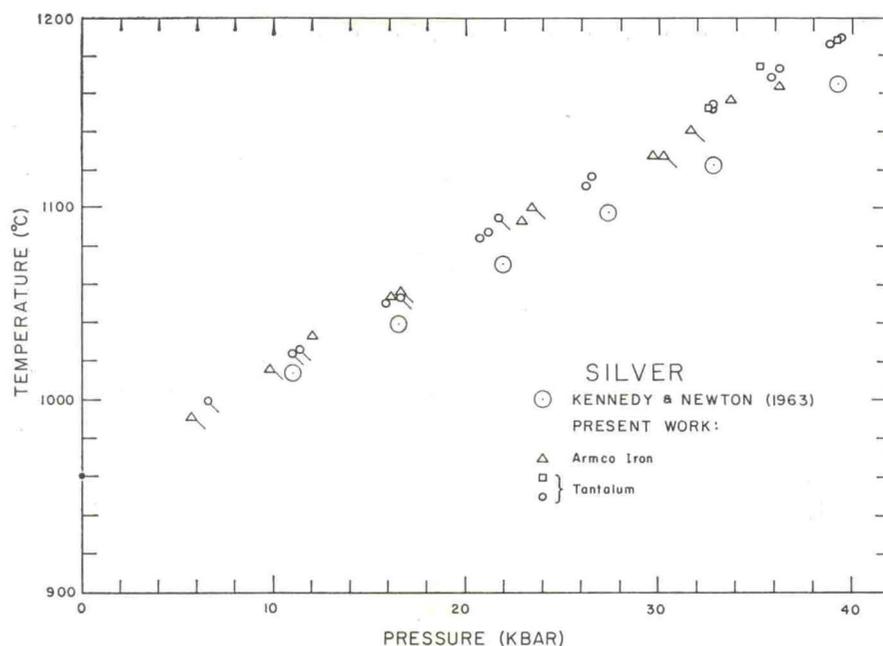


FIG. 2. Data for the melting of silver, together with the results of Kennedy and Newton. The various symbols correspond to different runs and container materials; the symbols with tails denote data obtained upon decompression cycles, those without tails refer to compression. The accepted zero-pressure melting point is indicated.



Armco iron and tantalum with Pyrex stoppers; there was no evidence for reaction between samples and containers, in accord with the more careful reports in the literature.⁷ Data in the range of 5 to 40 kbar were obtained and are shown in Fig. 2. Precise determinations of friction were made in each run and were less than 3 kbar, double-value. The data, uncorrected for any effects of pressure on thermocouple emf, are believed precise to $\pm 4^\circ$ and accurate to ± 1.0 kbar (Fig. 2).

The present data for silver, uncorrected for the effect of pressure on thermocouple emf, can be fitted with

straight lines of slope $5.87 \pm 0.27^\circ/\text{kbar}$ passing through the zero-pressure melting point of 960.8°C (Fig. 2).

If the thermocouple corrections according to the data of Hanneman and Strong⁸ are made, the slope is increased to $\sim 6.9^\circ/\text{kbar}$; according to Getting and Kennedy,⁹ the slope is altered to $\sim 6.0^\circ/\text{kbar}$. Kennedy and Newton³ reported data for the melting of silver in iron¹⁰ capsules up to 40 kbar; the melting temperatures, determined with chromel-alumel thermocouples, increased linearly with pressure at the rate of $5.0^\circ/\text{kbar}$ (Fig. 2). There are at least several possible reasons why

TABLE I. Pertinent thermodynamic data near the zero-pressure melting points.

	Copper	Silver	Gold
Entropy of fusion (cal/g atom) ^a	2.3 ± 0.1	$\sim 2.3_1$	$\sim 2.2_1$
Volume (cm ³ /g atom)	liquid	7.951 ± 11^b	11.543 ± 13^c
	solid	7.601^e	10.969^f
Volume change of fusion (cm ³ /g atom)	0.350 ± 11	0.574 ± 13	$\sim 0.6_1; \geq 0.56_0^h$
$(\partial V/\partial T)_P (10^{-4} \text{ cm}^3/\text{g atom}^\circ)$	liquid	$\sim 7.9_7^b$	11.20 ± 2^c
	solid ⁱ	6.02^e	9.69^f
$(\partial \Delta V/\partial T)_P (10^{-4} \text{ cm}^3/\text{g atom}^\circ)$	liquid	$\sim 1.9_8$	1.51 ± 2
	solid	~ 7.5	~ 7.3
C_p (cal/g atom ^o) ^a	liquid	~ 7.5	~ 7.0
	solid	7.4_7	7.7_0
ΔC_p (cal/g atom ^o)	$0.0_8 (\pm 0.1?)$	$-0.4 (\pm 0.2?)$	$-0.3 (\pm 0.1?)$
(dT/dp) ($^\circ/\text{kbar}$) calculated	3.65 ± 0.27	$\sim 5.9_4 (\pm 0.3?)$	$\sim 6.0-6.6$

^a R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values for the Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).

^b J. A. Cahill and A. D. Kirshenbaum, *J. Phys. Chem.* **66**, 1080 (1962).

^c A. D. Kirshenbaum, J. A. Cahill, and A. V. Grosse, *J. Inorg. Nucl. Chem.* **24**, 333 (1962).

^d R. O. Simmons and R. W. Baluffi, *Phys. Rev.* **129**, 1533 (1963).

^e R. O. Simmons and R. W. Baluffi, *Phys. Rev.* **119**, 600 (1960).

^f R. O. Simmons and R. W. Baluffi, *Phys. Rev.* **125**, 862 (1962).

^g See Ref. 16.

^h See Ref. 13.

ⁱ Values deduced from measurements of macroscopic volume, not from lattice-parameter measurements.

¹⁰ R. C. Newton (private communication).

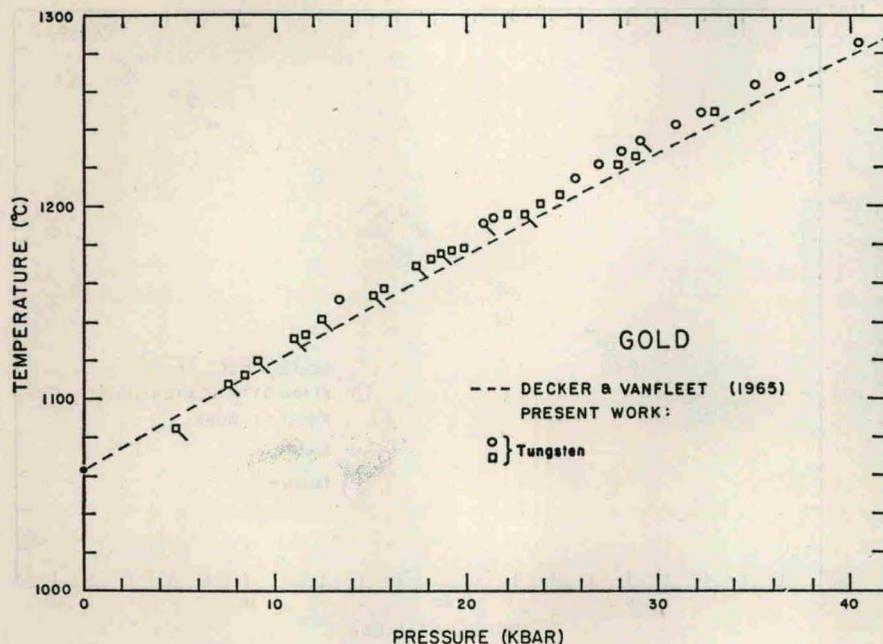


FIG. 3. Data for the melting of gold, together with the curve suggested by Decker and Vanfleet (see text). The two symbols correspond to separate runs in tungsten containers; the symbols with tails denote data obtained upon decompression, those without tails refer to compression. The accepted zero-pressure melting point is indicated.

the Kennedy-Newton data³ do not agree with the present results: first, their use of chromel-alumel thermocouples at the upper limit of their calibration and in the range of possible chemical deterioration; second, their probable slight overestimate of pressure at the higher pressures as evidenced, for example, by intercomparison of data¹¹ for antimony. The differing effect of pressure on the emf of chromel-alumel and Pt versus Pt+10% Rh thermocouples increases the discrepancy because of difference in the algebraic sign of the correction.^{8,9,12} The zero-pressure data (Table I) suggest an initial slope of $\sim 5.9_4^\circ/\text{kbar}$, with an uncertainty difficult to estimate but probably less than $\pm 0.3^\circ/\text{kbar}$.

Gold

Gold of 99.999% purity from American Smelting and Refining Company was run in capsules of Pyrex with a 5-mil thick tungsten disk between sample and thermocouple. There was no indication of any reaction between samples and containers. Gold apparently alloys with most metals, making it one of the more difficult materials to contain in metallic capsules, but no reaction was obvious with tungsten; unfortunately, there seem to be few data for the Au-W alloy system. The data from the two runs are shown in Fig. 3. The double-value of friction was, in all cases, less than 2 kbar; again, data below about 7 kbar were not obtained. The precision is estimated as $\pm 4^\circ$ and the accuracy as ± 1.0 kbar for the data (Fig. 3).

In the effort to find a suitable container for gold, runs were made in tantalum, in molybdenum and in a

Pyrex capsule similar to that finally settled upon except that the tungsten disk was painted on the side in contact with the sample with TV Tube Koat, which is apparently colloidal carbon in an organic solvent. Runs in Mo and Ta were rejected because they showed signs of sample contamination. The run in Pyrex, with the carbon-coated tungsten disk, yielded good signals and a linear increase in temperature of $\sim 5.2^\circ/\text{kbar}$ up to about 30 kbar with a zero-pressure intercept of $1105 \pm 5^\circ\text{C}$. A fluorescence analysis of TV Tube Koat[®] did not indicate any constituents above atomic number 20. It is thus tentatively concluded that liquid gold reacts with carbon and that the course of peritectic or monotectic reaction had been followed in this particular run.

Decker and Vanfleet⁴ recently published data for the melting of gold to 70 kbar with the solid-liquid transition being detected by discontinuities in resistance. However, to obtain their smoothed melting curves, (i) they introduced shifts of the order of $\pm 10^\circ$ in temperature in order to accord with the zero-pressure melting point of 1063°C ; (ii) these shifts were combined with a juxtaposition of the raw data so that an assumed initial melting slope of $5.91^\circ/\text{kbar}$ was obtained, (iii) the room-temperature pressure calibration was corrected to the vicinity of the melting curve in a quantitatively obscure way; (iv) the pressure corrections above 40 kbar were made so that the data were consonant with a Simon equation fit of the data below 40 kbar, which in turn, depended, of course, on the assumptions made in the adjustment of the data near zero pressure.

The smoothed melting curve of Decker and Vanfleet for gold is plotted in Fig. 3, together with the results of this investigation. Disagreement is outside of the

¹¹ W. Klement, A. Jayaraman, and G. C. Kennedy, *Phys. Rev.* **131**, 632 (1963).

¹² F. P. Bundy, *J. Appl. Phys.* **32**, 483 (1961).