

Phase Diagrams of the Bismuth Trihalides at High Pressure¹

by A. J. Darnell and W. A. McCollum

Atomics International Division of North American Aviation, Inc., Canoga Park, California 91304
(Received October 10, 1967)

The phase diagrams of BiF₃, BiCl₃, BiBr₃, and BiI₃ were determined at pressures up to 36 kbars by differential thermal analysis, resistance, and dilatometric techniques. The phase diagrams for BiF₃ and BiCl₃ are relatively simple; no new polymorphs were detected between room temperature and the melting point. A new solid phase (γ) of BiBr₃ stable at high pressure was found. The triple point for BiBr₃ ($\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$) is 300° and 12.5 kbars. Both a new high-temperature (β) and a high-pressure (γ) form of BiI₃ are reported. The triple point for BiI₃ ($\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$) is 510° and 25.5 kbars, and for BiI₃ ($\beta \rightleftharpoons \gamma \rightleftharpoons I$) it is 800° and 25 kbars. The transition volumes for the phase changes ($\alpha \rightarrow \gamma$), ($\beta \rightarrow \gamma$), and ($\alpha \rightarrow \beta$) around the triple point are -5.3, -5.7, and 0.1 cm³/mole, respectively. The melting temperatures of these salts as a function of pressure are fitted to the Simon equation, $P - P_0 = A[(T/T_0)^c - 1]$. The respective values for P_0 (bars), A (bars), T_0 (°K), and c for these salts are: BiF₃, 0, 130,000, 1030, 1.01; BiCl₃, 0, 8660, 507, 2.70; BiBr₃ (β), 0, 14,400, 492, 1.85; BiI₃ (β), 0, 17,700, 681, 1.95; BiI₃ (γ), 25,000, 16,800, 1073, 2.38.

Introduction

The bismuth halides BiCl₃, BiBr₃, and BiI₃ have been well characterized at atmospheric pressure or under their own vapor pressure.²⁻⁶ This group of compounds offers a good example for study of transport properties of molten salts such as electrical conductivity and viscosity at constant volume for comparison with the existing data at constant atmospheric pressure. However, in order to maintain constant volume of the liquid state over a wide range of temperatures, it is necessary to maintain very high external pressure upon the salt. This paper gives the equilibrium melting curve of these salts as a function of pressure at pressures up to 36 kbars. The pressure-temperature dependence of the polymorphic transitions in the compounds BiBr₃ and BiI₃ is also reported.

Experimental Section

Materials. BiF₃. Bismuth trifluoride was prepared from reagent grade Bi₂O₃ and analytical reagent grade aqueous hydrofluoric acid.^{6c} The BiF₃ precipitate was washed and then vacuum dried at 100° for 24 hr. Its melting point was 755 ± 5°. The X-ray powder pattern agrees with the pattern for BiF₃ given by Swanson, *et al.*^{6c}

BiCl₃. Analytical reagent grade bismuth trichloride

was treated by bubbling HCl gas through the molten salt; this was followed by triple distillation under an atmosphere of pure argon.⁷ The salt thus prepared had a melting point of 233.6°, in good agreement with the literature value.

BiBr₃ and BiI₃. Bismuth tribromide and bismuth triiodide were synthesized by direct combination of the elements at high temperatures in a sealed evacuated

(1) (a) This work was supported by the Research Division of the U. S. Atomic Energy Commission. (b) Presented before the Division of Physical Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 11-15, 1967.

(2) (a) M. Blander, "Molten Salt Chemistry," Interscience Publishers, Inc., New York, N. Y., 1964; (b) B. R. Sundheim, "Fused Salts," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

(3) L. F. Grantham and S. J. Yosim, *J. Phys. Chem.*, **67**, 2506 (1963).

(4) (a) F. J. Keneshea and D. Cubicciotti, *ibid.*, **62**, 843 (1958); (b) J. W. Johnson and D. Cubicciotti, *ibid.*, **68**, 2235 (1964).

(5) J. D. Kellner, *ibid.*, **71**, 3254 (1967).

(6) (a) G. M. Wolten and S. W. Mayer, *Acta Cryst.*, **11**, 739 (1958); (b) H. E. Swanson, N. T. Gilfrich, and M. I. Cook, "Standard X-Ray Diffraction Powder Patterns," National Bureau of Standards Circular 539, Vol. 6, U. S. Government Printing Office, Washington, D. C., 1956, p 20; (c) H. E. Swanson, M. C. Morris, R. P. Stinchfield, and E. H. Evans, "Standard X-Ray Diffraction Powder Patterns," National Bureau of Standards Monograph 25, Vol. I, U. S. Government Printing Office, Washington, D. C., 1962, p 7.

(7) S. J. Yosim, A. J. Darnell, W. G. Gehman, and S. W. Mayer, *J. Phys. Chem.*, **63**, 230 (1959).

Vycor system.⁸ Each of the salts was triply sublimed under reduced pressure after removal of the excess halogen. The melting points of the tribromide and triiodide were 218.5 ± 0.5 and $407.5 \pm 1.0^\circ$, respectively, in good agreement with reported values.⁸ The X-ray powder pattern of this BiI_3 checks with the powder pattern for BiI_3 given by Swanson,^{6b} *et al.*

Experimental Methods and Procedure. The phase studies upon the bismuth trihalides at elevated pressures were carried out in a piston-cylinder high-pressure chamber similar to the apparatus of Coes,⁹ Hall,¹⁰ and Kennedy, *et al.*¹¹ A high-pressure chamber cell utilizing an internal graphite or metal strip heater similar to the design used by Kennedy and Newton¹² was used to carry out the high-temperature phase transition studies. A high-pressure, high-temperature cell of this design can attain pressures from a lower limit of approximately 2 kbars to an upper limit of approximately 55 kbars at temperatures from ambient to 1500° . Several experimental techniques were used to detect the phase transitions as no single technique was suitable for detection of the variety of phase transitions found in these salts. These techniques include (a) differential thermal analysis (dta), (b) electrical resistance measurements, (c) differential joule heating method, and (d) the volume discontinuity method.¹³ A description of these methods follows.

(a) A differential thermal analysis cell and technique similar to those used by Kennedy and Newton¹² and by Pistorius¹⁴ were used to determine the high-pressure melting points of the four halides. Nickel or boron nitride dta cells were used for BiF_3 . Platinum cells were used for BiCl_3 , and gold cells were used for BiBr_3 and BiI_3 . The dta method was found to have adequate sensitivity for the detection of the melting and freezing points of these salts. However, the solid-solid phase transitions in BiBr_3 and BiI_3 are difficult to detect by dta, because of a small heat of transformation and/or a slow transformation rate.

(b) Electrical resistance measurements were also used to detect phase changes in these salts. Both isobaric and isothermal measurements of the alternating current resistance as a function of temperature and pressure, respectively, were carried out at a frequency of 1000 Hz using a General Radio Type 1650-A resistance bridge. A phase change was signaled by a discontinuity or a change in slope of the resistance as a function either of temperature or of pressure.

(c) The differential joule heating method utilizes a change in resistance of the sample associated with a phase change to alter the heating or cooling rate. This is accomplished by placing the salt sample in a parallel resistance path with the graphite or nickel furnace heating element. The heat generated by the alternating current passing through the sample contributes to the heat generated by the furnace heating element and thus a relatively small change in the

resistance of the sample affects the heating rate. Experimentally this is done by placing a solid cylindrical sample directly inside a tubular furnace heating element. The advantage of this method is its simplicity and high sensitivity. The techniques and equipment used for this method are the same as for ordinary thermal analysis, but with a much greater sensitivity to phase transitions than ordinary thermal analysis and much simpler experimentally than the dta method.

(d) The volume discontinuity method has been used by Bridgman¹³ and by Kennedy and LaMori¹¹ to detect solid-solid phase transitions. This method works well on transitions which have a large transition volume and a large dT/dP term such as the $\alpha \rightleftharpoons \gamma$ and $\beta \rightleftharpoons \gamma$ transitions in BiI_3 . This volumetric method is complementary to the thermal method which is more satisfactory for detection of transitions with a large ΔH and a small dT/dP term. The principal reason, however, for use of the volume discontinuity method here is the additional thermodynamic information gained from measurement of the ΔV of the phase transition.

Temperature measurements were made with chromel-alumel thermocouple junctions located within the pressure chamber in direct contact with the sample ampoule. The effect of pressure on the thermoelectric potential of chromel-alumel junctions is relatively small (*i.e.*, $<1\%$) at pressures below 50 kbars and temperatures below 1000° .¹⁵ Therefore, the emf-temperature tables for atmospheric pressure have been used to obtain the temperatures reported here.

Results

BiF_3 . The melting curve of BiF_3 as a function of pressure from 2 to 15 kbars is shown in Figure 1. Melting points at higher pressures were not made because of the extreme corrosiveness of the molten BiF_3 at the correspondingly higher temperatures. The results shown in Figure 1 are from the first or second melting point determination on a given sample by the differential joule heating method in a nickel cell and by the dta method in a nickel or a boron nitride container. In general, melting points were not reproducible after

(8) S. J. Yosim, L. D. Ransom, R. A. Sallach, and L. E. Topol, *J. Phys. Chem.*, **66**, 28 (1962).

(9) L. Coes, *J. Amer. Ceram. Soc.*, **38**, 298 (1955).

(10) H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).

(11) G. C. Kennedy and P. N. LaMori in "Progress in Very High Pressure Research," F. P. Bundy, W. R. Hibbard, and H. M. Strong, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p 304.

(12) G. C. Kennedy and R. C. Newton in "Solids under Pressure," W. Paul and D. M. Warschauer, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963.

(13) P. W. Bridgman, "The Physics of High Pressures," G. Bell and Sons, London, 1958.

(14) C. W. F. T. Pistorius, *J. Phys. Chem. Solids*, **26**, 1543 (1965).

(15) F. P. Bundy in "Progress in Very High Pressure Research," F. P. Bundy, W. R. Hibbard, and H. M. Strong, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p 256.