Table I: Thermodynamic Properties of Fusion of the Bismuth Trihalides

Salt	$(dT/dP)_{P=0}$, deg/kbar	ΔS_f, eu	ΔV_f, cm³/mole (calcd)	V_l at mp, cm³/mole	V_s at mp $(V_l - \Delta V_f)$, cm³/mole	V_l/V_s
BiF₃	7.6	. . .	. . .	. . .	. . .	. . .
BiCl₃	15.5	11.2[23]	7.3	80.0[27]	72.7	1.11
BiBr₃ (β)	16.6	$\begin{cases} 10.55[24] \\ 10.1[25] \end{cases}$	7.2	95.2[28]	88.0	1.08
BiI₃ (β)	17.5	13.7[26]	10.1	126[29]	116	1.09
BiI₃ (γ)	25.0	. . .	. . .	. . .	. . .	. . .
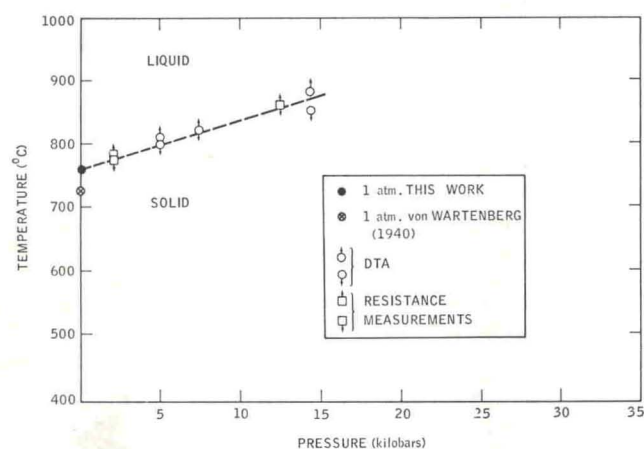
Figure 1. Pressure–temperature diagram for BiF₃.
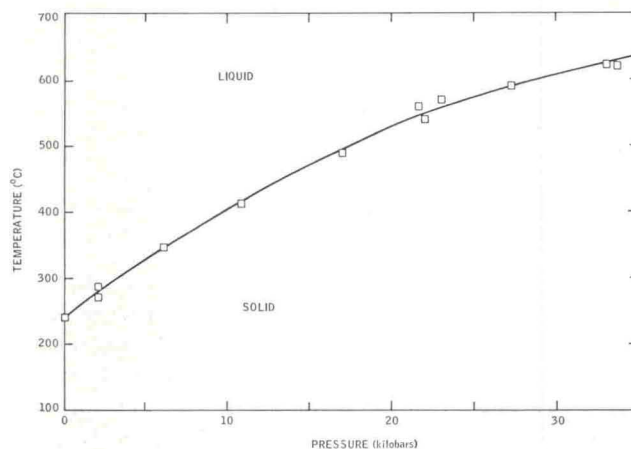
Figure 2. Pressure–temperature diagram for BiCl₃.

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 ± 5°, 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

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

(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 Fricke[17] 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

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

(16) H. von Wartenberg, *Z. Anorg. Allgem. Chem.,* **244,** 337 (1940).

(17) F. Hund and R. Fricke, *Z. Anorg. Allgem. Chem.,* **258,** 198 (1949).
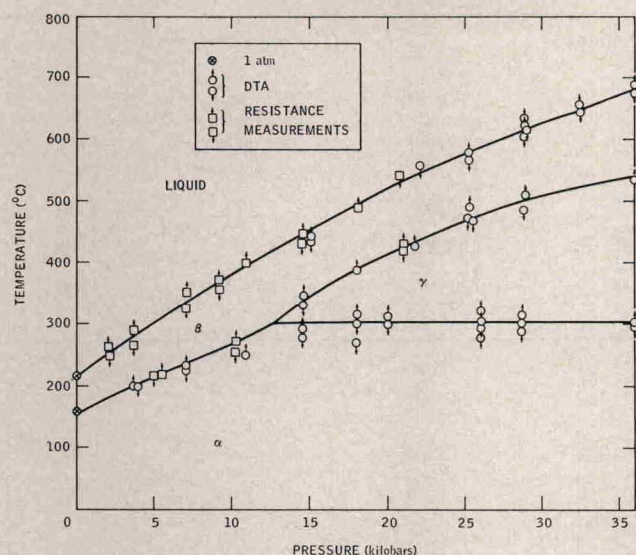
Figure 3. Pressure–temperature diagram for BiBr₃.

Figure 4. Pressure–temperature diagram for BiI₃.

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°/kbar. The $\alpha \rightleftarrows \beta$ transition reported at ambient pressure by Pushin[18] and by Wolten and Mayer[6a] was detected by dta and ac resistance methods. The temperature of this $\alpha \rightleftarrows \beta$ 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 $\alpha \rightleftarrows \beta$ transition in BiBr₃ 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°/kbar. Therefore, from eq 1 the $\alpha \rightleftarrows \beta$ transition volume should not be equal to zero. Wolten and Mayer[6a] have examined BiBr₃ 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 $\alpha \rightleftarrows \gamma$ 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.

BiI₃. Bismuth triiodide was examined by the same experimental techniques as were used for BiBr₃. The pressure–temperature phase diagram for BiI₃ is shown
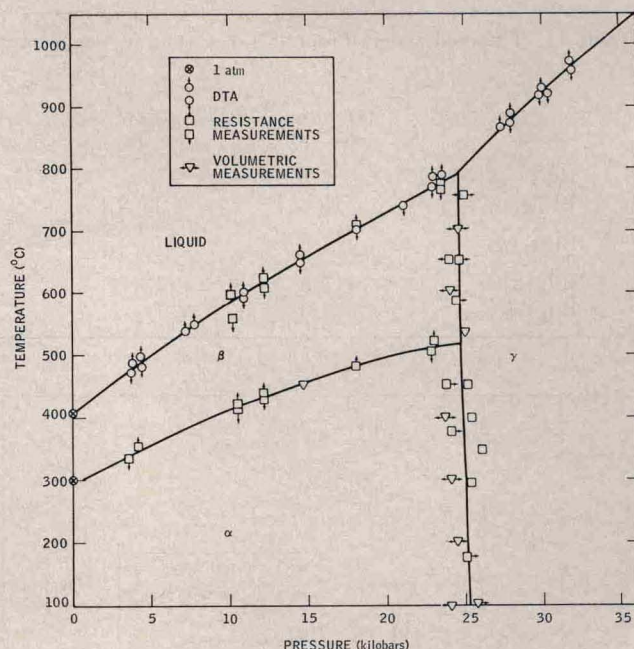
in Figure 4. Zahner and Drickamer[19] examined BiI₃ by optical adsorption at pressures up to 75 kbars but failed to detect the $\alpha \rightleftarrows \gamma$ transition at 25 kbars shown in Figure 4. This phase transition proceeds with a large volume change (~5%) but is very sluggish at room temperature. 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 BiI₃ 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 $\alpha \rightleftarrows \gamma$ transition. The volume *vs.* pressure curve also exhibits a similar hysteresis effect. The $\alpha \rightleftarrows \gamma$ 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).