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CHAPTER 4

High Pressure-Temperature Apparatus

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1. INTRODUCTION

There has been an explosive growth in high pressure-temperature research in recent years. In 1955 there were probably less than six laboratories in the entire world conducting research at pressures above 25 kb (1 kilobar, abbreviated kb, equals 986.9 atmospheres or 14,504 pounds per square inch) simultaneously with temperatures above 500ºC. Today at least 150 laboratories have this capability. Another indicator of present day interest in high pressure research is the number of papers that are being published. Figure 1 shows the number of papers appearing each year from 1954 through 1961 wherein research conducted at 10 kb or above (static pressure) was reported. Without question, the great interest currently manifest in this field stems from the February 15, 1955 diamond synthesis announcement of the General Electric Company.

When considered in detail, there are perhaps as many high pressure devices as there are high pressure researchers, because each worker seems to develop certain aspects of the art to suit his own tastes. When considered in broad perspective, however, there are a limited number of basic apparatus types that have been developed for simultaneous use at high pressure and high temperature. They are: (1) Piston-cylinder, (2) Bridgman anvil, (3) Belt, (4) Multiple anvil, and (5) Supported piston apparatus. Following a discussion of general methods for generating pressure, these basic types and some variations thereof will be discussed.

In nature, pressure is universally generated by gravitational fields. This is the case whether the pressure is a transient generated when a meteor strikes or whether the pressure is static as exists in the interior of planets, stars or other celestial bodies. The maximum transient pressure generated when a meteor

falls to the earth is appreciable, being in excess of 150 kb. The pressure at the bottom of the deepest water on the earth's surface (seven miles in the Philippine Trench) is of the order of 1 kb, whereas the pressure at the center of the earth is of the order of 3.4×10^3 kb. Pressures at the center of some white dwarf stars are

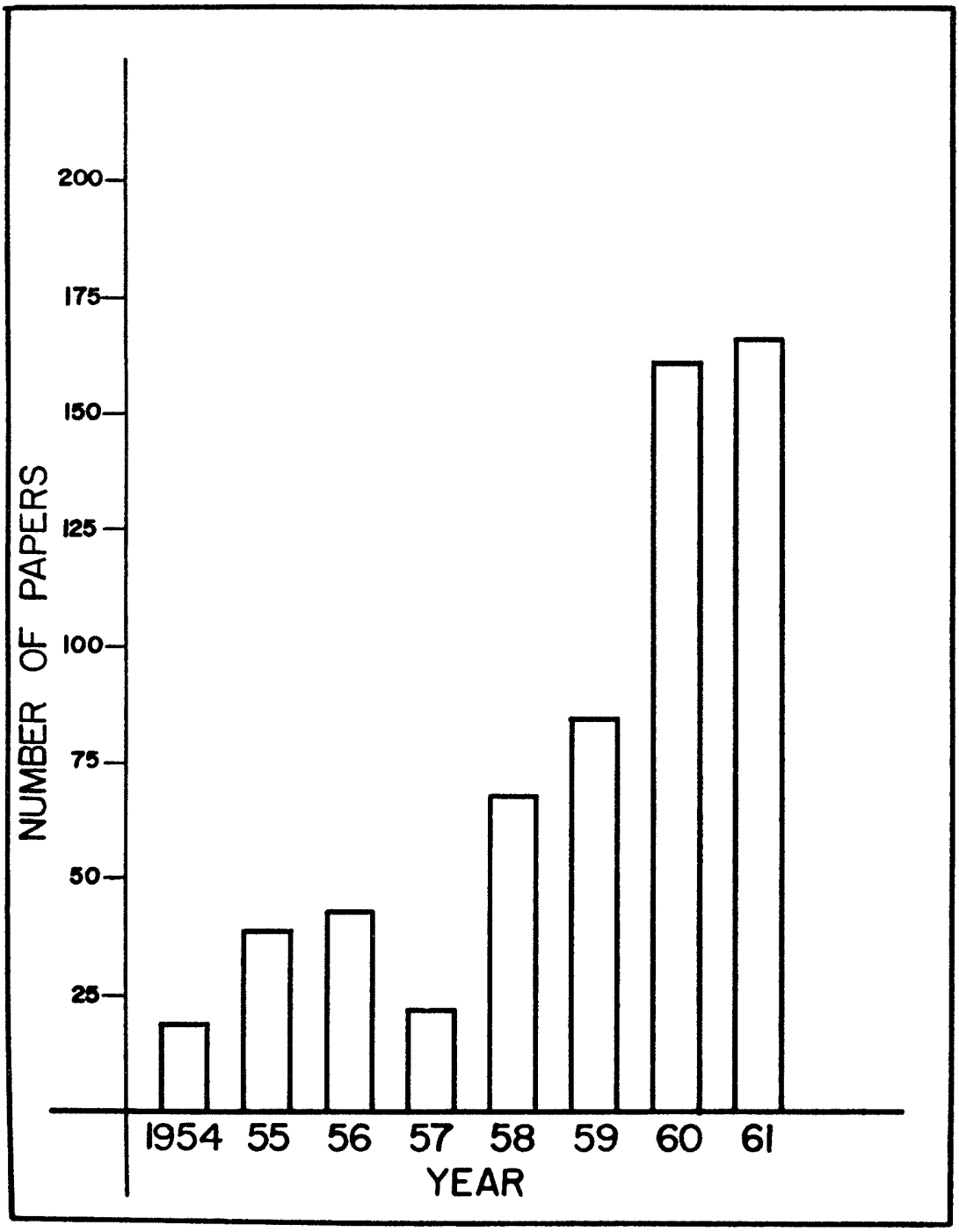

Fig. 1. High pressure papers (>10 kb) published each year from 1954 through 1961.

thought to be of the order of 10^{12} kb. Naturally existing pressures, many of them occurring simultaneously with very high temperatures, are of much greater magnitude than anything that can be produced in the laboratory.

One of the naturally occurring pressures can be rather readily utilized by man in his experiments--that being the pressure developed in the ocean depths. By lowering vessels containing the material to be studied into the sea, a plunger of some sort can be pushed into the vessel by the pressure of the surrounding water, or, alternatively, the vessel (when constructed of rubber, plastic, or thin metal) may be caused to collapse in order to generate a pressure inside. This procedure has been used in the past for some experiments, but with the progress of time, much superior and more convenient means have been developed for producing pressure.

A method akin to that of using the ocean depths to produce pressure is that of generating pressure by using the pull of gravity on a liquid contained in a long vertical tube. In times past, mercury columns were often used for this purpose because of the high density of this element. The substance to be compressed was placed at the bottom of the column, and the pressure exerted upon it was controlled by adjusting the height of the column. Very accurately measured, truly hydrostatic pressures were obtained in this way. However, the maximum pressures achieved were, by today's standards, very low.

In order to produce pressure there must be means for reducing the volume of a substance. This is usually accomplished, mechanically, by moving some confining walls, surrounding the sample, inward. If a very high pressure is to be developed, these walls must be very strong and relatively incompressible and, consequently, must be constructed in thick sections of the best materials. On moving confining walls inward, there is an immediate confrontation with problems involving heavily loaded sliding surfaces, gaskets, extrusion, plastic flow, friction, deformation, strength of materials, and design geometry. Attempts to meet these problems, particularly when high temperature as well as high pressure is involved, have brought forth considerable ingenuity in the design of high pressure devices.

2. PISTON-CYLINDER APPARATUS

The earliest type of high pressure apparatus consisted of a strong cylinder, fitted at one end with a sealing plug and at the other end with a movable, cylindrical piston. The sample to be compressed was placed inside the cylinder between the plug and the piston. Then the piston was driven into the cylinder, thus compressing the sample. When the sample was a liquid, as it usually was in the early days of high pressure research, it was necessary to provide some kind of a seal on the piston tip to prevent loss of liquid as pressure was developed.

One of the most famous seals is called the Bridgman Seal after its inventor, P. W. Bridgman[1]. One component of the seal is a mushroom-shaped plug. The stem of the mushroom, which is cylindrical in shape, fits accurately inside an axial hole in the tip of the piston. The head of the mushroom is also cylindrical and fits accurately to the internal diameter of the chamber. A soft ring of packing material is placed in the annular space between the stem and the chamber wall between the underside of the mushroom plug and the annular tip of the piston. When pressure is developed within the chamber, the pressure inside the packing exceeds the chamber pressure by virtue of the fact that the area of the annulus under the head of the mushroom plug is less than the area on top of the plug. Consequently this seal will not allow liquid to escape between the piston and the chamber wall. There are several other types of seals that are also satisfactory for sealing liquids in piston-cylinder devices, including a variety of "O"-ring seals.

When very high pressures are generated, the cylinder will expand. The piston will also expand, but under some conditions may not expand enough to prevent extrusion of fluid between the piston and the cylinder wall. In such instances it is sometimes possible to control the clearance between the piston and cylinder by compressing the outside of the cylinder at the same time that pressure is being generated by the advancing piston within the cylinder. One of the most convenient methods for compressing the cylinder is to provide a taper on the outer diameter of the cylinder which can be forced into a surrounding tapered ring at a suitable rate to offset the internal expansion due to pressure. Such a method was first used by Bridgman[2].

It seems that Charles Algernon Parsons was the first person to vigorously attack the problem of generating high pressure simultaneously with high temperature[34]. The driving force for Parsons' work was his great desire to synthesize diamonds. This desire also motivated most other researchers who entered the high pressure-temperature field before diamonds were finally synthesized. Parsons had excellent laboratory and shop facilities at his command and, consequently, conducted experiments on a grand scale. His pressure apparatus consisted of a piston and cylinder which used internal electrical resistance heating (see Figure 2). He used a solid pressure transmitting material which also served as thermal and electrical insulation and, probably, was the first person to utilize such a combination in a high pressure, high temperature device. His chamber diameters ranged from 3/8 to 6 in. The maximum pressures and

temperatures reported by Parsons were of the order of 15 kb and 3000ºC. Parsons actively pursued the diamond synthesis problem from 1887 to about 1920.

When solid substances are being studied in piston-cylinder devices, nothing is required, as a rule, in the way of a seal if the clearance between the piston and the cylinder is held to a low value (usually less than 0.0005 in.). If the material under study is a very soft solid with a very low coefficient of shear friction,

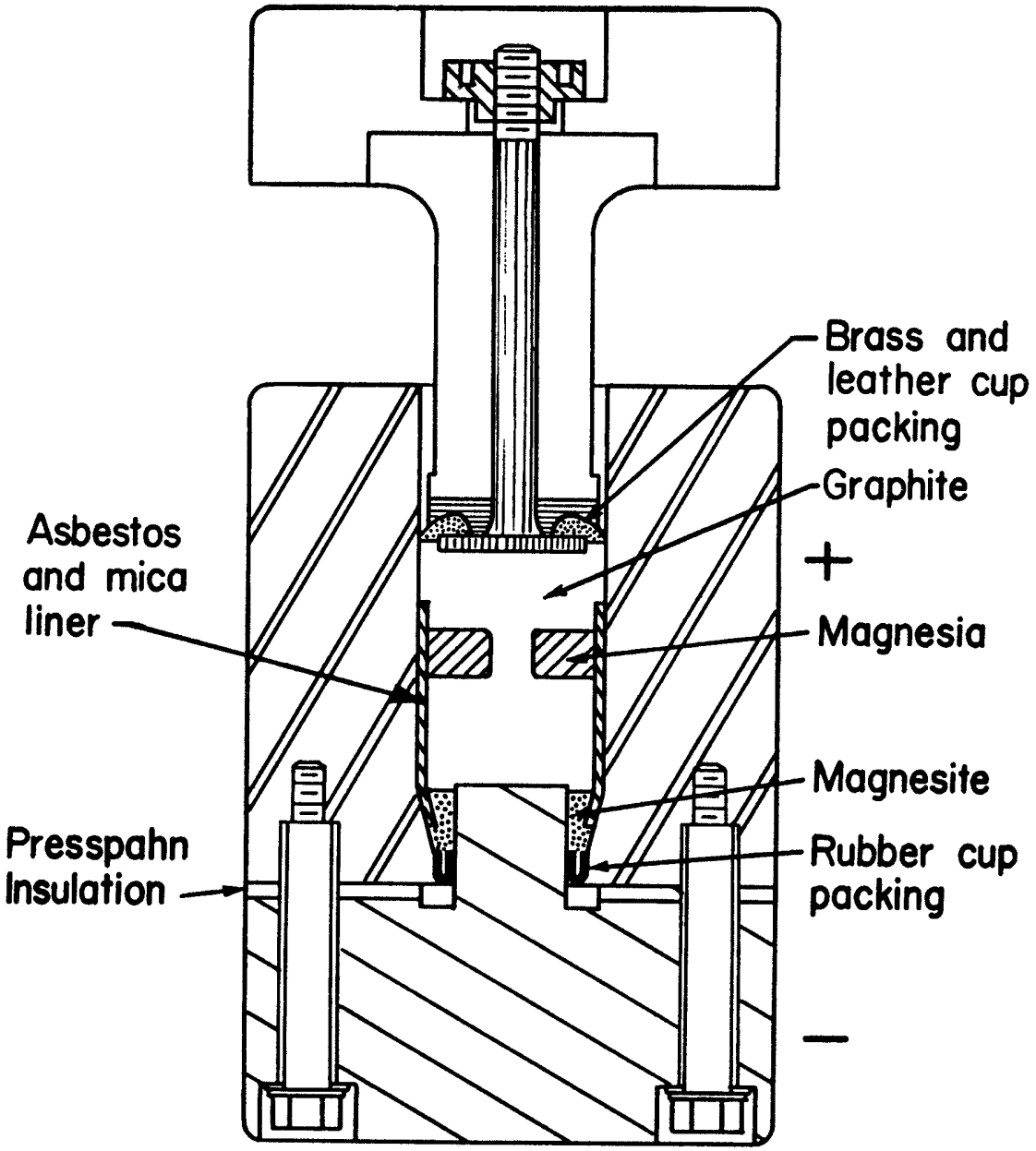

Fig. 2. One type of piston-cylinder device used by C. A. Parsons.

such as lead, tin, or indium, it will tend to extrude somewhat between the piston and cylinder even when the clearances are extremely small. Extrusion will also often occur with harder materials when passing through a pressure induced phase change, particularly when the volume decreases appreciably. This effect is apparently enhanced by the tremendous increase in reaction rate caused by the presence of a shear field. (It is also possible that there may be a reduction in the transformation pressure in a shear field.) A strong shear field exists near the periphery of the piston tip. In this region the sample is in contact with the cylinder wall and, because of friction, resists being moved by the advancing piston tip. This causes shearing

of the sample and, consequently, very rapid transformation in this region as compared to the rate of transformation in the bulk of the sample. Extrusion of the sample (because of the volume decrease accompanying transformation) into the annular clearance between piston and cylinder then occurs. The extrusion tends to be "explosive" because the shear increases tremendously during this process and further speeds the rate of transition. The above extrusion phenomenon is particularly apparent for bismuth metal. Extrusion of materials such as those described above can be prevented by use of a concave disk of cold-rolled steel sheet, approximately 0.005 in. thick of a diameter equal to that of the piston. This disk will, when placed between the piston tip and the sample, flatten under load thus expanding (because of its original concave shape) tightly against the cylinder wall to provide a simple, effective seal. Sometimes two or three disks are more effective than one.

In the early piston-cylinder devices, both the piston and cylinder were constructed of high quality tool steels. The piston was usually made glass hard, while the cylinder was somewhat softer. Maximum pressures attainable with steel pistons and cylinders were somewhere in the neighborhood of 25 kb. As piston-cylinder devices were improved, cemented tungsten carbides were substituted for steels. The usual cementing agent in cemented tungsten carbides is cobalt. For high pressure work the cobalt content is usually used in the range from 1 to 12 wt. %. Carbides with the lowest cobalt content have the highest compressive strengths. However, they are very brittle and are very subject to fracture under unbalanced loading. For most high pressure research, carbides containing about 6 wt. %. cobalt give the best results. Because tungsten carbides have limited tensile strengths (their tensile strengths are of the order of 1/50th of their compressive strengths), cylinders of this material must be supported by external steel binding rings. These are designed to keep the tungsten carbide under compression at all times, regardless of the pressure being developed inside. Cemented tungsten carbides have the highest compressive strength (of the order of 800,000 p.s.i.) of any engineering materials that can be fabricated into relatively large shapes. In addition to utilizing steel binding rings to give radial support to carbide cylinders, experience has shown that end-loading of cylinders made of brittle materials is important in order to prevent breakage in a plane perpendicular to the cylinder axis. Breakage usually commences in the vicinity of a piston tip because of the steep pressure gradient existing there. End loading is usually provided by an auxiliary hydraulic ram operating concentrically with the piston-driving ram or, alternatively, by a pair of heavy clamping plates that are forced together by tension bolts. Piston-cylinder devices, so constructed, can be routinely used at pressures in the neighborhood of 40 kb and can occasionally be taken to pressures in the neighborhood of 60 kb.

In order to heat a material being subjected to pressure in a piston-cylinder apparatus, it is generally most convenient to use an internal electrical resistance furnace and to place the material being studied within this furnace. Such furnaces usually require a rather large current for their operation. Consequently, it is necessary to have heavy electrical connections enter the working volume of the apparatus. It is quite practical to insulate the bottom plug from the cylinder and to use it as one of the electrical connections. The moving piston can then serve as the other.

Historically, Loring L. Coes, Jr., of the Norton Company, seems to have been the first person to develop a piston-cylinder device with simultaneous pressure-temperature capabilities considerably beyond those used by Parsons. Therefore, time will be taken to briefly discuss some of his work.

Coes reported the synthesis of a new dense silica in July of 1953[5]. This material, which has since been named coesite, is one of the most interesting materials that has been synthesized by high pressure, high temperature techniques. Coesite has a density of 3.01, whereas the density of quartz is only 2.65. Its refractive index is 1.60 while the refractive index of quartz is 1.54. It was discovered during a study of the minerals constituting eclogite, the material with which diamonds are associated in the diamond bearing pipes. Coesite was first synthesized at a pressure near 35 kb between 500-800ºC. (Incidentally, another SiO_2, stishovite, still more dense than coesite, was synthesized by S. M. Stishov and S. V. Popova in 1961 at a pressure of about 115 kb and a temperature of about 1300ºC. This material has the remarkably high density of 4.35 and refractive index of 1.81.)[6] Following the synthesis of coesite and stishovite, these materials were found in nature, in silicate materials, where huge meteorites had crashed to the earth.

Coes did not describe his high-pressure apparatus in the 1953 Science article. At the American Ceramic Society meeting April 21, 1954, in Chicago, Coes presented a paper on "High Pressure Minerals" that had been synthesized during the course of his research on the synthesis of diamonds. On this occasion, Coes, again, did not discuss the nature of the equipment used in this research. He did, however, describe the apparatus at the "Seventh Symposium on Crystal Chemistry as Applied to Ceramics," held at Rutgers

University, New Brunswick, New Jersey, June 4, 1954. Coes, however, did not personally publish a description of the apparatus until 1962.[7]

The apparatus consists of a special alumina cylinder that is force-fit into a steel binding ring as shown in Figure 3. The apparatus is double-ended, pressure being generated by pushing a tungsten carbide piston into each end of the alumina cylinder. Heating is accomplished by passing an electric current from one piston through a cylindrical graphite heating tube, in which the sample capsule is contained, and out

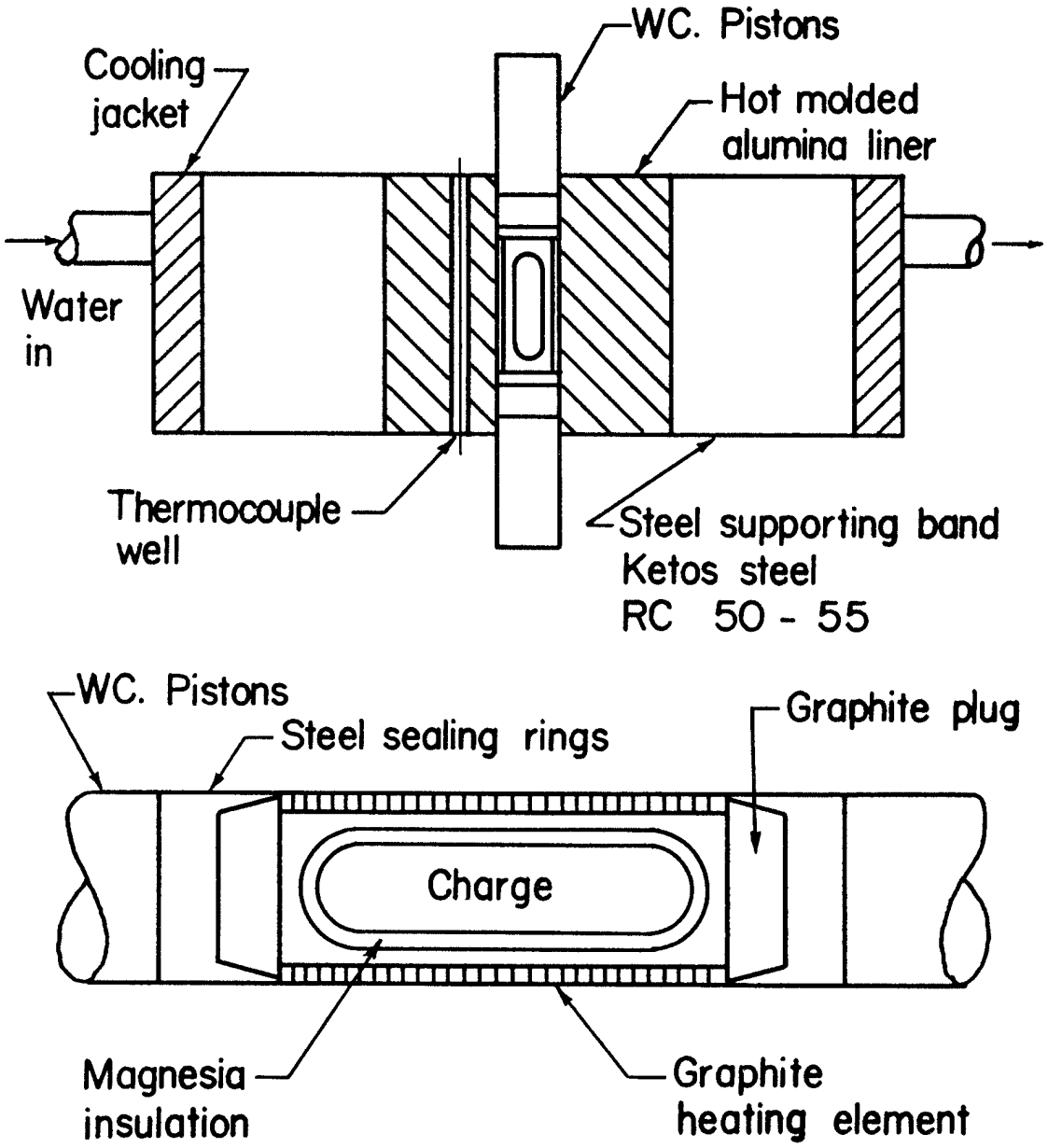

Fig. 3. Coes piston-cylinder apparatus.

through the opposite piston. The alumina cylinder insulates the two pistons from each other, thus making such resistance heating possible. The ultimate pressure capabilities of this apparatus are somewhere in the neighborhood of 45 kb at a temperature of 800ºC. At a pressure of 30 kb the temperature can be increased to the neighborhood of 1000ºC. Temperature is measured by means of a thermocouple located in a well adjacent to the cylindrical chamber as shown in the drawing. Of course the temperature at this point is lower than the temperature at the sample, but comparisons made with a thermocouple in the sample at 1 kb make it possible to correct the temperature reading of the thermocouple in the well.

Other variants of simple piston-cylinder devices for high pressure-temperature use have been described by Birch, Robertson, and Clark[8], Hall[9], and Boyd and England.[10]

3. HEATING METHODS

Only brief mention has been made, so far, of the procedures used in heating piston-cylinder apparatus. Before proceeding further, it would be well to discuss general heating methods. One method for heating material being subjected to pressure is to externally heat that part of the apparatus containing the material under study. This is done by immersing the equipment in a thermostated bath, or by surrounding the proper pressure components with some kind of a furnace. Thermostated baths containing silicone fluids have been used at temperatures to 300ºC. External furnaces have been used with anvil devices to temperatures as high as 1000ºC. The major problem connected with external heating of high pressure components is the loss of strength of materials. The upper temperature limit for steel high pressure components is about 300ºC. Cemented tungsten carbide components can be heated to the neighborhood of 700ºC, while cemented chromium carbide components will maintain considerable strength to about 1000ºC. In general, thermostat bath immersion has been used to heat piston-cylinder type devices, whereas external furnaces have been used with Bridgman anvils. In the case of Bridgman anvils, pressures of about 20 kb can be developed at temperatures of the order of 1000ºC when the anvils are made of cemented chromium carbide. Reducing the temperature will, of course, allow higher pressures to be generated.

It is sometimes possible and convenient to determine temperature coefficients for processes occurring at high temperature by working at low temperature. This is done by extrapolating the low temperature results to regions of higher temperature. Low temperatures can be generated in many types of high pressure devices by immersing the requisite parts of the apparatus in a cryogenic liquid or by circulating a cryogenic fluid through the apparatus. The steel and carbide parts are generally not weakened by low temperature. In fact, some materials may be strengthened when subjected to low temperatures.

Another procedure for heating material being subjected to pressure is to supply heat directly inside the apparatus. This heating can be accomplished by passing a steady current through a resistance element located inside the pressure chamber. Very high temperature transient heating can be obtained by discharging a capacitor through a resistance element. Another internal heating procedure, also transient in nature, utilizes the heat generated by chemical reactions. In this connection, Bridgman[11], in his diamond synthesis research, ignited a thermite charge inside a piston-cylinder apparatus thereby generating temperatures of about 3000ºC for a period of a few milliseconds. Nuclear reactions have been suggested for developing temperatures inside high pressure devices, but apparently have not yet been used in practice.

Electrical resistance heating, the most common form of internal heating for high pressure devices, is usually carried out by means of a tube or box type resistance furnace that surrounds the specimen under study. It is necessary, in the case of internal heating, to protect the chamber walls of the apparatus from the high temperature so that they will not be weakened or destroyed. The furnace must, therefore, be separated from the walls by some insulating media. The most common media used are thermally insulating solids which also provide electrical insulation, transmit the pressure, and often serve, in addition, as compressible gaskets. Besides filling these roles, the solid thermal insulator must be chemically inert and stable under the experimental conditions to which it is subjected.

It might be well at this juncture to point out that all liquids that are ordinarily liquids at room temperature, are frozen solid at pressures of 35 kb or less at room temperature. A 50-50 (by volume) mixture of normal pentane and iso-pentane freezes at 35 kb, this having the longest range of liquid existence (under pressure) of any known liquid. Most liquids freeze well below 10 kb. It would be most desirable to always use fluids to transmit pressure since they subject the sample to uniform pressure over its entire surface. Non-hydrostatic media such as solids can introduce pressure gradients on a sample's surface. Such gradients are undesirable for some experiments. At pressures above 35 kb (at room temperature), however, the only fluids existing are materials that are ordinarily gases at room temperature. Handling gases at such pressures has proved to be unfeasible up to the present time. Therefore, experimenters have turned to the use of solids as pressure transmitters. At very high pressures, there are many solids that behave in an approximately hydrostatic fashion. Their use greatly simplifies the problems of apparatus design and makes it possible to achieve pressures and temperatures that would otherwise be impossible. Examples of some of the solids used are pyrophyllite (a fine-grained, naturally occurring, hydrous aluminum silicate), hexagonal boron nitride (fine-grained, polycrystalline), silver chloride and sodium chloride.

In some high pressure, high temperature devices where fluids have been used to transmit pressure, the fluids are gases such as argon or nitrogen. In others, the fluids may be liquids such as kerosene. In these

instances, the sample is contained inside an electrical resistance furnace that is baffled externally to shield the walls of the containing vessel from the heat of the furnace. Sometimes the baffles are concentric, reflective metal shields. In other instances a granular, thermally insulating solid is loosely packed between the furnace and the chamber wall to serve as a baffle. In addition to the baffles, it is necessary to have adequate liquid cooling of the apparatus components. This is also true in instances where solid materials are used as the thermal insulator. Heat loss is much greater in fluid systems than in solid systems. Therefore, much more cooling is required when fluids are used to transmit pressure. The highest temperatures that have been reported to date in fluid systems are of the order of 1400ºC simultaneously with pressures of about 27 kb.

4. FRICTIONAL EFFECTS

With any type of high pressure device, due concern must be given to the problems arising from friction. Consideration must also be given to the phenomenon of hysteresis. Friction and hysteresis may be associated with sliding surfaces, or with solid substances being used to transmit pressure, or may be important in connection with a solid material being studied since all solids exhibit internal friction effects under pressure. In piston-cylinder devices, the friction at the interface between the piston and the cylinder wall is an item of some concern in determining, from the force on the piston and the area of the piston tip, the pressure transmitted to the sample. As the piston is pushed into the cylinder there will be a certain amount of frictional holdup so that the driving thrust transmitted to the piston is not completely transferred to the sample. When the thrust on the piston is released there will be a "backlash" region in which the frictional forces are reversing direction. Following this, friction will hinder the retraction of the piston from the cylinder; the net result being that pressure will be higher within the sample than that calculated from force/area relationships. There will be similar effects occurring in the ram of the hydraulic press that is used to drive the pistons or other pressure generating components. Hydraulic ram friction will, in general, however, be much smaller than the friction in the high pressure piston-cylinder system. The correct pressure applied to a sample would lie about midway between the force/area pressure calculated during the compression and decompression cycles and procedures have been worked out for determining the correct pressure on the sample.

At very high pressures, friction in piston-cylinder devices can absorb an appreciable fraction of the total applied load. Under these circumstances it becomes difficult to make an accurate friction correction. It is possible to considerably reduce the friction correction by using equipment in which the piston can be rotated while pressure is applied. The rotation need be only ± 1º or 2º to be effective.[12] Rotation of the piston in high pressure piston-cylinder devices is an application of the free piston gage principle.[13] In the free piston gage (a device used as a primary pressure standard), rotation of the calibrating piston allows it to settle to its equilibrium position thereby overcoming the frictional effects. When piston deflections are measured during compression and decompression cycles while the piston is being rotated, the deflections will be much closer together than deflections taken without piston rotation. In fluid systems at relatively low pressures the friction correction can be reduced to a negligible value. When solid materials are used to transmit pressure in high pressure devices, however, piston rotation is only partially effective in eliminating frictional errors. This is true because of the frictional lag (hysteresis) inherent in solid pressure transmitting materials. Many solids, particularly those composed of fine powders, will not transmit the total pressure to which they have been subjected to their interior regions. On the other hand, when the pressure on the exterior surface of the solid is reduced, the pressure on the interior remains unchanged at first (a backlash effect). Further reduction of exterior pressure leads to a situation wherein the interior pressure exceeds the external pressure. In some solids this can be a considerable effect.

5. MULTI-STAGING

In a piston-cylinder apparatus it is quite practical to effectively support all free surfaces of the cylinder (thus preventing it from breaking). When this has been done, the only free surface remaining is the exposed portion of the piston that protrudes from the cylinder. Piston breakage is reduced by keeping the length of the protruding portion as small as possible. It is usually the piston, however, that ultimately fails as higher and higher pressures are produced. Theoretically, extremely high pressures could be developed by a process known as multi-staging. In multi-staging, one high pressure apparatus is placed inside the chamber of a larger high pressure apparatus, and so on. In practice, true multi-staging has not been carried beyond two stages. P. W. Bridgman[14] was the only experimenter to ever build and operate a true two-stage piston-cylinder device. The theory of a two-stage apparatus is based on the idea that the pressure responsible for breakage of components is a differential pressure; namely the difference in pressure between the interior and the exterior of the apparatus. Therefore, if one apparatus which, for example,

could generate 50 kb as a single stage device, were placed inside the chamber of a larger apparatus (also capable of generating a pressure of 50 kb), it should be possible to generate 100 kb in the chamber of the inside apparatus since its exterior could be subjected to 50 kb by the outside apparatus. In Bridgman's two-stage apparatus, the inside piston had a diameter of 1/16 in. It was difficult to measure the frictional forces on the inside piston and to properly correct for them because they were very large. Bridgman did succeed, however, in measuring compressibilities of a large number of substances to 100 kb in this device. This work has not been duplicated by others, yet it is used as a basis for the calibration of high pressure equipment and as a basis for confirming theoretical work on the compressibilities of materials.

6. ANVIL APPARATUS

The first anvil apparatus was probably constructed by Wartman in 1859. This apparatus was described in an article entitled, "On the Effect of Pressure on Electrical Conductibility in Metallic Wires."[15]

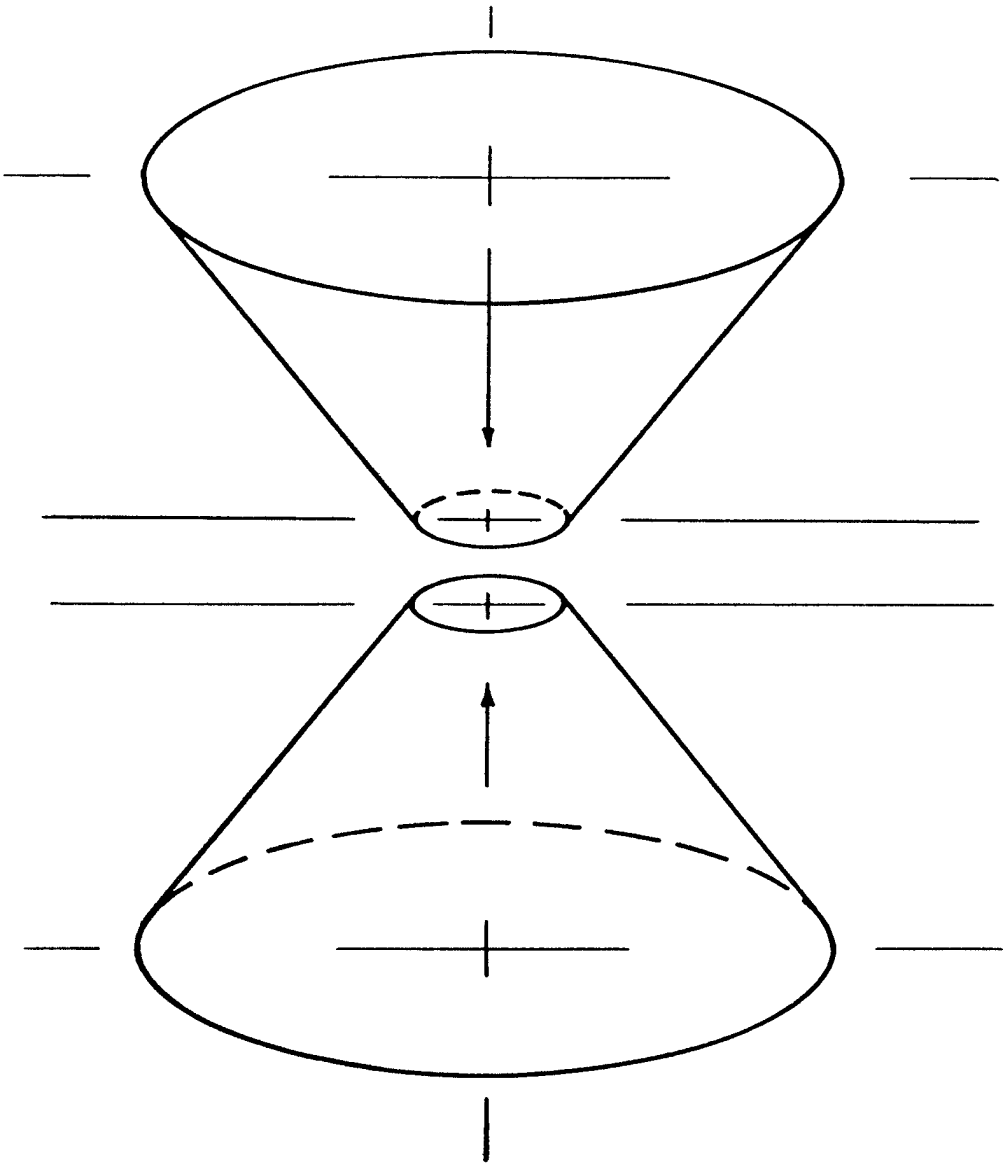

Fig. 4. Pair of truncated cones, illustrating principle of massive support.

The metal wires used in these experiments were embedded in guttapercha which was, in turn, compressed between the jaws of a hydraulic press. The pressure developed was estimated to be 0.4 kb. Following this work, the use of anvils in high pressure devices seems to have been abandoned for about 75 years—the next published anvil work, that of P. W. Bridgman, not appearing until 1935.[16]

Anvils are capable of producing the highest static pressures attainable at the present time. They are able to do this because of a principle known as "massive support." If a pair of truncated cones (see Figure 4) is designed so that the small circular faces (which bear on each other in an anvil device) have an area that is considerably smaller than the area of the cone bases, any axial thrust imposed on the abutting faces

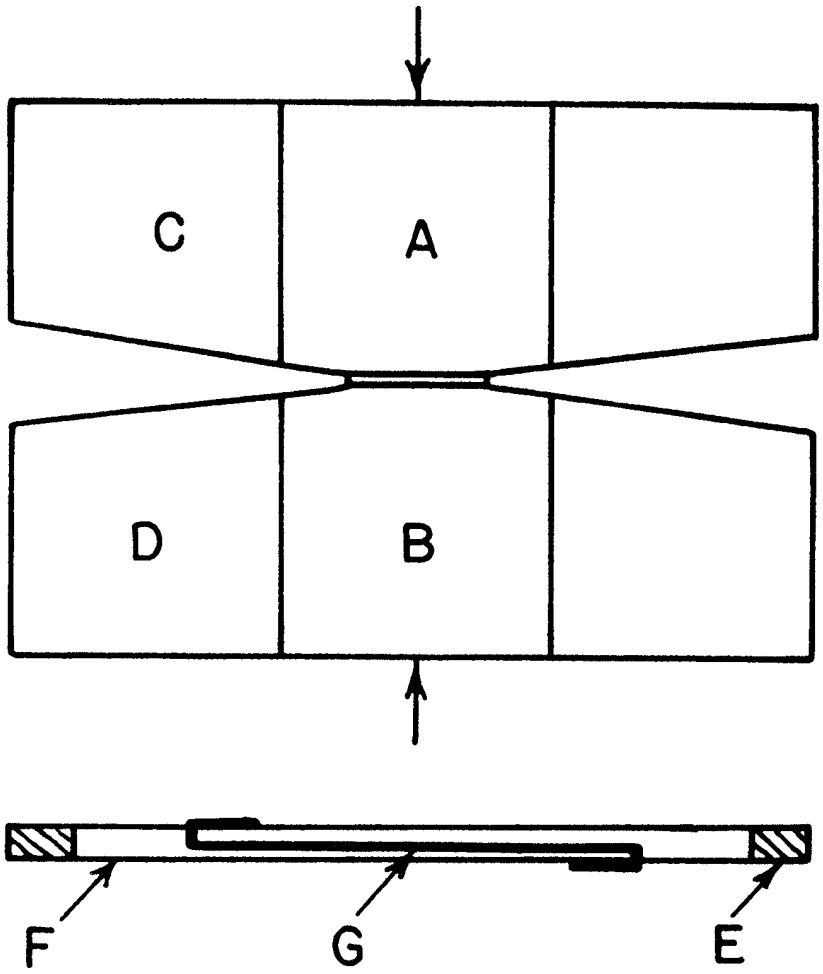

Fig. 5. Bridgman anvils (upper) and cell arrangement (enlarged, lower) for measuring electrical resistance. *A* and *B* are equivalent cemented tungsten carbide anvils, *C* and *D* are steel binding rings, *E* is a pipestone ring, *F* is silver chloride, and *G* is a ribbon of the metal under study.

is "fanned out" into the greater circular area behind the faces. Massive support is thereby provided to the faces and they are able to withstand a much greater load than would the face of a right circular cylinder of the same area. (Note that the mechanical ties to the face of a right circular cylinder reach back into an area that remains constant with distance.)

Bridgman anvils, as these devices have come to be known, are essentially "two-dimensional" in that the ratio of sample diameter to sample thickness, at the highest pressures, is of the order of 1:100. Common sample thicknesses range from about 0.002 in. to 0.010 in.

In order to accommodate a sample (in Bridgman anvils) and transmit pressure to it in a reasonably hydrostatic fashion, the sample is embedded in a silver chloride disk. The disk of silver chloride is surrounded by a pipestone gasket as shown in Figure 5. Pipestone is the common name of the fine-grained mineral catlinite. This mineral consists primarily of micron sized crystals of hydrous aluminum silicates with small amounts of iron oxide and other substances. For centuries this material has been used by American Indians to make smoking pipes; hence, the name pipestone. Other fine-grained solids with frictional and compressive characteristics similar to those of pipestone may also be used in constructing

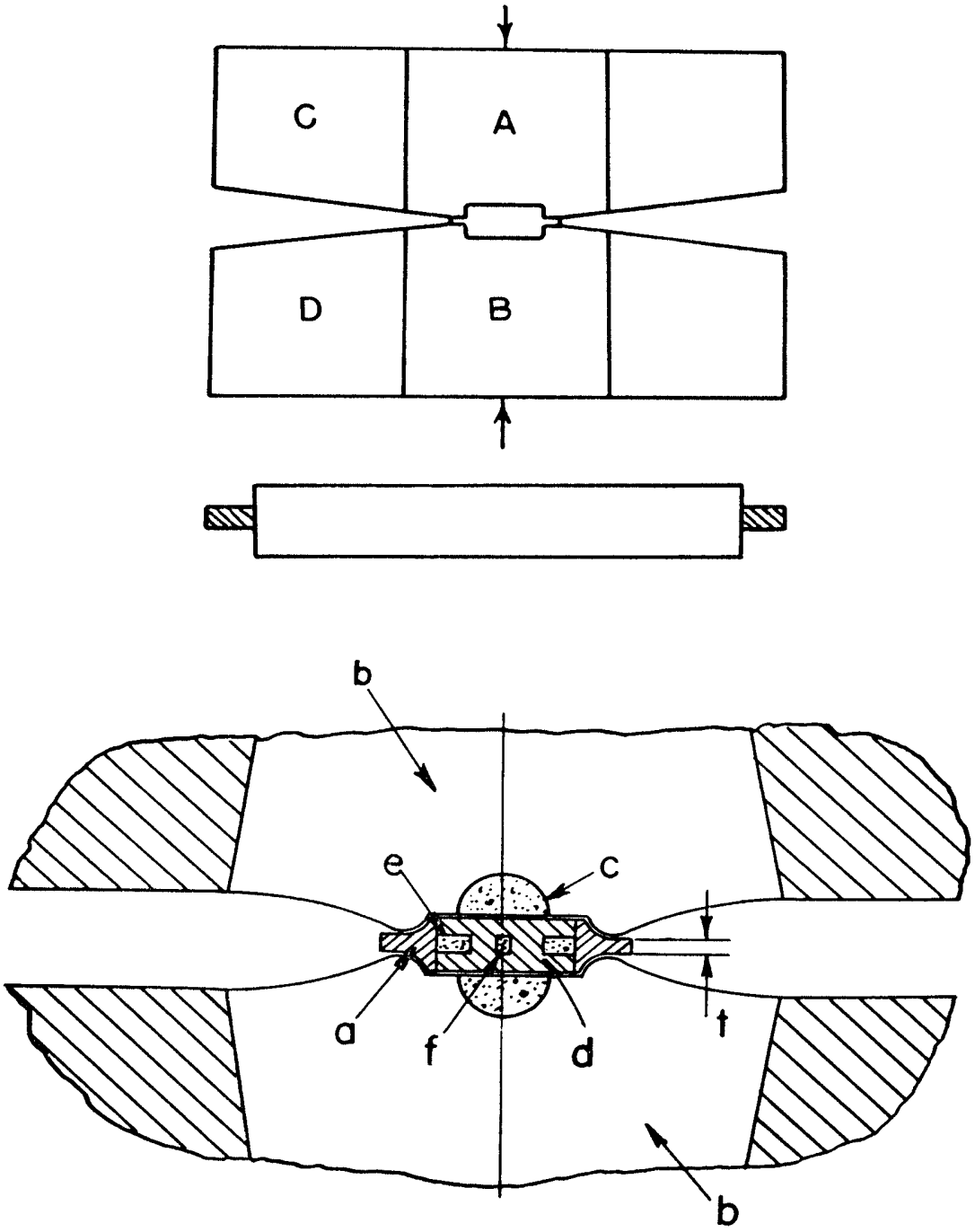

Fig. 6. Bridgman's "hollowed" anvils with an enlarged view of the sample and gasket immediately below (upper) and Bundy's "saucer" (lower). In the saucer *b* is steel or carbide, *c* and *e* are dense alumina, *d* is graphite, *f* is the sample, and *t* represents the initial gasket thickness.

gaskets for Bridgman anvils. Examples of such materials are the minerals pyrophyllite and talc, clay minerals and some oxides. Under load, a thin section of pipestone is very strong. Because of its frictional characteristics, it bites into the periphery of the anvil faces and effectively prevents extrusion of the silver chloride and its imbedded sample as pressure is developed between the advancing anvil faces.

In addition to using pipestone or similar stony gaskets, some researchers[17] have utilized metal gaskets constructed of materials such as nickel or platinum. These gaskets are usually used when water or some other liquid is being subjected to pressure since they can effectively contain liquids at high pressure and temperature in a Bridgman anvil device. Stony gaskets such as pyrophyllite or pipestone are porous and will not contain liquids under such conditions.

Bridgman anvils can be forced together until the force/area pressure is at least 200 kb. By providing support to the sloping anvil shoulders with liquid or solid media, various designs have been developed in which pressures as high as 500 kb have been generated.[18] In developing such pressures it is necessary to utilize rather small cemented tungsten carbide anvils. Apparently, large anvils contain a greater number of flaws or defects where cracks can begin to propagate. Therefore, the maximum pressure developed with large tungsten carbide pressure components is always less than that obtained with small components. It is also necessary in achieving the highest pressures to strengthen the anvils or analogous high pressure components by "coldwork." During cold-working, the anvils are deformed and, consequently, must be reground to proper dimensions before use.

The most common method for heating Bridgman anvils is to build an external furnace around the anvil system. Internal heating has also been used; for example, Balchan and Drickamer[19], working on a microscopic scale, have introduced internal electrical heaters into modified Bridgman anvil devices, and, by such means, have achieved temperatures as high as 400ºC at 200 kb. This apparatus is used for optical work and uses salt to transmit pressure, provide support to the Bridgman anvils, and to serve as optical windows. Another method for heating material between flat anvils (probably first used by F. P. Bundy, unpublished work, General Electric Research Laboratory, Schenectady, New York) is to discharge a

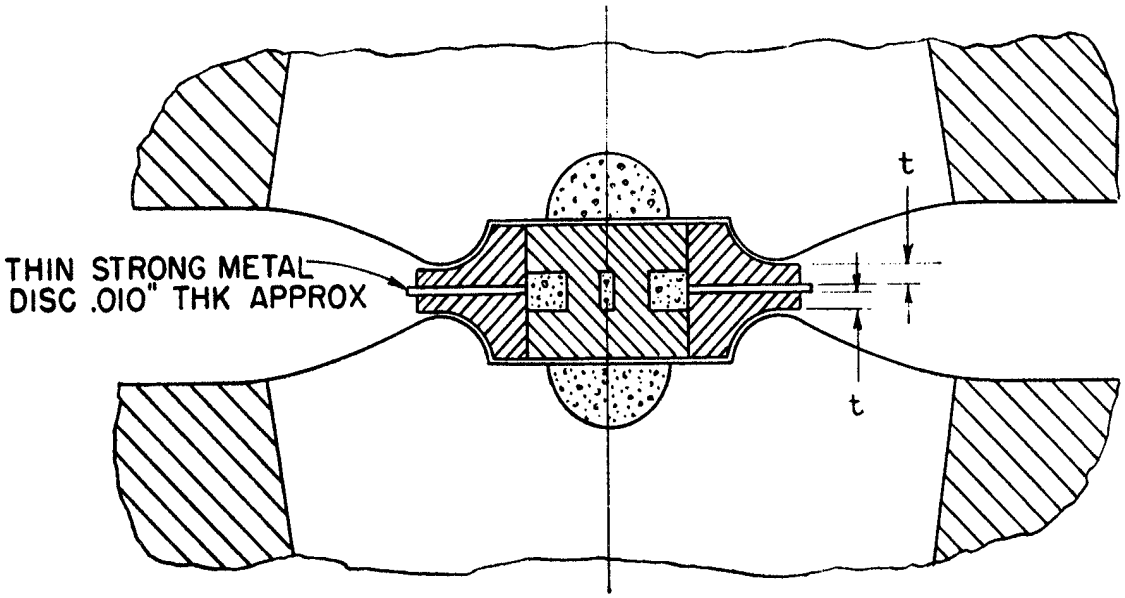

Fig. 7. Hall's sandwich gasket as used with "saucer" apparatus.

condenser through the anvils into an electrically conducting medium inside. Such a procedure, of course, limits the heating time to a few milliseconds, Consequently, maximum temperature is achieved for an extremely short period of time. Generation of high temperature by this procedure depends on the fact that the time required for conduction of heat away from the sample is large compared to the duration of the transient impulse from the condenser. It is of interest to note that F. P. Bundy has successfully synthesized diamond directly from graphite, in belt-type apparatus, utilizing condenser discharge heating.[20] The pressure and temperature required were about 130 kb and 3000ºC.

A serious shortcoming of Bridgman anvil type devices is their tiny working volume. Bridgman made an attempt to increase the thickness of the sample between his flat anvils, thereby increasing the volume of the specimen that could be subjected to pressure. This was done by hollowing the anvils as shown in Figure 6. Hollowing the anvils severely reduced the pressure that could be achieved because the ratio of total available anvil motion (initial gasket thickness was unchanged) to sample thickness was

greatly increased. In addition, considerable breakage was experienced because of the stress concentration points in this angular design.

F. P. Bundy (unpublished work) improved on Bridgman's hollowed anvils by rounding the edges as shown in Fig. 6. Bundy called his device the "Saucer." Thermal insulation was provided at the ends of

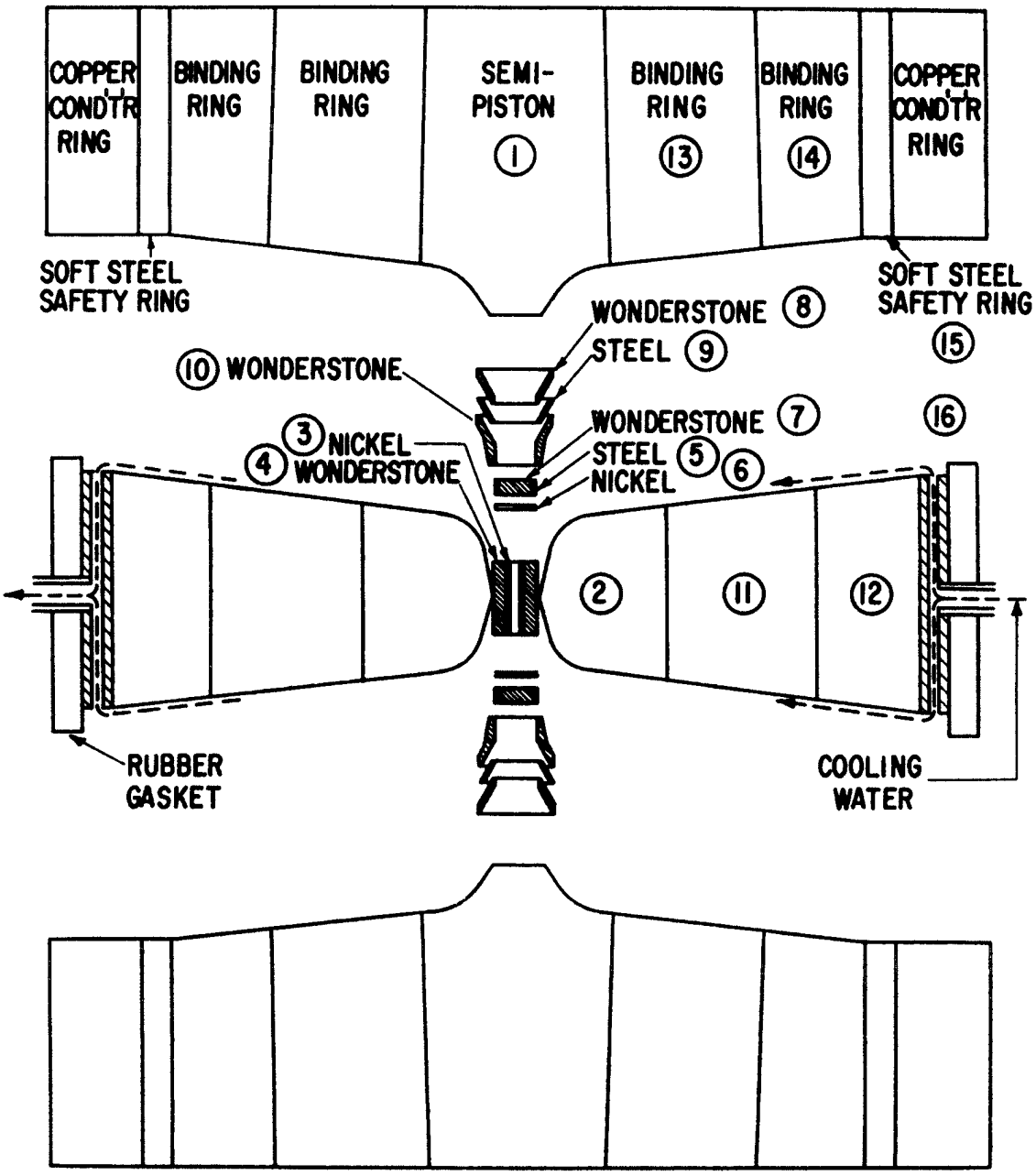

Fig. 8. "Exploded" view of belt apparatus.

the sample by an embedded slug of hot-pressed alumina located in the central portion of the saucer. Heating was accomplished by electrical resistance means. Temperatures as high as 2500°C were obtained, simultaneously with pressures in the neighborhood of 35 kb.

The pressure range of Bundy's device was extended somewhat and the volume was increased considerably by the author's invention of the sandwich gasket, composed of steel and pyrophyllite, as is shown in Figure 7.[21] When pyrophyllite is used alone as gasket material, there is, for any particular apparatus design, an optimum thickness for the gasket. When greater thicknesses than the optimum are

used, the pyrophyllite crumbles irregularly as the anvils are brought together and the pressure that can be developed is reduced. Two sections of pyrophyllite, with an intermediate section of steel (as in the sandwich gasket above), however, more than doubles the optimum gasket thickness. This doubles the available anvil motion and permits a larger sample to be accommodated. Additional layers in the sandwich are efficacious in some high pressure designs.

7. THE BELT APPARATUS

One of the most effective high pressure, high temperature devices that has been conceived is the Belt apparatus. The idea of using a conical piston and a conical shaped chamber together with a compressible, sandwich gasket to generate pressure was conceived and perfected by the author late in 1952 and early 1953. The Belt was first described in a General Electric Research Laboratory report no. RL-1064 in March of 1954. Distribution of this report, however, was limited within the company. The report was finally published six years later in the Review of Scientific Instruments. During the long interval prior to publication, however, there were some official and unofficial "leaks" concerning details of the Belt design.

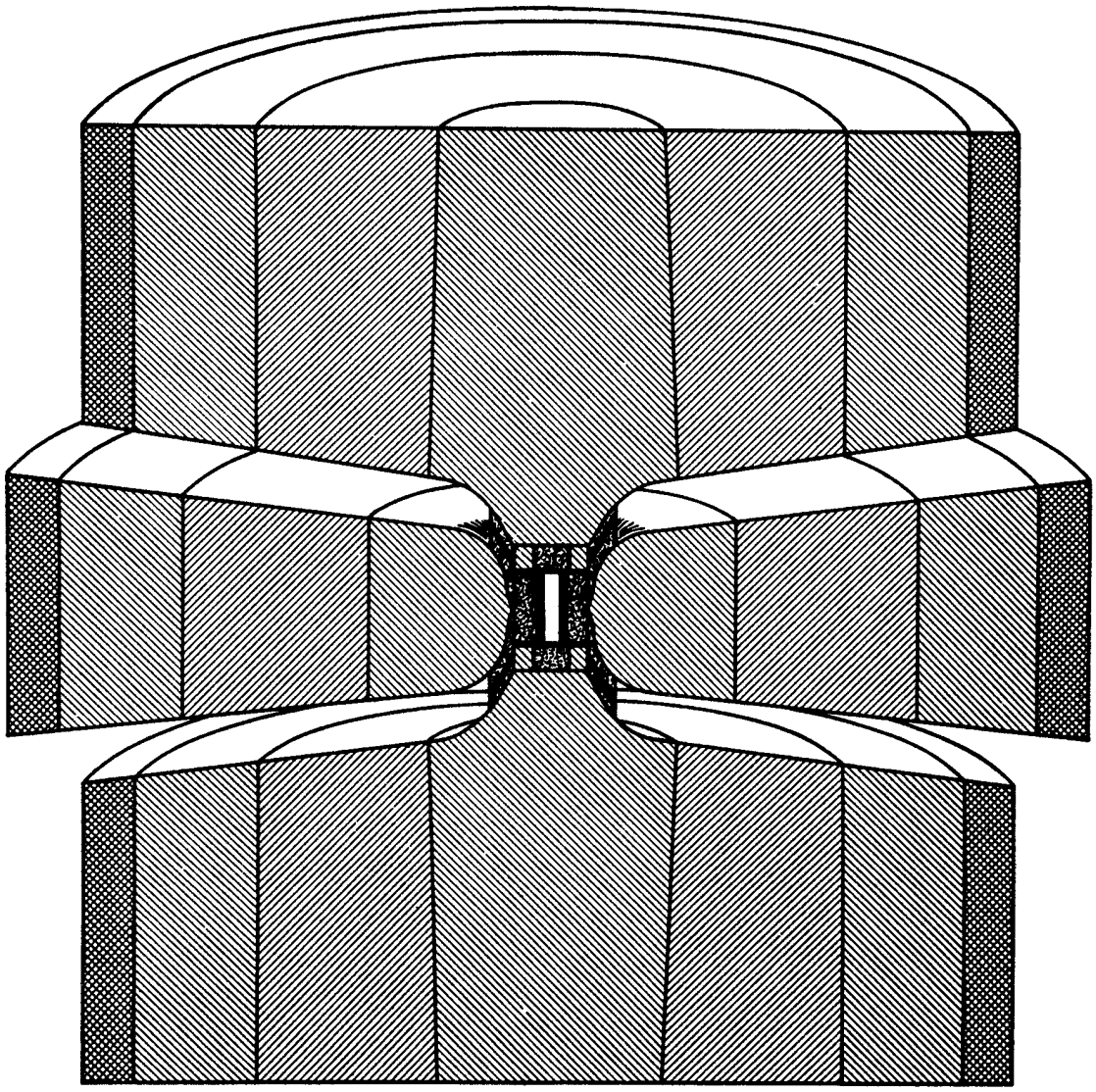

Fig. 9. "Assembled" view of belt apparatus.

For example, the original General Electric press release "Man Made Diamonds," February 15, 1955, included photographs which clearly showed the double-ended conical piston-chamber arrangement and the use of binding rings for support. In September of 1953, the Belt was shown to a prominent European high pressure worker visiting the General Electric Laboratory in Schenectady. He left with sketches and

dimensions. At about this same time, a G.E. research associate transmitted details of the device to his former professor who was working in high pressures at a midwestern university. Some minor information concerning the Belt was revealed in a paper published in 1955 on the melting point of germanium as a function of pressure.[22]

Diagrams of the Belt apparatus are shown in Figures 8 and 9, and a photograph of the first Belt is shown in Figure 10. The function of the various components can be explained by referring to Figure 8. The conical pistons (1) are thrust into each end of a conically shaped chamber (2) by a hydraulic press. Pressure generated by the advancing pistons is transmitted to the sample (contained in the sample-heater tube (3)) by

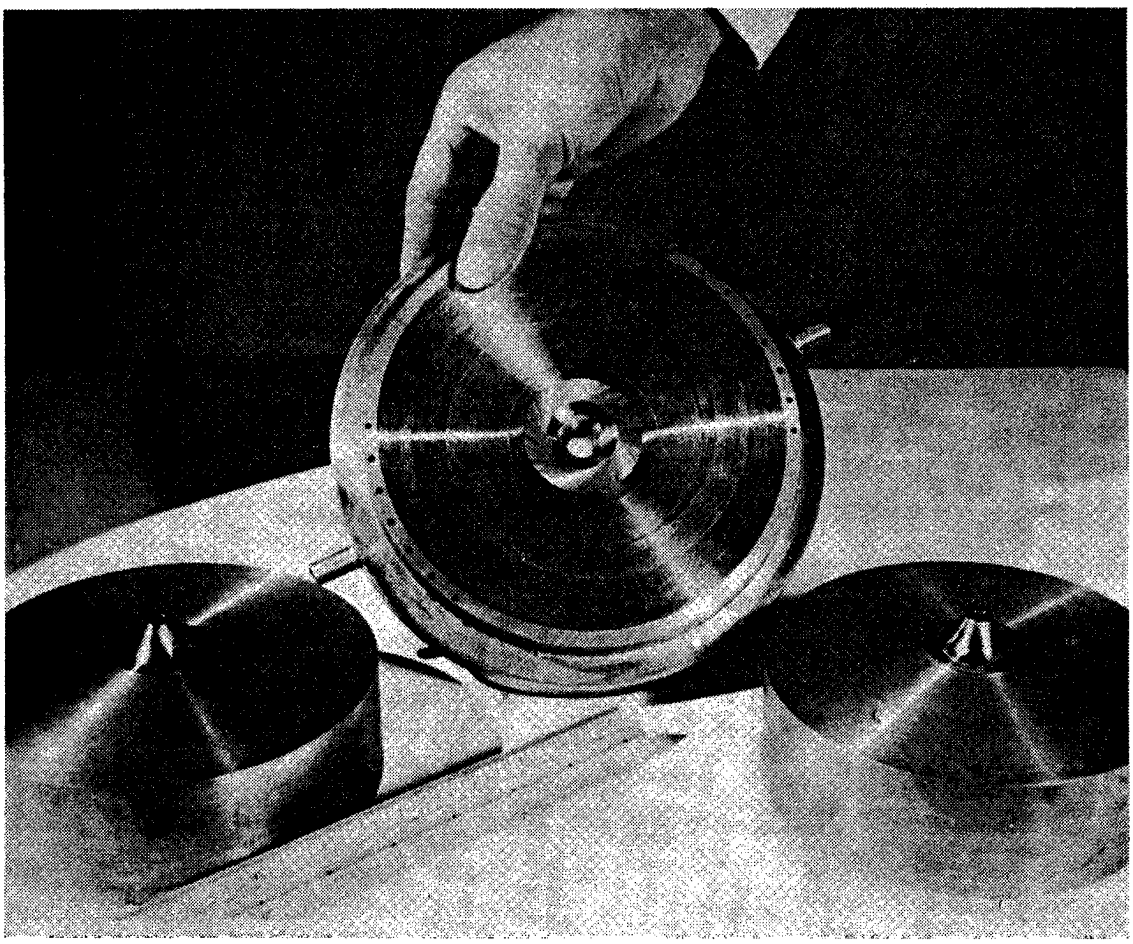

Fig. 10. Photograph of first belt apparatus.

pyrophyllite (4) or similar material, noted as wonderstone in Figure 8. In addition to transmitting pressure, the pyrophyllite also serves as thermal and electrical insulation. The sample is heated by passing an electrical current through the heater-sample tube (3). Current enters this tube from the pistons by way of hardened steel conducting rings (5) and metal end disks (6). The short cylindrical slugs of lava (7) provide thermal insulation at the ends of the heater-sample tube. The sandwich gasket, which consists of two pyrophyllite sections with a steel cone between them (parts 8, 9, and 10, respectively), compresses and extrudes under piston load thus allowing the pistons to generate pressure within the chamber. Hardened steel binding rings (11 and 12), which are stressed almost to their yield points by tapered, interference press-fits, maintain a compressive load on the cemented tungsten carbide chamber (2) to prevent it from breaking as pressure is developed within the chamber. The tapered piston is likewise strengthened by press-fit binding rings. Soft steel safty rings (15 and 16) surround the press-fit binding rings (13 and 14) as a protective measure against flying fragments should the binding rings fail. The chamber (2) and rings (11 and 12) form a toroidal "belt" around the sample, and it was from this that the apparatus received its name.

The Belt apparatus is capable of generating pressures on the new scale in the neighborhood of 150 kb simultaneously with steady state temperatures (with water cooling) of the order of 2000ºC.

Temperatures of at least 5000ºC can be maintained for millisecond periods. The basic principles operative in the Belt have been utilized by other researchers in constructing similar devices.[232425]

Brief mention of the pressure scale would be appropriate at this time. High pressure apparatus, such as the Belt, have been calibrated in terms of sharp electrical resistance transitions occurring in Bi, Tl, Cs, and Ba. These transitions, as measured in Bridgman's anvil apparatus, were originally reported to occur at pressures of 24.9, 44, 54, and 78 kb, respectively.[26] These values were used in the early calibrations of the Belt and other apparatus. Calibration based on these values is now referred to as the "old" pressure scale. The "new" pressure scale, now accepted by most workers in the field, is based on values of 25.4, 371 42, and 59 kb, respectively, for these transitions.

A secondary pressure calibration of the above type is necessary in systems which utilize compressible gaskets in order to ascertain the pressure being developed at the sample location. Part of the ram load is, of course, absorbed by the gaskets and, in the case where solid pressure transmitting materials are used, is also used in overcoming internal friction in the solid. In calibrating an apparatus, a silver chloride specimen carrying a calibrating wire is substituted for the sample. Silver chloride is used because, compared to most solids, it is very "hydrostatic" as a pressure transmitter. Oil pressure to the hydraulic rams which thrust the pressure generating components together is then slowly increased and recorded

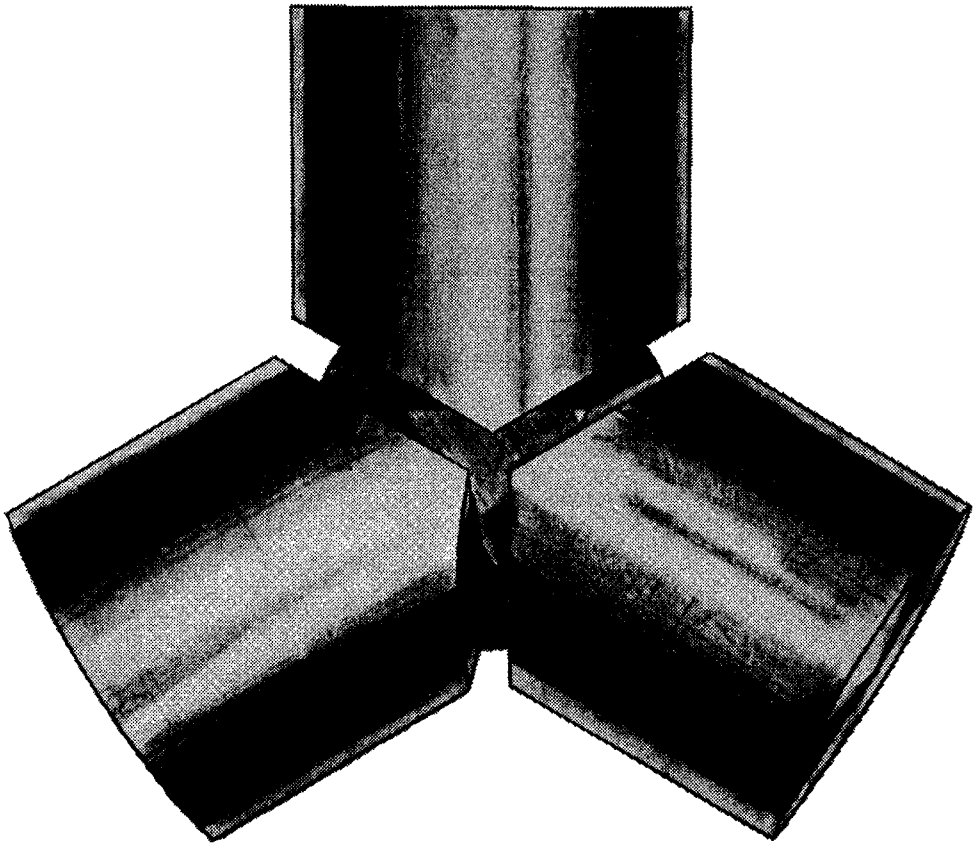

Fig. 11. Tetrahedral anvils.

simultaneously with a recording of the electrical resistance of the pressure sensing wire. The oil pressure required to induce each transition is then plotted vs the appropriate pressure value for the transition. A smooth curve through these points and the origin then serves as the pressure calibration curve for the apparatus.

The massive support principle is operative in the Belt in both the pistons and the chamber. In addition, the design allows the piston and chamber to support each other through the sandwich gasket. To develop the highest pressures in Belt type apparatus the length of the sample is shortened. This is done, of course, at a sacrifice in sample volume. Shortening the sample requires a slight modification of the conical pistons and chamber. The sandwich gasket of the Belt apparatus provides a pseudo multi-staging effect

which is also a contributory factor to the high pressures that can be developed. The multi-staging comes from the gradual drop of pressure along the gasket from the tip of the piston outward. Pressure is highest near the tip of the piston and drops off to atmospheric pressure at the outer rim of the gasket.

8. MULTI-ANVIL APPARATUS

The first member of a regular series of multi-anvil presses is the Tetrahedral Anvil Press. This press came into being as a matter of necessity when the Belt, because of unfortunate circumstances, could no longer be used for research by its inventor.

Immediately after leaving the General Electric Company in the fall of 1955 to accept employment

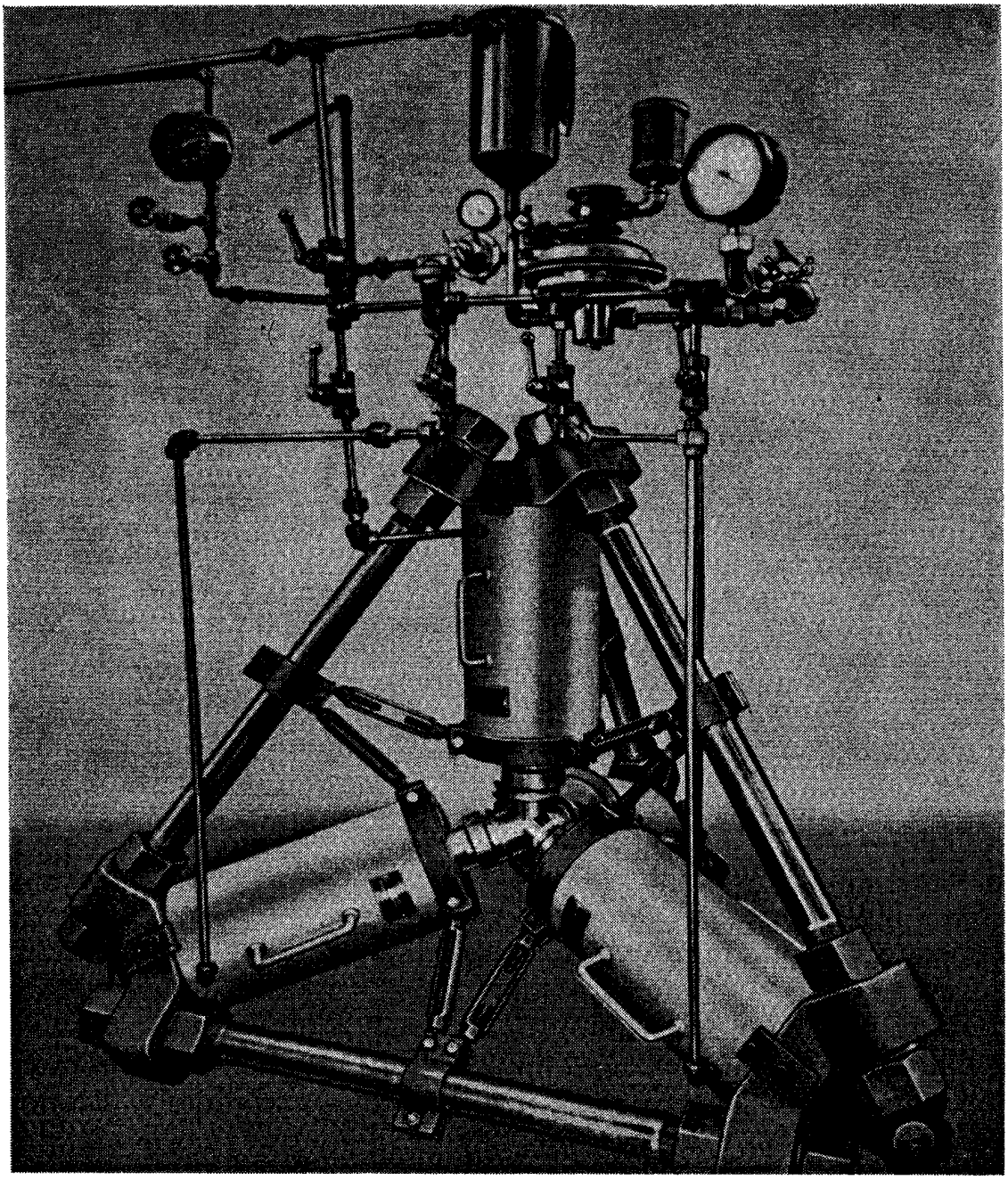

Fig. 12. Original tetrahedral press.

with Brigham Young University, the author was beseiged with requests from scientists to reveal the details of the Belt apparatus. Circumstances of secrecy, however, prevented disclosure. The situation was

discussed in the highest of scientific, governmental and military circles. A strong current of feeling against the secrecy quickly developed. It became apparent, however, that the problem would not be resolved for some time to come. Consequently, the author found himself being encouraged from all sides to develop another apparatus to take the place of the Belt and be made available to scientists everywhere. Solid support, in the form of dollars, was first made available for such an undertaking by the Carnegie Institution of Washington through the very much appreciated help of Philip H. Abelson and Paul A. Scherer. Additional financial aid followed, and the Tetrahedral Press slowly came into being. During the Christmas holidays of 1957 diamonds were made in this apparatus and thus it successfully passed the test that, at the time, seemed paramount for proving its worthiness as a high pressure-temperature machine.

The Tetrahedral Press is an extension of the "two-dimensional" Bridgman anvil concept to three dimensions. A "three-dimensional" device is necessary to overcome the problem of the small sample size in the Bridgman anvils. In the Tetrahedral Press and other multi-anvil devices, the principle of massive support is still at work but not to the same extent as in Bridgman anvils. This is so because the solid angle

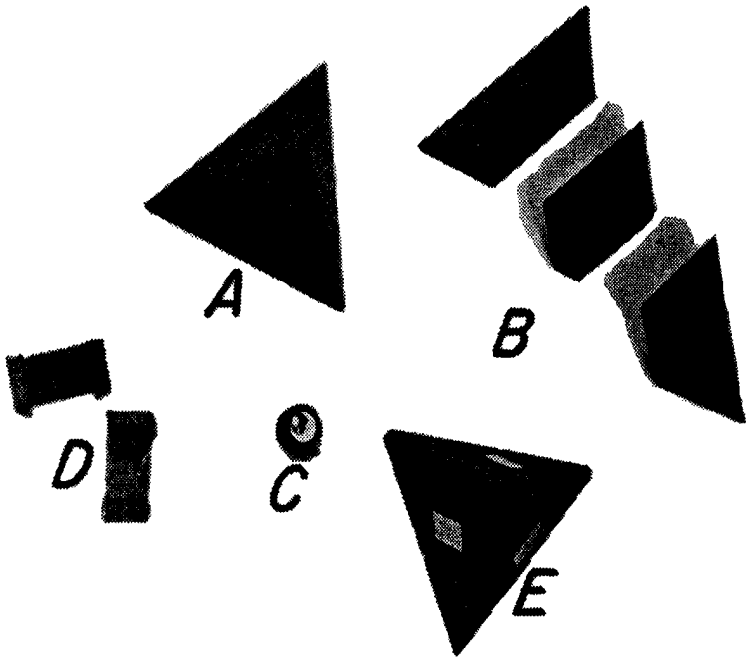

Fig. 13. Tetrahedral cell.

subtended by each anvil must decrease as the number of anvils used is increased. However, in multi-anvil devices the anvils tend to support each other through the gaskets, and this tends to compensate for the reduction in massive support given to the anvil faces.

In the Tetrahedral Press four anvils with triangular faces (see Figures 11 and 12) are driven toward a central point by hydraulic rams whose axes lie along lines normal to the triangular anvil faces. The anvil axes intersect at tetrahedral angles (109.47º) in the center of a regular tetrahedral volume enclosed by the anvil faces. The anvils are usually constructed of cemented tungsten carbide and are surrounded by a press-fit steel binding ring. The binding ring, as usual, absorbs the tensile loads developed within the body of the tungsten carbide.

The cell in which the pressure is generated consists of a regular pyrophyllite tetrahedron as shown in Figure 13. The edges of this tetrahedron are approximately 25% longer than the corresponding legs on the triangular anvil faces. The pyrophyllite within the tetrahedron transmits pressure to the sample, provides thermal and electrical insulation and, by extruding between the sloping shoulders of the advancing anvils, provides the necessary compressible gasket. The tetrahedral cell, A, is sawed from block "grade A lava" (pyrophyllite) obtained from the Tennessee Lava Corporation, Chattanooga 5, Tennessee. Typical edge length of a tetrahedral cell used for research is one inch. (The corresponding edges of the triangular

faced anvils are 3/4 in. long.) In order to place a sample within the lava tetrahedron, a central slab, B, 0.100 in. thick is cut from it with twin, pen-nib slitting saws 0.006 in. thick. The faces of this central slab are parallel to two opposite edges of the tetrahedron. A 0.188 in. diameter sample hole is then drilled through the center of the slab perpendicular to its faces. For calibration purposes a silver chloride cylinder, C, 0.100 in long and 0.188 in. diameter (to fit the above sample hole) is prepared with a small axial hole to receive a wire of calibrating material. For calibration this wire is connected to silver disks placed over the ends of the silver chloride cylinder. Electrical connection to these disks is made with 0.005 in. thick metal connecting

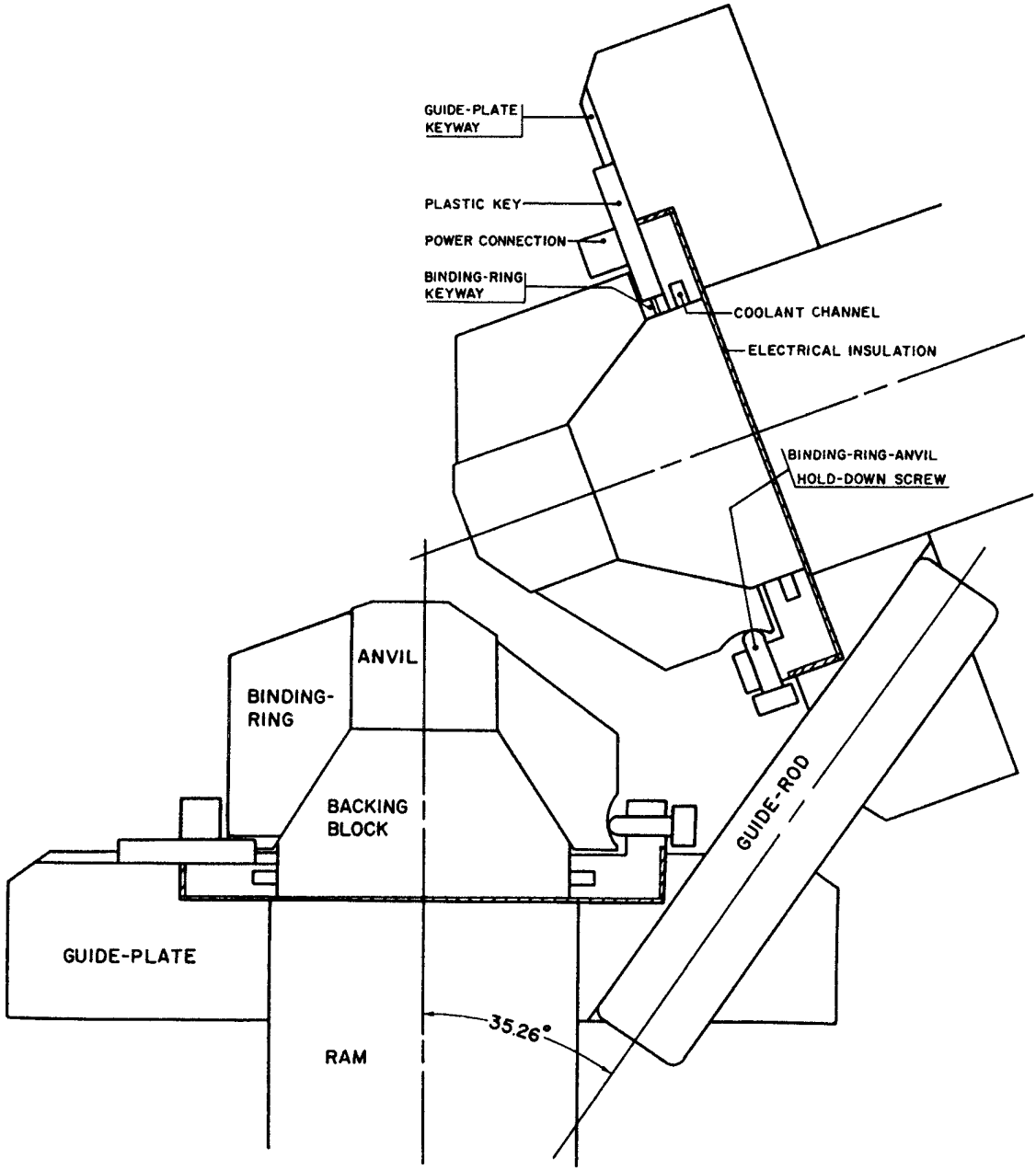

Fig. 14. Cross section of tetrahedral anvil guide device.

tabs, D, which, in turn, make electrical contact with the anvils. The cell is assembled, E, and held together with water soluble glue, used sparingly. The surface of the tetrahedron is then painted with rouge (thick suspension in ethanol) and dried at 95ºC for about two hours. The cell is then kept in a desiccator until used. The rouge increases the surface friction of the pyrophyllite and, for a given ram load, increases the pressure obtained by approximately 20%.

When an experiment is to be run in the Tetrahedral Press, the sample under study is substituted for the silver chloride assembly used in the calibration. In some instances the material may be contained in a tube through which an electrical current is passed to provide heating. In other instances indirect heating is

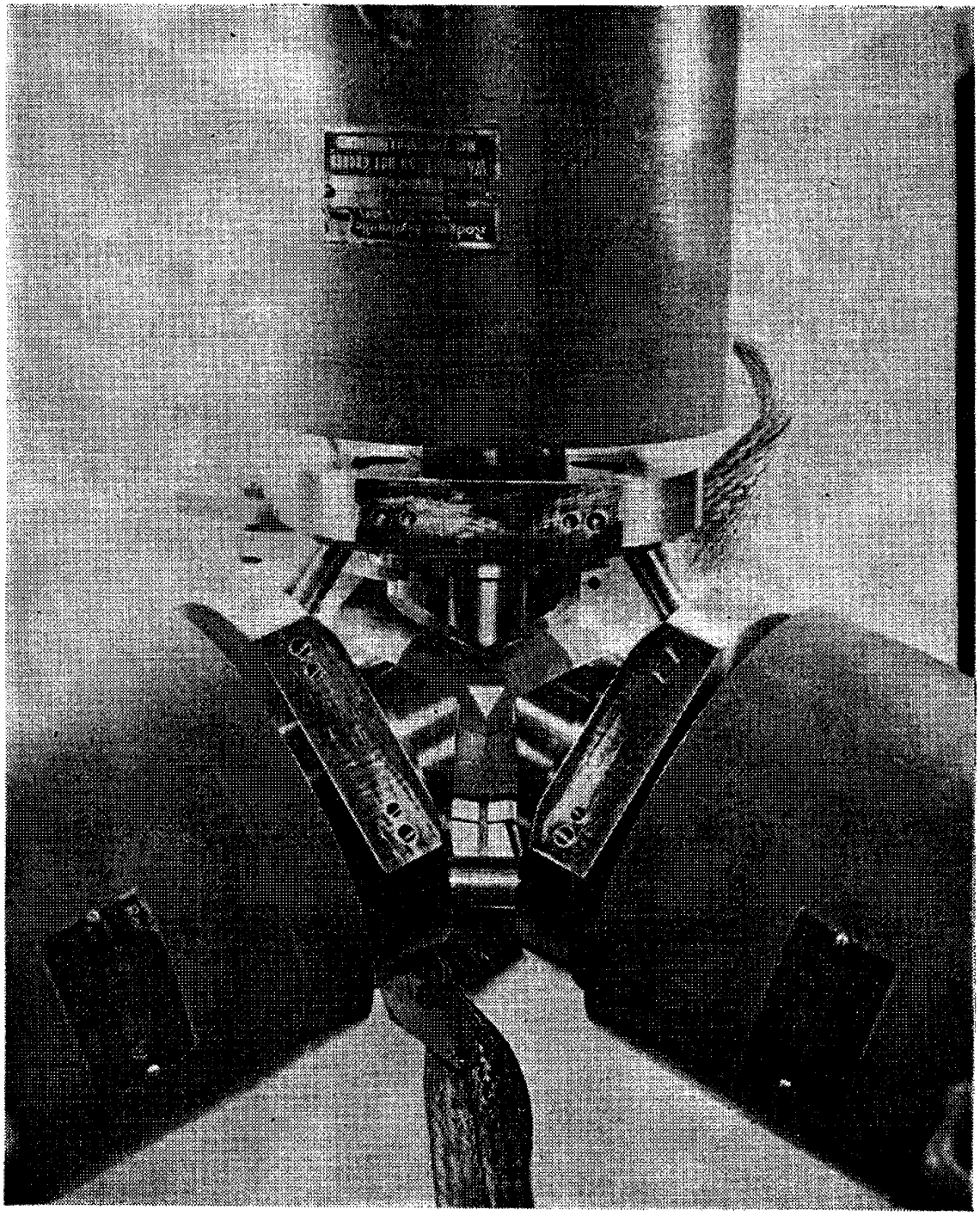

Fig. 15. Anvil guide installed on orginal tetrahedral press.

provided by passing a current through the metal tabs shown in Figure 13. Graphite-cloth strips are often used as heaters in place of the metal tabs.

The working volume of the cell just described is rather small, being only 2.3% of the initial tetrahedron volume and 5.6% of the volume of a tetrahedron formed by the completely closed anvils. This

small volume is used in most research applications in order that the average pressure exerted over the

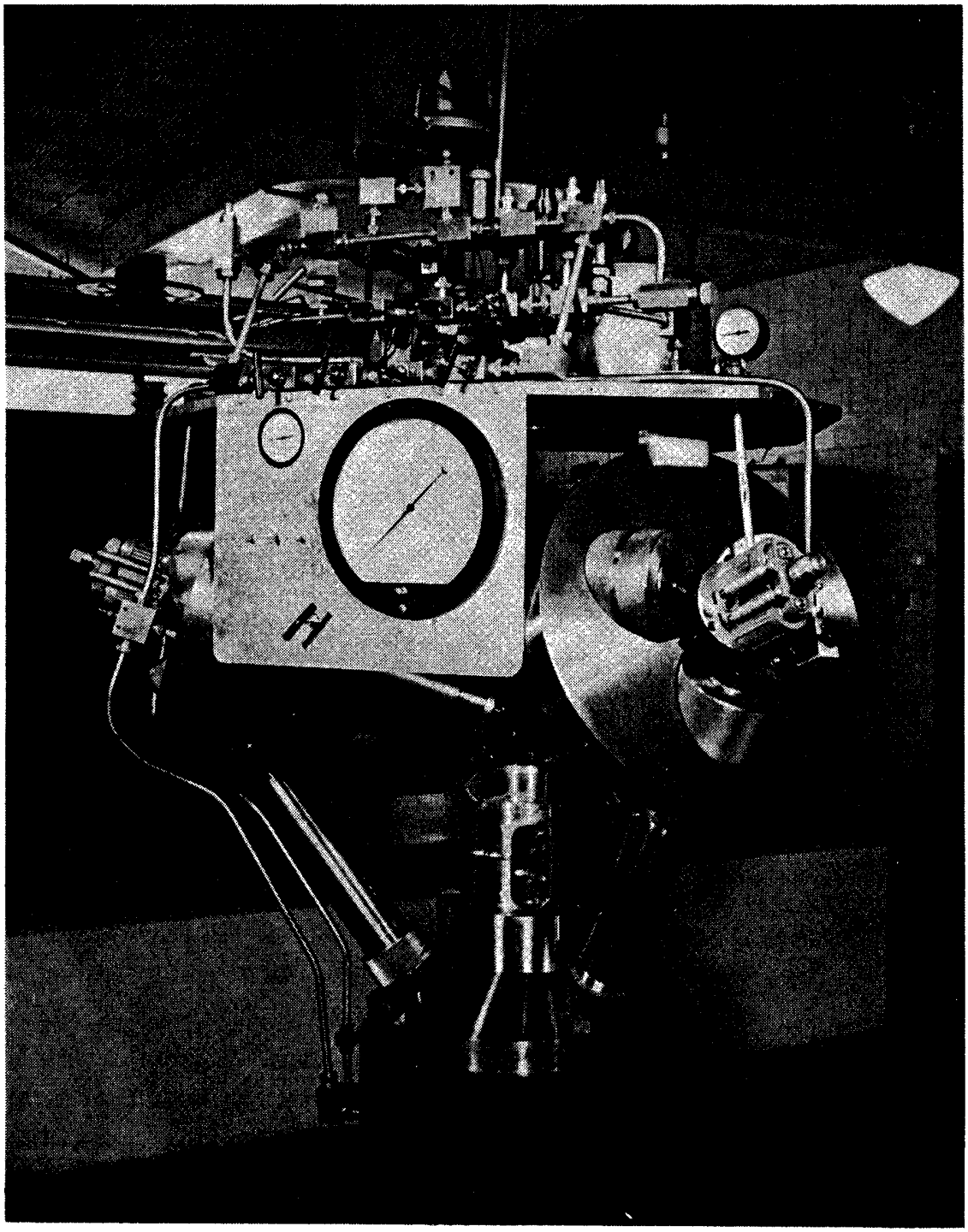

Fig. 16. Tetrahedral press mounted apex down.

surface of a sample, initially filling the space at one bar, will, for a given ram thrust, be the same regardless of the sample's compressibility. Also, in this small working volume a rather uniform pressure is distributed over the sample surface and its distortion is small. In certain instances a much larger working volume can be used, particularly when the above considerations are not important.

When electrical strip heaters are used to provide indirect heating, it may be important to isolate the heaters from the sample. This would be the case if the sample were electrically conducting or tended to react chemically with the strips. If the sample is a poor thermal conductor, it is desirable, in order to maintain a uniform temperature distribution, to encase the sample in a good thermal conductor. This will also tend to facilitate heat transfer to the sample from the heaters. In any high pressure apparatus utilizing electrical resistance heaters, it is desirable to use heaters with a relatively high electrical resistance. This is important in order to reduce the current density at the point where the electricity passes from a tungsten carbide anvil or related component to the conductor leading to the heating element. High local heating at this juncture caused by a high current density will cause cracking and breaking of carbide anvils.

Temperature inside the cell can be measured by locating a thermocouple in the immediate vicinity of the sample under study. Thermocouple leads are brought out through the edges of the tetrahedron in the space between the sloping anvil shoulders. Friction of the pyrophyllite gaskets on the fine wires (usually 0.005 or 0.010 in. diameter) is sufficient to hold them in place during high pressure operation. It is often helpful in preventing thermocouple wire "pinch-off" to sandwich the wires between two wafers of

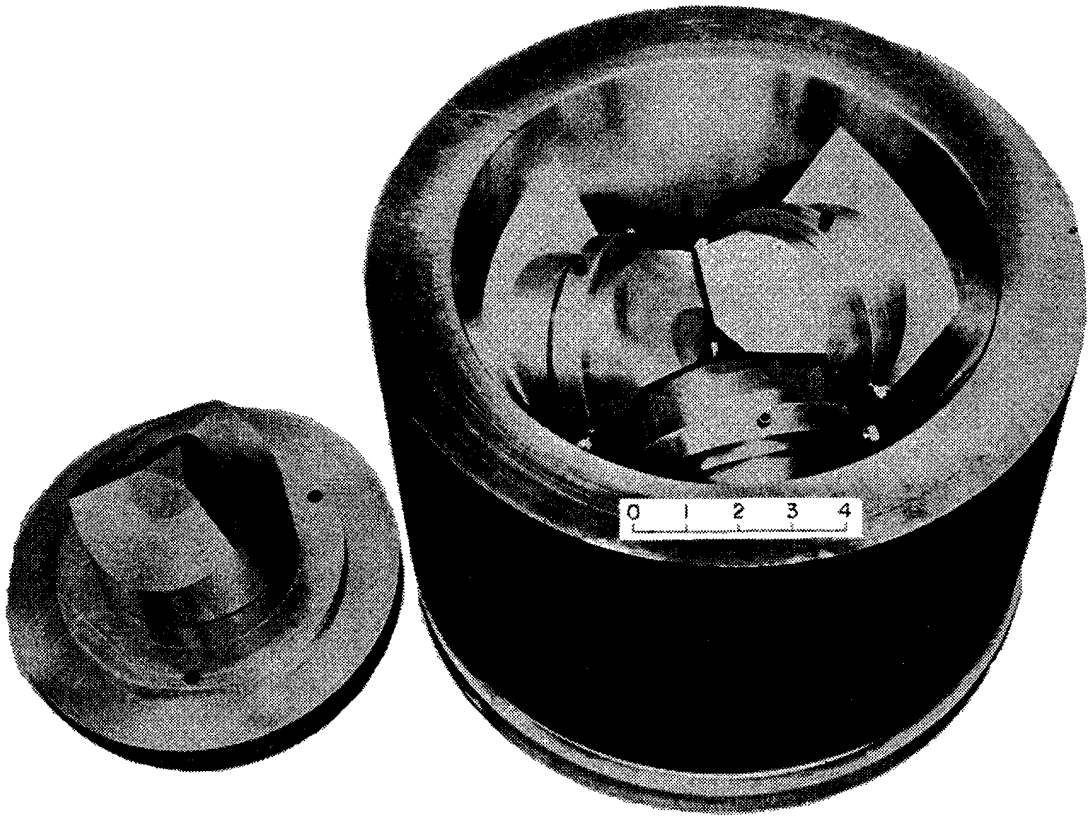

Fig. 17. Lloyd and Hutton's scheme for moving tetrahedral anvils together.

pyrophyllite. The total initial thickness of these wafers should equal the distance between the anvil shoulders at the moment they close on the tetrahedral cell. If desired, the thermocouple wires can make contact with two of the anvil faces thus eliminating the need for bringing leads out through the gaskets. When this is done only two of the anvils are used to bring in the heating current. Temperature readings taken with wires contacting the anvils are less accurate than those taken with the wires passing through the gaskets but are good enough for some purposes.

In the original tetrahedral press the anvils were brought together by independent valves which controlled each ram. The position of the anvils was indicated by dial gages. In the initial stages of pressure build up, while the gasket was being formed, the rams were advanced individually in small incremental

steps. After the gasket had formed, all control valves were opened thus supplying hydraulic oil simultaneously to the four hydraulic rams. Recently, tetrahedral presses have been equipped with an anvil guide device[27] that eliminates the need for incremental adjustment. This device causes all hydraulic rams to advance symmetrically and simultaneously toward the center of the Tetrahedral Press as oil pressure is applied to all four hydraulic rams from one valve. The anvil guide device for the Tetrahedral Press consists of six guide rods and four guide plates (Figures 14 and 15). A guide plate is fastened to the moving end of each hydraulic ram. The anvil, with its various supporting structures, is centrally mounted on the guide plate. Each guide plate contains three guide holes, symmetrically arranged at 120º angles to each other. The axis of each hole makes an angle of 35.26º with respect to the ram axis. When assembled, the guide rods are positioned within the guide holes in which they are free to slide as the rams advance. All rams, being interconnected by the guide rods and plates, are forced to move synchronously together as hydraulic oil is simultaneously applied to the rams. Anvil guides can also be used with other varieties of polyhedral presses.

In Tetrahedral Presses equipped with anvil guide devices it is convenient to mount the press apex down as shown in Figure 16. In such a configuration the tetrahedral cell can be placed on the triangular face of the lower tetrahedral anvil where it will remain as the anvils close on each other. In prior designs where the anvils could be independently controlled, the press was usually mounted apex up. To operate this press, a nest was formed by advancing the three lower anvils to the correct position for receiving the tetrahedral cell. After insertion of the cell (apex down) in the nest, the upper anvil was advanced until it touched the upward facing triangular base of the cell. At this point the rams were adjusted in small steps until the gasket was formed.

The four inward moving anvils of the Tetrahedral Press sweep out sufficient volume by compressing and extruding the gasket to allow pressures of at least 100 kb (new scale) to be generated. Higher pressures may be achieved by incorporating a truncated, regular tetrahedral pyramid with a base smaller than the triangular anvil face into the faces of the tetrahedral cell. This truncated tetrahedron should be made of cemented tungsten carbide, hot-pressed alumina, or some other relatively incompressible substance. Alternatively, higher pressures may be generated by modifying the triangular faces so that they protrude a greater distance toward the center of the tetrahedral cell.

Following the Tetrahedral Press in the regular series of polyhedral presses is the Cubic Press. In this press six hydraulic rams advance six anvils with square faces and 45º sloping shoulders toward the center of a cube. The Octahedral Press follows the Cubic Press in this sequence and so on. Regular polyhedral shapes are not always desirable in a high pressure device; consequently, the polyhedral press idea has been extended to include prisms and other less regular shapes.

It is possible to move tetrahedral anvils together by a mechanical scheme in which the upper anvil forces (through the gaskets) the lower triad of anvils into a tapered ring. With this arrangement only one hydraulic ram is required; namely, a ram to drive the upper anvil. (See Figure 17.) This idea has also been extended to cubic anvils.[28]

9. SUPPORTED-PISTON APPARATUS

The supported-piston apparatus approaches a two-stage, piston-cylinder device in its design and operation. The first equipment of this type to be described was that of Boyd and England.[29] In this apparatus the inner chamber is supported radially by binding rings and axially by bolted or hydraulically loaded end plates. The protruding portion of the piston (see Figure 18) is supported by a compressible, solid material such as KBr. Thus, three separate means are used to give support in this apparatus in contrast to the single support (a hydraulic fluid under pressure) utilized in Bridgman's two-stage apparatus.

The KBr is used as a preformed shape and is wrapped with indium or lead foil to reduce friction. The apparatus is designed so that the high pressure piston advances about 0.030 in. into the sample assembly before contact is made with the KBr. The stroke required is minimized by precompressing the cell assembly after it has been placed in the high pressure stage. Dimensions of the apparatus components are adjusted so that a pressure of about 80 kb is generated in the sample while a supporting pressure of about 18 kb is developed in the KBr. The KBr undergoes a phase transformation at approximately 18 kb with a volume decrease of about 10%. This tends to keep the support pressure constant at 18 kb.

The sample is centered in a pyrophyllite, talc, or hexagonal BN cell and is heated by an electrical resistance furnace in the usual manner. A sheathed thermocouple of external diameter 0.010-0.040 in. is used to measure temperature and is brought out of the high pressure region through a snugly fitting hole in the stainless steel or hardened steel end plug. Under pressure, frictional force between the hole and the

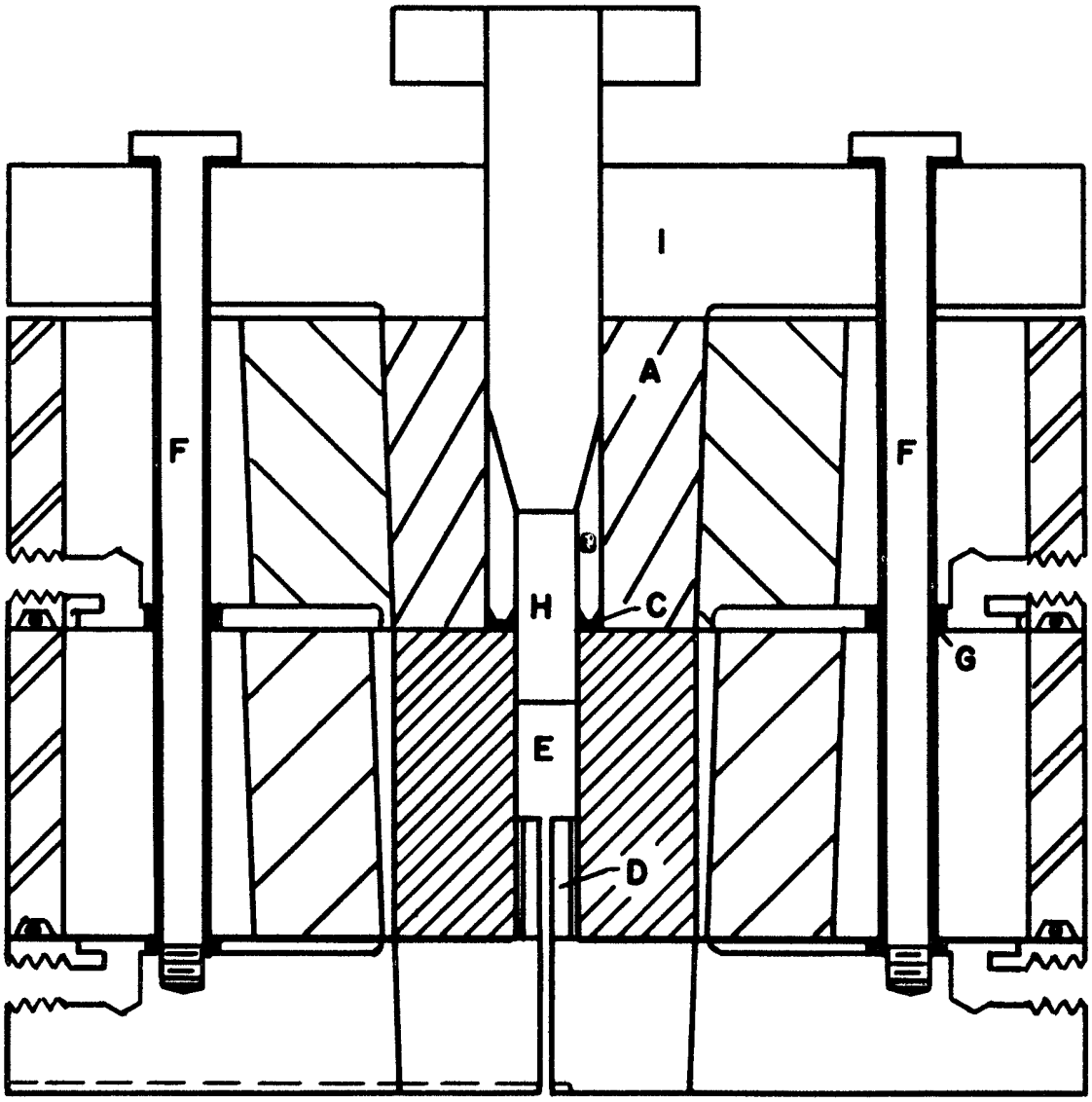

Fig. 18. Boyd and England's supported-piston apparatus. *A*, steel supporting stage core, LaBelle HT R_c 55; *B*, volume filled with KBr cell; *C*, sealing ring, R_c50; *D*, steel power lead, R_c 60, with 1/32 in. thick pyrophyllite insulating sleeve; *E*, volume filled by sample and furnace assembly; *F*, steel bolts (6), R_c 30, insulated with tape; *G*, neoprene washers; *H*, cemented carbide piston, 1% binder; *I*, end plate, 4340 R_c 50. All carbide parts are stippled and with the exception of *H* are 6% binder.

sheath is usually sufficient to prevent expulsion of the thermocouple assembly. As is the case in the Belt and multi-anvil apparatus, the cell assembly is nonrecoverable and a new one must be used for each run.

A device similar to that of Boyd and England above has been described by Giardini, Tydings, and Levin.[30] Maximum pressures of about 80 kb have been reported for supported-piston devices.

10. CONTAINERS FOR HIGH PRESSURE/TEMPERATURE WORK

Offhand it might seem that it would be difficult to handle liquid samples in high pressure, high temperature apparatus such as the Belt or the Tetrahedral Press. However, this is not the case. In many instances a liquid can be contained by a graphite tube, that is also being used as the heating element, simply by placing snug fitting graphite plugs into each end of the tube. Liquid is inserted into the tube, with one

plug in place, by means of a hypodermic needle. The other graphite plug is then inserted, excess liquid being squeezed out between the plug and the cylinder as the plug is pushed into place. When under pressure and surrounded by a material such as pyrophyllite, this simple assembly will usually not leak. As an example, coesite has been synthesized from sodium silicate solution confined in a graphite container, as described above, at a temperature near 700ºC at a pressure of 35 kb.

A similar procedure can be used in the case of a metal tube (which may also be used as the heating element in the same manner as graphite). In this case, cylindrical metal plugs are inserted into the ends of the metal tube. Alternatively, to increase the working volume, metal cups may be substituted for the plugs. In using metal cups, it is wise to fill one of the cups with liquid before inserting it in the metal tube to affect final closure. This is necessary in order to prevent the formation of an air bubble which occurs when an empty cup is put into place. The fit between the metal cup and cylinder may be sufficiently loose to allow extrusion of excess liquid between the mating interfaces. When under pressure, however, there will ordinarily be no leak between the cup and the tube.

When it is undesirable to use the tube containing the liquid as the heating element, it can, of course, be heated indirectly by a surrounding heating element that is separated from the container tube by a sheet of electrical insulating material. Solids that may become liquid at a sufficiently high temperature are confined in the same way as liquids. Some materials that are extremely fluid at high temperature will succeed in finding a place to leak from the capsule. Oftentimes the material simply goes through the pores of a graphite or boron nitride sleeve.

The "container problem" is difficult at very high pressure/temperature. Experience has shown that many materials that are adequate as containers at high temperature and atmospheric pressure are completely inadequate at high pressures because of increased solubility, chemical reactivity, diffusion, or because of increased rate of reaction. As an example, a container suitable for use in studying the melting point of silicon as a function of pressure has not been found. When a suitable container cannot be found for use in fusion curve studies, it is sometimes possible to perform "one-shot" experiments in which a single cell assembly is used for determining each point on the curve. In such experiments, the melting point is approached quickly and a temperature measurement taken before too much diffusion or chemical reaction can take place.

Some of the most useful, electrically conducting containers for high pressure, high temperature research are made of tantalum, molybdenum, platinum, nickel, or graphite. Useful nonmetallic containers are often made of hot-pressed hexagonal boron nitride, pyrophyllite, talc, crushable alumina or crushable magnesia.

The extreme speed of diffusion and rate of reaction that has been experimentally observed in many systems at high pressure and high temperature cannot be over emphasized. As has already been mentioned, these factors greatly aggravate the container problem. Diffusion can be particularly rapid. Consequently, materials thought to be well outside the reaction zone can quickly be transported into the reaction zone. This is especially true in systems containing mineralizers such as water or hydrogen sulfide, or in a system containing chemical compounds from which these mineralizers may be formed.

11. INSTRUMENTATION OF HIGH PRESSURE/TEMPERATURE EQUIPMENT

After a material has been subjected to high pressure and high temperature, it is necessary to determine what has taken place. Of course, in every instance where high pressure (at a uniform temperature) has been applied, thermodynamics dictates that there be a macroscopic decrease in volume. In addition to this, there may be a change in phase or state, and the properties of the material under study, such as electrical conductivity, thermal conductivity, or dielectric constant, may undergo a discontinuous change. When irreversible changes have occurred, it is possible to determine what has happened by an examination of the sample after pressure and temperature have been released. An example of such a change is the transformation of graphite to diamond. Such changes often involve metastable states. Diamond, for example, is thermodynamically unstable with respect to graphite at room temperature and atmospheric pressure by 685 calories per mole. (Under the pressure/temperature conditions where diamond is formed, however, diamond is stable with respect to graphite.) In many metastable states there has been a drastic change in the type of bonding so that the energy barrier for reversal to the stable state is very high. Thus, a very long time would be required for the transformation to the stable state to take place at room temperature. Usually, however, elevation of temperature can bring about the change in a short period of time. For example, the transformation of diamond to the thermodynamically stable graphite will progress rapidly at temperatures of the order of 1500ºC at atmospheric pressure. In "capturing" a metastable phase that has been produced at high pressure and high temperature, it is necessary to reduce the temperature

substantially before releasing the pressure. In some instances, the metastable phase can only be captured by cooling to cryogenic temperatures before pressure is released.

In cases where the changes produced by high pressure/temperature are reversible; i.e. the material reverts to its original form on removal to ordinary conditions, it is necessary to use some means for "seeing" into the high pressure apparatus to determine what has happened. This is often difficult because of the heavy components required to confine the high pressures (such things as cylinders, pistons, anvils, binding rings, etc.) and also because of the insulation and sealing problems encountered. One of the most common methods for detecting changes that occur is to follow the changes in the electrical resistance of the specimen under consideration. For metals, measurements are made with ordinary resistance meters. Resistance of nonmetals can be measured with special "meggers" designed for the purpose. Discontinuities in electrical resistance often indicate a change in phase or state. Changes in the slope of electrical resistance versus pressure plots can indicate second order phase changes, etc. Generally, resistance measurements give only limited information concerning the nature of phase changes.

Thermocouples can be used to detect changes when latent heat is released or absorbed. Fusion curves as a function of pressure have been determined by this means.[31] The differential thermal analysis (DTA) method of detecting latent heat effects has also been used to determine fusion curves and establish phase boundaries.[32] W. F. Claussen of the General Electric Research Laboratory has used differential thermal conductivity as a means for detecting phase changes.[33]

In externally heated piston-cylinder devices, measurement of piston displacement with sensitive micrometer gages can indicate volume discontinuities or abrupt changes in the slope of the compressibility and thus yield valuable information. This is more difficult in internally heated devices where solids are used to transmit pressure. However, in cases where the sample occupies a relatively large proportion of the total volume within the pressure generating portion of the apparatus, it is possible to obtain an indication of a phase change involving a large volume discontinuity.

By using diamond or sapphire anvils, it has been possible to perform optical measurements on materials subjected to high pressure over a temperature range from about -30ºC to 175ºC.[34] As has already been mentioned, Drickamer has used sodium chloride and other alkali-halide windows for optical measurements, at room and elevated temperatures, in modified Bridgman anvil apparatus. It should be possible to extend the use of optical detection methods, by means of salt gaskets or diamond windows, to the larger volume systems such as the Belt or the Tetrahedral Press.

The generation of noise during freezing has been used to detect this type of phase change.[35] In this work, an ultrasensitive microphone was attached to the container where freezing was taking place. The noise signal picked up by the microphone was then amplified and recorded on an oscilloscope. Attempts at Brigham Young University to adapt this method for use with the Tetrahedral Press have, up to the present time, been unsuccessful. However, this detection method warrants continued investigation.

Electron[36] and nuclear[37] magnetic resonance measurements have been used in anvil and piston-cylinder devices to detect changes taking place at high pressure.

Probably the most versatile type of instrumentation that could be used with a high pressure/temperature device would utilize x-ray diffraction techniques. X-ray diffraction methods are currently being used in connection with Bridgman anvil devices, the Tetrahedral Anvil Press, and piston-cylinder apparatus. In these devices, any gaskets or materials surrounding the specimen must be relatively transparent to x-rays. One version of the Bridgman anvil device utilizes tiny diamond anvils to provide the x-ray transparency. The primary x-ray beam is shot into the sample at a glancing angle through one of the diamonds and the diffracted beam is scanned by a spectrometer. Tiny piston-cylinder devices where the cylinder is constructed of diamond or beryllium have also been used. In these devices the primary x-ray beam enters the sample through the wall of the cylinder. The diffracted beam, after emerging from the cylinder wall, is recorded directly on film or is scanned by a spectrometer. In some Russian work, the x-ray film has been placed right inside the high pressure cylinder where it is immersed directly in the hydrostatic fluid surrounding the sample. A review of the above x-ray techniques has been presented by Jamieson and Lawson.[38]

A Tetrahedral Anvil X-ray Diffraction Press was conceived about four years ago by Dr. J. Dean Barnett and the author. The general approach to be taken was disclosed at the International High Temperature Symposium held at Asilomar, California, in October of 1959. A proposal to develop this equipment was submitted to the U.S. Army Research Office (Durham) and a grant to do the work was received in June of 1960. Design and construction were completed and preliminary tests begun in late summer of 1962. The basic apparatus (see Figure 19) consists of a standard Tetrahedral Press, built with

great precision, to which three geared scanning tracks have been attached. The tracks are mounted on the press so that diffracted x-rays that exit from spaces between the sloping anvil shoulders (the x-rays must

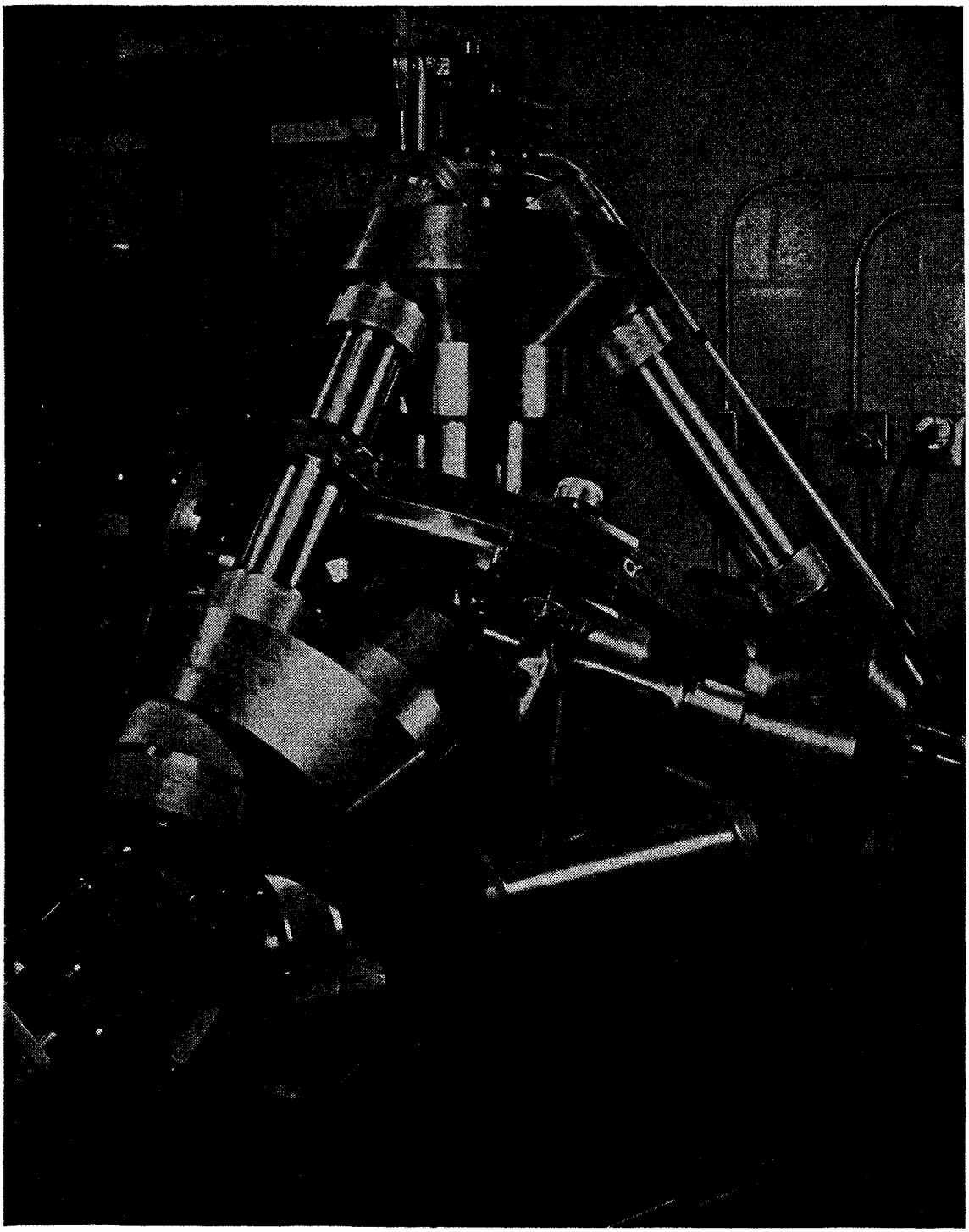

Fig. 19. Tetrahedral X-ray diffraction press.

penetrate the gasket formed between these shoulders) will be intercepted over about a 100º sector (see Figure 20). One of the hydraulic rams is hollow and contains an x-ray tube. The x-ray tube directs a primary beam of x-rays through a hole along the ram axis, through a collimating tube and thence through a 0.030 in. diameter hole along the axis of a tetrahedral anvil. The 0.030 in. hole is terminated on the

triangular face of the anvil by a 90º hollow cone which is 1/8 in. across at the anvil face. A solid beryllium cone fills this cone to prevent extrusion of cell material into the 0.030 in. hole.

It is not possible to use tetrahedral cells made of pyrophyllite in x-ray diffraction work because pyrophyllite is not sufficiently transparent to x-rays. It is necessary to make the cells from materials appearing in the upper left hand corner of the periodic table. Lithium hydride, boron, and mixtures of lithium hydride and boron have proved eminently satisfactory for x-ray use. Powders of these materials are compressed into dense tetrahedrons (1 in. on edge-the anvils are 3/4 in.) by a die designed for the purpose. The tetrahedrons are then drilled or sawed in the same manner as pyrophyllite cells in order to insert the sample, provide heating tabs, or whatever else may be necessary. In contrast to the ease with which pyrophyllite can be machined, however, compressed tetrahedrons of LiH or B or their mixtures machine with great difficulty. The specimen to be studied is located at the center of the tetrahedral cell. If the specimen is an electrical conductor, it may be placed there in the form of a thin sheet that can be heated directly by an electric current. Nonconductors can be heated indirectly by placement between flat sheets of graphite, beryllium or zirconium which are electrically heated. These materials are used because of their relative transparency to x-rays (molybdenum radiation is usually used).

A synchronous motor drives a carriage, on which a slit system, counter tube and cathode follower are mounted, along each x-ray track in typical spectrometer fashion. Signals from the cathode follower go to a nearby preamplifier and thence to electronic sensing and recording equipment. With the three identical

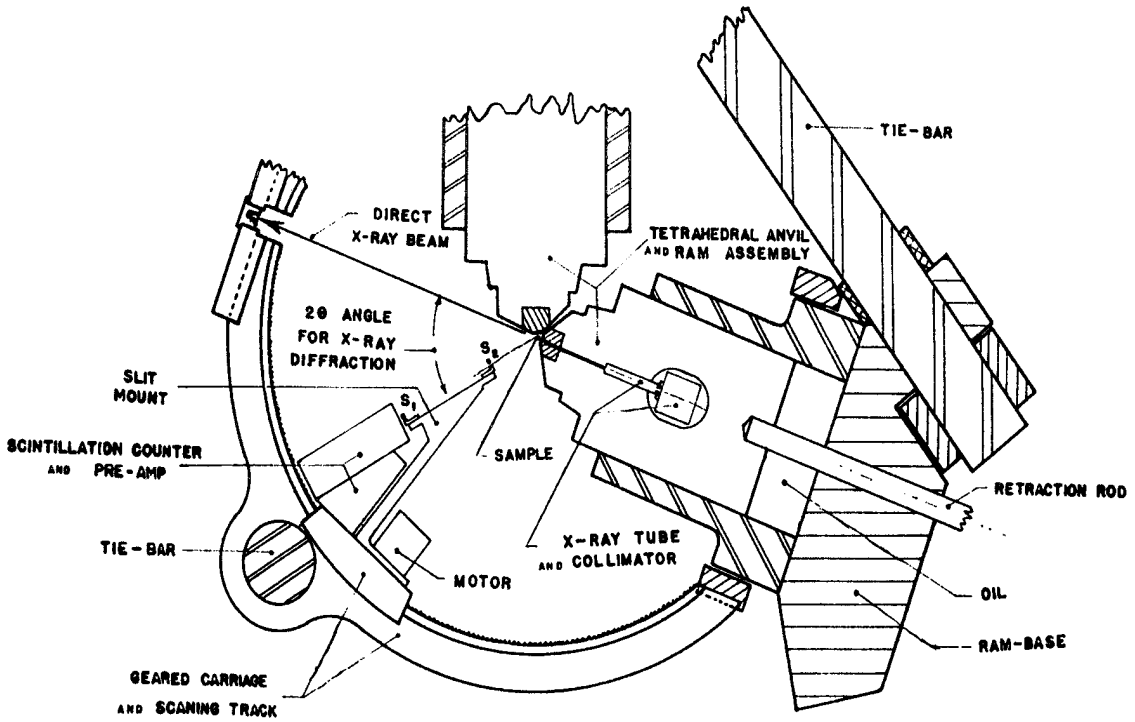

Fig. 20. Cross section through tetrahedral X-ray press.

track systems, it is possible to monitor the disappearance of one phase simultaneously with the appearance of another and, at the same time, monitor the pressure within the cell by observing the change in d spacing of a calibrating substance.

The Tetrahedral X-ray Press has proved to be a versatile and useful scientific tool. One of the early scientific findings coming from this equipment was the discovery that face centered cubic ytterbium transforms to body centered cubic at 40 kb, 25ºC.[39] The macroscopic volume decreases 3% at the transition while the volume of individual atoms decreases by 11%. This is the first pressure induced transition from a close-packed to non-close-packed structure to be observed and contradicts previous predictions that this transition would be found to be analogous to the face-centered cubic to face-centered-cubic transition in cerium.

12. SOME ADVANTAGES AND DISADVANTAGES OF VARIOUS HIGH PRESSURE/TEMPERATURE APPARATUS

Plain Bridgman anvil apparatus is the least expensive of the devices described above. This is particularly true if a hydraulic press of about 200-ton capacity is already available. The highest static pressures attainable are developed in Bridgman anvil type equipment. Some disadvantages connected with this device are its extremely small "two-dimensional" volume, the existence of large radial pressure gradients and the strong shearing and deformation of the sample that can take place. Attainable steady state temperatures are lower than in any of the other devices.

Piston-cylinder devices related to the Coes type device stand next to Bridgman anvils in initial cost. Research size equipment requires a hydraulic press of from 100-500 tons capacity for their operation. When used at the highest pressures, end loading is required. This can be provided by bolted clamping plates but is much more conveniently applied by a special hydraulic press. The special press is expensive. Piston-cylinder devices require a very accurately aligned press in order to prevent fracture of the carbide pistons. Such fracture readily occurs with a slightly off-axis load. These devices are somewhat troublesome, particularly when used at the highest pressures, because of a tendency for the piston to stick in the cylinder. The uniaxial loading of this type of device causes some distortion of the sample which may be disadvantageous for some experiments. These devices are at their best when used at pressures below 30 kb.

The supported piston apparatus works quite satisfactorily with regard to producing high pressure and temperature, but it is much more cumbersome than the Belt. Its cost is comparable to that of a Belt. Uniaxial distortion of the sample may, again, be a problem in this apparatus.

The Belt type apparatus is the best of very high pressure/temperature uniaxial devices. Its cost is modest if a hydraulic press is already available for its operation.

The Tetrahedral or Cubic Press, when equipped with anvil guide, is the easiest to operate of all the devices that have been described. There are no heavy parts to lift and handle as is the case with the Belt, piston-

TABLE I

Comparison of Anvil Contact Temperatures with Through-the-Gasket Temperatures

Chromel-Alumel Couples

Pressure kb	Through-the-Gasket Temperatures, ºC							
	100	200	300	400	500	600	700	800
	Anvil Contact Temperatures, ºC							
16	93	186	286	384	482	583	679	774
26	94	189	288	384	483	585	683	776
35	94	187	286	384	483	584	681	776
44	93	187	287	384	482	582	679	774
53	94	188	286	382	482	580	679	774
62	96	191	288	385	487	583	682	776
71	96	190	288	387	486	584	686	778
80	97	194	292	389	486	588	686	780

Pt/Pt 10% Rh Couples

Pressure kb	Through-the-Gasket Temperatures, ºC									
	100	200	300	400	500	600	700	800	900	1000
	Anvil Contact Temperatures, ºC									
16	89	183	279	375	473	572	669	769	869	968
26	84	191	288	385	481	578	674	771	868	966
35	93	190	287	384	481	577	674	771	868	966
44	93	192	289	384	483	578	675	773	870	966
53	93	191	288	383	481	577	673	769	569	966
62	93	190	288	384	480	577	674	769	870	965

71	94	189	290	382	481	578	675	770	871	961
80	94	186	280	378	372	571	668	762	864	963

cylinder and supported-piston apparatus. Note that the chamber with its associated heavy binding rings (and sometimes clamping plates) must be lifted in and out of the press in these three devices. Cost of the Tetrahedral Press is comparable to the cost of a Belt, plus the hydraulic press that is required to operate it.

In the Tetrahedral and Cubic Presses, the sample is compressed from four sides and six sides, respectively. This causes less sample distortion than occurs in the uniaxial devices and provides a more "hydrostatic" pressure. There are considerably fewer components in a tetrahedral or cubic cell than in the cell-gasket arrangement for Belt devices. When multi-anvil devices are opened, the cell falls cleanly and freely from the anvils and the press is immediately ready for another run. In Belt and cylinder type devices the cell is stuck fast inside the chamber at the conclusion of a run and must be driven out with some kind of a ram-rod. The chamber must then be scoured with steel wool to remove adhering cell or gasket fragments in order to prepare it for another run.

Multi-anvil devices provide four or more electrical connections into the sample through the anvils. Two connections can be used for heating current, leaving at least two additional connections for other purposes. These connections can serve as thermocouple connections (wires make pressure contact with anvil faces) thus eliminating the more difficult procedure of bringing thermocouple connections out through the gaskets. The thermocouple readings made through anvil contact are lower than those made directly with wires leading through the gaskets and, in addition, are not as reproducible. These readings, however, are satisfactory for many purposes. Table I gives a comparison of thermocouple temperatures taken through the gasket vs readings taken through anvil contact at various pressures. Values are given for Pt/Pt 10 % Rh thermocouples as well as chromel-alumel couples. The cemented tungsten carbide anvils consisted of 88 wt. % WC plus 12 wt. % Co binder. The reference temperature was 0ºC. No correction has been made for the effect of pressure on thermocouple *emf* inasmuch as experimental or theoretical means for making such corrections are not yet available. Neglecting this effect, use of the charts to convert anvil contact readings to through-the-gasket readings gives temperatures that are probably correct to ± 2%.

The reader who wishes additional information on high pressure-temperature apparatus beyond that presented here would do well to consult in detail the books listed in references (1), (7), and (12) and, in addition, reference (40)[40].

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