

Phase Diagrams of the Bismuth Trihalides at High Pressure¹

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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.

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(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

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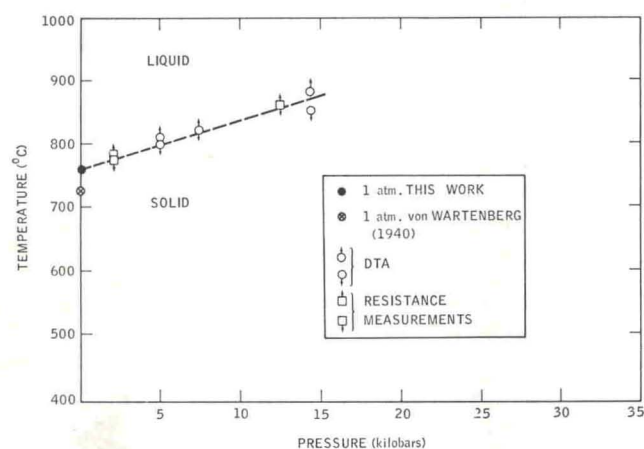
(13) P. W. Bridgman, "The Physics of High Pressures," G. Bell and Sons, London, 1958.

(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.

Table I: Thermodynamic Properties of Fusion of the Bismuth Trihalides

Salt	$(dT/dP)_{P=0}$, deg/kbar	ΔS_f , eu	ΔV_f , cm ³ /mole (calcd)	V_l at mp, cm ³ /mole	V_s at mp ($V_l - \Delta V_f$), cm ³ /mole	V_l/V_s
BiF ₃	7.6
BiCl ₃	15.5	11.2 ²³	7.3	80.0 ²⁷	72.7	1.11
BiBr ₃ (β)	16.6	$\left. \begin{array}{l} 10.55^{24} \\ 10.1^{25} \end{array} \right\}$	7.2	95.2 ²⁸	88.0	1.08
BiI ₃ (β)	17.5	13.7 ²⁶	10.1	126 ²⁹	116	1.09
BiI ₃ (γ)	25.0

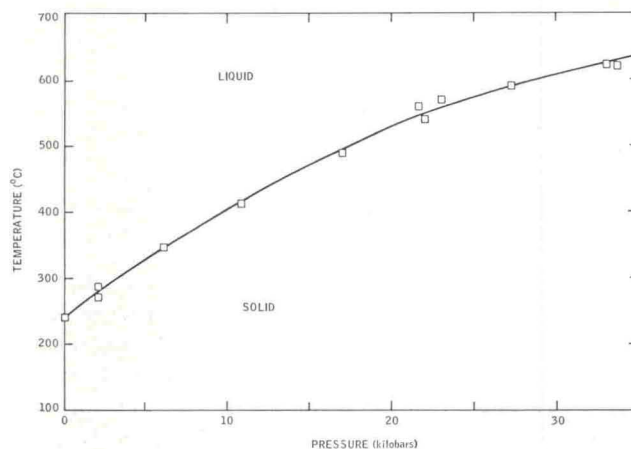
Figure 1. Pressure-temperature diagram for BiF₃.

the third successive run on a sample. Presumably, this is due to reaction with the container. The melting point data at elevated pressures extrapolate to a melting point of 760° at zero pressure. The melting point under an atmosphere of argon was $755 \pm 5^\circ$, which is higher than the melting point of 725° reported by von Wartenberg.¹⁶ The initial slope of the melting temperature dependence upon pressure is given in Table I. Data for the entropy ΔS and volume ΔV of fusion of BiF₃ at 1 atm are not available so that an independent check of the slope by the Clausius-Clapeyron equation

$$(dT/dP)_{P=0} = 23.9\Delta V/\Delta S \quad (1)$$

(where T is the melting temperature (°C) at a given pressure P expressed in kbars, ΔV and ΔS are the volume and entropy of fusion, respectively, in cm³ mole⁻¹ and cal mole⁻¹ deg⁻¹) cannot be made.

Solid BiF₃ was examined for phase transitions by the volume discontinuity and electrical resistance methods from room temperature to 700° at pressures up to 35 kbars. The $\alpha \rightleftharpoons \beta$ phase transition at 200° and at atmospheric pressure reported by Hund and Fricke¹⁷ was not detected by either method. The volume change for this transition may be too small to detect by our volumetric method. Below 400° the specific resistance of BiF₃ is so high that sample resistance exceeds the upper resistance limit of our cell and thus

Figure 2. Pressure-temperature diagram for BiCl₃.

we would not be able to detect a phase change occurring below 400° by this resistometric method.

BiCl₃. The melting temperature as a function of pressure for BiCl₃ is shown in Figure 2 over the pressure range from 2 to 32 kbars. This pressure-temperature melting curve was determined by DTA and ac resistance methods. These two methods give melting points which are in good agreement and which extrapolate to the melting point at atmospheric pressure. The initial pressure dependence of the melting temperature is 15.5°/kbar. The melting curve is given up to 625° since, at temperatures above this, successive melting points on a given sample are not reproducible. This is probably due to reaction of the molten bismuth trichloride with the platinum dta cells. No polymorphic transitions were observed in BiCl₃ by either of the above methods from room temperature up to the melting point at pressures from 2 to 32 kbars.

BiBr₃. The pressure-temperature phase diagram for BiBr₃ to pressures up to 36 kbars is shown in Figure 3. The phase transitions were obtained by dta, alternating current resistance, and differential joule heating techniques. Again, reasonably good agreement is obtained when more than one method was used to determine a particular phase boundary. The

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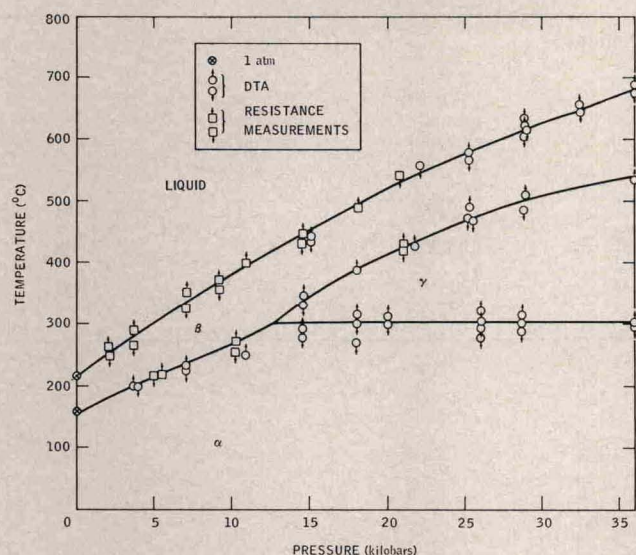


Figure 3. Pressure-temperature diagram for BiBr_3 .

melting point rises from 255° at a pressure of 2 kbars to 680° at a pressure of 36 kbars. The melting points at elevated pressure extrapolate to give a melting point of 215° at zero pressure which is in good agreement with the atmospheric melting point of 218.5° .⁸ The pressure dependence of the melting temperature (dT/dP) is $16.6^\circ/\text{kbar}$. The $\alpha \rightleftharpoons \beta$ transition reported at ambient pressure by Pushin¹⁸ and by Wolten and Mayer^{6a} was detected by dta and ac resistance methods. The temperature of this $\alpha \rightleftharpoons \beta$ transition was determined as a function of pressure up to a temperature of 300° and at a pressure of 12.5 kbars. This pressure and temperature define the triple point between α and β phases and a newly discovered γ phase. This γ phase lies between α and β phases at pressures from 12.5 kbars up to 36 kbars, the highest pressure examined. Since the $\alpha \rightleftharpoons \beta$ transition in BiBr_3 is detectable by thermal analysis,⁸ then the ΔH for this transition is not equal to zero. Our data show that the temperature dependence dT/dP of the phase boundary between α and β is $12^\circ/\text{kbar}$. Therefore, from eq 1 the $\alpha \rightleftharpoons \beta$ transition volume should not be equal to zero. Wolten and Mayer^{6a} have examined BiBr_3 by X-ray diffraction at 1 atm but found no change in structure up to 195° . Wolten and Mayer's explanation is that the $\alpha \rightarrow \beta$ transition, which occurs with an enthalpy and volume change but without a change in structure type, could arise from free rotation of the molecules without a change in crystal symmetry. The $\alpha \rightleftharpoons \gamma$ phase transition is also detectable by dta; however, the small size of the signal indicates that the heat of transition is small. The slope of this phase transition boundary dT/dP is zero and therefore from eq 1 ΔV for this transition is zero.

BiI_3 . Bismuth triiodide was examined by the same experimental techniques as were used for BiBr_3 . The pressure-temperature phase diagram for BiI_3 is shown

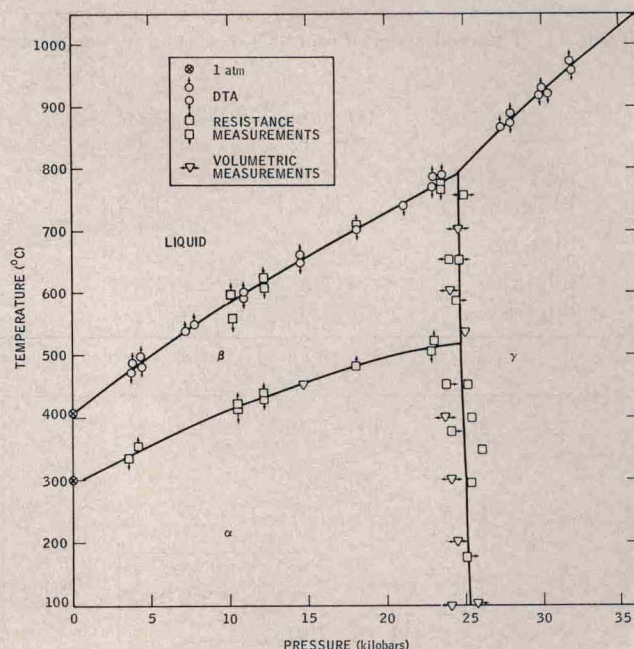


Figure 4. Pressure-temperature diagram for BiI_3 .

in Figure 4. Zahner and Drickamer¹⁹ examined BiI_3 by optical adsorption at pressures up to 75 kbars but failed to detect the $\alpha \rightleftharpoons \gamma$ transition at 25 kbars shown in Figure 4. This phase transition proceeds with a large volume change ($\sim 5\%$) but is very sluggish at room temperature. This sluggishness at room temperature probably explains why Zahner and Drickamer failed to detect it. The transition shows up distinctly and reversibly at temperatures above 100° by the volume discontinuity and ac resistance methods. A typical example of the behavior of the electrical resistance of BiI_3 as a function of pressure at constant temperature is shown in Figure 5. The displacement between the compression and decompression cycles indicates hysteresis to the $\alpha \rightleftharpoons \beta$ transition. The volume *vs.* pressure curve also exhibits a similar hysteresis effect. The $\alpha \rightleftharpoons \beta$ phase transition appears to occur over a pressure interval of approximately 4 kbars, on both the compression and decompression cycles. Part of this pressure interval is due to the pressure differential along the length of the sample since the system is not hydrostatic. Part is attributed to sluggishness toward phase transformation from one solid phase to another. This behavior is exhibited by many substances and has been termed "pressure range of indifference" by Bridgman.¹³ We have assumed the equilibrium pressure for the phase transformation to be the average of the pressures indicated for the compression and decompression cycles. Points midway between the onset and the completion of the phase

(18) N. A. Pushin, *Zh. Obshch. Khim.*, **18**, 1599 (1948).

(19) J. C. Zahner and H. G. Drickamer, *J. Phys. Chem. Solids*, **11**, 92 (1959).

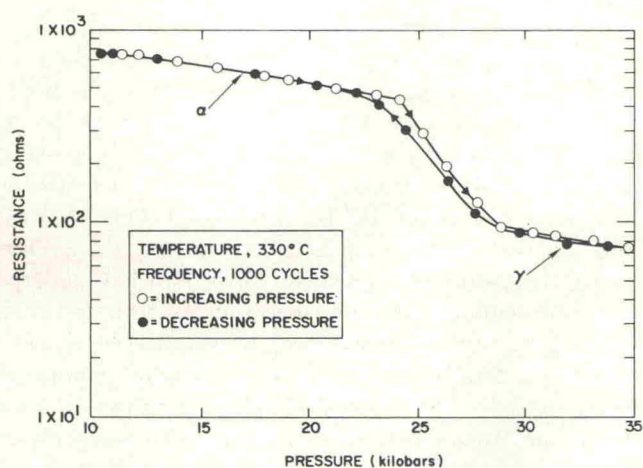


Figure 5. Electrical resistance of BiI_3 as a function of pressure at constant temperature.

transformation were taken as the transformation pressure for each cycle.

The existence of an $\alpha \rightleftharpoons \beta$ transition in BiI_3 shown in Figure 4 was indicated in the phase diagram work on the Bi- BiI_3 system by Yosim, *et al.*,⁸ although these authors could not unambiguously assign their thermal halts at 285 and 298° to definite phase transitions. No indication of a phase change in BiI_3 was found here which corresponds to the thermal halt at 285° in the Bi- BiI_3 system. However, it appears that the thermal arrest reported by Yosim, *et al.*,⁸ at 298° corresponds to the $\alpha \rightleftharpoons \beta$ transition in BiI_3 shown in Figure 4. This transition is not readily detected by thermal analysis but exhibits a discontinuity in the resistance *vs.* temperature curves. This is seen in Figure 6, which shows the electrical resistance of BiI_3 as a function of temperature at a constant pressure of 10.8 kbars. The $\alpha \rightleftharpoons \beta$ transition occurs at 405° at this pressure. The $\beta \rightleftharpoons$ liquid transition occurs over the temperature interval from 545 to 595°. The principal cause of this melting or freezing over such a wide interval is due to the pressure drop across the relatively long sample used in the resistance measurements. As stated above, this pressure drop may be of the order of 2-3 kbars. Since dT/dP for BiI_3 ($\beta \rightleftharpoons l$) is 17.5°/kbar (Table I), such a pressure differential might be expected to give a melting range of 35-55°. The dta method gives a sharper indication of the melting and freezing points at elevated pressures than the above resistance method since in the former case the salt sample is contained in a relatively short ampoule which is in direct contact with the thermocouple junction. Nevertheless, as shown in Figure 4, relatively good agreement is obtained between the two methods.

This resistance discontinuity in BiI_3 at the $\alpha \rightleftharpoons \beta$ transition was found by Fischer²⁰ at atmospheric pressure but was attributed by him to a "premelting" phenomenon. However, our measurements indicate that this is a solid-solid phase transition. Rosztoczy

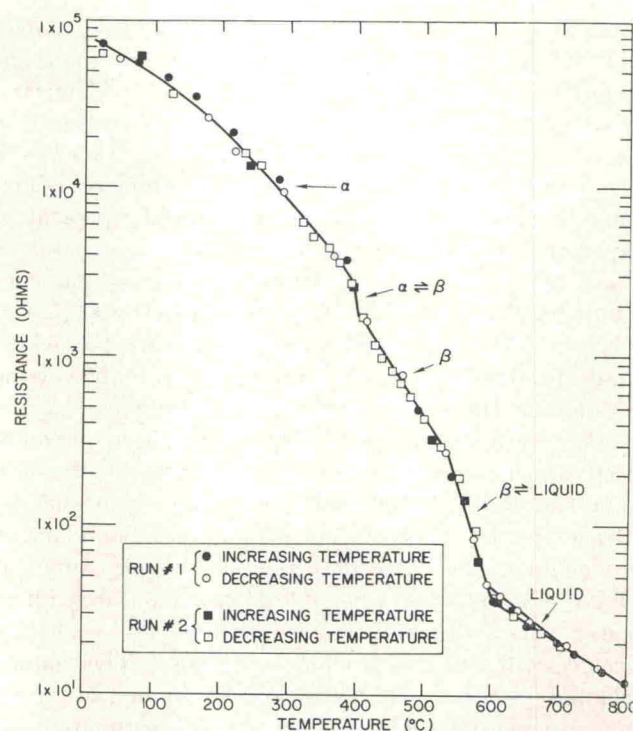


Figure 6. Electrical resistance of BiI_3 as a function of temperature at a constant pressure of 10.8 kbars.

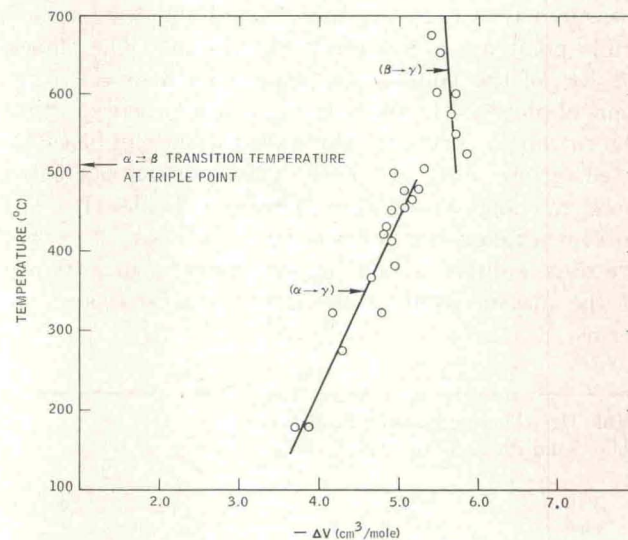


Figure 7. Transition volumes for the $(\alpha \rightarrow \gamma)$ and $(\beta \rightarrow \gamma)$ phase changes in BiI_3 .

and Cubicciotti²¹ and Cubicciotti and Eding²² failed to find this $\alpha \rightleftharpoons \beta$ transition in BiI_3 by thermal analysis²¹ and by drop calorimetry.²² The $\beta \rightleftharpoons \gamma$ transition, like the $\alpha \rightleftharpoons \gamma$ transition, was detected by both the volume discontinuity (Figure 5) and ac resistance techniques. The triple point for solid phases $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$ occurs at

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25.5 kbars and at 510°. The phase boundary slopes, dT/dP , for the phases in equilibrium around the triple point are: $\alpha \rightleftharpoons \beta$, 5.5°/kbar; $\alpha \rightleftharpoons \gamma$, -375°/kbar; and $\beta \rightleftharpoons \gamma$, -1000°/kbar. The transition volumes for the $\alpha \rightleftharpoons \gamma$ or $\beta \rightleftharpoons \gamma$ transitions were measured from 175 to 675° by the volume discontinuity method of Bridgman.¹³ The data points shown in Figure 7 represent an average of the transition volumes (ΔV_{tr}) obtained from the compression and decomposition processes at constant temperature. The discontinuity in the ΔV_{tr} vs. T curve at 510° is in agreement with resistance data which indicate a triple point at this temperature. The volume change for the $\alpha \rightleftharpoons \beta$ transition was measured at one temperature only, 450°. These transition volumes were measured isothermally while varying the pressure. The results illustrated in Figure 4 show that the isotherm at 450° intersects this $\alpha \rightleftharpoons \beta$ phase boundary at an acute angle. The detection or the measurement of ΔV of a transition when dT/dP is small is difficult to carry out isothermally. Nevertheless, the transition was carried out in this manner at 450°. The volume change for the $\alpha \rightarrow \beta$ transition determined by direct measurement is 0.1 cm³/mole with an estimated uncertainty of ± 0.1 cm³/mole. This is in fair agreement with $\Delta V(\alpha \rightarrow \beta)$ from $\Delta V(\beta \rightarrow \gamma) - \Delta V(\gamma \rightarrow \alpha)$ of 0.4 ± 0.4 cm³/mole. Thus the three independently measured transition volumes around the $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$ triple point are approximately additive. The slopes, dT/dP , of the boundaries between each of the three pairs of phases in equilibrium were also measured; thus the entropies, ΔS , of the three transitions can be calculated by use of eq 1. These values of ΔS calculated from ΔV and dT/dP are shown in Table II. The entropy changes around the triple point $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$ are thus additive within the experimental uncertainty of the measurement of the separate dT/dP and ΔV terms.

Table II: Thermodynamic Properties of Solid-Solid Phase Transitions in BiI₃

Phase change	dT/dP , deg/kbar	ΔV , cm ³ /mole	ΔS , eu
$\alpha \rightarrow \gamma$	-375	-5.3 ± 0.2	0.33
$\beta \rightarrow \gamma$	-1000	-5.7 ± 0.2	0.13
$\alpha \rightarrow \beta$	5.5	0.1 ± 0.1	0.43

Discussion

If data are available for ΔV and ΔS of fusion, then an independent check of the pressure dependence of the melting temperature dT/dP can be made by means of eq 1. Neither volumetric nor entropy data are available for the fusion of BiF₃. Data for the entropy of fusion are available for BiCl₃,²³ BiBr₃,^{24,25} and BiI₃.²⁶ However, no direct determination of the volume of fusion of the bismuth trihalides has been

reported. An indirect determination of ΔV_f is sometimes made from density of the liquid and of the solid phases at the melting point. Densities for the liquid salts BiCl₃, BiBr₃, and BiI₃ near their melting points have been determined by Cubicciotti and co-workers.²⁷⁻²⁹ Data necessary to calculate the densities of the solid phases of BiCl₃, BiBr₃, and BiI₃ at their melting points are not available. Lattice parameters at 25° are available;⁶ however, BiBr₃ and BiI₃ undergo phase transitions between room temperature and their melting points. Furthermore, the necessary thermal expansion data between 25° and the melting points are not available. It is noted that the densities of solid BiCl₃ and BiBr₃ calculated from the room temperature lattice parameter and space group assignments of Wolten and Mayer^{6a} are less than the densities of the corresponding liquid salts at their melting points.^{27,28} The densities of solid BiCl₃ and BiBr₃ calculated from Wolten and Mayer's data are 3.86 and 3.80 g/cm³, while the densities of the liquid salts at their melting points measured by Keneshea and Cubicciotti^{27,28} are 3.94 and 4.72 g/cm³. From the slopes of the fusion curves, Figures 2 and 3, however, we see that the solids must be denser than the liquids.

On the other hand, if the experimentally determined³⁰ densities of 4.75 and 5.7 g/cm³ for BiCl₃ and BiBr₃, respectively, and 5.78 g/cm³ for BiI₃(α)^{6b} are compared with Cubicciotti's densities for these molten salts, then it is seen that an over-all volume increase of about 20% occurs in going from the solid at room temperature to the liquid state at its normal melting temperature.

The initial pressure dependence of the melting temperature $(dT/dP)_{P=0}$ and the entropy of fusion data available from the literature have been used to calculate the volume of fusion ΔV_f of BiCl₃, BiBr₃(β), and BiI₃(β) by eq 1. These are shown in Table I. The volume of the solid phase at the melting point was computed from density data of Cubicciotti, *et al.*,²⁷⁻²⁹ and from the calculated values of ΔV_f , *i.e.*, $V_{solid} = V_{liquid} - \Delta V_{fusion}$. The ratios of molar volumes of liquid and solid BiCl₃, BiBr₃, and BiI₃ at their normal melting points are shown in Table I. These ratios for the bismuth halides are comparable to the ratios obtained for typical salts such as the alkali halides.³¹

Melting curves have commonly been reported in the form of the Simon³² equation

(23) L. E. Topol, S. W. Mayer, and L. D. Ransom, *J. Phys. Chem.*, **64**, 862 (1960).

(24) L. E. Topol and L. D. Ransom, *ibid.*, **64**, 1339 (1960).

(25) D. Cubicciotti and H. Eding, *J. Chem. Eng. Data*, **12**, 548 (1967).

(26) D. Cubicciotti and H. Eding, *J. Phys. Chem.*, **69**, 3621 (1965).

(27) F. J. Keneshea, Jr., and D. Cubicciotti, *ibid.*, **62**, 843 (1958).

(28) F. J. Keneshea, Jr., and D. Cubicciotti, *ibid.*, **63**, 1112 (1959).

(29) F. J. Keneshea, Jr., and D. Cubicciotti, *ibid.*, **63**, 1472 (1959).

(30) O. Honigschmidt and L. Birckenbach, *Ber.*, **54B**, 1873 (1921).

(31) H. Spindler and F. Sauerwals, *Z. Anorg. Allgem. Chem.*, **335**, 267 (1965).

(32) F. E. Simon and G. Glatzel, *ibid.*, **178**, 309 (1929).

$$(P - P_0)/A = (T/T_0)^c - 1 \quad (2)$$

where T is the melting temperature at pressure P , T_0 is the melting temperature at a triple point $s \rightleftharpoons l \rightleftharpoons g$ or $s \rightleftharpoons s' \rightleftharpoons l$, P_0 is the pressure at which $T = T_0$, and A and c are empirical constants. The Simon equation parameters were determined for each of the bismuth trihalides and are reported in Table III.

Table III: Parameters in the Simon Equation for the Melting Curves of the Bismuth Trihalides

Salt	T_0 , °K	P_0 , bars	A , bars	c
BiF ₃	1030	0	130,000	1.01
BiCl ₃	507	0	8,660	2.70
BiBr ₃ (β)	492	0	14,400	1.85
BiI ₃ (β)	681	0	17,700	1.95
BiI ₃ (γ)	1073	25,000	16,800	2.38

Kraut and Kennedy^{33,34} have recently proposed an equation relating the melting temperature T_m to the room-temperature compression, $-\Delta V/V_0$, of the solid phase in the form

$$T_m = T_m^0 \left(1 + C \frac{\Delta V}{V_0} \right) \quad (3)$$

where T_m^0 is the melting temperature at zero pressure and C is an empirical constant. Equation 3 gives a linear variation in T_m with $\Delta V/V_0$ for many simple substances such as metallic elements³⁴ and the alkali halides³⁵ over the pressure and temperature range for which melting and compression data are available. Vaidya and Gopal³⁵ have modified eq 3 so that the melting temperature of a high-pressure polymorph in equilibrium with the liquid is related to the temperature of the triple point and the compression of the high-pressure solid phase. The melting temperature of the bismuth trihalides at a given pressure have been plotted *vs.* the isothermal compression, $-\Delta V/V_0$, for the salt at this same pressure from compression data taken at 25°. ³⁶ These data of T_m *vs.* $-\Delta V/V_0$ for the bismuth trihalides are shown in Figure 8. Only BiI₃ (γ) exhibits a linear relationship between T_m and $\Delta V/V_0$. The melting point data for the other bismuth trihalides exhibit an upward curvature similar to the data for helium and argon shown by Kraut and Kennedy.³⁴ The effects of ultrahigh pressures on liquids such as the bismuth trihalides may be complex and sufficiently large so that representation of the melting temperatures by an equation with only one adjustable parameter may not yield a linear relationship in T_m *vs.* $-\Delta V/V_0$ as was found in the case for the alkali metals and the alkali halides.

Summary and Conclusions

The pressure-temperature phase diagrams in Figures

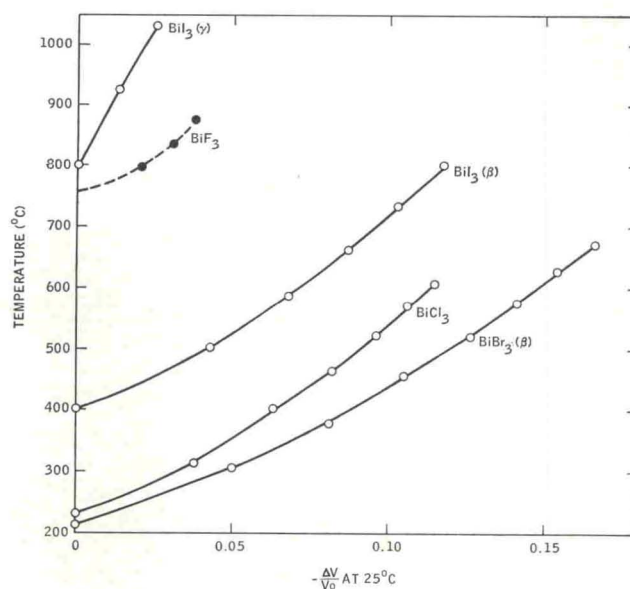


Figure 8. Melting temperature *vs.* compression ($-\Delta V/V_0$) for bismuth trihalides (Kennedy equation).

1 through 4 outline the P - T boundaries for the liquid and various solid phases of the bismuth trihalides. No really satisfactory container was found for molten BiF₃ since not more than two or three reproducible melting points could be obtained with the containers employed. A similar problem was encountered with BiCl₃ at temperatures above $\sim 650^\circ$. The melting points of the bismuth trihalides were found to rise as a function of pressure in a manner typical of a solid which expands during the melting process. The initial slopes of the melting curves (dT/dP) decrease in the order BiI₃ > BiBr₃ > BiCl₃ > BiF₃. This same order in dT/dP is observed for the halides of the alkali metals.³¹ This sequence probably arises as a result of an increase in the volume of fusion with increasing atomic weight of the halogen. A direct measurement of the volume of fusion of the bismuth trihalides would be welcomed in order to check the consistency of the ΔS_f , dP/dT , and ΔV_f terms. An increase in complexity in the pressure-temperature diagrams is noted (Figures 1 through 4) as the atomic number of the halide increases. Additional structure data on the high-temperature and high-pressure polymorphs of BiBr₃ and BiI₃ would be useful toward a better understanding of these systems. We observe that the high-pressure (γ) form of BiI₃ can be retained in a metastable state if the temperature is

(33) E. A. Kraut and G. C. Kennedy, *Phys. Rev. Letters*, **16**, 608 (1966).

(34) E. A. Kraut and G. C. Kennedy, *Phys. Rev.*, **151**, 668 (1966).

(35) S. N. Vaidya and E. S. R. Gopal, *J. Phys. Chem. Solids*, **28**, 1074 (1967).

(36) A. J. Darnell and B. B. Owens, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 51V.

lowered and kept below -40° before the pressure is released to atmospheric. The γ form rapidly and spontaneously reverts to the α form with the evolution of heat when the temperature is raised to -30° . This metastability makes the γ form available for character-

ization studies at atmospheric pressure, if the temperature is kept below -30° .

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