

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

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

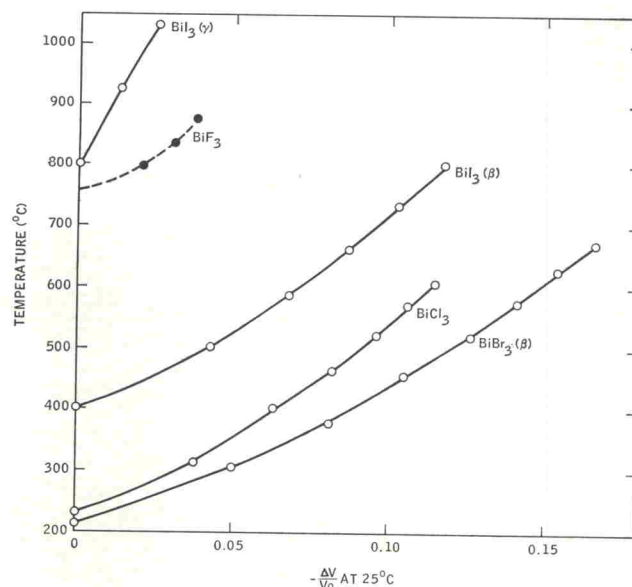


Figure 8. Melting temperature vs. compression ($-\Delta V/V_0$) for bismuth trihalides (Kennedy equation).

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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