maximum in the melting curve of Glauber's salt $(Na_2SO_4 \cdot 10H_2O)$.[15] As a sequel to Tammann's work, Bridgman[24] considered the problem of the general shape of the melting curve in detail in two papers, giving measurements on a number of substances to 12 kbar. On the basis of his experimental results he concluded that the normal shape of the melting curve embodies a monotonic rise in the melting temperature with pressure. Schames[25] proposed that at high pressures the melting curve asymptotically approaches some limiting temperature.

Simon[26] suggested an empirical equation for a melting curve, normal with respect to Bridgman's conclusions. The Simon equation,

$$P_m/a = [T_m/(T_m)_0]^c - 1,$$

where $a$ and $c$ are positive constants and $(T_m)_0$ is the temperature-axis intercept of the curve, has often been used to fit experimental data. Several investigators have found the Simon equation appropriate only over moderate pressure ranges.[21]

Experimental determinations of melting under pressure in recent years have led to further questioning of the validity of the idea that the normal curve has a positive slope and thus conforms to the general Simon shape. Fusion curves with negative slopes have been reported for bismuth,[21] gallium,[27] water,[15] antimony,[21] silicon,[28] germanium,[29] indium phosphide,[28] indium arsenide,[28] indium antimonide,[28,30] gallium arsenide,[28] gallium antimonide,[28] and aluminum antimonide.[28] Fusion curve maxima have been reported for tellurium, rubidium,[31] cesium,[32] barium,[33] bismuth telluride,[34] lead telluride,[11] antimony telluride,[11] europium,[35] potassium nitrate,[36] and carbon.[37] Jayaraman[35] has just recently reported the first minimum in a fusion curve, that of cerium. Thus, what were once considered anomalous occurrences appear to have become rather widespread phenomena. It therefore appears that the Simon equation does not represent a general fusion curve as it does not allow a maximum, minimum, or negative slope.

The inapplicability of the Simon curve is not surprising if one considers the limitations on its validity. Although originally an empirical relationship, the Simon equation has been derived independently by several investigators.[38,39] All of these theoretical developments assume an isotropic, monatomic solid. However, most of the substances known to possess anomalous melting curves (i.e., not having a slope greater than zero) have rather open, anisotropic crystal structures. Furthermore, Gilvarry[39] has stated that even when theoretically applicable, the Simon equation should be viewed more as an interpolation formula than as a basic fusion equation.[39a]

Voronel[40] also obtained the Simon equation by arbitrarily assuming a linear dependence on pressure of the ratio of the heat of fusion to the volume change, in the Clapeyron equation. More recently Voronel[41] modified the general Simon formula to permit melting curves with negative slopes by introducing an effective temperature (the absolute temperature reduced by an additive constant).

No general fusion-curve equation which would allow maxima and/or minima has been proposed. However, Knopoff has arbitrarily regarded the Simon constants as a function of pressure, thus arriving at a fusion curve allowing maxima.[42] Such an assumption is just a higher order approximation of Voronel's procedure.

At present, it would seem then that a melting curve more specific than the Clapeyron equation, yet maintaining the desired generality, does not exist. Thus, various fusion curve phenomena are best interpreted and correlated in terms of specific characteristics of the material involved and general properties of substances demonstrating similar behavior.

## B. Group VI B Melting Curves

As might be expected on the basis of the above discussion, little success was achieved in correlating the results presented here and the Simon equation. Obviously, it cannot be used to represent the tellurium melting data, since it does not allow for a maximum. Although Babb[4] fitted his selenium data up to 10 kbar and found Simon constants of $a = 11.1 \pm 0.7$ kbar and $c = 2.04 \pm 0.1$, the upper portion of the curve shown in

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TABLE I. Comparison of experimental melting curve slopes with those calculated on the basis of the Clapeyron equation.

| | | Atmospheric pressure values | | | |
|---|---|---|---|---|---|
| Element | Melting point $T_m$(°K) | Entropy of melting $S\left(\dfrac{\text{cal}}{\text{°K g atom}}\right)$ | Relative volume change on melting $\Delta V/V$ | Clapeyron $\dfrac{dT_m}{dP_m}\left(\dfrac{\text{°K}}{\text{kbar}}\right)$ | Experimental $\dfrac{dT_m}{dP_m}\left(\dfrac{\text{°K}}{\text{kbar}}\right)$ |
| S (rhombic) | 386 | 1.06[a] | 0.055[b] | 32 | 30[d] |
| Se | 490 | 3.04[b] | 0.159[b] | 21 | 24 |
| Te | 725 | 5.80[b] | 0.054[e] | 4.6 | 5.4 |

[a] Estal D. West, J. Am. Chem. Soc. 81, 29 (1959).
[b] O. Kubaschewski, Trans. Faraday Soc. 45, 931 (1949).
[e] See Ref. 11.
[d] See Ref. 15.

Fig. 2 departs significantly from the Simon equation using these constants. For sulfur the error involved in arriving at values for $a$ and $c$ is so large that such a calculation is meaningless. Mills and Grilly[43] have observed similar difficulties in arriving at unique and accurate values for $a$ and $c$. Considering the complexity of the crystal lattices of S, Se, and Te, and the previous discussion, the failure of the Simon curve to fit the data presented is not surprising.

Knowledge of the volume change and latent heat upon melting at atmospheric pressure permits the calculation of the initial slope of the fusion curve from Clapeyron's equation. Table I gives, for the Group VI B elements, a comparison of the experimental initial slopes and the initial slopes calculated using the Clapeyron equation and latent heats and volume changes of indicated source. The agreement between the two slopes is good considering the accuracy of the $\Delta V$ and $\Delta S$ values given. Also given in Table I are the atmospheric-pressure melting points.

One of the most interesting characteristics of the data presented is the maximum in the melting curve of tellurium. The Clapeyron equation requires $\Delta V$ to be zero at the maximum and negative at all points in this phase beyond the maximum. Thus, at pressures beyond the maximum, the density of the liquid at the melting point is greater than that of the solid. Two immediately apparent explanations for a melting curve maximum are: (1) increases in the coordination of the liquid concomitant with pressure at such a rate that the density of the liquid becomes greater than that of the solid; and (2) a solid-state phase boundary intersecting the melting curve at the maximum. Since support for the latter alternative has not, in general, been found, most observers have turned to the former. Ball[11] and Jayaraman[35] have supported the first alternative as constituting the most fruitful approach.

In the case of tellurium, Kalbakina et al.,[19] have explained the melting curve maximum by the existence of an apparent second-order phase transition at 15 kbar and room temperature. However, as previously pointed

out, McWhan and Jamieson[20] failed to observe this transition, even with careful compressibility measurements made using an x-ray diffraction apparatus. Also, measurements of electrical resistance and electronic energy gap by the authors[10] gave no indication of this transition. There is, therefore, some doubt concerning the presence of this phase transition.

Several investigations of the structure and properties of liquid tellurium at atmospheric pressure have been undertaken.[44-46] X-ray studies[44] indicate that the chain structure with covalent bonding and a coordination number of 2 is retained just above the melting point. Due to this persistence of the chain structure, hole conduction dominates conduction by electrons, the Hall coefficient and thermoelectric power being positive.[46] As the temperature is increased, the number of covalent bonds (and thus holes) decreases and the number of tellurium ions and free electrons increases. The Hall coefficient is found to reverse sign at about 575°C, showing that electrons are beginning to dominate the conduction process. The semiconducting behavior is observed up to 625°C where the resistivity becomes constant, remaining so until 670°C at which point metallic behavior begins.[46] Furthermore, liquid tellurium has a minimum[47,48] in the temperature dependence of its volume. Mokrovskii and Regel[47] observed kinks in the dependence of the electrical resistance and viscosity on the temperature, at the temperature of the volume minimum. All of the above properties of liquid tellurium can be understood by considering its structure.[46] Just above the melting point, the chain structure dominates. As the temperature increases the chains are progressively broken, yielding ionized atoms and electrons free to conduct. Johnson[45] successfully developed an expression for the electrical conductivity of tellurium

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