Melting of Copper, Silver, and Gold at High Pressures*

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The melting points of copper, silver, and gold have been determined up to about 40 kbar by means of differential thermal analysis in piston-cylinder apparatus. The melting curve of gold shows definite curvature in the explored pressure range, and slight curvature is suggested for copper; the melting temperature of silver rises linearly with pressure. The experimentally determined initial slopes, without any corrections attempted for the effects of pressure on thermocouple emf, are (in °/kbar): Cu, $\sim 3.9_5$; Ag, 5.87 ± 0.27; Au, $\sim 6.1_2$. Previous results of Gonikberg, Shakhovskoi, and Butuzov for copper, of Kennedy and Newton for silver and of Decker and Vanfleet for gold agree inadequately with the present data. Comparison of initial melting slopes with those predicted from thermodynamic data allows evaluation of proposed pressure corrections to emf of Pt versus Pt+10%Rh thermocouples; those proposed by Hanneman and Strong are shown to be too large. The linearity of the melting curve of silver, combined with its ease of containment, suggests its use for high-pressure, high-temperature calibration. Bounds for the initial variations in the volume changes of fusion with pressure may be estimated from the present results and zero-pressure data. The Lindemann relation for melting is examined for copper, silver, and gold by comparing the present results for melting with the 300°K data for the elastic moduli and their variation with pressure; agreement does not appear to be adequate.

INTRODUCTION

COPPER, silver, and gold comprise a group of metallic elements with well-investigated physical, chemical, and structural similarities. As with many other groups of related elements,[1] investigation at high pressures should serve to elucidate many of the similarities and differences in better detail. Some of the most important data which are unique to high-pressure experimentation are determinations of the trajectories of phase boundaries. Since copper, silver, and gold crystallize, insofar as is known, only in the face-centered cubic structure, the study of phase relations reduces to a determination of the melting curves. One report each for the melting of copper,[2] silver,[3] and gold[4] at high pressures exists in the literature; the present experiments were undertaken to test and extend these data, if possible, and to compare them with the predictions calculated from zero-pressure data. From an experimental and engineering viewpoint, precise and accurate determination of such phase transitions would be extremely useful in the calibration of many types of high-pressure apparatus at high temperatures. From a more fundamental point of view, the data for melting can be usefully compared with similar data for other series of elements and with theory in the search for generalizations.

GENERAL EXPERIMENTAL PROCEDURES

Quasi-hydrostatic pressure was generated in piston-cylinder apparatus, with the furnace assembly similar to the design described elsewhere[5] except that fired boron nitride was used instead of talc inside the carbon heating element. The metallic capsules employed to contain samples in the copper and silver experiments were sealed with stoppers of Pyrex, which softened at the operating temperatures and prevented escape of the liquid. For experiments with the more reactive gold, the capsule was almost entirely Pyrex. Transitions were detected by differential thermal analysis[6] using Pt versus Pt+10% Rh thermocouples. At a given pressure, the melting and freezing signals were reproducibly observed at leas three times, with a typical precision and reproducibility of ±1°, before the datum point was considered as determined. The signal on heating, at a given pressure, was taken as the equilibrium temperature for the transition. Often on decompression, the initial heating signal was observed to lie higher in temperature than the subsequent, reproducible signals, this effect probably being due to relaxation of friction in the apparatus. As discussed elsewhere,[6] the initial datum in a given run is taken only at pressures above 10 kbar or so because of mechanical limitations. The

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[1] W. Klement and A. Jayaraman, Progr. Chem. Solid State (to be published).
[2] M. Gonikberg, G. Shakhovskoi, and V. Butuzov, Zh. Fiz. Khim. 31, 350 (1957).
[3] G. C. Kennedy and R. C. Newton, *Solids Under Pressure* (McGraw-Hill Book Company, Inc., New York, 1963).
[4] D. L. Decker and H. B. Vanfleet, Phys. Rev. 138, A129 (1965).
[5] W. Klement, L. H. Cohen, and G. C. Kennedy, J. Phys. Chem. Solids 27, 171 (1966).
[6] L. H. Cohen, W. Klement, and G. C. Kennedy, J. Phys. Chem. Solids 27, 179 (1966).

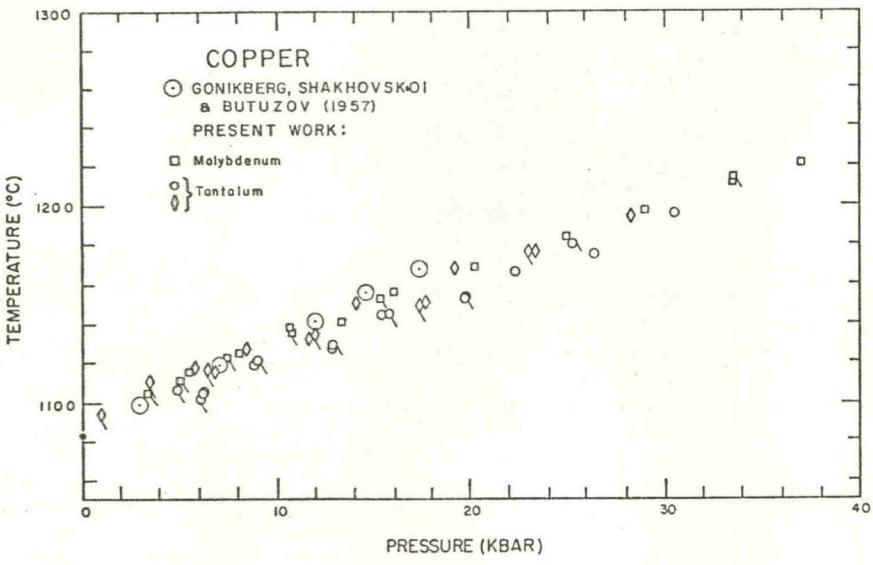

FIG. 1. Data for the melting of copper, together with the results of Gonikberg, Shakhovskoi, and Butuzov. The various symbols correspond to different runs and container materials; the symbols with tails denote data obtained upon decompression cycles, those without tails refer to compression. The accepted zero-pressure melting point is indicated.

transitions are then observed at various pressures on compression. On release of pressure, the transitions are again observed at several pressures. The difference in pressure, or "double-value of friction," is estimated for the same transition temperature as observed on compression and decompression. Friction is assumed to be symmetrical and the true pressure is thus obtained by interpolation. Datum-by-datum corrections for friction were made in order to enhance accuracy except at the lowest and highest pressures where this was not possible. In most cases, two or more compression and decompression cycles were run on the same sample in order to verify reproducibility of the data and to identify any progressive variation in the transition temperatures due to contamination.

EXPERIMENTS, RESULTS AND DISCUSSION

Copper

Copper of 99.999% purity from American Smelting and Refining Company was run in capsules of molybdenum and tantalum with Pyrex stoppers. There was no indication of any reaction between samples and containers; the scanty zero-pressure data[7] for the Cu-Mo and Cu-Ta binary systems suggest little alloying. The data from the several runs are shown in Fig. 1. The double-value of friction was, in all cases, less than 2.5 kbar; the friction corrections below about 5 kbar were, however, not precisely established because of the difficulty in obtaining data at low pressures.

The data for copper, uncorrected for the effect of pressure on thermocouple emf, can be fitted with a straight line of slope $\sim 3.9_5$°/kbar with a scatter of about $\pm 10°$ *if* an intercept at the zero-pressure melting point of 1083°C is assumed (Fig. 1). A better linear fit of the data is obtained for a line of slope $\sim 3.6_2$°/kbar and scatter about $\pm 7°$, but a zero-pressure intercept of $\sim 1090°$ is required. If some curvature, $d^2T/dp^2 < 0$, is allowed, an even better fit is possible. A critical evaluation of the copper data suggests that the data below about 5 kbar are less reliable than the others because of the difficulty in applying corrections for friction; the possibility of slight (even 1–2%) alloying of the liquid with the containers is not excluded and such a reaction could alter the zero pressure intercept to a temperature other than 1083°C; the possibility of curvature in the melting line is certainly present but the various uncertainties suggest that any deviations from a linear fit are not yet thoroughly established.

Corrections for the effect of pressure on thermocouple emf according to Hanneman and Strong[8] or Getting and Kennedy[9] would alter the melting slope from the uncorrected $\sim 3.9_5$°/kbar to $\sim 4._9$ or ~ 4.3°/kbar, respectively. Previous data for the melting of copper, published by Gonikberg, Shakhovskoi, and Butuzov,[2] suggest a linear increase of temperature with pressure, with a slope of 4.6°/kbar (uncorrected for the pressure effect on the emf of "platinum–platinum-rhodium" thermocouples) from experiments up to 18 kbar (Fig. 1). Besides the disagreement with the present results, the data[2] of Gonikberg *et al.*, are outside the range allowed by the zero-pressure data. A likely source of error is reaction between the copper and the "steel" they used to sheathe the thermocouple. The zero-pressure data for the volume and entropy change of fusion (Table I) bound the initial slope between about 3.3_8 and 3.9_2°/kbar.

Silver

Silver of 99.99+% purity, obtained from American Smelting and Refining Company, was run in capsules of

[7] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

[8] R. E. Hanneman and H. M. Strong, J. Appl. Phys. 36, 523 (1965).

[9] I. C. Getting and G. C. Kennedy (private communication).

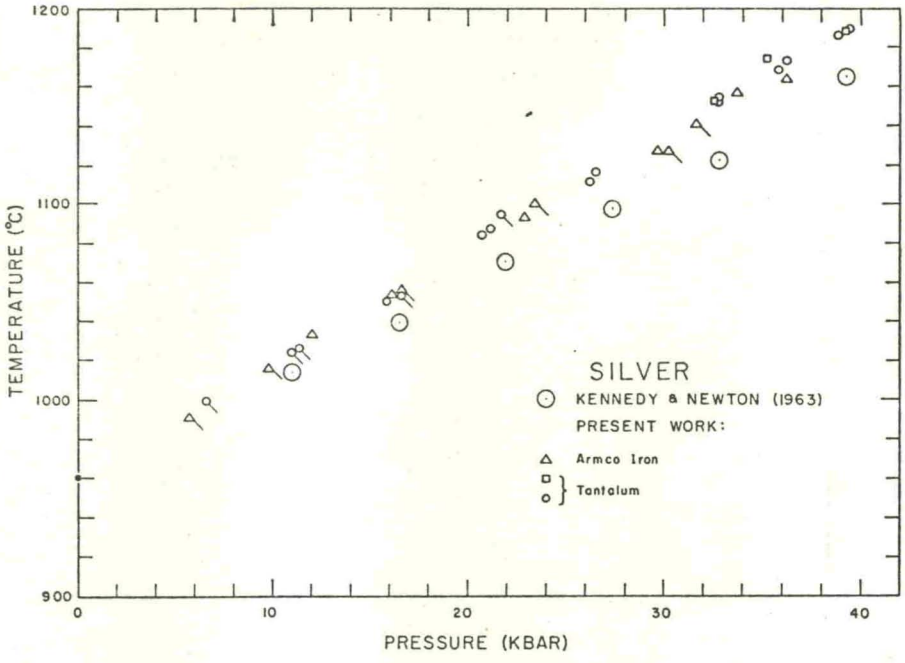

FIG. 2. Data for the melting of silver, together with the results of Kennedy and Newton. The various symbols correspond to different runs and container materials; the symbols with tails denote data obtained upon decompression cycles, those without tails refer to compression. The accepted zero-pressure 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 $\pm 4°$ 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 ± 0.27°/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 Strong[8] are made, the slope is increased to ~ 6.9°/kbar; according to Getting and Kennedy,[9] the slope is altered to ~ 6.0/kbar. Kennedy and Newton[3] reported data for the melting of silver in iron[10] capsules up to 40 kbar; the melting temperatures, determined with chromel-alumel thermocouples, increased linearly with pressure at the rate of 5.0°/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 (cm³/g atom)	liquid	7.951 ± 11[b]	11.543 ± 13[c]	11.4_0[d]
	solid	7.601[e]	10.969[f]	10.789[g]
Volume change of fusion (cm³/g atom)		0.350 ± 11	0.574 ± 13	$\sim 0.6_1$; $\gtrsim 0.56_0$[h]
$(\partial V/\partial T)_p$ (10^{-4} cm³/g atom°)	liquid	$\sim 7.9_7$[b]	11.20 ± 2[c]	~ 7.9[d]
	solid[i]	6.02[e]	9.69[f]	7.31[g]
$(\partial \Delta V/\partial T)_p$ (10^{-4} cm³/g atom°)		$\sim 1.9_5$	1.51 ± 2	~ 0.6
Cp (cal/g atom°)[a]	liquid	~7.5	~7.3	~7.0
	solid	7.4_7	7.7_0	7.3_1
ΔCp (cal/g atom°)		0.0_3 (± 0.1?)	-0.4 (± 0.2?)	-0.3 (± 0.1?)
(dT/dp) (°/kbar) calculated		3.65 ± 0.27	$\sim 5.9_4$ (± 0.3?)	~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. Balluffi, Phys. Rev. 129, 1533 (1963).
[e] R. O. Simmons and R. W. Balluffi, Phys. Rev. 119, 600 (1960).
[f] R. O. Simmons and R. W. Balluffi, 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).

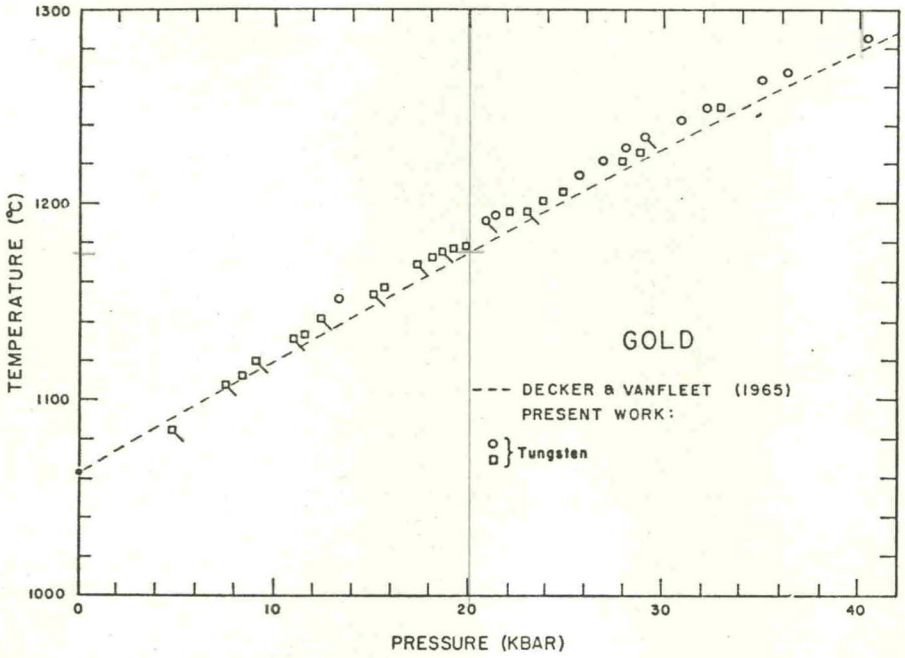

FIG. 3. Data for the melting of gold, together with the curve suggested by Decker and Vanfleet (see text). The two symbols correspond to separate runs in tungsten containers; the symbols with tails denote data obtained upon decompression, those without tails refer to compression. The accepted zero-pressure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

the Kennedy-Newton data[3] 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 data[11] 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 $\sim 5.9_4$°/kbar, with an uncertainty difficult to estimate but probably less than ±0.3°/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 ±4° 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 ~5.2°/kbar up to about 30 kbar with a zero-pressure intercept of 1105±5°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 Vanfleet[4] 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 ±10° 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°/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).

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]	~ 4.9	~ 4.3	4.6[e]	3.65±0.27
Silver	5.87±0.27	~ 6.9	~ 6.6	5.0[f]	$\sim 5.9_4(\pm 0.3?)$
Gold	$\sim 6.1_2$	~ 7.2	~ 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 ~ 7.2°/kbar; corrections according to Getting and Kennedy suggest a value of ~ 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, ~ 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

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

[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 $dT/dp \gtrsim 0$ and $d^2T/dp^2 \lesssim 0$. Among melting curves, there are a few[1] with $dT/dp < 0$ and but one (cerium[15]) thus far with $d^2T/dp^2 \gtrsim 0$. 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 $(\partial \Delta V/\partial T)_p > (dT/dp)\Delta Cp/T$ 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 cm³/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

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

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

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

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 cm³/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

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

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

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

$d\Delta S/dp \approx 0.1 \pm 0.3$ 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

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

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.

[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).

From the Lindemann relation,

$$\frac{1}{3V}\left(\frac{\partial V}{\partial p}\right)-\frac{1}{2T}\left(\frac{\partial T}{\partial p}\right)+\frac{1}{\vartheta}\left(\frac{\partial \vartheta}{\partial p}\right)=0, \qquad (9)$$

if the "constant" is indeed assumed to be constant.

For the calculation of the relative variation in the Debye temperature with pressure,

$$\frac{1}{\vartheta}\left(\frac{\partial \vartheta}{\partial p}\right)_{300°K}=-\frac{1}{3V}\left(\frac{\partial V}{\partial p}\right)_{300°K}+\frac{1}{v_m}\left(\frac{\partial v_m}{\partial p}\right)_{300°K}, \qquad (10)$$

where v_m is the averaged velocity of sound. This velocity variation with pressure is most conveniently computed from the observed elastic moduli variation by the method presented by Anderson[19]; although this method is less accurate than several others proposed, the over-all uncertainty in the calculation is perhaps not much more than the ca. 2% uncertainty in the elastic moduli data. Taking the zero-pressure, 300°K elastic moduli for copper from Schmunk and Smith,[20] for silver from Bacon and Smith[21] and from Neighbours and Alers[22] and for gold from Neighbours and Alers[22] and from Daniels and Smith,[18] $(1/v_m)(\partial v_m/\partial p)_{300°K}$ is estimated as 3.9 for Cu, 6.3 for Ag, and 7.3 for Au in units of (Mbar)$^{-1}$. The elastic moduli for these solid elements are not known near the melting points, but may be assumed to be similar to (or slightly less than) the 300°K values. Then, from Eqs. (9) and (10), $(1/2T)(dT/dp)$ should be approximately equal to $(1/v_m)(\partial v_m/\partial p)_{300°K}$. However, the experimental values for $(1/2T)(dT/dp)$ are ~1.5 for Cu, ~2.4±0.1 for Ag, and ~2.4 for Au, in units of (Mbar)$^{-1}$. Thus, from the viewpoint of the Lindemann relation, the observed increase of the melting point with pressure is from two to three times too small. Since this conclusion is based on an analysis of 300°K data, there is a possibility that better agreement might be achieved with high-temperature elastic moduli data. It is unlikely, however, that such large discrepancies could be removed without anomalously large variations in the moduli as temperature is increased.

Despite the extensive theoretical treatments, mostly by Gilvarry[23] and recently by Babb,[24] the Simon equation has not proved to be reliable in estimating the courses of melting curves; it seems to be at best a convenient two-parameter representation for data over an explored interval. The inadequacies in the theoretical derivations of the Simon equation are probably due mostly to the inadequacies of the Lindemann relation. In addition to the outright failures for the several elements with liquids more dense than the solids along the melting curves, the above calculations suggest that little confidence can be vested in the relation even insofar as elements as "normal" as copper, silver, and gold are concerned. The great difficulty of course is that this relation effectively ignores the properties of the liquid by imputing to it a structure rigidly related to that of the solid. This is in inadequate agreement with the data (Table I) which indicate volume changes of fusion of 4.60±0.15%, 5.23±0.12% and 5.2–5.7% for copper, silver and gold, respectively.

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