TABLE II. Data for the initial melting slopes (in °/kbar).

	Present work				
		Corrected for the effects of pressure on Pt versus Pt+10%Rh thermocouples according to:			
	Experimental data	Hanneman-Strong[b]	Getting-Kennedy[c]	Previous work[a]	Predicted value
Copper	$\sim 3.9_5$[d]	$\sim 4._9$	$\sim 4._3$	4.6[e]	3.65 ± 0.27
Silver	5.87 ± 0.27	$\sim 6._9$	$\sim 6._0$	5.0[f]	$\sim 5.9_4(\pm 0.3?)$
Gold	$\sim 6.1_2$	$\sim 7._2$	$\sim 6._5$	5.91[g]	$\sim 6.0 - 6.6$[d]

[a] See Table I.
[b] See Ref. 9.
[c] See Ref. 10.
[d] See text.
[e] See Ref. 2.
[f] See Ref. 3.
[g] Assumed by Ref. 4; see text.

present experimental error. The melting data from the present investigation do indicate curvature, beyond experimental uncertainty, at the highest pressures. With an assumed zero-pressure intercept of 1063°C, the present data suggest an initial melting slope of $\sim 6.1_2$°/kbar. If thermocouple corrections according to Hanneman and Strong[8] are applied, this slope is increased to $\sim 7._2$°/kbar; corrections according to Getting and Kennedy suggest a value of $\sim 6._5$°/kbar. The effort to estimate the initial melting slope of gold from zero-pressure data (Table I) is hampered by what is believed to be an inadequate knowledge of the volume change of fusion. Sufficiently precise data for the density of liquid gold, for comparison with the density of the solid, appear to be unavailable and thus Losana's direct measurement[13] of the volume change must be considered; since the volume changes for copper and silver, as determined in a similar way as gold and reported in the same paper,[13] are low compared to the preferred values (Table I), it is exceedingly likely that the volume change for gold is also low. Thus a lower bound of ~ 6.0°/kbar seems to be the best estimate possible; an upper bound for the melting slope may be in the vicinity of 6.6°/kbar (Table I).

IMPLICATIONS FOR THE DETERMINATION OF THE EFFECTS OF PRESSURE ON THERMOCOUPLE EMF

Hanneman and Strong[8] have given an extensive and detailed discussion of corrections to be applied to thermocouple emfs at high pressures and temperatures so as to obtain true temperatures. An important step in their analysis[8] is the comparison of various phase trajectories calculated from zero-pressure data with the actual high-pressure determinations; the discrepancy in such a comparison is then mostly attributed to the effect of pressure on thermocouple emf and an absolute correction is thus obtained. It seems clear, however, that the uncertainties are such in the calculations and experiments for the melting of germanium, the α-γ iron transition and the graphite-diamond equilibrium line—the phase transformations treated by Hanneman and Strong[8]—that only uncertain corrections can be obtained. The present results offer a further, perhaps more reliable basis for such a comparison.

The silver data are probably the most precise. Comparison of the predicted value for the melting slope, $\sim 5.9_4(\pm 0.3?)$°/kbar, shows good agreement with the experimental value of 5.87 ± 0.27°/kbar but profound disagreement with the value obtained by modifying the data according to the Hanneman-Strong correction, $\sim 6._9$°/kbar. The data for copper are less certain but a similar disagreement of Hanneman-Strong corrections of the present data with the predicted values seems clear. The predicted value for gold is too uncertain to allow any comparison. It thus appears undeniable that the proposed correction for Pt versus Pt+10% Rh thermocouples is too large, at least in the temperature range immediately above 1000–1100°C. The recent preliminary data of Getting and Kennedy[9] on the effect of pressure on thermocouple emf yield corrected slopes (Table II) at less variance with the predicted values.

CONSIDERATIONS FOR THE CURVATURE OF MELTING CURVES

The curvature, or change in slope with pressure, of the phase boundary for a first-order transition is

$$\frac{d^2T}{dp^2} = \frac{1}{\Delta V}\left(\frac{dT}{dp}\right)\left\{\left(\frac{\partial \Delta V}{\partial p}\right)_T + 2\left(\frac{dT}{dp}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_p - \left(\frac{dT}{dp}\right)^2 \frac{\Delta C_p}{T}\right\}. \quad (1)$$

Bridgman[14] has suggested that

$$-\left(\frac{\partial \Delta V}{\partial p}\right)_T \geqslant \left(\frac{dT}{dp}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_p \geqslant \left(\frac{dT}{dp}\right)^2 \frac{\Delta Cp}{T} \quad (2)$$

and

$$-\left(\frac{\partial \Delta V}{\partial p}\right)_T - \left(\frac{dT}{dp}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_p \geqslant \left(\frac{dT}{dp}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_p - \left(\frac{dT}{dp}\right)^2 \frac{\Delta Cp}{T} \quad (3)$$

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[13] L. Losana, Gazz. Chim. Ital. 68, 836 (1938).

[14] P. W. Bridgman, *The Physics of High Pressures* (The Macmillan Company, New York, 1931).

for the physical situations, where $dT/dp \geqslant 0$ and $d^2T/dp^2 \leqslant 0$. Among melting curves, there are a few[1] with $dT/dp < 0$ and but one (cerium[15]) thus far with $d^2T/dp^2 \geqslant 0$. The thermodynamic data for the melting of copper, silver and gold (Table I) are probably more precise and extensive than those for other elements with relatively high melting points. One of the most uncertain of the data in Table I is probably the value for the thermal expansion of liquid gold,[16] which is believed to be an overestimate because the values given in the same paper[16] for copper and silver are higher than the presently preferred values. There do not appear to be direct measurements of any type for the compressibilities of the liquids and solids near the melting points. The present experimental results and the data collected in Table I allow, however, estimates of $(\partial\Delta V/\partial p)$ via Eqs. (1), (2), and (3).

The suggested inequalities of Eqs. (2) and (3) must be subject to empirical testing for each material considered. For copper, silver, and gold, the inequality $(\partial\Delta V/\partial T)_p > (dT/dp)\Delta C_p/T$ is satisfied beyond doubt. *If* it is assumed that Eqs. (2) and (3) are valid, the following lower limits for $-(\partial\Delta V/\partial p)_T$ are estimated as (in units of cm^3/g atom Mbar) Cu, 1.6; Ag, 2.6; Au, 1.2 at the respective zero-pressure melting points. The bounds implied for $(\partial\Delta V/\partial p)$ via Eq. (1) may be examined by writing an equation for the melting curve as an expansion about the zero-pressure melting point, viz

$$T = T_0 + p(dT/dp)_{p=0} + \tfrac{1}{2}p^2(d^2T/dp^2)_{p=0} + \cdots. \qquad (4)$$

If the experimentally determined initial slopes are identified with $(dT/dp)_{p=0}$ and the deviations from linearity and/or experimental uncertainties are identified with the next term, estimates can be obtained for $(d^2T/dp^2)_{p=0}$. Thus

$$-2|\Delta T|/p^2 \lesssim (d^2T/dp^2)_{p=0}, \qquad (5)$$

where the right-hand side may be estimated from Eq. (1). The upper bounds for $-(\partial\Delta V/\partial p)_T$, obtained in this way, are: Cu, 7.5; Ag, 3.9; Au, 3.4 (in units of cm^3/g atom Mbar).

The validity of these bounds for $(\partial\Delta V/\partial p)_T$ is difficult to assess since the estimates are based on empirical relations [Eqs. (2) and (3)] and on experimental data uncorrected for the effects of pressure on thermocouple emf. Nevertheless, knowledge of $(\partial\Delta V/\partial p)_T$ is of great importance in any understanding of the course of the melting curve beyond the explored region since this term, involving the difference in compression between liquid and solid, is probably the dominant one in the expression for the variation in volume change with pressure, viz

$$\frac{d\Delta V}{dp} = \left(\frac{\partial\Delta V}{\partial p}\right)_T + \left(\frac{dT}{dp}\right)\left(\frac{\partial\Delta V}{\partial T}\right)_p. \qquad (6)$$

It is more likely that the pertinent zero-pressure data are available for estimating the variation in entropy change with pressure, viz

$$\frac{d\Delta S}{dp} = -\left(\frac{\partial\Delta V}{\partial T}\right)_p + \left(\frac{dT}{dp}\right)\frac{\Delta C_p}{T}. \qquad (7)$$

$d\Delta S/dp \approx 0.1 \pm 0.3$ for copper, -2 ± 1 for silver, and -1.4 ± 0.4 for gold (in units of cal/g atom Mbar). It can be readily appreciated that the standards for these types of data must be very high. Only highly precise zero-pressure determinations combined with careful high-pressure experiments can give a proper basis, beyond the accumulated uncertainty, for internally self-consistent results and for any extrapolation to higher pressures and temperatures. It is doubtful whether very many of the high-pressure, high-temperature data in the literature could meet such stringent requirements.

CONCERNING THE LINDEMANN RELATION

Most of the theoretical rationalizations of the Simon equation are based on some form of the Lindemann relation, which may be expressed here as

$$M^{1/2}V^{1/3}T^{-1/2}\vartheta = \text{“constant”}, \qquad (8)$$

where M is the mass of the element, V the volume of the solid at the melting point, T the absolute melting point, and ϑ the Debye temperature. For related series of elements, the "constant" often varies by less than 10%. For copper, silver and gold, the variation in the "constant" is about in this range for the Debye temperatures[17] derived from specific heat, elastic moduli, resistivity, thermal expansion and x-ray intensity measurements. For the Debye temperatures deriving from elastic-moduli data, as computed by Gschneidner,[17] the variation in the "constant" is less than 2%.

It should be possible to investigate the utility of the Lindemann relation for theories of melting at high pressure if measurements allowing the derivation of Debye temperatures at high pressure were available for comparison with data for the compression and melting curve of the element. In general, there are only limited data allowing estimation of the Debye temperatures at high pressure except that, fortunately, the elastic moduli at 300°K of copper, silver, and gold have been measured by Daniels and Smith[18] to 10 kbar.

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[15] A. Jayaraman, Phys. Rev. **137**, A179 (1965).

[16] W. Krause and F. Sauerwald, Z. Anorg. Allgem. Chem. **181**, 347 (1929).

[17] K. A. Gschneidner, Solid State Phys. **16**, 275 (1964).

[18] W. B. Daniels and C. S. Smith, Phys. Rev. **111**, 713 (1958).