



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 data⁷ 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 $\sim 3.9^\circ/\text{kbar}$ with a scatter of about $\pm 10^\circ$ 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 $\sim 3.62^\circ/\text{kbar}$

and scatter about $\pm 7^\circ$, but a zero-pressure intercept of $\sim 1090^\circ$ 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 Strong⁸ or Getting and Kennedy⁹ would alter the melting slope from the uncorrected $\sim 3.9^\circ/\text{kbar}$ to ~ 4.9 or $\sim 4.3^\circ/\text{kbar}$, 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 $4.6^\circ/\text{kbar}$ (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 data² 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_3 and $3.9_2^\circ/\text{kbar}$.

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).