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

	Present work: Experimental data	Present work, corrected for the effects of pressure on Pt versus Pt+10%Rh thermocouples according to: Hanneman-Strong[b]	Present work, corrected for the effects of pressure on Pt versus Pt+10%Rh thermocouples according to: 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.

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

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

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

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