Arsenic Triselenide: Boiling-point Relation at Elevated Pressures

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Arsenic triselenide glass of good quality has been prepared by reacting the elements together under argon in a high-pressure radio-frequency furnace. The boiling points of the selenide thus produced have been measured over the pressure range 0.065—10 atm; the normal b.p. is 846 °C. The variation of log P against $1/T$ can be expressed satisfactorily by a linear relation.

CHALCOGENIDE glasses are of increasing interest in the electronic field, arsenic triselenide (As_2Se_3) in particular being used in i.r. optical devices. For the latter application, however, the selenide should have a low oxygen-impurity content and from this standpoint Savage and Nielson[1] showed that distillation of glasses of this type in hydrogen could be used as a method of purification. A knowledge of the vapour pressure of arsenic triselenide is therefore useful, and the aim of the present work is the

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[1] J. A. Savage and S. Nielson, *Phys.Chem. Glasses*, 1965, **6**, 90.

evaluation of the vapour pressure–temperature relation by a boiling-point method over a larger temperature range than has previously been explored.

EXPERIMENTAL

Preparation of Arsenic Triselenide, As_2Se_3.—An internally heated pressure vessel was used which incorporated radio-frequency (r.f.) heating instead of resistance heating as used previously.[2] With r.f. heating a higher power input is possible which necessitates less thermal insulation around the sample and allows a fairly fast cooling rate in the glass-transition region. A diagram of the r.f. furnace which operates at 450 kHz has been published.[3] The silica reaction vessel was similar to that used for making other chalcogenide glasses and consisted of a bulb (volume *ca.* 12 cm^3) surmounted by a vertical tubular outlet.[3] The silica thermocouple sheath passed down the latter, leaving an annular space of only *ca.* 0.1 mm in which the high-pressure argon present could act as a diffusion barrier and virtually eliminate vaporization loss from the sample. Weights of arsenic and selenium of 99.9999% purity were employed to give *ca.* 20 g of the selenide.

After evacuating and flushing with high-purity argon, the r.f. furnace was pressurized to 70 atm and the temperature raised.* The selenium melted at 220 °C and with further heating some of the arsenic dissolved; the remainder of the arsenic dissolved at its triple point (recently confirmed [4] to be at 816 °C and 35.5 atm). The melt was heated at 8° min^{-1} to 950 °C, held there for 45 min to establish homogeneity, cooled to 600 °C, and depressurized at this temperature over a period of 1 h. The final cooling rate at atmospheric pressure in the temperature region 250—150 °C was 7° min^{-1} which was fast enough to produce a glass of good homogeneity. Three batches of arsenic triselenide were made.

Determination of Boiling Points.—The internally heated pressure vessel employed was that used for studying the vapour pressure of sulphur;[5] ancillary equipment for measuring temperature and pressure has also been described.[6] The silica b.p. vessel consisted of a cylindrical bulb 11 mm in diameter and 15 mm long surmounted by a vertical tube 20 cm long and 5 mm in bore. The annular clearance between the tube and the silica thermocouple sheath which passed down it was *ca.* 0.1 mm, and the pointed end of the sheath containing the thermojunction (Pt–Pt + 13% Rh) dipped 3 mm below the surface of the selenide (*ca.* 1.8 g).

With a heating rate of 2—3° min^{-1} a b.p. was shown by a marked arrest in the temperature plot from the thermocouple in the sample when the latter's vapour pressure equalled that of the applied pressure of argon. Since vapour loss from the sample occurs predominantly at the b.p., at the instant a b.p. was recorded the system was pressurized to the next pressure. With this precaution and limitation of the number of determinations in a run to two or three, only *ca.* 2% of the sample was lost during a run so that any incongruency of the vaporization would have negligible effect on the sample's composition. To obtain satisfactory b.p. arrests at the highest pressures it was advantageous to incorporate *ca.* 5% of alumina powder as nucleating agent. No significant differences were found with the three batches of selenide, and from several determinations at atmospheric pressure the normal b.p. was found to be 846 ± 1 °C.

The normal b.p. was also checked by the method of Fischer and Rahlfs [7] in which the temperature of the vapour is measured by a movable thermocouple. Just below the point where most of the vapour condensation occurs there is a region where the temperature is constant and is considered to be representative of the true vapour–liquid equilibrium. For this measurement the vertical boiling tube used had a uniform bore of 12 mm, the weight of the selenide was 6 g, and the furnace had a constant-temperature zone 2 cm long. With a heating rate of 4° min^{-1}, the temperature plot from the sample showed an arrest at 846 °C but rose to 849 °C by superheating over a time interval of 4 min. During this period, however, the thermocouple in the vapour showed a constant temperature of 847 °C with fluctuations of ±1 °C at a distance of 2.5—3 cm above the liquid surface.

RESULTS AND DISCUSSION

The boiling points of arsenic triselenide at different pressures are shown in the Table. A plot of log P against $1/T$ was linear, any curvature being negligible within experimental error, and the results can be expressed by relation (1). For pressures in kN m^{-2}, the constant term

$$\log (P/\text{atm}) = -(5\,620/T) + 5.0217 \qquad (1)$$

becomes 7.0274. In deriving this relation a weighting was applied to take account of the accuracy being generally better near the middle of the temperature range. Calculated b.p.s from (1) are compared in the Table with those observed.

Observed pressures (atm) and boiling points (°C) for arsenic triselenide

P	B.p.*	P	B.p.*
0.0658	634 (633)	2.03	919 (919)
0.184	699 (703)	3.48	983 (981)
0.313	743 (744)	4.95	1 028 (1 025.5)
0.371	759 (757.5)	5.80	1 049 (1 046.5)
0.438	771 (771.5)	6.12	1 052 (1 054)
0.632	803 (803)	7.18	1 074 (1 076)
0.825	827 (827.5)	9.10	1 115 (1 110)
0.870	831 (832.5)	9.90	1 124 (1 123)
1.00	846 (846)	10.00	1 123 (1 124)
2.01	918 (918)		

* Calculated values are given in parentheses.

From (1) the mean heat (ΔH_v) and mean entropy of vaporization (ΔS_v) for the temperature range in the Table are respectively 25.71 kcal mol^{-1} and 22.97 cal K^{-1} mol^{-1}. Although departure of the vapour from ideal behaviour was ignored in the derivation, it is not likely to be great so that these values should be accurate within a few %. They refer, however, to the mean molecular weight of the vapour. It is interesting to note that the above value of ΔS_v is approximately that expected from Trouton's rule.

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* 1 atm = 101 325 Pa, 1 cal = 4.186 J.

[2] L. M. Webb and E. H. Baker, *J.C.S. Dalton*, 1972, 769.

[3] E. H. Baker and L. M. Webb, *J. Materials Sci.*, 1974, **9**, 1128.

[4] E. H. Baker, *Trans. Inst. Min. Metal*, 1974, **C83**, 237.

[5] E. H. Baker, *Trans. Inst. Min. Metal*, 1971, **C80**, 93.

[6] E. H. Baker, *J. Chem. Soc.*, 1962, 464.

[7] W. Fischer and O. Rahlfs, *Z. anorg. Chem.*, 1932, **205**, 1.

Ustyugov and his co-workers[8] made molecular-weight measurements on the unsaturated vapour and were able to obtain a rough measure of the dissociation of the selenide at different temperatures. Although dissociation of the selenide is marked at lower pressures, extrapolation of their results to the saturation vapour pressures obtained here suggests that dissociation will only occur to the extent of *ca.* 10%, so that the predominant species in the saturated vapour appears to be monomeric As_2Se_3.

The b.p.s obtained by Ustyugov *ct al.* for pressures below atmospheric were measured by means of a quartz Bourdon gauge,[9] and their results yield values of ΔH_v and ΔS_v of 26.00 kcal mol^{-1} and 22.92 cal K^{-1} mol^{-1} respectively; these lead to a value for the normal b.p. of 861 °C, somewhat higher than that obtained here. Any physical interaction between the buffer gas and the vapour in the method used here will be negligible at these moderate pressures so that the vaporization conditions in the dynamic and static measurements should be similar and it is not clear why the two sets of results show a discrepancy. Although the latter is not vast, it is greater than usually found between these types of measurement (*cf.* arsenic[4] and selenium[10] for example).

Measurements of the electrical conductivity of arsenic triselenide prepared previously by a high-pressure method[2] agreed well with those obtained by Edmond,[11] who prepared the selenide at lower pressures by reacting the elements in a sealed tube at *ca.* 600 °C for a long time. Material supplied by this author was found to have a normal b.p. of 845 °C, whilst at 5.80 atm its b.p. was 1 049 °C (Table). Physicochemically, the materials prepared by the high- or low-pressure method can be considered identical.

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[8] B. M. Kuadzhe, G. P. Ustyugov, and A. A. Kudryavtsev, *Tidskr. Mosk. Khim. Tekhnol. Inst.*, 1968, **58**, 29.

[9] G. P. Ustyugov, A. A. Kudryavtsev, B. M. Kuadzhe, and E. N. Vigdorovich, *Izvest. Akad. Nauk S.S.S.R., Neorg. Materialy*, 1969, **5**(**2**), 378.

[10] H. Rau, *J. Chem. Thermodynamics*, 1974, **6**, 525.

[11] J. T. Edmond, *Brit. J. Appl. Phys.*, 1966, **17**, 979.