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

Element	Melting point T_m(°K)	Atmospheric pressure values			
		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[c]	4.6	5.4

[a] Estal D. West, J. Am. Chem. Soc. 81, 29 (1959).
[b] O. Kubaschewski, Trans. Faraday Soc. 45, 931 (1949).
[c] 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 ΔV and ΔS 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 ΔV 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

[43] R. L. Mills and E. R. Grilly, Phys. Rev. 99, 480 (1955).

[44] R. Buschert, I. G. Geib, and K. Lark-Horovitz, Phys. Rev. 98, 1157(A) (1955); Bull. Am. Phys. Soc. 1, 340 (1956).
[45] V. A. Johnson, Phys. Rev. 98, 1567(A) (1955).
[46] A. S. Epstein, H. Fritzsche, and K. Lark-Horovitz, Phys. Rev. 107, 412 (1957).
[47] N. P. Mokrovskii and A. R. Regel, Zh. Techn. Fiz. 25, 2093 (1955) [English abstract transl.: Chem. Abstr. 50, 3028e (1956)].
[48] W. Klemm, H. Spitzer, W. Lingenberg, and H. J. Junker, Monatsh. Chem. 83, 629 (1952) [English abstract transl.: Chem. Abstr. 46, 10747b (1952)].