H. T. Hall

Equipment

APPARATUS FOR PHASE-EQUILIBRIUM MEASUREMENTS AT PRESSURES UP TO 50 KILOBARS AND TEMPERATURES UP TO 1750°C

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Apparatus for Phase-Equilibrium Measurements at Pressures up to 50 Kilobars and Temperatures up to 1750°C

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Abstract. Construction and calibration of apparatus utilizing a solid pressure medium for phase-equilibrium studies at elevated temperatures and pressures are described. Pressure calibration is carried out by measurement of the Bi I–Bi II and Tl II–Tl III transitions. A new determination of the thallium transition, 37.1 ± 1.3 kilobars, is given. Tests indicate that talc is superior to pyrophyllite and boron nitride as a solid pressure medium for high-temperature work.

INTRODUCTION

The apparatus described below was developed to permit study of phase equilibria in the ranges of pressure and temperature present in the upper part of the earth's mantle. Such studies can help define and solve a variety of geophysical and petrological problems. The chemical and mineralogical constitution of the mantle and the nature of the Mohorovicic discontinuity are matters of great current interest. Many lavas have originated in the mantle, and their temperatures of formation and compositions must have been influenced by high pressure. Phase-equilibrium determinations at high temperatures and pressures can put limits on the mineralogical nature of the mantle and may provide data on the melting relations at these pressures that will be of considerable significance in understanding the origins of lavas. Although this paper covers only the construction and calibration of the apparatus, some results on the quartz–coesite transition are presented in the following paper in this issue.

Studies of silicate equilibria at high temperatures and at pressures in excess of 10 kb are most conveniently carried out with a pressure system utilizing a solid pressure medium. *Coes* [1955] developed a simple, internally heated high-pressure system of this sort for use up to 1000°C and 45 kb. (The details of his apparatus have not yet been published.) *Hall* [1958] has shown that this design may be modified to reach temperatures above 2000°C. The apparatus described in this paper is based on the Coes-Hall design. Developments made by the present authors include chiefly the method of introducing thermocouple leads into the pressure chamber. This apparatus can be used up to a pressure of about 50 kb at a temperature of 1750°C. The measurable temperature range may be extended by using thermocouples that melt at higher temperatures than platinum/platinum–10 per cent rhodium.

APPARATUS

The apparatus consists of an internally heated tungsten carbide pressure vessel supported by a steel ring. The pressure vessel is end-loaded during a run with a thrust of 150 to 250 tons delivered by a hydraulic press. Pressure is applied to the run and furnace assembly with a carbide piston driven by a second hydraulic press. The assembly is illustrated in Figure 1.

The carbide core of the pressure vessel is ground in the form of a tapered cylinder approximately 2 in. long, 2 in. in diameter, and with a bore of 0.500 in. The taper on the outside of the carbide cylinder is 1° included angle. The core is forced into a steel supporting ring with an interference of 0.018 to 0.022 in. on the diameter. The steel supporting ring has an outside diameter of 6¼ in. and is jacketed with a soft-steel safety ring ⅜ in. thick.

We have used Carboloy grade 883 for the core of the pressure vessel. A variety of steels have been employed for the supporting ring;

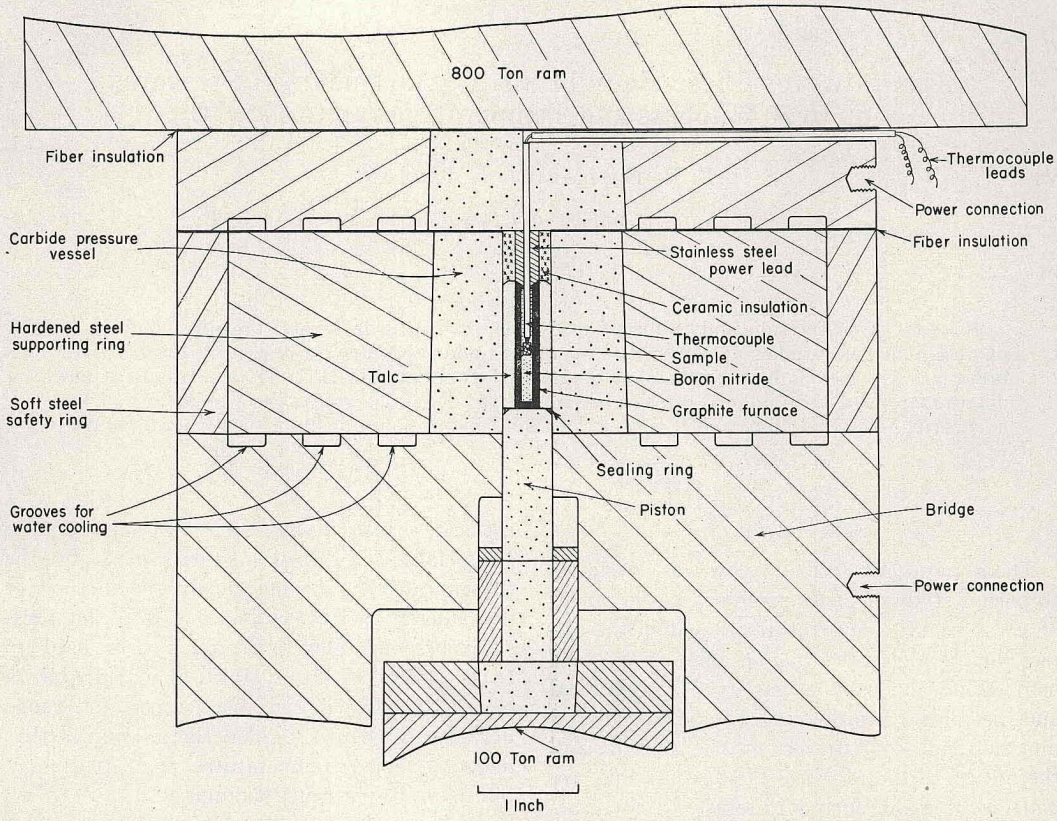

Fig. 1. Apparatus for use in the pressure range up to 50 kb at temperatures up to 1750°C. Carbide parts are stippled; steel parts are ruled.

satisfactory results have been obtained using AISI E4340 forged as rings and hardened to Rockwell C44–46. The bores of the 4340 rings are stretched about 1 per cent on a steel mandrel after hardening. Autofrettaging a ring substantially increases its yield point.

The core of a pressure vessel constructed in this manner ordinarily lasts up to 60 runs at high temperature. Fracture starts in the first few runs with the development of radial cracks in the central part of the bore and with cracks normal to the axis of the bore forming opposite the ends of the piston and base plug. These fractures fill up with lead (used as a jacket on the furnace assembly, Fig. 2) during a run and do not interfere with the operation of the apparatus. Eventually chips spall off the end of the core adjacent to the base plug, and the end loading becomes less effective. When the ends of a core are well chipped the lateral cracks in the bore can expand and the core becomes unusable. The core can then be pressed out and the ring fitted with a new one.

Pistons can be made conveniently from standard carbide inserts 0.500 in. in diameter by 1.5 in. long. The bore of the pressure vessel is ground to a diameter 0.0005 to 0.001 in. larger than the piston. The end of the piston that bears on the ram of the press is jacketed with steel to prevent chipping. Pistons last indefinitely at pressures below 30 kb; they last up to 40 runs in the range 30 to 50 kb.

Grooves are cut in the base plate and bridge, adjacent to the faces of the pressure vessel, to permit water cooling. Without water cooling the steel supporting ring expands away from the carbide core on high-temperature runs and causes its rapid deterioration.

The furnace and base plugs assembly is illustrated in detail in Figure 2. The run in the

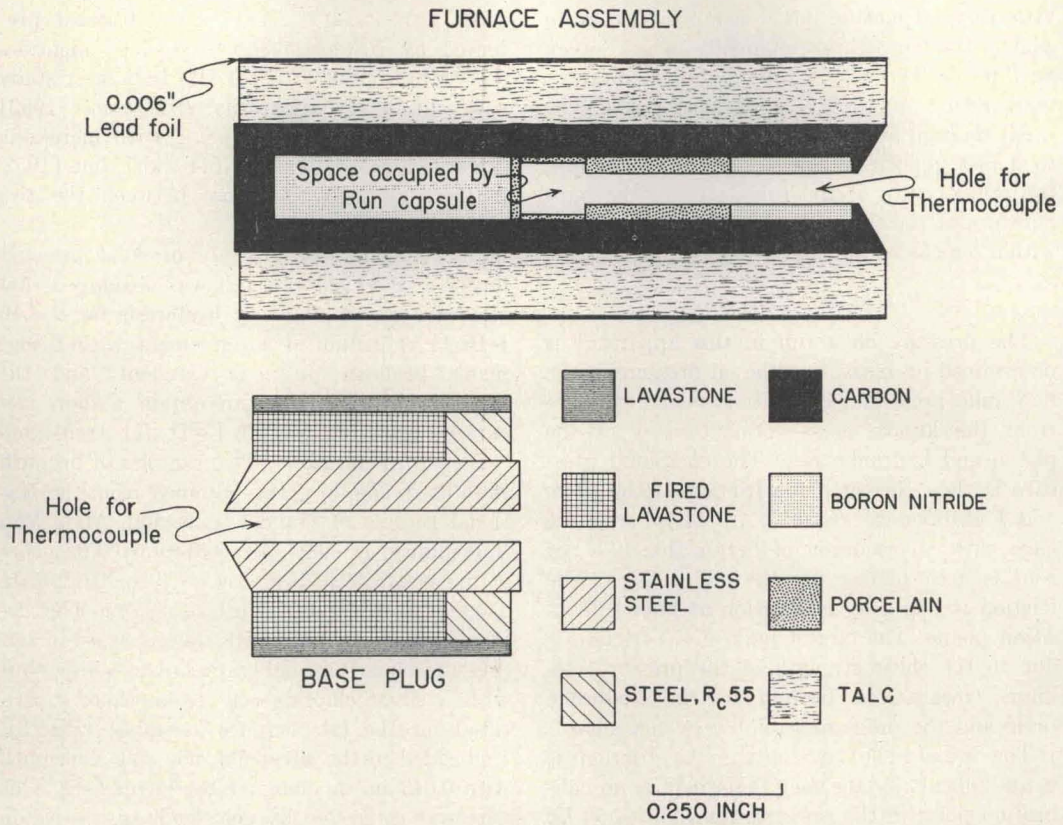

Fig. 2. Detail of furnace and base plug assembly used in apparatus shown in Figure 1. The assembly is not recoverable, and a new unit is used for each run.

form of a powder is loaded in a platinum capsule with a wall thickness of 0.003 in. The run and capsule are then compressed in a pellet press to a diameter of 0.096 in. and a length of 0.100 to 0.125 in. The furnace is a graphite tube, ¼ in. in outside diameter, with a bore of ⅛ in. and a length of 1⅛ in. Talc is used for an insulating sleeve and pressure medium. Boron nitride and high-temperature porcelain are used for inserts within the furnace. Boron nitride, which is isostructural with graphite, was found to be soluble in platinum and lowers its melting point by an amount on the order of 400°C. Hence the thermocouple and platinum capsule around the run are shielded from contact with boron nitride by porcelain inserts.

The base plug consists of a stainless-steel power lead insulated by a ceramic sleeve. The power lead can be made conveniently from pressure tubing, but it must be annealed before using. The thermocouple is introduced in a ceramic tube through a hole in the power lead and is held in place by friction. The hardened-steel washer at the base of the assembly is designed to reduce stress at the vulnerable edge of the bore. Fired pyrophyllite tends to chip the bore on release of pressure; hence the base-plug assembly is surrounded with a thin sleeve of unfired pyrophyllite. For consistent results clearances between the various parts of the furnace and base-plug assembly must be held to about 0.001 in.

The power supply consists of a 220-volt 50-amp variable transformer, the output of which is fed through a 5-kw transformer with a winding ratio of 20 : 1. Maximum power output is thus about 500 amp at 10 volts. Fine adjustment of the power is achieved by adding a small votage, in phase, through a second variac. The furnace illustrated in Figure 2 has very

little thermal inertia, but it has proved easy to control the temperature manually to ±5°, even at 1700°C. The power required to maintain a temperature of 1700°C is about 1.8 kw. The small thermal inertia of the furnace contributes to a fast quench. When the power is shut off, the temperature of the run drops to the temperature of the pressure vessel wall (< 500°C) within 5 seconds.

Pressure Calibration

The pressure on a run in this apparatus is determined by measuring the oil pressure in the hydraulic press and computing a load pressure from the known cross-sectional areas of the piston and hydraulic ram. The computed pressure is then corrected for friction in the press and high-pressure assembly. A 1400-bar Heise gage with an accuracy of better than 0.1 per cent is used to measure the oil pressure. The friction is found by calibration at known transition points. The largest part of the friction is due to the shear strength of the pressure medium; mechanical friction in the hydraulic press and the pressure assembly is very small.

The problem of evaluating the friction is made difficult by the fact that there is no calibration point in the pressure range 10 to 50 kb at high temperature. Since, however, the shear strengths of solid pressure media decrease with temperature, values of friction measured at room temperature form upper limits for the friction actually present at high temperatures. The friction in the hydraulic press and piston assembly itself is independent of run temperature and may be taken as a lower limit. As is described below, it is possible to make the difference between these limits as small as 10 per cent.

There are two calibration points at room temperature in the pressure range 10 to 50 kb that can conveniently be used. These are the transition Bi I–Bi II at about 25 kb and the transition Tl II–Tl III at about 37 kb.

The transition Bi I–Bi II has been located by *Bridgman* [1940] at 24.9 kb at 30°C and used by him as a primary calibration point. There is a second transition in bismuth (Bi II–Bi III) at 26.4 kb that is less convenient to measure. *Bridgman* [1935] located a transition in thallium by volume discontinuity at 41,000 kg/cm² (40.2 kb) at 30°C. The phase diagram presented by *Bridgman* [1935, p. 899] identifies this transition as Tl II–Tl III. In a later study with an anvil apparatus *Bridgman* [1952] found this transition occurring with increasing pressure at 45,000 kg/cm² (44.1 kb), but [1952, p. 208] declined to choose between the two values.

In the course of a study of solid pressure media a silver chloride cell was developed that yielded a remarkably low hysteresis for the Bi I–Bi II transition. The agreement with Bridgman's bismuth point is excellent, and the method has been used to obtain a more accurate value for the Tl II–Tl III transition.

Bismuth transition. Two samples of bismuth were used. One of them, obtained from the National Bureau of Standards through Alvin Van Valkenburg, is 99.99 per cent pure. The other is the electrolytic bismuth used by Bridgman. These samples gave identical results. The determination was made with the same piston and pressure vessel assembly described above but with a silver chloride cell ⅛ in. thick substituted for the talc furnace assembly (Fig. 3). Embedded in the silver chloride was a bismuth wire 0.013 in. in diameter by ⅜ in. long. This wire was connected by gold leads to the piston and to an insulated base plug. The transition was detected by the change in electrical resistance.

A run across the transitions Bi I–Bi II is illustrated in Figure 3. The hysteresis shown in

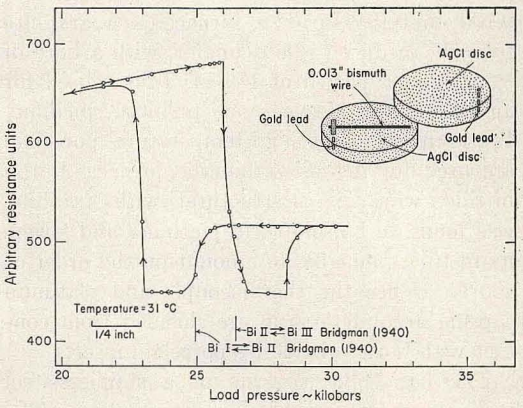

Fig. 3. The transitions Bi I ⇄ Bi II ⇄ Bi III as shown by the change in electrical resistance of a bismuth wire in an AgCl cell.

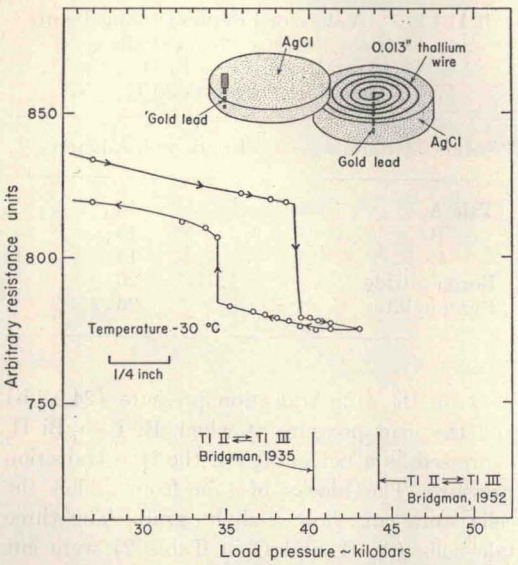

Fig. 4. The transition Tl II ⇄ Tl III as shown by the change in electrical resistance of a thallium wire in an AgCl cell.

Figure 3 for the transition I–II is 11.6 per cent. By balancing on the transition, with I and II present, increasing the pressure until I → II and releasing the pressure until II → I, it was possible to reduce the hysteresis to 3.1 per cent about a mean value of 25.2 kb, in good agreement with Bridgman's value of 24.9 kb.

Thallium transition. The II–III transition in thallium is sharp, and it occurs at a pressure sufficiently higher than the bismuth transitions to make it of interest as a calibration point. The chief difficulty in working with the thallium point is that the change in electrical resistance is only 28 per cent [*Bridgman,* 1952, p. 208], smaller by a factor of 20 than the change at the Bi I–Bi II point.

One sample of thallium was obtained, through Alvin Van Valkenburg, from the National Bureau of Standards. It is 99.9 per cent pure. A second sample was obtained from the Fisher Scientific Company. It is listed as 'purified.' Shavings of these materials were extruded through a die into Nujol to form 0.013-in.-diameter wires. It was necessary to use 2½ in. of wire to obtain a sufficiently large resistance change. For establishing the calibration point the silver chloride cell sketched in Figure 4 was used. The thallium wire was wound in a spiral between two disks of silver chloride. The change in resistance with pressure on one run is shown in Figure 4. By balancing on the transition in the manner described above for bismuth it was possible to reduce the hysteresis below that shown.

TABLE 1. The Transition Tl II ⇄ Tl III
Temperature 29° ± 1°C

Thallium	Pressure,* kb	Hysteresis, %
NBS	37.15	6.8
NBS	37.10	7.2
Fisher	37.15	8.7

* Mean of the pressures at which the transition started on increasing and decreasing the load.

Results obtained for three set-ups, two with the National Bureau of Standards thallium and one with the Fisher thallium, are given in Table 1. The agreement of the means on the three set-ups is excellent, and there is clearly no measurable difference between the two samples of thallium. From these data the Tl II–Tl III point can be taken to be 37.1 kb ± 3.5 per cent.

Pressure Media

A pressure medium for high-temperature runs not only must have a low shear strength but also must be an electrical insulator and a good thermal insulator. Silver chloride is by far the best solid pressure medium tried by the authors at room temperature, but it melts at 455°C (at 1 atm) and becomes an electrical conductor. At high temperatures other materials must be used.

To explore the suitability of various solid pressure media we have used cells of the sort illustrated in Figure 5. These cells, patterned after a design by *Hall* [1958, Fig. 3], give values of friction equivalent to those obtained with actual furnace assemblies. Data are presented below for talc, pyrophyllite, and boron nitride. The talc and the pyrophyllite, obtained from the American Lava Corporation in the form of pressed cakes, are respectively Lava Grade 1136 and Lava Grade A. The boron nitride was obtained in similar form from Union Carbide Corporation.

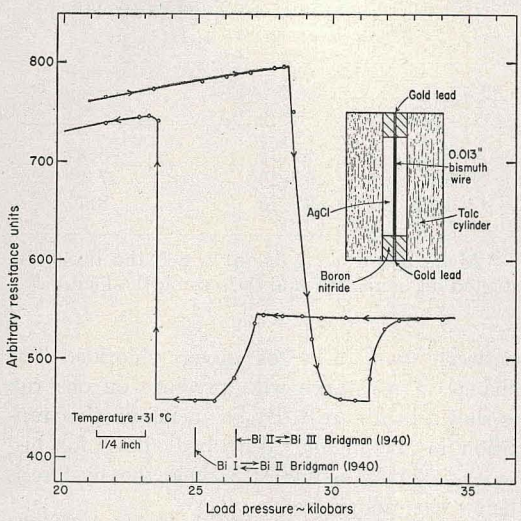

Fig. 5. The transitions Bi I ⇄ Bi II ⇄ Bi III as shown by the change in electrical resistance of a bismuth wire in a talc cell.

A typical run with bismuth in a talc cell is illustrated in Figure 5. The point at which Bi I starts to invert to Bi II is sharp and reproducible to about ±0.5 per cent of the pressure. Measurement of this point is unaffected by holding the cell at a pressure slightly below the transition pressure for periods up to half an hour. It can be noted in Figure 5 that the hysteresis loop is not symmetrical about the true inversion point. This phenomenon is characteristic of these pressure media; it results from the fact that a part of the deformation is elastic rather than plastic. The phenomenon may be understood by imagining the sleeve of pressure medium as a spring which must be compressed in bringing pressure to bear on the bismuth wire; when the pressure is released the 'spring' snaps back, causing an unsymmetrical hysteresis loop. With some set-ups we have observed the reverse reaction Bi II → Bi I proceeding at a load pressure actually slightly higher than the true transition pressure. With these media the pressure at which Bi II → Bi I is not so reproducible as the advance reaction and is dependent on how long the sample is held above the transition pressure.

Data on identical cells of talc, pyrophyllite, and boron nitride are presented in Table 2. These cells were jacketed with 0.006-in.-thick lead foil. The listed frictions are the difference

TABLE 2. Values of Friction Obtained with Various Pressure Media at the Transition Bi I → Bi II 24.9 kb, temperature 30°C

Pressure Medium	Friction on Advance, %
Talc A	13
B	13
C	14
Boron nitride	20
Pyrophyllite	26

between the true transition pressure (24.9 kb) and the load pressure at which Bi I → Bi II, expressed as a percentage of the true transition pressure. The blocks of talc from which the cells were cut show a slight grain. The three talc cells (A, B, and C in Table 2) were cut from mutually perpendicular slices in a block to test any possible effect of grain; no significant effect was found. These data show that talc is considerably better than boron nitride or pyrophyllite as a pressure medium. Talc has an additional advantage over pyrophyllite in that it is stable to higher temperatures.

A talc cell has also been tested at the thallium transition. The friction at the point Tl II → Tl III measured relative to the equilibrium point (37.1 kb, see above) is 13.6 per cent, in excellent agreement with the results obtained with bismuth. It is evident that at least over the range 20 to 40 kb the friction in a talc cell is a constant percentage of the load pressure.

To be certain that the type of cell illustrated in Figure 5 adequately models a high-temperature furnace assembly a run was made with an actual furnace assembly in which the sample and platinum capsule were replaced with a cylinder of AgCl the same size as the run containing a ⅛-in. length of bismuth wire. No other changes were made. The friction at the Bi I → Bi II point was found to be 13.4 per cent, in agreement with the results in Table 2.

For runs at high temperatures a correction of −13 per cent to the load pressure is taken as one limit and a correction of −3 per cent (estimated minimum friction) as the other. These limits involve two assumptions: that the friction should be counted as negative, and

that at high temperature the friction decreases from its room-temperature value.

During high-temperature runs in this apparatus the piston continually advances, and pumping is necessary to maintain the pressure. This results from creep in the base plug assembly and from extrusion of lead into cracks in the wall of the pressure vessel. At pressures above 15 kb these effects dominate the temporary effect of thermal expansion as the furnace is heated to temperature. Since the piston is continually advancing on the furnace assembly, the correction for friction should be negative.

At high temperature the shear strengths of these pressure media decrease, and, hence, so also should the friction. This effect may be slightly offset by chemical changes. At temperatures above 1000°C a thin zone of the talc adjacent to the graphite furnace breaks down to enstatite and quartz (or coesite). At a run temperature of 1700°C this zone has a maximum thickness of 0.018 in. It is unlikely that this shell could be strong enough to materially influence the pressure transmitted to the run. Moreover, at high temperature the enstatite and quartz are crystallizing in a hydrous environment (H_2O given off by the talc) and may have essentially no strength.

Temperature Measurement

Temperature measurement in high-pressure apparatus is subject to error due both to gradients within the apparatus and to the effect of pressure on the temperature-sensing element. There are no direct measurements of the effect of pressure on the emf of a thermocouple in the ranges of temperature and pressure utilized with this apparatus. Measurements at lower temperatures and pressures and some indirect experiments, reviewed below, indicate that the effect of pressure on the emf of a platinum/platinum–10 per cent rhodium thermocouple is small, and the effect is probably negligible in comparison with the precision of measurement now attainable. Error due to thermal gradients can be more directly evaluated.

We have measured the temperature gradient in a furnace of the design in Figure 2 in a series of runs by introducing two platinum/platinum–10 per cent rhodium thermocouples with their junctions either 1/8 or 1/16 in. apart and arranged as nearly as possible along the axis of the furnace. In these experiments one of the junctions was placed in the same position in the furnace as the thermocouple on a routine run; the position of the other, depending on the set-up, corresponded to either the center or the opposite end of a run capsule. The differences between the couples, therefore, approximate the gradient across an actual run.

As can be seen in Figure 6 the maximum difference found was 15°. Making no correction to the reference couple reading, runs can be assigned an uncertainty of ±10° below 1500°C and ±15° above.

Birch [1939] has examined the effect of pressure on chromel-alumel and platinum/platinum–10 per cent rhodium thermocouples at pressures up to 4000 bars and temperatures up to 500°C. Birch found no effect for the chromel-alumel couple, but measured a small decrease in the emf of the platinum couple with increasing pressure. The correction for the platinum couple was found to be a linear function of both temperature and pressure, reaching a maximum value in his measurements of 15μv (1.5°) at 470°C and 4100 bars. Extrapolation of Birch's data to higher temperatures and pressures can be expected to give a measure of the maximum possible correction, since most pressure effects tend to decrease with increasing

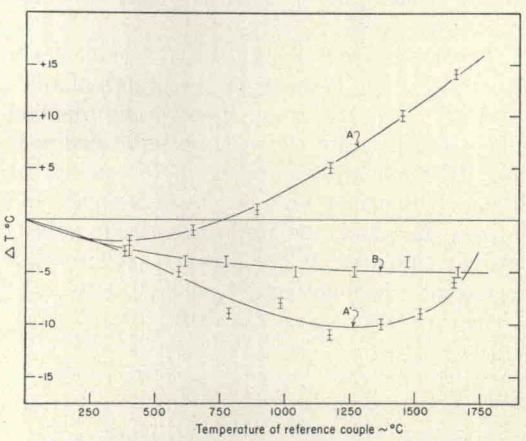

Fig. 6. Temperature gradients measured in the furnace assembly shown in Figure 2. For runs *A* and *A'* the reading couple was mounted 1/8 in. from the reference couple; for run *B* the reading couple was 1/16 in. from the reference couple.

presure. The correction at 40,000 bars and 1700°C would be +48°.

Hall [1955, p. 1145] compared a platinum/platinum–10 per cent rhodium couple and a chromel-alumel couple at temperatures up to 900°C and pressures up to 100,000 atm. He found an average deviation from the mean temperature of ±3° at 900°C. We have repeated Hall's experiment up to a pressure of 45 kb. A measurable effect was found; its magnitude is in rough agreement with Hall's data and is substantially less than that predicted by extrapolation of Birch's measurements.

A chromel-alumel couple and a platinum/platinum–10 per cent rhodium couple were run with their junctions, separated by ceramic approximately 0.030 in. thick, placed in the position normally occupied by a run capsule. Changes in emf of the two couples were then read as a function of temperature and pressure. Two set-ups were made with a number of runs. At high temperature and pressure the chromel-alumel couple read a higher apparent temperature than the platinum couple. The maximum difference was 10° ±1° at 955°C and 45.5 kb. An average of three runs at about 950°C gave a change with presure in the range 17 to 45.5 kb of 0.27°/kb; one run at 500°C in the same pressure range gave 0.07°/kb. The two couples, therefore, read measurably different at high temperature and pressure, and the difference increases with temperature and pressure.

The experiment described above indicates a small difference between the two types of thermocouple but yields no positive information about the pressure effect on an individual couple. In making these runs, we repeatedly set the potentiometer on one of the couples and rapidly increased the pressure without adjusting the power input. The platinum/platinum–10 per cent rhodium couple showed either no change or a small erratic drift; the chromel-alumel couple invariably drifted to a higher emf. This suggests that the difference in reading between the couples is largely due to a pressure effect on the chromel-alumel couple.

Clearly, present data are too limited to make a meaningful correction for the effect of pressure on the emf of a thermocouple at pressures above 10 kb and temperatures above 1000°C. Hall's data and ours, nevertheless, indicate that the correction will be of the same order as the present precision of temperature measurement in this pressure range.

Acknowledgments. The construction of much of the apparatus described above was carried out with skill and ingenuity by Mr. O. R. McClunin, and his work is gratefully acknowledged. Dr. Alvin Van Valkenburg of the National Bureau of Standards supplied samples of pure bismuth and thallium, and Professor P. W. Bridgman sent us some of his stock of electrolytic bismuth. Drs. Sydney P. Clark and H. S. Yoder and Professor Francis Birch have read this manuscript and offered many helpful suggestions.

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