PREPARATION, VAPOR PRESSURE AND THERMOCHEMISTRY
OF
TIN(II) BROMIDE

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ABSTRACT

The synthesis of high-purity tin(II) bromide from the elements is outlined. The vapor pressure of liquid SnBr₂ from 576 to 923 K is measured by the quasistatic method. Previous Knudsen effusion mass spectrometric studies are reviewed. A critical evaluation of the literature values for melting temperature and enthalpy of fusion is presented. The molar heat capacities of SnBr₂(s) and SnBr₂(l) are evaluated, and an expression for the molar heat capacity of SnBr₂(g) is derived from spectroscopic constants and structural data. A complete set of thermochemical data useful in the modelling of discharge arcs containing SnBr₂ is derived from the vapor pressure measurements.

Tin(II) bromide is of considerable interest as a source of radiation in metal halide discharge lamps. This is due in part to the continuum (molecular) radiation in the visible spectrum of arcs containing tin halides (1). When an alkali metal halide, such as NaBr, is also introduced to the arc, the total Na concentration in the vapor phase can be enhanced by formation of vapor phase complexes such as NaSnBr₃ (2). These effects can lead to increased luminous efficacy and improved color rendition, particularly where a warm, lower color temperature light is desired. In spite of the widespread use of SnBr₂ in lamps, only a few references to its use in lamps have appeared in the literature in the last 20 years (1,3-10).
Satisfactory lamp life and performance require metal halides with extremely low levels of oxygen-, hydrogen- and carbon-containing impurities. We describe here the preparation of high-purity SnBr₂ from the elements which yields material suitable for discharge lamps. This method is compared with previously applied methods for the synthesis of SnBr₂, and the advantages and disadvantages of each method are discussed.

The accurate modelling of discharge lamps containing SnBr₂ requires a detailed knowledge of the vapor phase species present above the condensed phase, and requires accurate thermochemical data for the vaporization process and for vapor phase processes such as dimerization or dissociation. We have thus performed total vapor pressure measurements above SnBr₂ over the temperature range 576 to 923 K by the quasistatic method (11). This is a wider temperature range than that reported in previous total vapor pressure studies (12,13).

Also included is a brief review of previous Knudsen effusion mass spectrometric studies, and a review of previous melting temperature and enthalpy of fusion results for SnBr₂. Recommended values for the melting temperature and the enthalpy of fusion are based on a critical evaluation of the literature data.

Recommended values for the molar heat capacities of solid, liquid and gaseous SnBr₂ are also reported. The recommended molar heat capacities for the condensed phases are based on literature values. The calculation of the molar heat capacity for the gaseous phase is based on a critical evaluation of spectroscopic constants and the product of the principal moments of inertia from the literature.

The vapor pressure data from this study are then used to derive a complete set of thermochemical data useful in the modelling of discharge arcs containing SnBr₂. Enthalpies and entropies of vaporization are derived using both second- and third-law treatments, and are compared with previous literature values. Recommended values for the standard enthalpies of formation of solid, liquid and gaseous SnBr₂ are also reported.

A more detailed account of this work will be published elsewhere.

EXPERIMENTAL

Synthesis of Tin(II) Bromide

Tin(II) bromide was prepared from Sn metal shot (99.999%, Cominco Electronic Materials), and reagent ACS grade bromine. Both were used as received, without further purification. The reaction vessel is fabricated from a fused silica tube, 48 mm o.d. by 50 cm long, closed on the left end, with a depression in the center. A 90 degree cross with 2 necks and a bromine bulb is attached to the right end of the vessel, as shown in Figure 1. The vessel is cleaned with 10% HF, rinsed with deionized H₂O, followed by reagent grade ethanol. It is then evacuated and heated to about 500 K to remove solvent residues.

While holding the main reaction vessel vertically, about 150 g of Sn metal is introduced through neck A, and the vessel is sealed off at point 1 (see Figure 1). The vessel is then heated to about 500 K with a broad-flamed torch and evacuated and refilled with inert gas three times through neck B. It is allowed to cool under vacuum (< 1 Pa) and is then filled with inert gas.
An amount of Br₂ equal to 99% of that required to form SnBr₂ is poured into the bulb through neck B. A partial vacuum is then applied through neck B until the bromine begins to boil. The vessel is refilled with He and evacuated to this pressure three times. The bromine bulb is then immersed slowly in liquid nitrogen, a hard vacuum (< 1 Pa) is applied, and the vessel is sealed off at point 2.

The vessel is placed into a two-zone tube furnace as shown in Figure 1. The sealed-tube reaction is carried out behind a blast shield in a fume hood. Each temperature controller is equipped with a temperature overshoot protection circuit (operating from a second, independent thermocouple) which will disconnect power from all furnaces in the event of an overshoot. The left hand (L.H.) zone is heated to 395 K, the right hand (R.H.) zone and bromine bulb being held at ambient temperature until all of the bromine has reacted to form SnBr₄. The vessel is then sealed off at point C, leaving only the large vessel section in the furnace, and the L.H. zone is heated to 395 K to drive all of the SnBr₄ to the R.H. side. The L.H. zone is then raised to 675 K and the R.H. zone to 395 K for 48 hours. The L.H. zone is then raised to 775 K for a minimum of 72 hours until all traces of SnBr₄ have reacted to form SnBr₂.

The final step in the preparation of SnBr₂ consists of melting the product, scrubbing with inert gas and filtering through a porous silica frit. The details of this process have been described in the literature for other metal halides (14). The filtered liquid is jetted through a small orifice, and the molten particles are rapidly quenched. This provides spherical particles with a small surface area to mass ratio, thus reducing potential water or oxygen contamination.

Chemical analysis of the product for total tin by iodometric titration gave (42.46 ± 0.21)% Sn (theory 42.62%), and for bromide by argentometric titration with potentiometric endpoint gave (57.15 ± 0.29)% Br (theory 57.38%), thus confirming the stoichiometry to within experimental uncertainty.

Vapor Pressure Measurements

The vapor pressure measurements were made using the quasistatic method of Rodebush and Dixon (11).

The SnBr₂ was loaded into the measurement cell in an inert atmosphere dry box. The cell itself was fabricated from Thermal Syndicate grade four electrically fused silica. No interaction was observed between the sample and this material.

The sample was then heated in a platinum-wound vertical furnace, regulated by a Stanton Redcroft LVP controller. The temperature was maintained within ±0.2 K. The temperature of the sample was monitored independently by a platinum-to-(platinum +13% rhodium) thermocouple. Cold junction compensation was made with a second thermocouple immersed in an ice/water bath. The potential difference was monitored by a Thurlby 1905a voltmeter with a resolution of 1 μV.

The pressure measurements were made with a Baratron 170 capacitance gauge with a precision of 0.1 Pa in the range up to 1.3 kPa, 1 Pa in the range from 1.3 to 13.3 kPa, and 10 Pa in the range from 13.3 to 133 kPa.
RESULTS AND DISCUSSION

Synthesis

Previous approaches to the synthesis of anhydrous SnBr₂ include: direct reaction of the elements (15-20), reaction of tin metal with anhydrous HBr (13,21-25), reaction of tin metal with aqueous HBr followed by dehydration (26-33), reaction of tin with butyl bromide and butyl alcohol (34), and simple vacuum distillation of commercial samples (35-38).

Preparations in aqueous and organic media are undesirable from the point of view of potential solvent contamination. Dehydration of commercial samples may also suffer from incomplete removal of water, hydroxide and oxide impurities. The possibility of a volatile SnOBr₂ species has been suggested (37), although its existence at high temperatures has not been established.

Reaction of the elements and reaction of tin with anhydrous HBr are most attractive for preparation of high-purity SnBr₂. The anhydrous HBr route suffers from very low rates of production and limited batch sizes (23). Synthesis from the elements is easily scaled up to moderate batch sizes (300-500 g) and has the advantage that reactants or solvents containing oxygen, hydrogen or carbon are unnecessary. Higher valent halides (SnBr₄) are potential contaminants (37), but can be minimized by sufficient reaction time at high temperature and by the melting and inert gas scrubbing process employed in this work. Mass spectral analysis of material prepared from the elements shows only SnBr₂ as the product (16).

Vapor Pressure Measurements

The vapor pressure above SnBr₂(l) was measured over the range 576 to 923 K, and the values were first fitted by linear regression to the form:

\[ \ln(p/Pa) = -A \cdot (K/T) + B \]  

Figure 2 shows the experimental points and the linear least squares fit to equation (1). Table 1 contains the coefficients of this regression and the corresponding coefficients reported in previous vapor pressure studies (12,13).

The data were also subjected to a more accurate regression analysis of \( \ln(p/Pa) - (\Delta C_p/R) \cdot \ln(T/K) \) against \( K/T \), where \( \Delta C_p = C_p(g) - C_p(l) \) accounts for the change in the difference in heat capacities with temperature. This gives an equation of the form:

\[ \ln(p/Pa) = -A' \cdot (K/T) + (\Delta C_p/R) \cdot \ln(T/K) + B' \]

A constant value of \( \Delta C_p/R = -7.500 \) was chosen to give the best fit to the data. The coefficients and 95 per cent confidence limits of both regression equations are given in Table 2.

There is generally good agreement between the results presented here and the work of the other authors. However, our results include a considerable increase in the measurement range and a general improvement in the precision of the measurements. The results of Karpenko (12) cover the range 723 to 893 K, and there is very close agreement with our results in this range. The results of Fischer and Gewehr (13) cover the range 729 to 884 K, but the measured
pressures are all about five percent lower at each temperature. There is no obvious reason for
this discrepancy. We have not included the results of the Knudsen effusion mass spectrometric
studies of Hilpert (2) due to the very limited temperature range of the measurements.

It is interesting to note that coefficients of the linear fit of equation (1) from this work are
closer to Fischer's values than to Karpenko's (see Table 1). This odd result is due to the wider
temperature and pressure range measured in this work, and to the fact that the simple linear
regression of equation (1) does not include the change in heat capacity (i.e. the
$(\Delta C_p/R) \ln(T/K)$ term of equation (2)).

Knudsen Effusion Mass Spectrometry

Table 3 lists the appearance potentials for ions detected above solid tin(II) bromide from
several sources. Although some mass spectrometric studies (16,39) have not reported ions
derived from dimers, the presence of $\text{Sn}_2\text{Br}_4(\text{g})$ has been confirmed by references (2) and (21).
In an elegant study Hilpert (2) has determined the partial pressures of $\text{SnBr}_2$ and $\text{Sn}_2\text{Br}_4$
over the solid (373 to 501 K) and liquid (501 to 573 K). The enthalpy and entropy for the
dissociation of the dimer, equation (3), were found to be $(106.8 \pm 3.6) \text{kJ} \cdot \text{mol}^{-1}$ and $(153.7$
$\pm 8.8) \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ respectively at 298.15 K.

$$\text{Sn}_2\text{Br}_4(\text{g}) = 2 \text{SnBr}_2(\text{g}) \quad (3)$$

Melting Temperature and Enthalpy of Fusion

The reported melting temperature of tin(II) bromide ranges from a low of 489 K to a high
of 509 K as shown in Table 4. These melting temperatures have been measured in the course of
a wide variety of synthetic and physico-chemical studies, and represent data gathered over a 67
year time period. The value reported most often in the literature and in reviews is 505 K,
which is also that reported in the early work of Kendall et al. (32) and Fischer et al. (13). The
fact that many recent investigations (ostensibly using carefully-prepared, pure materials) report
values considerably less than this is a bit disturbing and is not easily explained. A critical
evaluation of these data leads us to recommend a value of 507 K as shown in Table 4.

Reported values for the enthalpy of fusion of tin(II) bromide also cover a considerable
range as shown in Table 4. The recent differential scanning calorimetric data of Gardner and
Preston (45) suggests that the previously reported values may be high. Their data, and further
calculations, lead us to recommend a value of $\Delta_f^{\text{H}}(298.15 \text{K}) = 13.2 \text{kJ} \cdot \text{mol}^{-1}$. This
corresponds to a value of 15.1 kJ·mol⁻¹ at 507 K.

Molar Heat Capacities

Molar heat capacities for the condensed phases of $\text{SnBr}_2$ reported in compilations of
thermochemical parameters (e.g. reference (43)) are estimates based on extrapolation of the
low-temperature values reported in reference (19). Recently Gardner and Preston (45) have
determined the molar heat capacities of the solid from 350 K to 500 K and of the liquid from
520 K to 800 K using differential scanning calorimetry. We have used their values together
with the values from reference (19) to represent the molar heat capacity of the solid, 298.15 K.
to 507 K, and the liquid, 507 to 1000 K. The coefficients for the polynomials representing the molar heat capacities are listed in Table 5.

We have assessed critically the spectroscopic constants \( \nu_1, \nu_2, \nu_3 \) (the vibration frequencies) and \( I_{ABC} \) (the product of the principal moments of inertia) required to calculate the molar heat capacity of SnBr\(_2\)(g). The molar heat capacity and entropy were calculated using the method described in the JANAF tables (47).

The spectroscopic constants for SnBr\(_2\)(g) and many other species listed in the review of thermodynamic properties of gaseous metal dihalides by Brewer et al. (48) were estimated primarily because very few experimental values were available at that time. We have selected the vibration frequencies obtained by matrix isolation-Raman spectroscopy together with depolarization measurements (49,50). There is a significant dependence of the vibrational frequencies on the matrix, the values being lower in a nitrogen matrix than in an argon matrix. In this work we have used the frequencies obtained from an argon matrix. Values for \( \nu_1 \) and \( \nu_3 \) measured using matrix isolation-infrared spectroscopy in argon (51) are very similar to those in reference (50). Beattie and Perry (52) report a value for \( \nu_2 \) similar to that used here from an analysis of the resonance fluorescence spectrum.

The first evidence for the non-linear geometry of SnBr\(_2\)(g) came from high-temperature electron diffraction in 1941 (53). The equilibrium bond length and Br-Sn-Br angle used here are those derived from detailed analysis of electron diffraction data from a series of non-linear symmetric triatomic molecules (54).

Calculations using self-consistent field (SCF) and configuration interaction (CI) theory have yielded vibrational frequencies close to experimental values, but gave larger values for the bond length and bond angle (55). Force constants have been derived from electron diffraction and spectroscopic data (56).

We have assumed the multiplicity of the ground state to be 1 and that there are no low-lying electronic levels that make significant contributions to the partition function below 1500 K.

The selected spectroscopic constants for SnBr\(_2\)(g) are listed in Table 6. The coefficients for the polynomial describing the molar heat capacity are given in Table 5. \( S^0_m(\text{SnBr}_2\text{,g,298.15 K}) \) is presented in Table 10.

**Thermochemical Parameters**

We have derived a comprehensive set of thermochemical parameters for tin(II) bromide assuming that the vapor above the liquid contains only monomers. The literature contains two reports of the monomer-dimer equilibrium for tin(II) bromide. Hilpert’s study (2) covers the range 373 to 573 K and reports that the mole fraction of dimer above the liquid decreases with increasing temperature from \( x(\text{Sn}_2\text{Br}_4) = 0.016 \) at 510 K to 0.014 at 573 K. Conversely, Karpenko’s (12) results indicate that \( x(\text{Sn}_2\text{Br}_4) \) increases from 0.056 at 773 K to 0.094 at 893 K. We have shown previously (57) that it is essential to carry out studies of monomer-
dimer equilibria over the same temperature range as vapor pressure measurements. In view of the low mole fraction of the dimer and the large uncertainties in the values for the monomer-dimer equilibrium, we feel the most reliable treatment of our results is to regard the vapor as containing only monomer.

Thermodynamic quantities for the vaporization of tin(II) bromide derived from the second-law treatment are given in Table 7. The enthalpy of evaporation, $\Delta_{\text{evap}} H^0_{m}(T)$, is calculated from the slope of the linear regression of $\ln(p/Pa)$ against reciprocal temperature, $T$ being the mid-point temperature of the range of measurement. Similarly, the entropy of evaporation, $\Delta_{\text{evap}} S^0_{m}(T)$, is calculated from the intercept of the linear regression. The corresponding values at 298.15 K are derived using the molar heat capacities for the liquid and gas given in Table 5.

The enthalpy of evaporation can also be calculated by using the third-law method whereby each experimental measurement gives a value for $\Delta H^0_{m}(298.15 \text{ K})$. The third-law treatment for evaporation can be expressed in the form:

$$\Delta_{f} H(298.15 \text{ K})/T = -\Delta_{f} H^0_f /T - \{S^0_f (298.15 \text{ K}) - S^0_f (298.15 \text{ K})\} - R \ln(p/p^0) \quad (4)$$

The molar heat capacities for the liquid and gas were taken from this work (Table 5) as was $S^0_m(\text{SnBr}_2, g, 298.15 \text{ K})$. The entropy of liquid tin(II) bromide, $S^0_m(\text{SnBr}_2, l, 298.15 \text{ K})$ was determined from $\Delta_{\text{evap}} S^0_m(298.15 \text{ K})$ and $S^0_m(\text{SnBr}_2, g, 298.15 \text{ K})$. The average of the third-law values differs from the second-law value by only 1 kJ·mol$^{-1}$. The third-law values show no temperature dependence. A strong dependence of the third-law values on temperature can be taken to be indicative of an incorrect value for $S^0_m(298.15 \text{ K})$ (58). The enthalpy of sublimation, $\Delta_{\text{sub}} H^0_m(298.15 \text{ K})$, is calculated from the enthalpies of evaporation and fusion at 298.15 K.

Values for the thermodynamics of evaporation from second-law treatments are compared in Table 8, and are in close agreement. We have not included the enthalpy and entropy values calculated from the Knudsen effusion mass spectrometric studies of Hilpert (2) and Ciach et al. (37) due to the very limited temperature range of the measurements.

Reported values for the enthalpy of formation of SnBr$_2$(s) at 298.15 K differ considerably and are listed in Table 9. We have selected the value from reference (59), $\Delta_f H^0(\text{SnBr}_2, s, 298.15 \text{ K}) = -252.923$ kJ·mol$^{-1}$. Values for the enthalpy of formation for SnBr$_2$(l) and SnBr$_2$(g), derived from this work, are listed in Table 10 together with $S^0_m(298.15 \text{ K})$ for solid, liquid and gas.

Vapor pressures above liquid tin(II) bromide calculated using the thermochemical parameters given here are in close agreement with those calculated from equation (2) using the nonlinear coefficients from Table 2.
REFERENCES

1. D.M. Speros, R.M. Caldwell and W.E. Smyser, *High Temp. Sci.*, 4, 99 (1972).
2. K. Hilpert, *J. Electrochem. Soc.*, 136, 2099 (1989).
3. Z.K. Krasko, *J. Illum. Eng. Soc.*, 11, 162 (1982).
4. T. Shintani, S. Nagano, T. Ishigami and H. Sasaki, U.S. Patent No. 4,027,190, 31 May 1977.
5. P.C. Drop, J.J. Ge Groot and J.H. Verduin, *Proc. Int. Conf. Phenom. Ioniz. Gases, 13th*, 2, 491 (1977).
6. Philips Electronic and Associated Industries, Ltd., British Patent No. 1,484,468, 01 Sep 1977.
7. General Electric Co., Fr. Demande 2,195,063, 01 Mar 1974.
8. T. Takada, M Tsuchihashi and K. Watanabe, *Mitsubishi Denki Giho*, 46, 407 (1972).
9. P.D. Johnson, U.S. Patent No. 3,497,754, 24 Feb. 1970.
10. Z.N. Kobina, E.L. Korotkov and A.V. Leonidov, *Svetotekhnika*, 16, 7 (1970).
11. W.H. Rodebush and A.L. Dixon, *Phys. Rev.*, 26, 851 (1925).
12. N.V. Karpenko, *Vestn. Leningrad. Univ., Fiz. Khim.*, (2), 77 (1969).
13. W. Fischer and R. Gewehr, Z. *Anorg. Allgem. Chem.*, 242, 188 (1939).
14. S. Anderson, U.S. Patent Numbers 3,676,534, 11 July 1972; 3,948,793, 06 April 1976; 4,010,000, 01 March 1977; 4,201,739, 06 May 1980.
15. H. Han, *Huaxue Tongbao*, (8), 44 (1989).
16. C. Hirayama and R.D. Straw, *Thermochim. Acta*, 80, 297 (1984).
17. G.G. Gospodinov, *Zh. Neorg. Khim.*, 29, 2461 (1984).
18. N.N. Zhamskaya, *Zh. Neorg. Khim.*, 26, 1449 (1981).
19. G.A. Berezovskii, Yu.G. Stenin and I.E. Paukov, *Zh. Fiz. Khim.*, 54, 1871 (1980).
20. H. Chakurov and G. Gospodinov, *Dokl. Bolg. Akad. Nauk.*, 32, 185 (1979).
21. S.A. Mucklejohn and N.W. O’Brien, *Proc. 10th Int. Mass Spec. Conf.*, 999 (1985).
22. R.A. Deans, R.A. Geanangel and W.W. Wendlandt, *Thermochim. Acta*, 30, 364 (1979).
23. R.A. Deans and R.A. Geanangel, *Synth. React. Inorg. Met.-Org. Chem.*, **8**, 345 (1978).
24. S. Prasad, K.S.R. Krishnahai and V. Hariharan, *J. Indian Chem. Soc.*, **37**, 347 (1960).
25. J.D. Corbett and S. von Winbush, *J. Am. Chem. Soc.*, **77**, 3964 (1955).
26. B. Clever and S.P. Kumar, *J. Chem. Soc. Faraday Trans.*, **86**, 123 (1990).
27. A. Wojakowska, *J. Therm. Anal.*, **35**, 91 (1989).
28. A. Wojakowska and J. Terpilowski, *Pol. J. Chem.*, **56**, 641 (1982).
29. J. Andersson, *Acta Chem. Scand., Ser. A*, **A29**, 956 (1975).
30. A. Wojakowska and J. Terpilowski, *Rocz. Chem.*, **47**, 1621 (1973).
31. G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed., Vol. 1, pp. 732-733, Academic Press, New York (1965).
32. J. Kendall, E.D. Crittenden and H.K. Miller, *J. Am. Chem. Soc.*, **45**, 963 (1923).
33. F. Freyer and V. Meyer, *Z. Anorg. Chem.*, **2**, 1 (1892).
34. V.D. Pomeschichkov, V.P. Stel’makh, I.V. Isakov, and V.V. Pozdeev, *Zh. Neorg. Khim.*, **26**, 1958 (1981).
35. I. Novak and A.W. Potts, *J. Electron Spectrosc. Relat. Phenom.*, **33**, 1 (1984).
36. A.W. Potts and M.L. Lyus, *J. Electron Spectrosc. Relat. Phenom.*, **13**, 327 (1978).
37. S. Ciach, D.J. Knowles, A.J.C. Nicholson, and D.L. Swingler, *Inorg. Chem.*, **12**, 1443 (1973).
38. I.N. Belyaev and E.A. Shurginov, *Zh. Neorg. Khim.*, **15**, 883 (1970).
39. D.J. Knowles, A.J.C. Nicholson and D.L. Swingler, *J. Phys. Chem.*, **74**, 3642 (1970).
40. S. Evans and A.F. Orchard, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 207 (1975).
41. A.P. Popov, N.N. Zhamskaya and G.A. Kokovin, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **(6)**, 160 (1974).
42. T.N. Sves’tyanova and N.V. Karpenko, *Zh. Fiz. Khim.*, **45**, 1834 (1971).
43. L.B. Pankratz, "Thermodynamic Properties of Halides", U.S. Department of the Interior, Bureau of Mines Bulletin 674, U.S. Government Printing Office, Washington, D.C. (1984).
44. A.K. Molodkin, M. Rabbani, A.G. Dudareva, and A.I. Ezhov, *Zh. Neorg. Khim.*, **24**, 1073 (1979).
45. P.J. Gardner and S.R. Preston, *Thermochim. Acta*, **185**, 219 (1991).

46. A.G. Dudareva, Yu.E. Bogatov, E.V. Galenko, A.K. Molodkin and V.Ya. Lityagov, *Zh. Neorg. Khim.*, **20**, 2860 (1975).

47. JANAF Thermochemical Tables, 3rd Edition. Editors: M.W. Chase, C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald and A.N. Syverud. *J. Phys. Chem. Ref. Data*, **14**, Supplement 1 (1985).

48. L. Brewer, G.R. Somayajulu and E. Brackett, *Chem. Rev.*, **63**, 111 (1963).

49. H. Huber, G.A. Ozin and A. Vander Voet, *Nature*, **232**, 166 (1971).

50. G.A. Ozin and A. Vander Voet, *J. Chem. Phys.*, **56**, 4769 (1972).

51. D.M. Jenkins and S.J. Ogden, Personal communication.

52. I.R. Beattie and R.O. Perry, *J. Chem. Soc. (A)*, **2429** (1970).

53. M.W. Lister and L.E. Sutton, *Trans. Faraday Soc.*, **37**, 406 (1941).

54. A. Ya. Nasarenko, V.P. Spiridonov, B.S. Butayev and E.Z. Zasorin, *J. Mol. Struct. (Theochem)*, **119**, 263 (1985).

55. J.M. Ricart, J. Rubio, and F. Illas, *Chem. Phys. Letters*, **123**, 528 (1986).

56. A.G. Gershikov, E.Z. Zasorin, A.V. Demidov and V.P. Spiridonov, *Zh. Struktur. Khim.*, **27**, 36 (1986).

57. N.W. O’Brien and S.A. Mucklejohn, *J. Chem. Thermodynamics*, **19**, 1065 (1987).

58. S.A. Mucklejohn, N.W. O’Brien and T.R. Brumleve, *J. Phys. Chem.*, **89**, 2409 (1985).

59. Yu.G. Stenin, G.A. Kokovin and N.N. Zhamskaya, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk.*, **(2)**, 91 (1977).

60. D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-3, U.S. Government Printing Office, Washington, D.C. (1968).

61. "Thermodynamic Constants of Substances—Part 4 (C,Si,Ge,Sn,Pb)", V.P. Glushko, ed., No. 1, pp. 458-459, USSR Academy of Sciences, Moscow (1970).
TABLE 1
Pressure-temperature relationship above SnBr₂(l)

Coefficients of \( \ln(p/\text{Pa}) = -\frac{A}{T} + B \)

| Reference and Year | Range/K | A \( \times 10^4 \) | B |
|--------------------|---------|----------------|---|
| Karpenko (12) 1969| 723-893 | 1.2182        | 24.991 |
| Fischer (13) 1939 | 729-884 | 1.2324        | 25.026 |
| This work 1990    | 576-923 | 1.2566        | 25.500 |

TABLE 2
Vapor pressure equations for SnBr₂ with the limits of the coefficients at the 95% confidence level.

Linear Form:
\[
\ln(p/\text{Pa}) = - (1.2566 \pm 0.0247) \times 10^4 \cdot \frac{K}{T} + (25.500 \pm 0.332)
\]

Nonlinear Form:
\[
\ln(p/\text{Pa}) = - (1.8071 \pm 0.0136) \times 10^4 \cdot \frac{K}{T} - (7.500) \cdot \ln(T/K) + (82.555 \pm 0.184)
\]

60
### TABLE 3

Appearance potentials for ions detected above SnBr₂(s)

| Ion  | Precursor          | Appearance potential/eV | Reference |
|------|--------------------|--------------------------|-----------|
| Sn⁺  | SnBr₂(g) (a)      | 12.8 ± 1.0               | (39)      |
| Sn⁺  | SnBr₂(g) (b)      | 14.5 ± 1.0               | (39)      |
| Sn⁺  | SnBr₂(g) (b)      | 14.9 ± 0.3               | (16)      |
| SnBr⁺ | SnBr₂(g) (c)     | 11.0 ± 0.4               | (39)      |
| SnBr⁺ | SnBr₂(g) (c)     | 11.2 ± 0.2               | (16)      |
| SnBr⁺ | SnBr₂(g) (c)     | 11.0 ± 0.5               | (21)      |
| SnBr₂⁺ | SnBr₂(g) (d)    | 10.0 ± 0.4               | (39)      |
| SnBr₂⁺ | SnBr₂(g) (d)    | 10.6 ± 0.2               | (16)      |
| Sn₂Br₃⁺ | Sn₂Br₄(g) (e) | 10.6 ± 0.5               | (21)      |

(a) SnBr₂(g) + e⁻ = Sn⁺ (g) + Br₂⁻ (g) + 2e⁻
(b) SnBr₂(g) + e' = Sn⁺ (g) + 2Br(g) + 2e⁻
(c) SnBr₂(g) + e²⁻ = SnBr⁺ (g) + Br⁻ (g) + e⁻
(d) SnBr₂(g) + e² = SnBr₂⁺ (g) + 2e⁻
(e) Sn₂Br₄(g) + e⁻ = Sn₂ Br₃⁺ (g) + Br⁻ (g) + e⁻

### TABLE 4

Reported values of the melting temperature and enthalpy of fusion for SnBr₂. Melting temperature values have been rounded to the nearest K.

| Reference(s) | Melting Temperature/K | Δ_{fusion}H°_m(T)/kJ·mol⁻¹ |
|--------------|-----------------------|-----------------------------|
| (40)         | 489                   | -                           |
| (38)         | 499                   | -                           |
| (22)         | 501-502               | -                           |
| (41)         | 503                   | -                           |
| (42)         | 504                   | 17.2 (19.3) *               |
| (30)         | 504                   | 20.6                        |
| (43)         | 504                   | 17.2                        |
| (13,18,25,28,31,32,44) | 505                   | -                           |
| (45)         | 507                   | 14.3                        |
| (46)         | 509                   | -                           |
| **Recommended value** | 507                   | 15.1                        |

* Of two values reported, the first, 17.2 kJ·mol⁻¹, was preferred
TABLE 5

Coefficients for the temperature variation of the molar heat capacities of SnBr₂ using the equation:

\[ C^0_{p,m}(T)/J \cdot K^{-1} \cdot mol^{-1} = A + B(T/K) + C(T/K)^2 + D(T/K)^2 \]

|       | A         | B         | C         | D         |
|-------|-----------|-----------|-----------|-----------|
| SnBr₂(s) | 4.10970 \cdot 10^1 | 1.21581 \cdot 10^{-1} | -6.36180 \cdot 10^{-5} | 6.47550 \cdot 10^5 |
| SnBr₂(l) | 8.83280 \cdot 10^1 | -4.69880 \cdot 10^{-3} | 4.08791 \cdot 10^{-5} | -5.40900 \cdot 10^4 |
| SnBr₂(g) | 5.81690 \cdot 10^1 | 1.54000 \cdot 10^{-5} | -1.71000 \cdot 10^{-9} | -1.59110 \cdot 10^5 |

TABLE 6

Spectroscopic constants for SnBr₂(g)

| Vibrational frequencies | \( \nu_1 \) | \( \nu_2 \) | \( \nu_3 \) |
|-------------------------|-------------|-------------|-------------|
|                         | 244 cm⁻¹   | 82 cm⁻¹    | 231 cm⁻¹   |

| Sn-Br bond length       | 2.504 Å     |
| Br-Sn-Br bond angle     | 98.6 °      |
| \( I_{ABC} \)           | 3.760 \cdot 10^{-112} g³ cm⁶ |
TABLE 7
Thermodynamics of vaporization for SnBr₂

|                          | Δ$_{\text{evap}}$H°$_m$(750 K) | (105 ± 2) kJ·mol⁻¹ | Δ$_{\text{evap}}$H°$_m$(298.15 K) (a) | (121 ± 3) kJ·mol⁻¹ | Δ$_{\text{evap}}$H°$_m$(298.15 K) (b) | (122 ± 3) kJ·mol⁻¹ | Δ$_{\text{evap}}$S°$_m$(750 K) | (116 ± 3) J·K⁻¹·mol⁻¹ | Δ$_{\text{evap}}$S°$_m$(298.15 K) | (152 ± 5) J·K⁻¹·mol⁻¹ | Δ$_{\text{sub}}$H°$_m$(298.15 K) | (135 ± 5) kJ·mol⁻¹ |
|-------------------------|-------------------------------|--------------------|--------------------------------------|-------------------|--------------------------------------|-------------------|-----------------------------|--------------------------|--------------------------------|--------------------------|--------------------------------|--------------------------|
| (a) Second-law treatment|                               |                    |                                      |                   |                                      |                   | (a) Second-law treatment  |                          | (b) Third-law treatment    |                          | (b) Third-law treatment    |                          |

TABLE 8
Enthalpies and entropies of evaporation for SnBr₂

| Reference        | T/K  | Δ$_{\text{evap}}$H°$_m$(T)/kJ·mol⁻¹ | Δ$_{\text{evap}}$S°$_m$(T)/J·K⁻¹·mol⁻¹ |
|------------------|------|---------------------------------|----------------------------------|
| Fischer (13)     | 811  | 102 ± 2                         | 112 ± 2                          |
| Karpenko (12)    | 808  | 101 ± 1                         | 112 ± 1                          |
| This work        | 750  | 105 ± 2                         | 116 ± 3                          |

Table 9
Reported values for the enthalpy of formation of SnBr₂(s) **

| Reference         | ΔH°$_m$(SnBr₂,s,298.15 K)/kJ·mol⁻¹ |
|-------------------|----------------------------------|
| Brewer (48)       | -266.102                         |
| Wagman et al. (60)| -243.509                         |
| Glushko (61)      | -259.994                         |
| Stenin et al. (59)| -252.923                         |

** Values reported to 3 decimal places as in the usual convention. This does not represent the precision.
TABLE 10

Enthalpies of formation and entropies at 298.15 K for SnBr$_2$ **

| Phase     | $\Delta H^\circ_{m}(298.15 \text{ K})/\text{kJ mol}^{-1}$ | $S^\circ_{m}(298.15 \text{ K})/\text{J K}^{-1}\cdot\text{mol}^{-1}$ |
|-----------|---------------------------------------------------------|----------------------------------------------------------|
| SnBr$_2$(s)| -252.923                                                | 153.000                                                  |
| SnBr$_2$(l)| -239.723                                                | 176.900                                                  |
| SnBr$_2$(g)| -118.383                                                | 328.764                                                  |

** Values reported to 3 decimal places as in the usual convention. This does not represent the precision.

Figure 1. Vessel and furnace arrangement for synthesis of tin(II) bromide
Figure 2. Vapor pressure (p/kPa) versus temperature (T/K) for tin(II) bromide. Solid curve is the linear least squares fit of equation (1). Boxes are experimental points.