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Calibration Techniques in Ultrahigh-Pressure Apparatus

Pressure and temperature calibration of ultrahigh-pressure apparatus is described. Pressure calibration up to 30 kilobars has been established accurately. Above this pressure are not known with sufficient absolute accuracy to compare results reliably with theoretical predictions of behavior of matter. The effect of pressure on temperature-sensing devices, like thermocouples, have been measured over temperature intervals of 100 deg C up to pressures of the order of 100 kilobars. The effect on some thermocouples is appreciable.

(see discussion)

Introduction

WITHIN the past few years several kinds of apparatus have been developed which are capable of maintaining, simultaneously, pressures up to about 100 kilobars¹ and temperatures above 2000 C for periods of minutes or hours. This development has expanded tremendously the field of investigation of chemical reactions, phase changes, and physical properties of materials under extreme conditions. In order that the results obtained from these investigations may be compared properly with theory, and with the results of other methods of subjecting matter to very high pressures and temperatures—shock pressure-wave technique for example—it is important that the pressures and temperatures be known in absolute terms. The purpose of this paper is to present the origins of the pressure and temperature scales used in this field, to describe some of the calibration techniques, to point out some of the weaknesses and discrepancies existing today, and to suggest some ways in which improvements might be realized.

Primary Pressure Calibration

Pressure is force per unit area. Therefore a primary pressure calibration must measure accurately a definite force acting uniformly on a definite area. In hydraulic systems this is usually accomplished by having a known weight resting on a free piston of accurately known area, and rotating the piston assembly to eliminate frictional drag. At pressures above 30 kb, at room temperature, all substances except perhaps helium are in the solid state so that one has to deal with solids. Since solids can sustain shear stresses, difficulties arise regarding friction and uniform pressure loading of the gage piston.

P. W. Bridgman of Harvard University spent over 40 years of his career investigating physical phenomena at high pressures, and his measurements of certain sharp phase-transition phenomena are used widely today for calibration points for our pressure scales.

In 1942 [1]² and later in 1948 [2], Bridgman reported detailed work on the compressibilities of a large number of substances, measured in a two-stage apparatus. In the first paper he reported abrupt volume changes in bismuth at 24.9 kb, in thallium

at 39 kb, and in barium at 59 kb. In the second paper he reported a sharp 11 per cent volume decrease in cesium at 44 kb. The frictional hysteresis between loading and unloading this apparatus was about 10 per cent at 100 kb. Bridgman believed his pressure values on a force-to-area basis were correct, in the 100-kb region to ± 2 or 3 per cent, and in the 25-kb region to ± 0.2 per cent. Bridgman's volume data are shown in Fig. 1.

In a 1952 paper [3] Bridgman reported the measurement of resistance behavior of a large number of materials up to 100 kb using a simple flat-face-anvil apparatus. He found sharp resistance discontinuities in bismuth at 24.9 kb, thallium at 44 kb, cesium at 54 kb, and in barium at 78 kb. These are shown graphically in Fig. 2. In bismuth the resistance transition was definitely associated with the volume change. It seemed reasonable to suppose that the volume changes and resistance changes should also be the same events in the other metals, but Bridgman believed the pressure calibrations of each of the two kinds of apparatus used were accurate enough that 78 kb as measured on the flat-face-anvil apparatus could not be the same pressure event as 59 kb measured in the two-stage apparatus. Hence he concluded that the volume discontinuity and the resistance discontinuity in barium were separate physical events. Likewise for cesium and for thallium. The reader is referred to Bridgman's papers for detailed description of the apparatuses and discussion of the accuracy of the pressure calibration.

As resistance measurements are more easily made than volume measurements in most apparatuses, most people working in the field of high pressure have used the resistance discontinuities of bismuth, thallium, cesium, and barium for pressure calibration of their apparatuses.

Recently Boyd and England [4], using a modified piston-and-cylinder apparatus of their own design, have checked the pressures at which the bismuth and thallium resistance transitions occur. They observed the bismuth transition at a force/area pressure of 25.2 ± 0.4 kb which is in satisfactory agreement with Bridgman's value of 24.9 kb. Their value for the thallium resistance transition was 37.1 ± 1.3 kb, which is considerably lower than Bridgman's value of 39 kb for the volume transition measured in a two-stage piston-and-cylinder apparatus.

At the June, 1960, Lake George Conference on Very High Pressure, sponsored by the Air Force (WADC) and General Electric Company [5], G. C. Kennedy reported some recent experiments he had carried out in his laboratory, using piston-and-cylinder apparatus in which the piston could be rotated slightly about its axis to relieve axial frictional drag. He found the bismuth transition at the same pressure as Bridgman, and to the same accuracy. His tests on thallium and barium, though incomplete, led him to believe that the volume change and resistance change

¹ The kilobar (abbreviated kb) is 10^9 dynes/cm.² It is equivalent to 1020 kg/cm² or 987 atm. This unit will be used in this paper since most workers in the field have adopted it.

² Numbers in brackets designate References at end of paper.

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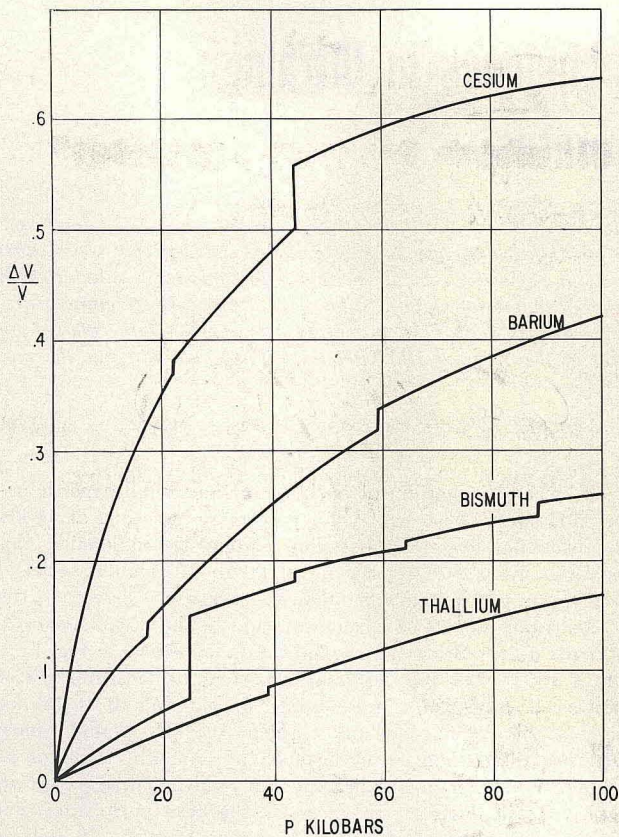


Fig. 1 Volume transitions observed by P. W. Bridgman

phenomena occur simultaneously for each of the four metals discussed, and that the pressures at which they occur are the $\Delta v/v$ pressures first reported by Bridgman. Thus Kennedy believes that the pressure values Bridgman used for the flat-face-anvil apparatus are too high.

More careful work will be required to resolve this discrepancy. Until it is resolved, workers in the field should indicate the method of pressure calibration they use, and comparison of results with theory, or the results of other types of experiments, should be made only with this possible discrepancy in mind.

Pressures generated in explosive shock-wave experiments are determined from measurements of particle velocity, shock-wave velocity, and application of conservation of energy and momentum. These pressures can be measured with an absolute accuracy of several tenths of a per cent. Temperature rise of the sample in shock-wave experiments also can be derived with considerable accuracy [6]. Thus the calibration of shock-wave experiments is in quite a satisfactory state.

Some Techniques of Pressure Calibration

The main purpose of a pressure calibration is to know what the chamber pressure is in a "working cell"; that is, a cell used to produce phase changes or reactions in the material under test. Since cell geometry, temperature, temperature distribution, compressibilities of the cell materials, and so on, can all affect the pressure attained in the working part of the pressure chamber, the geometry of the cell used for calibration should be similar to that of the working cell. This requirement practically eliminates the use of volume-change phenomena for calibration because to make a volume-change calibration point observable a large fraction of the volume of the pressure chamber must be filled with the calibration substance. On the other hand, very small wires of the calibration substance serve well to

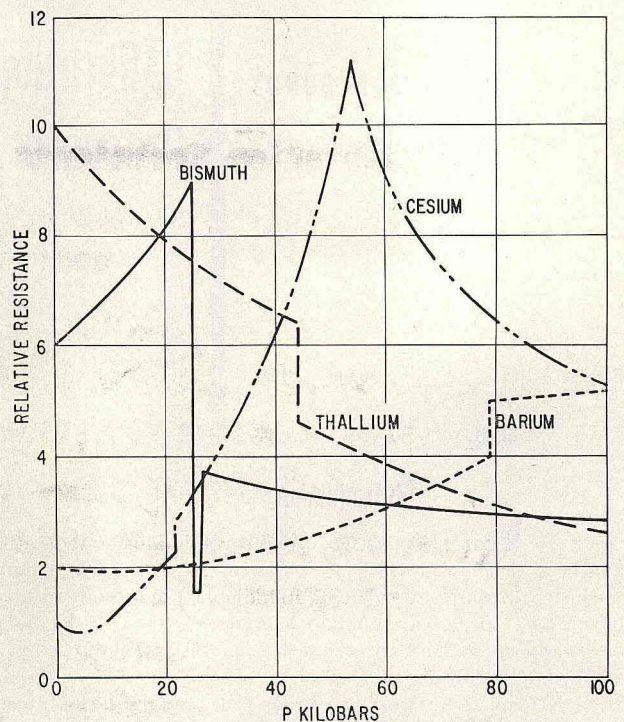


Fig. 2 High-pressure resistance behavior of bismuth, cesium, thallium, and barium (Bridgman)

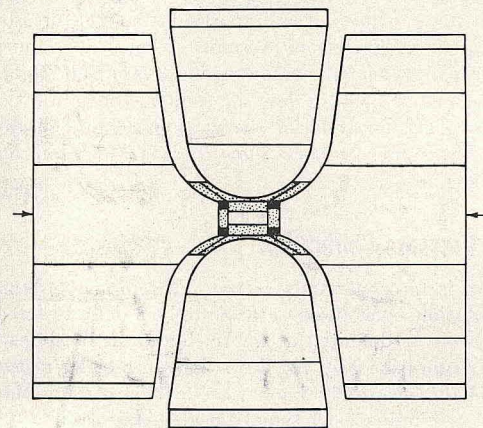


Fig. 3 Belt high-pressure, high-temperature assembly

give a resistance transition calibration point. Thus a small conductor of bismuth, thallium, cesium, or barium, surrounded by a low-shear-strength insulating material, like silver chloride, may be passed through the region of interest in a cell of similar structure to the working cell.

Because of the author's considerable experience with the "belt" type of superpressure apparatus [7] examples of its calibration will be used here. Fig. 3 shows a cross section of the belt apparatus. In this apparatus roughly half the press load is carried by the piston face and about half by the gasket region. With this large gasket loading it is obvious that the chamber pressure cannot be calculated with much accuracy from the press load and bore area. A typical calibration cell is made as shown in Fig. 4. A slender conductor of bismuth, thallium, cesium, or barium is located on the axis. This is surrounded by a sleeve of silver chloride which, being soft at all pressures, provides a fairly uniform field of pressure around the test wire. The silver chloride is surrounded by a sleeve of pyrophyllite stone and by the pyrophyllite "flower pots." The cell assembly is inserted in

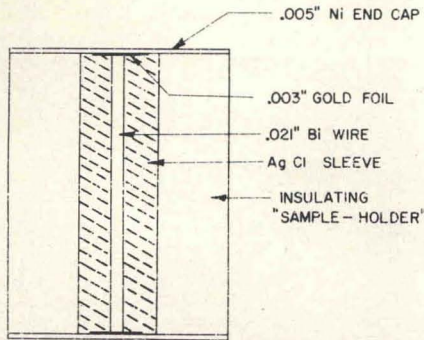


Fig. 4 Calibration cell for belt apparatus

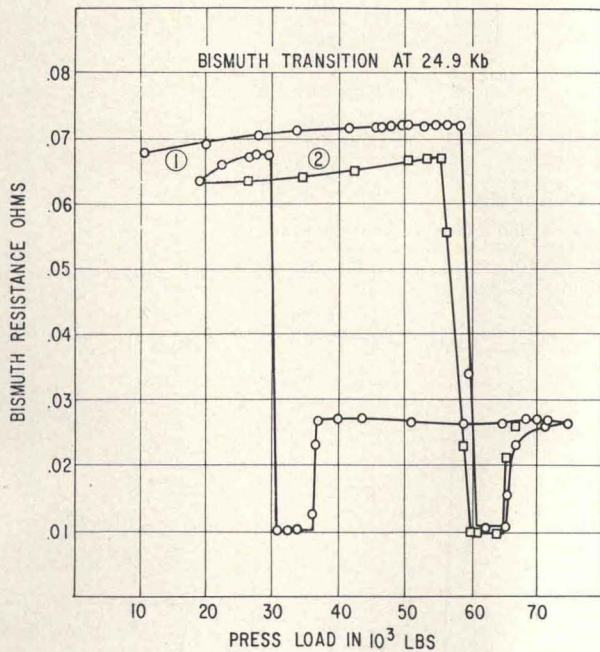


Fig. 5 Bismuth transition at 24.9 kb

the apparatus, the pistons closed in on it, and the resistance between the top and bottom pistons is measured as the press load is increased.

A typical resistance versus press-load curve for bismuth is shown in Fig. 5. The I → II transition at 24.9 kb is characterized by the large abrupt drop in resistance. The II → III transition is accompanied by a sharp increase in resistance. The "high" VI → VIII transition, reported by the author in 1958 [8], involves a drop in resistance. It is more drawn out than the other two, probably because of the gasket becoming thin and stiff at the very high press loading required and because of increased pressure gradients in the cell itself. Upon unloading, the reverse transitions occur at much lower press loads. This large "hysteresis" is believed to be due mainly to two things: (1) the reversal of the friction forces between the stone cell material and the walls of the pressure vessel, and (2) the different "spring constant" of the column of material lying between the piston faces as compared to that of the materials between the gasket regions. The latter is comprised mainly of cemented tungsten carbide while the former is chiefly of stone and silver chloride, both of which are much more compressible than cemented tungsten carbide. Thus, as unloading proceeds, the gasket zones unload more rapidly than the piston-face area and a given pressure can be held in the cell with considerably less press load. This large hysteresis shows that the pressure in the cell is not

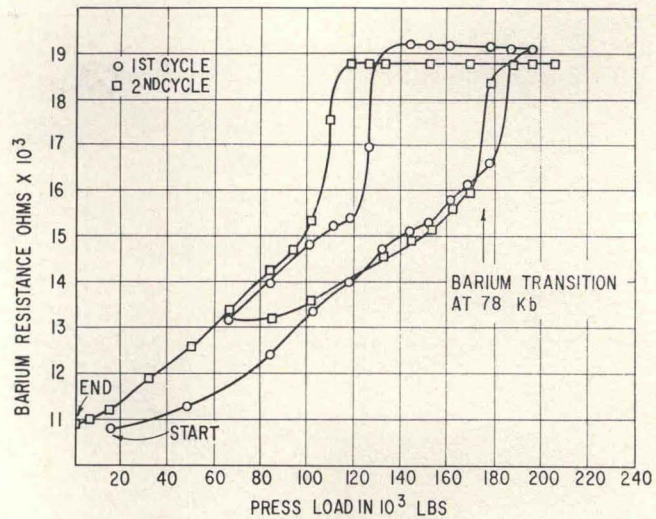


Fig. 6 Barium transition at 78 kb

a single-valued function of the press load and some convention must be agreed upon about how the operating point is to be approached. In the flat-face-anvil apparatus which has similar characteristics, Bridgman concluded that meaningful data could be taken only on the first up-loading cycle. In our laboratory we came to the same conclusion regarding the belt apparatus. Thus our pressure calibrations and "work runs" have always been made on the up-loading cycle.

A typical resistance versus press-load curve for barium in a belt apparatus is shown in Fig. 6. The same hysteresis effect between loading and unloading appears again.

Cesium, being extremely reactive with air and moisture, cannot be handled like ordinary wire materials. For long time periods it must be kept in a vacuum. For short periods it is protected adequately by white mineral oil. A technique successfully used by several workers is to draw molten cesium (warm room temperature) into long, slender, thin-walled glass capillary tubes. These are kept under mineral oil and used as needed by inserting the tube into an appropriate hole in the calibration cell, also under oil, when needed. A cell for cesium calibration is shown in Fig. 7. Before the cell is removed from the protecting oil the ends of the cesium column are plugged with little "nails" of metal, and these capped with gold foil. Then the cell may be removed from the oil, the excess oil blotted away, and placed immediately in the pressure apparatus.

After the resistance-transition data are obtained, the pressure versus press-load curve for the apparatus may be plotted as

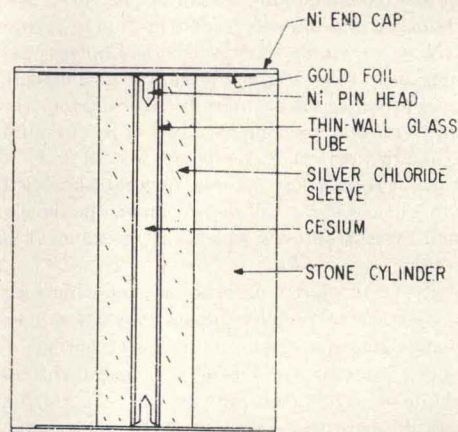


Fig. 7 Calibration cell containing cesium

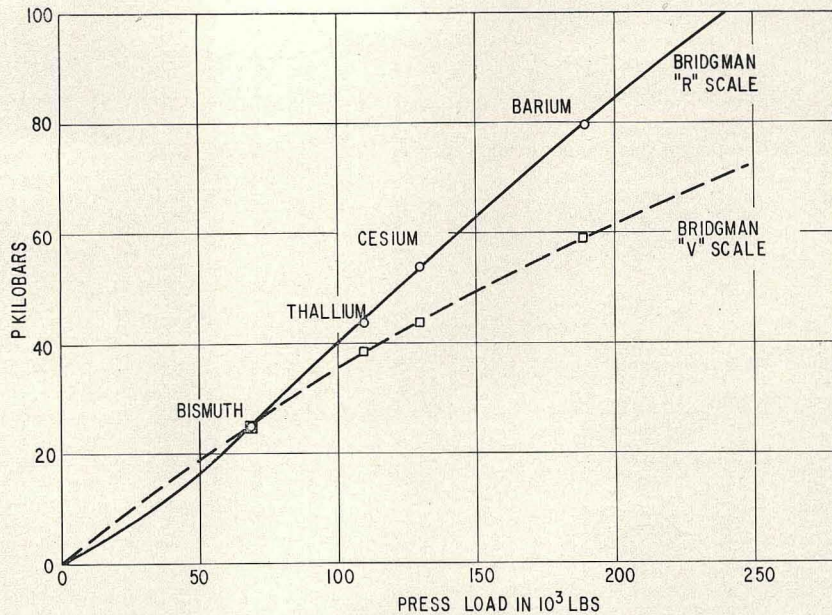


Fig. 8 Pressure versus press load plotted for volume and resistance-transition data

in Fig. 8. Two scales are shown. The upper one is according to Bridgman's resistance-transition scale and the lower one according to his volume-transition scale, the assumption being made that the resistance and volume changes are the same event in each of the metals. The R-scale is the one used by most workers in the field.

If the calibration wire is surrounded by materials like pyrophyllite, glass, alumina, or magnesia, instead of silver chloride, the resistance transitions drag out over larger press-load intervals, as shown in Fig. 9. This effect is almost certainly due to increased pressure gradients in the cell. In addition, the press load at which the transition starts is higher because of the shielding strength of the ceramic tube against the pressure field around it.

Determination of reaction-chamber pressures at elevated temperatures is more uncertain than it is at room temperature. After a working cell is compressed to pressure at room temperature its core is heated while holding the press load constant. As the core is heated several phenomena occur which affect the local pressure: (1) The rise of core temperature causes it to try to expand against its cooler, stiffer, environment and thus increase the local pressure. (2) Volume-reducing phase changes or reorganization of the core material caused by the higher temperature tend to decrease the local pressure. (3) Increased temperature of the surrounding material may decrease its shear strength, resulting in a more even distribution of pressure within the entire cell. (4) Gas generated in the hottest parts of the cell may migrate to the outer cell or gasket regions and alter the pressure distribution in the entire cell. It is obvious that the net result of these various phenomena on the core pressure depends upon the geometry, materials, temperature, and time. No broad generalizations can be safely made. Accurate knowledge of the local pressures in hot cores will depend upon the development of reliable small pressure probes which are operable at high temperatures.

An estimate of the order of pressure rise which may be expected from increasing temperature at constant volume may be made by balancing compressibility against thermal expansion. Using the data available for nickel, a temperature rise of 1000 deg C would increase its pressure to 200 kb. A 200 deg C rise of bismuth I would increase its pressure 2 kb. Of course the walls of a superpressure vessel cannot maintain the core at constant

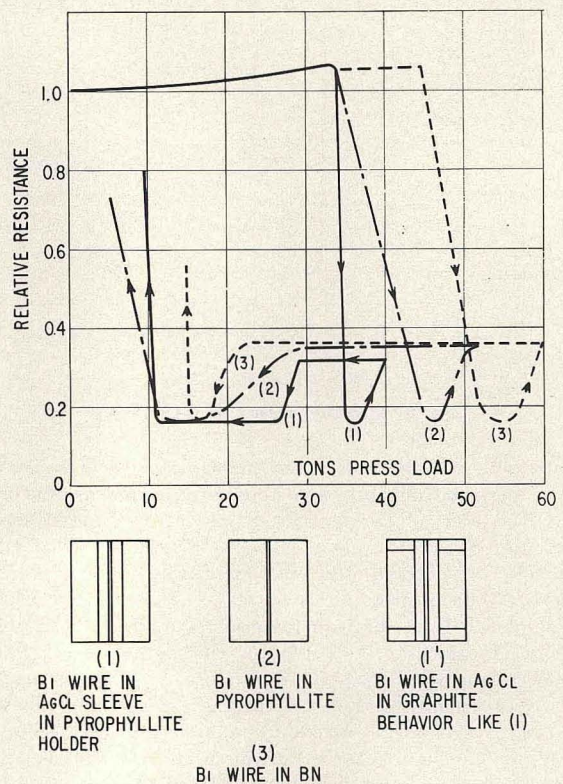


Fig. 9 Bismuth resistance-transition behavior in different kinds of sample holders

volume so the actual pressure rise would be less than calculated in the ideal case.

A technique that has been used to smooth out pressure inequalities in long hot runs is to preheat the core, after cold compression, to a temperature just safely short of the desired reaction conditions for a time long enough to anneal out porosity and to complete most of the volume-reducing phase transitions in the hot wall material; then allow the cell to cool off under full press load; then reheat to the desired reaction temperature.

Some observations by H. M. Strong, of our laboratory, using a manganin-wire pressure gage placed at the cool periphery of the cell, indicated that, following the preheating and cooling of the core, the reheating to full reaction temperature increased the pressure at the location of the manganin from about 70 to about 90 kb. During the 40-min reaction period the manganin showed a gradual pressure drop of about 5 kb and upon final cool-off a further drop of about 16 kb.

Temperature Calibration and Measurement

Thermocouples have proved to be the most satisfactory indicators of temperature in internally heated ultrahigh-pressure cells. One cannot be sure of their absolute accuracy, however, because of lack of knowledge of the effect of pressure on their normal emf. Bridgman [9], in 1918, reported some extensive measurements of this effect on a number of metals for the temperature range 0 to 100 C and pressures up to 12 kb. In 1939, Birch [10] published results of measurements on Pt/Pt 10 per cent Rh, and on chromel/alumel thermocouples, for temperatures up to 470 C and pressures up to 4 kb. Recently the author [5] reported an adaptation of the Bridgman experiment to the belt superpressure apparatus which yielded data on eight common thermocouple metals over the temperature range 30 to 130 C and pressures up to 100 kb (Bridgman R-scale). Since the Bridgman and Birch data do not extend to the ultrahigh-pressure region, only the latter work will be described here.

Fig. 10 shows the belt apparatus adapted to "pressure" thermal emf measurements. The top piston assembly was heated by a wrapping of nichrome resistance-heating wire. The bottom piston assembly was cooled by an air blast. An insulated wire of the metal to be tested was led through the gasket adjacent to the top piston, but electrically insulated from it; then down the axis of the pressurized region along the temperature gradient; and finally out through the bottom gasket adjacent to the bottom piston. Temperatures at the faces of the top and bottom pistons were measured by chromel/alumel thermocouples (not shown) which were brought in through the bottom gasket. The chromel/alumel thermocouples had already been found to have a small pressure effect by Birch, and this was verified by the present work. Ideally, the passage of the test wires through the pressure gradient in the gaskets should have been isothermal. This was not possible, but measurements showed that under the test conditions the temperature increased about 6 to 8 deg C from inside to outside the hot gasket and decreased about 2 deg C at the cool gasket. It was estimated that these deviations from ideal would produce an error of less than 5 per cent in the total result.

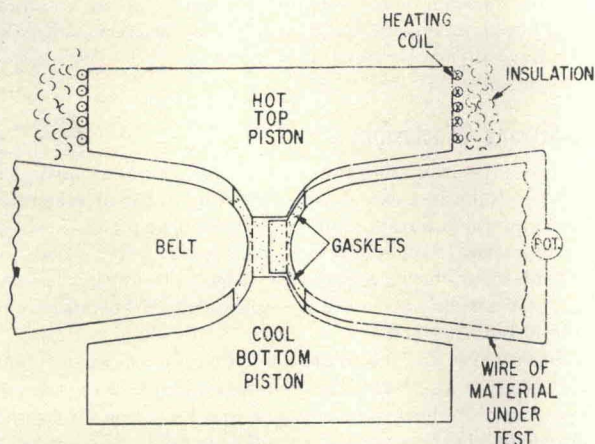


Fig. 10 Arrangement for "pressure" thermal emf measurements in belt apparatus

Since this thermocouple circuit is all of the same kind of metal its principle should be explained. The "hot junction" is where the metal wire goes through the pressure seal at the hot piston; the "cold junction" is where it goes through the pressure seal at the cool piston. One branch of the thermocouple is the pressurized wire extending along the temperature gradient between the hot and cool ends of the cell. The other branch is the same kind of wire at atmospheric pressure extending through the same temperature difference as the pressurized branch of the wire. Both terminals of the potentiometer, and the potentiometer itself, are at uniform temperature so no emf can be generated in that part of the circuit. Since the pressurized branch of the wire has a different thermoelectric coefficient than the unpressurized branch, there is a net thermal emf which is measured by the potentiometer. This is the "pressure" thermal emf. It is defined as positive if electrons tend to go from the pressurized to the unpressurized metal at the hot junction.

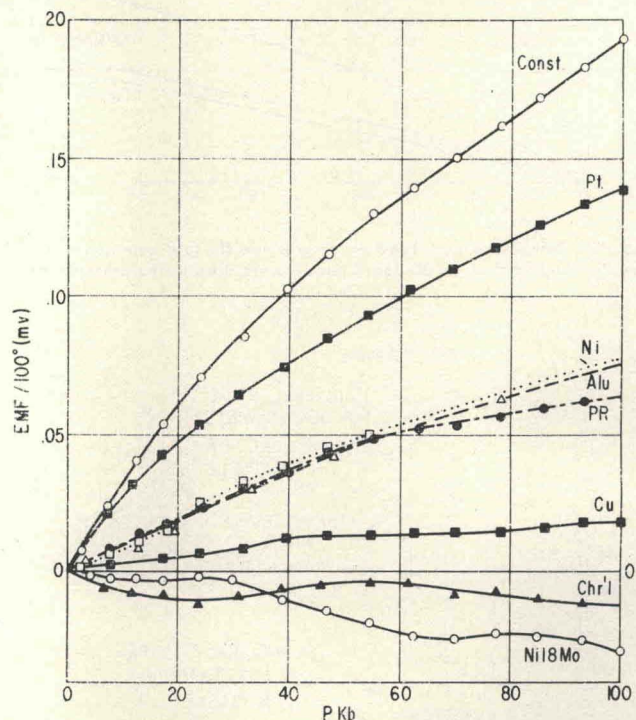


Fig. 11 Pressure thermal emf's for several frequently used thermocouple metals to 100 kb for a ΔT of 100 deg C

The results of the measurements are shown in Fig. 11. Constantan and platinum show the strongest effects; nickel, alumel, and Pt 10 per cent Rh show about the same medium effect. Copper has a weak positive effect, while chromel and Ni 18 per cent Mo have weak negative effects. These pressure thermal emf's may be used to find the effect of pressure on the net emf of regular thermocouple pairs. The difference of the pressure emf's in each branch of the thermocouple must be added to the normal thermal emf if it aids the normal emf—or subtracted if it opposes the normal emf. Of the 28 thermocouple pairs that may be made from the eight metals tested, only three pairs have additive pressure emf's. The corrections, in deg C, to four common thermocouples which are subject to ΔT of 100 deg C within the pressure field, are shown in Fig. 12. The pressure effect causes these four to read too low, so the corrections shown on the graph should be added to the temperatures derived from the standard temperature/millivolt tables.

The temperature range over which pressure thermal emf's can

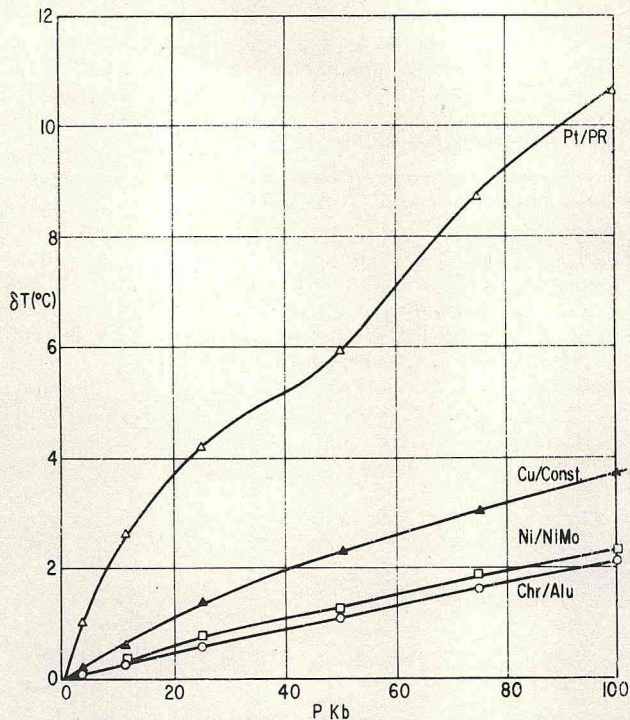


Fig. 12 Corrections as a function of pressure for four common thermocouples subjected to a 100-deg-C temperature drop in the pressure zone

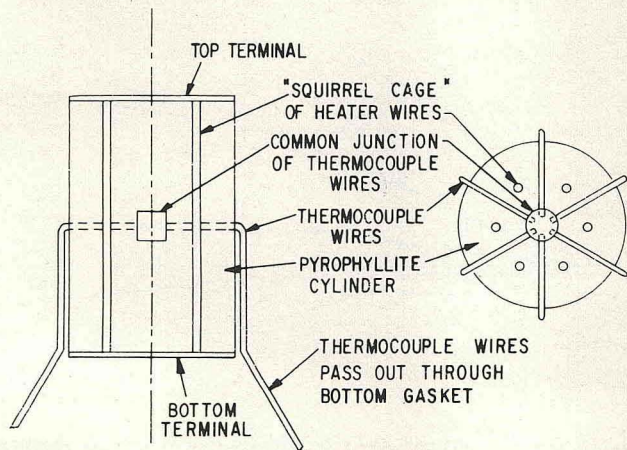


Fig. 13 Six-wire common-junction thermocouple in a squirrel-cage heater

be measured directly, as in Fig. 10, is limited by the temperature to which the top piston and gasket assembly can be heated without mechanical or electrical failure. There is little hope of carrying this above 300 to 350 C at 100 kb. Thus this setup is probably not capable of yielding the data required to correct thermocouple readings above the 500-C level. It is not safe to extrapolate very far above the actual low-temperature data, as has been shown by common-junction thermocouple tests which will now be described.

A cell was made with a six-wire "squirrel-cage" heater, and six thermocouple wires extending radially inward on the equatorial plane to a common junction at the center, as shown in Fig. 13. The thermocouple wires were brought out through the bottom gasket of the belt apparatus. The temperature and pressure fields of each thermocouple wire were the same, due to the symmetry of the system. After the cell had come to thermal equilibrium at a given power setting, the emf's between

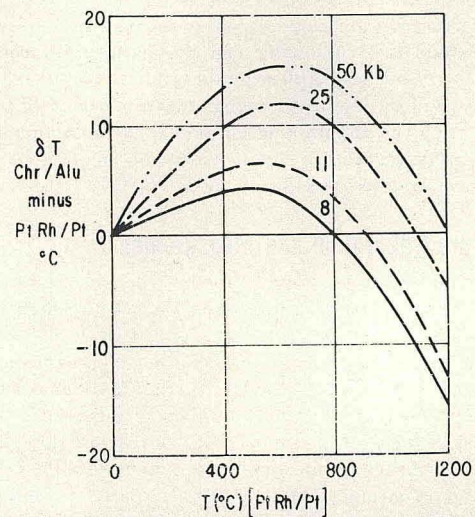


Fig. 14 Comparison of "standard table temperatures" of a common-junction chromel/alumel/platinum/platinum-10 per cent rhodium thermocouple set

the different thermocouple pairs were measured, and their "standard millivolt table temperatures" looked up and compared.

Fig. 14 shows the difference between the "temperatures" indicated by the chromel/alumel and Pt/Pt 10 per cent Rh thermocouples plotted against the Pt/Pt 10 per cent Rh temperature for four different pressures. Below 400 C these temperature differences are consistent with the data presented in Figs. 11 and 12. Above 400 C it is obvious that some other effect takes over on one, or both, of the thermocouples. Since there are no absolute data on which to base corrections in this higher temperature region it has been customary to report temperatures as given by the standard temperature/millivolt tables, naming the kind of thermocouple used, and assuming the true correction to be less than 10 per cent. This obviously causes an unreliable situation when one attempts to measure the effect of pressure on melting points, or phase equilibrium lines, at high pressures and temperatures.

Resistance thermometers offer even more uncertainties than thermocouples because of the unknown effects of plastic strain, and/or pressure, on the temperature coefficient of resistance.

There is a possibility that true temperatures can be measured from the thermal electronic noise generated in a resistor placed in the hot core of a pressure cell. The noise level would depend only on the resistance and the temperature. The resistance and noise spectrum could be measured from outside the cell, and from these the true temperature could be derived. Garrison and Lawson [11] have already demonstrated the feasibility of this method in lower pressure systems.

Summary and Conclusions

Absolute-pressure calibration of static-pressure apparatus above 30 kb is not in a very satisfactory state at the present time. In reporting their results, workers should specify the basis of their calibration. The most-used scale today—that based on Bridgman's values for resistance transitions in bismuth, thallium, cesium, and barium—is certainly accurate at 25 kb but may be 25 per cent high at 100 kb.

In shock-wave work absolute pressures are known to about 1 per cent accuracy. When the pressure ranges of static-pressure apparatus and of shock-wave systems can be made to overlap enough, some sharp phase change may be observable on both. This would be of great help in the absolute calibration of the static system.

Thermocouple readings up to about 400 C can be fairly reliably corrected for pressure effects. Above 400 C little is known for certain, so that workers should explain how they obtained any temperatures they quote.

A large effort and some new approaches are very much needed to extend the range of absolute calibration in both pressure and temperature measurement in ultrahigh-pressure apparatus.

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