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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, $\sim 3.9_6$; 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 least 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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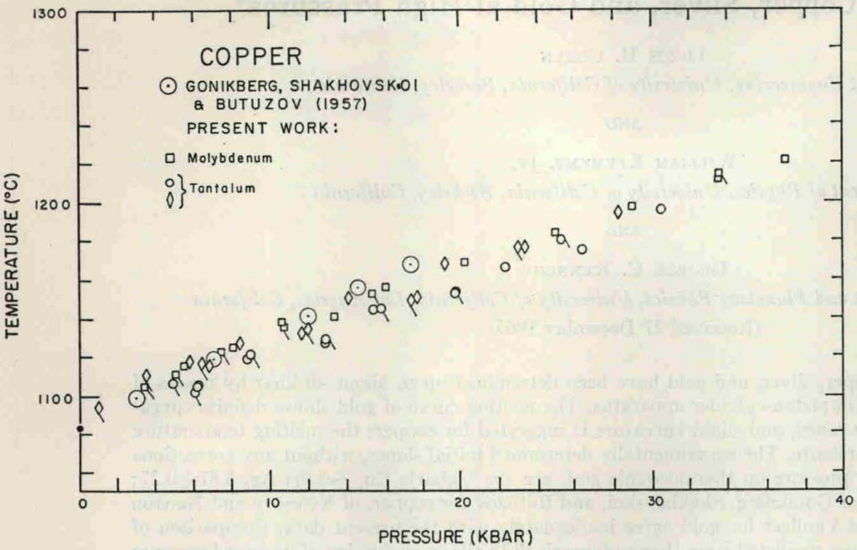

FIG. 1. Data for the melting of copper, together with the results of Gonikberg, Shakhovskoi, and Butuzov. The various symbols correspond to different runs and container materials; the symbols with tails denote data obtained upon decompression cycles, those without tails refer to compression. The accepted 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 ±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 ±7°, but a zero-pressure intercept of ~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 $\sim 4._3$°/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).