

the wire suddenly increased by a factor of about 2.2. Thus the melting temperature was sharply defined at each pressure.

Because the wire was tightly confined at these pressures it was possible to melt the wire successively many times, changing the pressure after each melting. The ram loading was calibrated to indicate pressure by measuring the resistance transitions in Bi (25.4 kbar), Tl (37 kbar), and Ba (58 kbar), and interpolating between these values with a smooth curve.

### III. MELTING CURVE

The temperature of melting was taken as the temperature at the beginning of the sudden resistance rise as indicated in Fig. 2. Because of the sharpness of the break in the resistance curve one can determine this point to better than  $\pm 2^\circ\text{C}$ . The accuracy of any temperature measurement however is probably only about  $\pm 10^\circ\text{C}$ , even though the thermocouple calibration at atmospheric pressure was accurate to  $\pm 5^\circ\text{C}$  at these temperatures, because no pressure correction to the thermal emf was attempted.<sup>23</sup>

Each run consisted of a set of melting points at various pressures. The results of the four successful melting runs did not all lie on the same curve. This could be due to variation in the thermocouple calibration or to thermal gradients along with the difficulty of placing the thermocouple junction at a point corresponding to the hottest region along the gold wire. Temperature gradients, large enough to account for the differences, are evident from the width of the transition which was between 20 and 30°C. In order to correct for this uncertainty the temperatures of each run were all raised or lowered by an amount such that the melting curves extrapolated to the correct melting point at atmospheric pressure with the slope calculated from Clapeyron's equation.<sup>24</sup> The corrections amounted to -13, -11, +5, and +11°C for the four runs. After this correction all points from all runs lay on a single smooth curve with a maximum scatter less than  $\pm 7^\circ\text{C}$ .

Another correction should be applied to the raw data because the pressure calibration was at room temperature rather than at the temperature of the experiment. The pressure cell expands with increasing temperature causing the pressure to rise. This does not appear as an increase on the oil pressure behind the rams because of internal friction in the pyrophyllite and friction in the pistons themselves. Above 40 kbar the gaskets are essentially immovable and it was assumed that the pressure increase due to heating was proportional to the temperature change from room tempera-

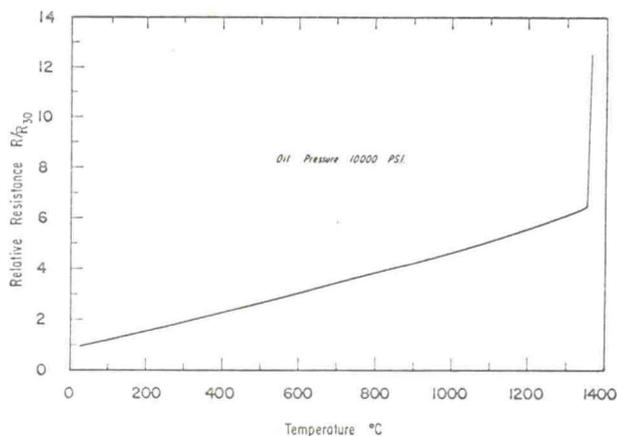


Fig. 2. Relative resistance of gold as a function of temperature at 10 000-psi oil pressure. (10 000-psi oil pressure corresponds to 52.2 kbar for the sample at room temperature.)

ture to the melting point. Below 15 kbar the gaskets are still forming and as the volume expands more material is forced into these gaskets between the anvils giving no pressure increase in this range. Between 15 and 40 kbar the correction was assumed to vary smoothly from 0 to the value at 40 kbar. Evidences for the above assumptions are: (a) Upon cooling the sample after melting at a pressure less than 15 kbar one notes a drop in the oil pressure. This indicates that the volume after the heating cycle is less than before allowing the rams to move in and the oil pressure to drop. (b) The raw melting curve between 15 and 40 kbar shows a slight upward curvature which is removed by applying the proposed pressure correction. The amount of the pressure correction above 40 kbar is not known so it was determined from the melting curve itself by assuming that this curve should have the form of Simon's equation.

The method of obtaining the pressure correction along with the coefficient  $c$  in Eq. (9) is outlined below. Substitution of  $T_m = T_{m,0} + \delta T$  into Eq. (9) and expanding in a power series in  $\delta T/T_{m,0}$  yields the following equation after some manipulation:

$$P_m - P_0' \delta T = \frac{(c-1)P_0' (\delta T)^2}{2 T_{m,0}} \left[ 1 + \frac{c-2}{3} \frac{\delta T}{T_{m,0}} \dots \right]. \quad (10)$$

If one plots experimentally measured values of  $(P_m - P_0' \delta T)$  versus  $(\delta T)^2$  as in Fig. 3 the points indicated by the open circles are obtained. The desired pressure correction is applied to the measurements above 40 kbar so as to cause them to fall along a curve satisfying (10) with a least-mean-square deviation. The final results are represented by the closed circles with  $c = 2.2 \pm 0.1$  and a maximum pressure correction of 3.9 kbar at 66.7 kbar. The corrected results are finally graphed in Fig. 4.

<sup>23</sup> F. P. Bundy, J. Appl. Phys. 32, 483 (1961).

<sup>24</sup> It is to be noted that one set of measurements, shown by the point numbers 2, 3, 4, 5, 7, 8, and 10 in Fig. 4, extend down to 3.5 kbar and have an initial slope of  $5.9 \pm 0.2^\circ\text{C}/\text{kbar}$  in excellent agreement with the value  $5.91^\circ\text{C}/\text{kbar}$  calculated from Clapeyron's equation.