko[15] are contradictory and indicate that *x* increases from 0.056 at 773 K to 0.094 at 893 K. In view of the low mole fraction of the dimer above the liquid and the large uncertainties for this (monomer + dimer) equilibrium, the recommendation in ref 11 has been adopted, and the gas phase above liquid tin(II) bromide has been treated as though it contained only monomers.

Similar contradictions are apparent in published reports for the tin(II) iodide system.[14,16] In this case, the temperature variation of the (monomer + dimer) equilibrium derived above the solid[14] has been used for the liquid range. From these data, the mole fraction of the dimer, *x*, is predicted to range from 0.0014 at 596 K to 0.0050 at 973 K.

For the selection of thermochemical parameters, in this study, the following sources have been used for the saturated vapor pressures: tin(II) chloride from Mucklejohn;[17] tin(II) bromide from Brumleve;[11] tin(II) iodide from the combination of Fischer,[18] Karpenko,[16] Voropaeva,[19] and Zhamskaya.[20] Vapor pressure data for reaction 5 above a mixture of $SnBr_2$ and SnI_2 with an excess of tin present were taken from Hilpert.[21]

Molar enthalpies and entropies of evaporation for the binary halides and for reaction 5 were calculated using the second law method, eq 6. The value for the molar entropy of the mixed halide SnBrI(g), $S^\circ_m(\text{SnBrI, g, 298.15 K})$, calculated from the second law enthalpy of evaporation and the result obtained using statistical thermodynamics show excellent agreement being within 1.3 $J \cdot K^{-1} \cdot mol^{-1}$ of one another. The molar enthalpies of evaporation and reaction 5 additionally were calculated using the third law method, eq 7. The molar enthalpies of formation for the species $SnCl_2(g)$, $SnBr_2(g)$, $SnI_2(g)$, and SnBrI(g) were determined from the results of both second and third law calculations. For the gaseous species, the standard molar entropies and temperature-dependent molar heat capacities from Tables 2 and 3 were used. The molar heat capacities of the binary halides in the solid and liquid phases were taken from Gardner.[22] The melting temperatures and enthalpies of fusion for the binary halides were taken from refs 11 and 22 with the exception of the enthalpy of fusion of SnI_2 which was chosen in the present work. The standard molar enthalpies of formation and entropies for the solid phase of the binary halides were selected in accordance with their ability—when used in conjunc-

Table 5. Selected Condensed Phase Transition Data

species	T_M K	$\Delta_{fus}H^o_m(T_M)$ kJ·mol^{-1}
$SnCl_2$	519.8[a]	14.100[a]
$SnBr_2$	507.0[b]	15.100[b]
SnI_2	593.25[a]	17.991
SnClBr	513.3	14.600
SnClI	512.3[c]	16.200
SnBrI	521.9[c]	17.700

[a] Ref 22. [b] Ref 11. [c] Ref 24.

Table 6. Coefficients of Heat Capacity Function, $C_p(T) = A + BT + CT^2 + DT^{-2}$/J·K^{-1}·mol^{-1}, for SnClBr in the Condensed Phases[a]

species	*A*	*B*	*C*	*D*
SnClBr(s)[b]	$6.4299 \cdot 10^{01}$	$4.7182 \cdot 10^{-02}$	0.0000	0.0000
SnClBr(l)[c]	$7.1951 \cdot 10^{01}$	$4.5543 \cdot 10^{-02}$	0.0000	0.0000

[a] Constants are shown to four decimal places by convention and do not represent their accuracy. [b] Valid in the temperature range $360 \le T$/K $\le T_M = 513.3$ [c] Valid in the temperature range $T_M = 513.3 \le T$/K ≤ 800.

tion with all other necessary data—to accurately reproduce the vapor pressures above the liquid phase of the respective species. For both $SnCl_2$(s) and $SnBr_2$(s), suitable parameters (Table 4) could readily be identified from the self-consistent set given in Table 1 since they were able to reproduce the vapor pressure data very satisfactorily. In the case of SnI_2(s), however, *none* of the self-consistent combinations in Table 1 could accurately reproduce the vapor pressure data. There are a number of possible explanations for this: the (monomer + dimer) ratio above the liquid may not be the same as that above the solid; the vapor pressure measurements themselves may be in error; or the published values for $\Delta_f H^o$(298.15 K) and S^o_{298}(298.15 K) for SnI_2(s) may be incorrect. Standard molar entropy data rely on low temperature molar heat capacity measurements for their derivation. Anisimov[23] provides the only published measurements of low temperature [(12 to 310) K] molar heat capacity data for SnI_2, from which the published values, Table S2 (Supporting Information), of the molar entropy have been derived. Extrapolating these data to very low temperature actually results in a negative value of the molar heat capacity at 0 K, which is clearly incorrect. Given this uncertainty at very low temperatures, this latter heat capacity has been reinvestigated by considering various extrapolations made of the data. For example, by assuming a linear relationship to C_p between (0 and 12) K, that as $T \to 0$ then $C_p(T)/T \to 1$ or assuming that $C_p(0\text{ K}) = 0$ J·K^{-1}·mol^{-1} and then refitting the experimental data. The Debye extrapolation method proved to be unsuccessful in this case. Using the reassessed C_p data to determine S^o_m(298.15 K) leads to values in the range: $170 \le S^o_m(SnI_2, s, 298.15\text{ K}) \le 188$ J·K^{-1}·mol^{-1}. Given this potential range of values, the selected value of S^o_m(298.15 K) made for SnI_2(s) (Table 4) is that which predicts the vapor pressure measurements, along with all other necessary data. The value selected yields an average absolute uncertainty of 6 % across the temperature range of the published measurements. The selected value for $\Delta_f H^o_m$(298.15 K) of SnI_2(s) was then chosen in conjunction with that of S^o_m(298.15 K). The selected values for the condensed phase binary halides are listed in Table 4.

The selected melting temperatures and enthalpies of fusion, given in Table 5, for $SnCl_2$ and $SnBr_2$ are those of ref 22 and ref 11, respectively. The selected melting temperature of SnI_2 is also that of ref 22, and the enthalpy of fusion selected here is the value that, in conjunction with other data, best predicts the observed vapor pressure of SnI_2. The selected melting temperatures of SnClI and SnBrI are those of ref 24, and the selected enthalpies of fusion are also those of ref 24 adjusted to make them consistent with the difference between the values selected here and the ref 22 values of $\Delta_{fus}H^o_m(SnCl_2, T_M)$ and $\Delta_{fus}H^o_m(SnBr_2, T_M)$. The recommended molar heat capacities for SnClI and SnBrI in the solid and liquid phases are those of ref 24. The molar heat capacity coefficients, corresponding to eq 1 of SnClBr(s) and SnClBr(l), are given in Table 6, and the melting temperature and enthalpy of fusion, given in Table 5, were estimated from SnClI and SnBrI by weighting the corresponding data according to the perceived influence of iodine relative to chlorine and bromine. There are currently no vapor pressure measurements available for the condensed phases of the mixed halides. Consequently, the molar enthalpies of formation and molar entropies for the solid phase of the mixed halides (see Table 4) have been selected based on their ability—when used in conjunction with the selected gas phase data—to be able to predict vapor pressures that lie within an expected region. This same criterion was used to select the molar enthalpies of formation of SnClBr(g) and SnClI(g) (see Table 2). In connection with this approach, it is worth, briefly, noting the large sensitivity found in the predicted vapor pressure when changes are made in $\Delta_f H^o_m$(298.15 K) and S^o_m(298.15 K). For example, at 900 K, changing $\Delta_f H^o_m$(298.15 K) by 1 kJ·mol^{-1} or S^o_m(298.15 K) by 1 J·K^{-1}·mol^{-1} (the latter at any temperature as the change is actually independent of *T*) has the effect of altering the predicted vapor pressure by approximately 13 %!

The data derived in this work for the mixed halide species in the solid and gas phases at 298.15 K using the calculations described above (Tables 2 and 4) and the estimation techniques described in section S3 of the Supporting Information are compared in Table S12 where uncertainties are summarized.

Secondary Indicative Methods used to Estimate Data

Empirical techniques and correlations have been employed in the Supporting Information, Section S3, of this paper with the purpose of providing additional (secondary) estimates and seeking validation of the magnitudes selected in this study in Tables 2 and 4 of the data for the condensed phases of the mixed tin(II) halides and for the gas phases.

Conclusions

It will be evident from our discussion above that there is much contradiction concerning information obtained for the tin(II) halide systems discussed here. A selected set of thermochemical parameters have been derived for the tin(II) halides, SnXX′ (X, X′ = Cl, Br, I) according to the chosen benchmark that the selected parameters should be those that accurately predict measured experimental vapor pressures. It is our intention that this paper should achieve clarification of the thermodynamics of these complex systems. In so, this work offers a route to further research, in lighting applications. A similar study on indium compounds is about to be begun. The selected parameters at 298.15 K for the gaseous and solid phases are those in Table 2 and 4, respectively. The values which have been estimated using various approximations in the Supporting Information of this paper (see Section S5) are validated since *at least one* of the various estimates made of their magnitudes does not differ by more than 5 % from the cited values, and often the difference is considerably less. The selected condensed phase transition data are those in Table 5. Selected coefficients describing the temperature dependence of the heat capacity for the gas phase species, and SnClBr in the solid and liquid phases, are listed in Tables 3 and 6, respectively. As is shown in the final Supporting Information Table S12, percentage uncertainty differences between the selected and the estimated data sets are never greater than about 10 % and in the majority of cases usually considerably less being sometimes in total agreement with our assignments.

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Supporting Information Available:

As well as a containing a significant amount of supporting detail, the Supporting Information section to this paper has, appended to it, a number of useful further references (S28 to S35) to tin halide chemistry to which the reader is further referred. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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