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 $a=11.1\pm0.7$ kbar and $c=2.04\pm0.1$, the upper portion of the curve shown in

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