pinched off during the formation of the gasket, it was found necessary to use protecting sheaths of pyrophyllite. (See Fig. 3.) When these sheaths, each of thickness 0.040 in., are placed on each side of a thermocouple lead where it enters the pyrophyllite tetrahedron, the incoming carbide anvils clamp down on the sheaths before the gaskets are formed, and the securely held sheaths prevent undue flowing of the pyrophyllite adjacent to the thermocouple wire. It was found possible to keep a thermocouple intact in this manner over the entire pressure range, as long as the pressure was increasing. However, the thermocouple would invariably break as the pressure was being released, indicating that considerable flowing of the pyrophyllite was taking place as the pressure was decreased.

The measurement of the sample temperature depends upon the reliability of the P-PR thermocouple over the entire pressure range. Strong[9] reports that in the General Electric Research Laboratories, several different thermocouples were compared on the "Belt" apparatus over a wide pressure and temperature range. It was concluded there that the handbook tables for P-PR probably agree with the true high-pressure calibration to within $\pm 10\%$. Further details on these tests are given in a later paper.[10] In a previous experiment at General Electric, Hall[14] had compared a P-PR thermocouple with a chromel-alumel thermocouple up to 100 000 atmospheres and 1000°C, and found agreement within 0.3% over the entire range. The question still seems to be largely unsettled.

As in the "Belt" apparatus, the pressure cannot be measured directly, but must be determined in terms of the applied load from a previous calibration of the apparatus. The pressure chamber can be calibrated by means of certain elements which undergo sharp resistance changes at certain fairly well-known pressures. These elements, for which the transitions and pressures at which they occur were measured by Bridgman,[15] are Bi (24 800 atm), Tl (43 000 atm), Cs (53 500 atm), and Ba (77 400 atm). Because of the difficulty encountered in working with cesium (extremely reactive, spontaneously igniting when exposed to air, and a liquid above 28.5°C), and because of some uncertainty in the transition pressure of thallium, only the bismuth and barium transitions were used for calibration purposes. The calibration curve is plotted in Fig. 4. The pressure calibration is thought to be accurate to $\pm 5\%$.

EXPERIMENTAL PROCEDURE

At a given pressure, the melting temperature is detected essentially by means of an electrical resistance change in the sample. The resistivity of molten indium, for example, is about three times that of the solid, and liquid tin has a resistivity of about four times that of the solid. (See *International Critical Tables*, Vol. 1, pp. 103–104.) In an experimental run, the heating power is

[14] H. T. Hall (unpublished).
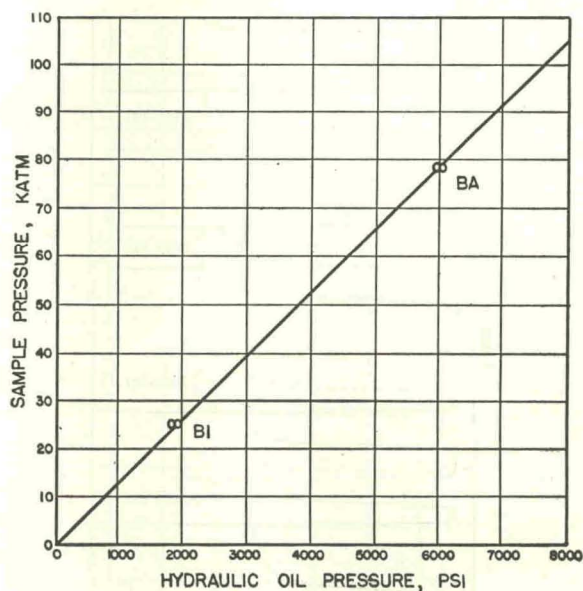[15] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, 165 (1952).

FIG. 4. Calibration curve for tetrahedral-anvil apparatus.

increased very slowly as the melting point is approached, in order to approximate a condition of equilibrium as far as heat flow and temperature distribution are concerned. Under this condition, the maximum temperature of the sample should occur at its center, near the thermocouple junction. As the melting temperature is attained at this hottest point, the sample begins to melt at its center, and increases in resistance. Now the resistance of the entire sample is a fairly small fraction of the total resistance in the leads, connections, etc., in the heating circuit, so that even though the sample resistance may increase by several times its initial value, the effect on the total circuit resistance is small. This means that the current remains nearly constant as the sample melts, while the voltage drop through the sample increases significantly. Hence, as the sample begins to melt, the heating power is sharply increased in the molten portion, and the temperature accordingly undergoes a sharp increase. This effect causes the entire sample to quickly melt from the center outwards, in a sort of "avalanche effect," and the strip-chart recorder indicates a sharp increase in the thermal emf, corresponding to a jump of about 55°C in indium, or about 85°C in tin. (See Fig. 5.) The melting temperature is taken to be the thermocouple-recorded temperature at which the "avalanche" begins; that is, the value of the temperature at the initial point of its sudden increase.

The lowest pressure at which melting point measurements were made was about 6500 atmospheres. Readings at pressures below this point were found to be inconsistent and inaccurate. Gasket formation takes place from about 3000 to 5000 atmospheres, and evidently pressure is not effectively transmitted from the anvils in to the sample until the gaskets are fully formed. The melting temperature was usually measured at about
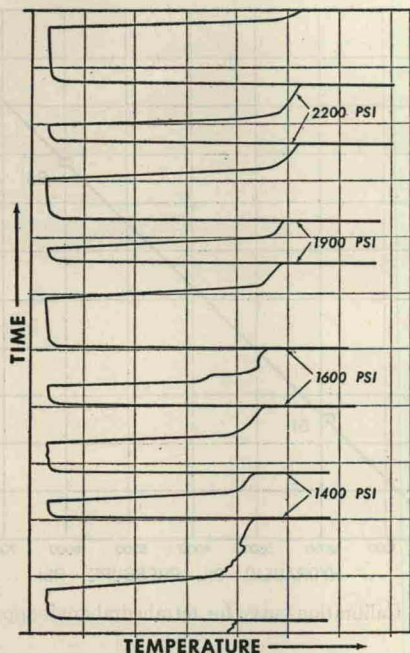
FIG. 5. Typical strip-chart record of melting.

every 6500 atmospheres, although on some runs measurements were made at about every 1300 atmospheres. (The 6500-atmosphere increment corresponds to an increment of 500 psi in the oil pressure of the hydraulic rams. This means that measurements were made at every 500 psi up to a maximum of 8000 psi, which corresponds to 105 000 atmospheres.)

Considerable variance existed in the measured fusion curves for a given substance, due to the difference in heat loss of the various samples. For example, out of the fusion curves that were measured for indium (three with graphite sleeves, two with Nichrome sleeves, and two without any sleeves, the sample being placed directly in the pyrophyllite with the thermocouple junction in the center of the sample), the measured melting temperatures at about 80 000 atmospheres were as follows: for the three with graphite sleeves, 335°C, 329°C, and 301°C; for the two with Nichrome sleeves, 308°C and 303°C; and for the two without sleeves, 336°C and 259°C. This represented a spread of about 25%, compared to the average.

In order to correct for this heat loss (due in this case to thermal conduction radially outwards from the midpoint of the sample), the following first-approximation correction formula was used:

$$t = t_m + k(t_m - t_a),$$ (1)

where t is the corrected temperature at the center of the sample where melting begins, t_m is the measured temperature recorded by the thermocouple, and t_a is the ambient temperature of the anvils, taken to be the temperature to which the thermocouple immediately drops just when the power is shut off after detection of a

melting point. The proportionality constant k for a given sample was determined by extrapolating the fusion curve for that sample into the temperature axis, comparing the extrapolated value of the normal melting temperature with its known value, and using Eq. (1). The gratifying and rather astonishing result of applying this temperature correction to the measured fusion curves of both indium and tin was a very close correspondence of the corrected curves in each case over the entire pressure range. For example, the total spread in the corrected values of the melting temperature for a given pressure was less than 4% of the average. (Compare this to 25% for the uncorrected values.)

The largest source of error in the corrected values of melting temperature was considered to be the extrapolation involved in the temperature correction. This involved a rather arbitrary extension of the measured
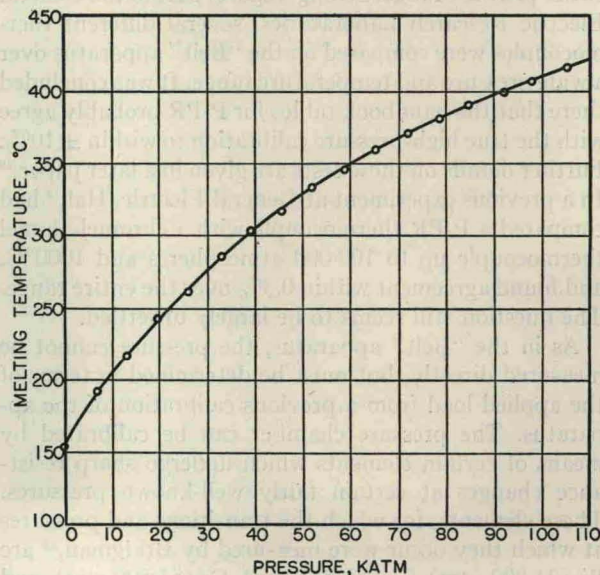

FIG. 6. Fusion curve of indium.

fusion curve from a pressure of about 6500 atm down to zero, where the variation of reasonably extrapolated values (in the case of indium) was as great as ±6% from the value finally used. This variation led to uncertainties of up to ±4% in the corrected temperatures, and it is estimated that the total uncertainty in corrected temperatures, taking into account the extrapolation, heat loss through the thermocouple wires, uncertainty in temperature readings at the beginning of the melting "avalanche," etc., is about ±5%.

RESULTS AND CONCLUSIONS

The experimental fusion curve for indium is shown in Fig. 6. It is found to rise smoothly with increasing pressure from the normal melting temperature of 156°C at atmospheric pressure to about 416°C at 105 000 atmospheres. The curve is normal in the sense of Bridgman over the entire pressure range; it is concave towards