High Pressure Methods

H. Tracy Hall*
Brigham Young University, Provo, Utah

Man is ever emulating nature. In his attempts to duplicate pressures that exist in the universe, however, he falls short of the tremendous pressures that are to be found. For example, the pressures thought to exist at the centers of the white dwarf stars are of the order of 10^{15} atmospheres. At the present time the highest static pressures attainable by man are about 2 x 10^5 atmospheres. It is somewhat paradoxical that the tremendous pressures that are found at the centers of the white dwarf stars are produced by one of nature's weakest forces, namely, the force of gravitation. In our own small section of the universe it is of interest to note that the pressure at the center of the sun is about 10^{11} atmospheres, while the pressure at the center of the earth is of the order of 10^6 atmospheres.

Before proceeding with a discussion of high pressure methods, it will be enlightening to consider pressure in terms of energy. All forms of energy can be represented as the product of two conjugate quantities, one of which is intensive and the other capacitive. For example, heat energy may be represented as the product of an intensive factor, temperature, by a capacitive factor, heat capacity. Similarly electrical energy, commonly expressed in watts, may be represented by the product of voltage and amperage. Pressure is the intensive factor associated with a type of mechanical energy . Its corresponding conjugate quantity is the volume change accompanying the application of pressure. The range of phenomenological changes that can be produced in matter by the application of energy is qualitatively dependent on the magnitude of the intensive quantity associated with the energy. In order to explore the range of phenomena that might exist, it becomes important to vary the parameters of temperature, voltage, pressure, frequency, etc. over as wide a range as possible. Indeed, pushing the extrema to the greatest possible limits is recognized today as one of the best ways to advance the frontiers of science. Until recently the pressures available to man have not been intense enough to do more than effect small perturbations upon matter. To obtain an idea of the pressures that might be required to produce significant changes in matter, it is helpful to contrast pressure with temperature. Temperatures of the order of 1000 to 2000°C have been available for thousands of years and are of sufficient intensity to readily produce chemical changes. The energies required to produce chemical changes in matter are of the order of 10,000 to 100,000 calories. In order to inject this amount of energy into a condensed system by the use of pressure it is necessary to have pressures available greater than 100,000 atmospheres. Energywise, 1 cc. kiloatmosphere is equivalent to 12.19°K.

In many respects pressure and temperature are opposites of each other. For example, increasing the temperature of a system causes the entropy of the system to continually increase and the system, as a general rule, continues to expand or open up. On the other hand, pressure causes a system to decrease in volume and causes the entropy to decrease. As a general rule, increasing temperature will increase the rate of reaction in a chemical system. Likewise increasing pressure in a condensed system will generally decrease the rate of reaction. To effect chemical reactions, then, it becomes necessary when working at very high presses; i.e., of the order of 100,000 atmospheres, to be able to simultaneously subject the system to rather high temperatures.

Within the past five years high pressure apparatus has been designed that is capable of reaching sustained pressures as high as 200,000 atmospheres simultaneously with sustained temperatures as high as 2500°C. Temperatures as high as 10,000°C may be achieved in some of these devices for periods of one or two seconds. This apparatus development has opened many research possibilities in the fields of chemistry, metallurgy, physics, geophysics, etc. One well publicized result arising from this apparatus development is the production, on a commercial scale, of man-made diamonds.

The most convenient way to utilize the energy associated with pressure is to transmit the pressure from a central location (the pumping

---

* Alfred P. Sloan Foundation Research Fellow, 1959-61.

station) by means of hydraulic lines to the points of use. The upper limit of pressure at which fluids can be transmitted from place to place at the present time is of the order of 20,000 atmospheres. At this pressure small, stainless steel capillary tubing has been successfully used as a conduit for the fluid.[1]

At pressures greater than 20,000 atmospheres it is necessary to produce the pressure directly within the reaction vessel. The simplest type of reaction vessel wherein this is done consists of a cylinder fitted with a plug at one end and a movable piston at the other. In operation the specimen to be subjected to pressure is located between the confining plug and the piston and is surrounded by some type of pressure transmitting medium. To generate pressure the piston is driven, usually by means of a hydraulic press, into the cylinder, thereby compressing the pressure transmitting medium which in turn compresses the sample. Of course, in many instances, the pressure transmitting medium may itself be the specimen of interest. The limitation on the transmission of pressure from one point to another to pressures below 20,000 atmospheres is imposed by the strength of the necessary plumbing and also by problems connected with valving of the pumps. The simple piston and cylinder device, just described, is useful at pressure to approximately 50,000 atmospheres. Problems associated with leakage past the piston can usually be solved by use of various types of seals now available. It is possible to introduce various electrical leads into the working chamber by use of conical seals so that various types of electrical measurements can be made. Friction of the piston against the wall of the cylinder constitutes an appreciable fraction of the total load being exerted on the piston by the hydraulic press. Allowance for this friction is usually determined by making measurements with increasing and also with decreasing loads. There have been many versions of the simple piston and cylinder apparatus. Apparatus for use from room temperature to about 250°C (the higher temperatures are obtained by immersion of the entire apparatus in a thermostated bath) has been adequately described by P.W. Bridgman.[2] Such apparatus is fairly common and will not be described here.

Birch et al[3] have described an apparatus capable of achieving pressures to 27,000 atmospheres simultaneously with temperatures to 1500°C. This apparatus utilizes a gaseous pressure medium. Gas at 2000 atmospheres is admitted to the chamber of a piston and cylinder device in which the advance of the piston increases the gaseous pressure to the final maximum pressure of 27,000 atmospheres. A resistance furnace is located within the cylindrical chamber and the sample to be heated and compressed is located inside this furnace. Electrical leads used to carry heating current to the furnace winding, to measure temperature, etc. are brought in through conical seals insulated with thin pyrophyllite cones. Necessary lateral support for the cylindrical chamber is provided by tapered binding rings. This support is increased as the pressure inside increases by means of a second hydraulic ram (the first ram drives the piston) that forces the conical binding rings over the external conical surface of the cylindrical chamber. Loring Coes of the Norton Company[4] has devised a simple piston and cylinder device capable of reaching pressures to 45,000 atmospheres simultaneously with temperatures of about 1200°C. This device uses an internal resistance furnace to heat the sample. There is a problem in designing high pressure apparatus with an internally heated furnace because these furnaces generally require rather large currents for their operation. This makes it difficult to introduce large leads into the high pressure region. Coes circumvented this problem by constructing the cylinder of fused alumina. Two cemented tungsten carbide pistons, one at each end of the cylindrical chamber, are driven into the chamber to generate pressure. Electrical connection is made with each of these pistons, and they, in turn, make connection with the heating element inside. The cross sectional area of the pistons is entirely adequate to carry the currents required, and the alumina cylinder electrically insulates each piston from the other. Pressure in this case is transmitted to the sample by solid, powdered refractory materials. More will be said about the use of solids to transmit pressure later.

I have described a device[5] very similar to Coes' except that the chamber is constructed of cemented tungsten carbide rather than alumina. The carbide has superior compressive strength to that of the alumina but creates a problem because it is a very good electrical conductor. Heating current is brought into the chamber in this system via a carbide piston at one end and via a carbide plug at the other. This plug is insulated from the tungsten carbide chamber by a thin electrically insulating film. This device is capable of a maximum pressure of 50,000 atmospheres and when water cooled can operate over long periods of time at temperatures near

2000°C. For very short periods of time temperatures upwards of 5000°C are possible.

Maximum pressures are obtained in simple piston and cylinder devices by constructing the pistons and the cylindrical chamber of cemented tungsten carbide. These materials are known by such trade names as Kennametal, Carboloy, Talide Metal and so on. These materials have the highest resistance to crushing; i.e., the highest compressive strength, of any engineering material currently available. As usually measured these crushing strengths are of the order of 750,000 pounds per square inch which is the equivalent of about 50,000 atmospheres. Although cemented tungsten carbides have extremely high compressive strengths, their resistance to breakage in tension is very low. A cylindrical chamber constructed of cemented tungsten carbide would, of course, be subjected to strong tensile forces. In order to offset these forces it is necessary to provide lateral support to the carbide chamber. This is usually obtained by the use of hardened steel binding rings. These binding rings may be of the tapered, interference fit, fixed type described by Hall or they may be of the type used by Birch in which a tapered binding ring is pushed over a tapered chamber by increasing amounts as the pressure is increased inside. The latter type is advantageous in attempting to keep the inside diameter of the chamber constant as the pressure inside is increased. However, the frictional forces along the tapers are such that the surfaces tend to gall after relatively few loading and unloading cycles. Of course, the load on the piston tends to make the piston increase in diameter, and this tends to compensate for the increased diameter of the cylinder. Thus it is quite feasible to utilize a fixed set of compound binding rings. They have the advantage of having a very long lifetime.

It is now appropriate to consider the problem of obtaining pressures beyond the 50,000 atmospheres obtainable in simple piston and cylinder devices. With a properly supported chamber, the limitation on the ultimate pressure obtainable in these devices is set by failure of the piston. If the piston is a good fit to the cylindrical chamber surface, that portion of the piston inserted within the cylinder receives some support from the cylinder wall. However, in order that there be motion of the piston, a certain portion of the piston must protrude beyond the end of the cylinder. This portion is unsupported and it is here where failure will occur. If materials with greater crushing strength than the cemented tungsten carbides were to become available, the pressures that could be obtained with a simple piston and cylinder would be increased by an amount corresponding to the increased compressive strength. Therefore, an important endeavor, in the effort to push pressures to higher levels, is research in the area of high strength materials. Of materials currently known to man, diamond has the highest compressive strength. However, diamond is not available in sizes large enough to fill most needs in high pressure apparatus construction. Diamonds have been used for the cylindrical confining vessel in high pressure x-ray diffraction work[6] because of their relative transparency to x-rays. However, in this use, the diamond is subject to tensive forces rather than to compressive loading and the maximum pressures obtained in such devices have been in the neighborhood of 35,000 atmospheres. Diamonds have also been fashioned into tiny Bridgman anvils (this type of apparatus will be described later).

Although diamond in large pieces is not obtainable, fine diamond powder is quite abundant and relatively inexpensive. Diamond powder might be used in a manner similar to that in which tungsten carbide powder is cemented together (by cobalt) to give cemented tungsten carbide. Such a material could conceivably have a compressive strength about twice that of the cemented carbide. However, a suitable bonding agent for the fine diamond particles has not yet been discovered. Any bonding agent that would have sufficient strength would of necessity be rather high melting. If the cemented diamond composition were fabricated in a manner similar to that used for the cemented tungsten carbides, the diamond powder and the cementing agent would be intimately mixed by grinding them together in a ball mill. The mixture would then be pressed to shape and heated at a temperature slightly below the melting point of the bonding agent until the bond had formed. This temperature would very likely be above 1000°C. At this temperature very fine diamond powder readily graphitizes. Of course, the resultant structure would have low strength. If a sufficiently high pressure were applied to the mixture of diamond powder and bonding agent, a region could be reached wherein the diamond would be thermodynamically stable over graphite, and as the temperature was raised to the sintering point the diamond would not graphitize. In practice it is not necessary to increase the pressure to a value high enough to make diamond stable over graphite. High pressure does slow down the rate of transformation of diamond to graphite and so it is only necessary to increase the pressure to a point where the rate of transformation is extremely slow. Some research at Brigham Young University has been directed towards producing a cemented diamond material. At the present time, the best cementing agent found is silicon. However, the product produced so far, is inferior to the commercially available cemented carbides. Further research in this direction is highly desirable.

It is quite likely that materials of greater crushing strength than those presently available will be eventually produced by high pressure, high temperature research. For example, my associates and I have recently, produced ¼ inch diameter x ½ inch long pieces of silicon carbide under high pressure, high temperature conditions with a compressive strength of 700,000 pounds per square inch. Ordinary hot-pressed silicon carbide has a compressive strength of only 25,000 pounds per square inch.

Theoretically, it should be possible to obtain extremely high pressures by multi-staging. In such a process, one pressure apparatus would be placed entirely within the chamber of another pressure apparatus. Since the pressure that can be obtained by a vessel depends only on the difference in pressure between that existing inside the vessel and that pressure that completely surrounds it, a two stage apparatus should make it possible to reach twice the pressure that can be obtained in a single stage. The mechanical difficulties connected with the design of a multi-stage apparatus are rather formidable. Consequently, at the present time an apparatus with greater than two stages has not been described. P. W. Bridgman[7] has described a two stage device in which the inner piston is only 1/16 of an inch in diameter. In spite of the difficulties encountered, Bridgman has reported many successful measurements with this device. One factor responsible for some of these difficulties is the fact that friction of the inner piston against the cylinder wall absorbs as much as 40% of the total load on this piston. The two stage device described by Bridgman could not be heated internally nor could electrical leads be inserted into the inner chamber. Its primary usefulness was in measuring pressure volume relations at room temperature.

In 1950,[8] P. W. Bridgman reported the construction of an anvil apparatus utilizing two important principles: the principle of massive support and the principle of motion by means of a compressible gasket. The principle of massive support can be readily visualized from Fig. 1 where a broad truncated come is depicted alongside of a right circular cylinder. The surface areas of the circular section marked a and a´ are equal. If the cone and the cylinder are subjected to compressive load between flat plates, it will be discovered that the pressure on a´ will be much greater than the pressure on a at destructive failure of the cone and cylinder respectively. The reason for this lies in the fact that the circular tip near the apex of the cone has mechanical ties fanning out into a greater volume behind the tip than is the case in a right circular cylinder. The greater the included angle of the cone, the greater will be the pressure to which the tip can be subjected. Bridgman anvils, utilizing this principle, are shown in Fig. 2. Such anvils can be forced together until the force over area pressure existing on the two contact faces is as high as 200,000 atmospheres before failure of the carbide occurs. Bridgman immersed two such anvils in a hydrostatic medium at 30,000 atmospheres and succeeded in obtaining a pressure between carbide anvil faces as high as 450,000 atmospheres before failure. No experiments, however, have been performed to the present time in such a two stage device. The maximum pressures above are possible only when the carbide binding rings are surrounded by shrunk-on or interference fit steel binding rings. These provide lateral support to the carbide and absorb some of the tensive load that is fanned out from the truncated surface near the apex into the volume immediately behind.

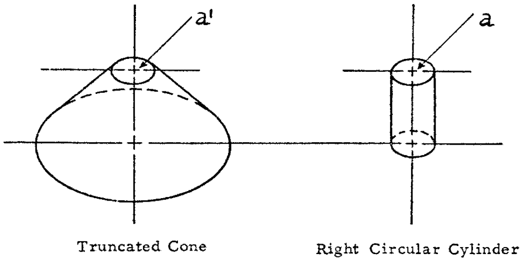

Fig. 1—The Principle of Massive Support

Bridgman's earliest experiments with anvils were conducted by placing thin wafers of materials to be compressed between the anvil faces. As the anvils were forced together, material would extrude from between the faces until the lateral friction near the edges of the specimen was sufficient to balance the pressure towards the center of the specimen. In general, the higher the internal friction of a substance the thicker would be the resultant specimen when equilibrium between the frictional forces and the

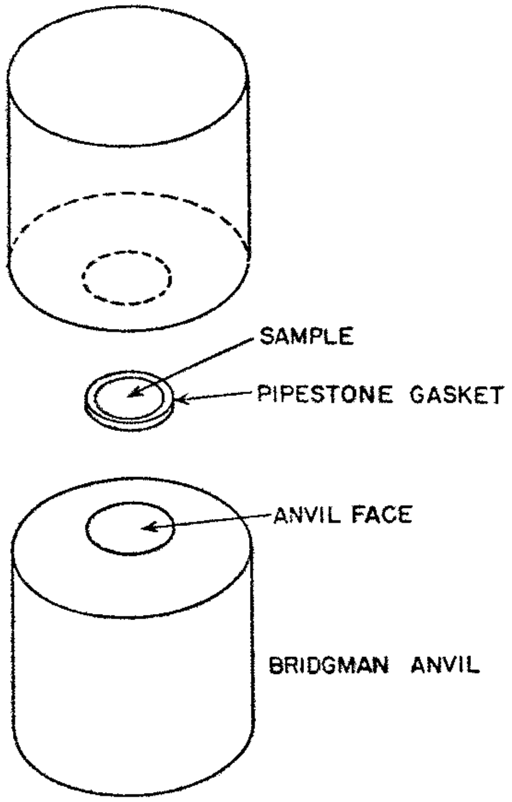

Fig. 2—Bridgman Anvils

pressure would be attained. The type of experiment just described was not particularly useful. A device utilizing massive support was needed in which relative motion could obtained and controlled. Bridgman solved this problem by surrounding a wafer like disc of the sample by a pipestone* ring as shown in Fig. 2. Pipestone's frictional and compressive properties are such that the ring would form a seal around the wafer-like sample preventing its extrusion from between the anvils, and, at the same time, it would compress with the anvil advance allowing motion to be obtained. It so happens that the relative compressions of pipestone and silver chloride are about the same. Therefore, if the specimen were made of silver chloride, the pressure within the silver chloride could be taken as equal to the force exerted on the anvils divided by the area of the anvil faces. Silver chloride if a very excellent solid pressure transmitting medium. More will be said concerning this later. Any material embedded in the silver chloride would thus be subjected to the calculated pressure. Bridgman used this device to measure the electrical resistance of metals by embedding a ribbon of the metal in the silver chloride and providing means for the ends of the ribbon to make electrical contact with the anvils.[9] These measurements were made at pressures up to 100,000 atmospheres. These measurements could have been extended to higher pressures at a sacrifice in anvil life. The upper pressure limit for these anvils is in the neighborhood of 200,000 atmospheres. It is likely that one out of three sets of anvils would succeed in achieving this pressure before failure. The anvils would eventually fail at 100,000 atmospheres but many dozens of runs are possible before this would occur.

Bridgman anvils have been adapted[10] for use in high pressure synthesis by surrounding the anvils with a furnace. It has been possible to reach a temperature as high as 1000°C with such an arrangement. At 1000°C, the highest attainable pressure is about 20,000 atmospheres. As the temperature is reduced towards room temperature the corresponding pressure that can be obtained is increased towards 100,000 atmospheres.

There are limitations in the Bridgman anvil device that it would be desirable to overcome for some purposes. One limitation, of course, is the smallness of the sample. Another is the simple geometry (the sample is, in effect, two dimensional). For many purposes it would be desirable to have a sample whose depth was of the same order of magnitude as its length and breadth. This would be particularly important in an apparatus design wherein the specimen were to be heated internally by an electrical resistance furnace. Another limitation in this design is the fact that it is not possible to measure volume of the sample as a function of pressure. The principle of massive support was so effective in increasing the ultimate pressure obtainable in a single stage apparatus that several attempts have been made to utilize this principle in other ways in order to obtain an apparatus that was free from one or both of the aforementioned limitations.

One of these designs the stepped-piston[11] utilizes the principle in the following manner (refer to Fig. 3). The working volume of this apparatus consists of an annular space *F* formed by the stepped-piston *D* and the stepped-cylinder

---

[*] Pipestone or catlinite (a red, indurated clay from the upper Missouri region) is found at Pipestone National Monument, a part of the Sioux Indian Reservation in Minnesota. As the name implies, the Indians carve smoking pipes from the material. The physical properties of pipestone are similar to those of pyrophyllite and talc.

E. (Although not shown in the figure, the cylinder is surrounded by a set of binding rings.) The annular area of the piston step is approximately 1/5 of the area of the large diameter portion of the piston. This annular area has mechanical ties reaching back into areas of larger cross section and will therefore, by the massive support principle, support a greater load than would a right circular cylinder of the same area. This same principle applies to the annular step of the cylinder. A force applied as shown at *A* of the figure will cause a specimen in the annulus to be compressed. Experience with this device shows that pressures in the annulus near 45,000 atmospheres cause the cemented tungsten carbide piston to break at the step in a plane perpendicular to the center line of the assembly. This is, no doubt, a manifestation of the pinch-off effect previously described by Bridgman.[12] A piston clamping force applied as shown at *B* will prevent the pinch-off effect. The sum of the forces *A* plus *B* when divided by the area of the large diameter portion of the piston must not exceed the compressive strength of the cemented tungsten carbide. With forces applied as thus far described the apparatus is operable to about 70,000 atmospheres. At this pressure a lateral break beginning at the step occurs in the carbide cylinder. This can be prevented by a clamping force shown as *C* in the figure. By utilization of these clamping forces it has bee possible to compress solid materials to annular loadings corresponding to 200,000 atmospheres. At this loading piston failure occurs. Hardened steel rings of triangular cross section *G* are used as gaskets when necessary. All sliding surfaces, including the external surfaces of any solid specimen to be compressed, are lubricated with molybdenum disulfide powder. In this design the piston and cylinder should fit within plus or minus 0.0002 inch above and below the step. This of course requires rather expert workmanship. In the form just described the stepped-piston apparatus is useful for making compressibility measurements at room temperature. If increased considerably in size, it might be adapted to internal heating. In the apparatus used at Brigham Young University forces *A* and *B* are provided by hydraulic rams while force *C* is provided by a mechanical clamp. This clamp consists of two heave hardened plates which are drawn together by heavy tension bolts. While this design seems rather complex, it is, nevertheless, somewhat simpler than a two stage piston and cylinder apparatus. The stepped-piston design has preserved the massive support principle but at the same time has made it possible to obtain large relative motion between mechanical

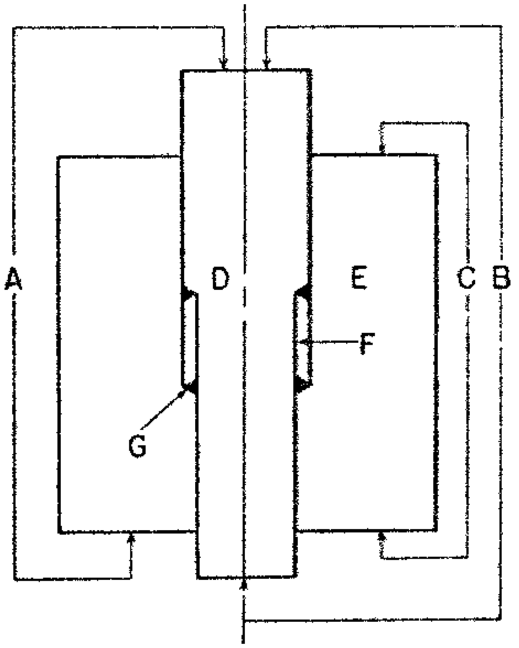

Fig. 3—Stepped Piston Apparatus

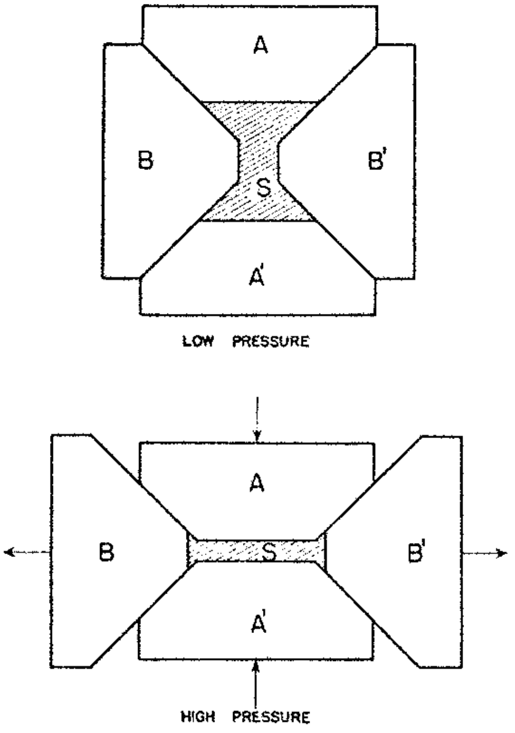

Fig. 4—"Blackhawk Special"

components of the system. Piston displacement, with proper correction for deformation of piston and chamber, gives directly the change in volume of sample as a function of pressure.

Another device utilizing the massive support principle which at the same time allows considerable relative motion is shown in Fig. 4. Construction of this device was begun at Brigham Young University in 1956 but was never completed due to the press of other business. We refer to the device as the "Blackhawk Special" because of the large number of Blackhawk hydraulic rams that were used to supply the many forces that were needed. These rams are one of a number of commercially available brands that have been designed principally for use in auto body repair. In addition to the rams, there are various pumps, hoses, valves, and fittings readily adaptable to high pressure work. This equipment and similar, but heavier, equipment designed for use in the construction industry are common sights in many high pressure laboratories today. The Blackhawk Special consists of a number of flat wedges located between two flat plates. The flat plates are maintained at a fixed distance corresponding to the thickness of the wedges. Pressure is generated by causing alternated wedges to advance or recede as indicated in the diagram. The wedges and plates are constructed of cemented tungsten carbide and are lubricated on all surfaces with a dry film lubricant. Electrical leads could conceivably be brought into the working volume through a cone and sleeve arrangement located in the flat plates.

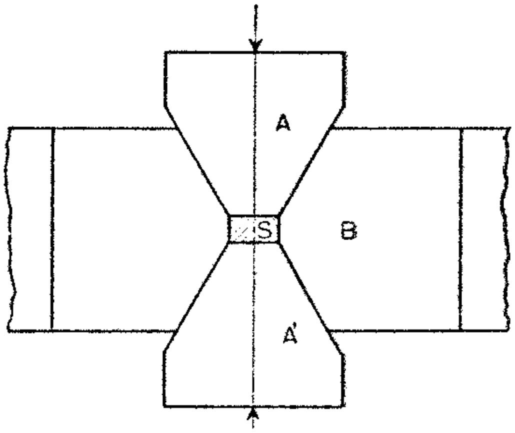

FIG. 5—"The Girdle"

Wendell B. Wilson[13] has recently described a device which utilizes massive support and obtains relative motion by allowing two cone shaped pistons to be forced into both ends of a conical chamber (refer to Fig. 5). As the conical pistons *A* and *A*′ are pushed together the wedge effect of the cones forces the conical chamber *B* to expand. The geometry operative in the die is shown in Fig. 6. As the pistons advance an increment Δh into the die, the die must expand by an increment Δr. From the drawing $\Delta r = \Delta h \tan \Theta$. In order for pressure to build within the die the disk volume swept out as the pistons advance must be larger than the increase in annulus volume caused by the increase in radius of the cylinder. Neglecting second order terms these volumes are found to be equal when $r = h \tan \Theta$. For a fixed Θ, h must be made smaller than this equal volume value if pressure is to be generated. Wilson has named this device "The Girdle." He has experimented with several designs including one in which Θ was set at 35° and h was set at ¼ inch. In this, he reported obtaining pressures of at least 80,000 atmospheres. One of the conical pistons is insulated from the conical chamber with a layer of red iron oxide. (Thermocouple leads may be brought out through this layer.) Heating current can be passed from the insulated piston through a furnace located inside the chamber, thence out through the piston at the opposite end. The latter piston is lubricated with a dry film lubricant (usually molybdenum disulfide) to facilitate its entry into the conical surface of the chamber.

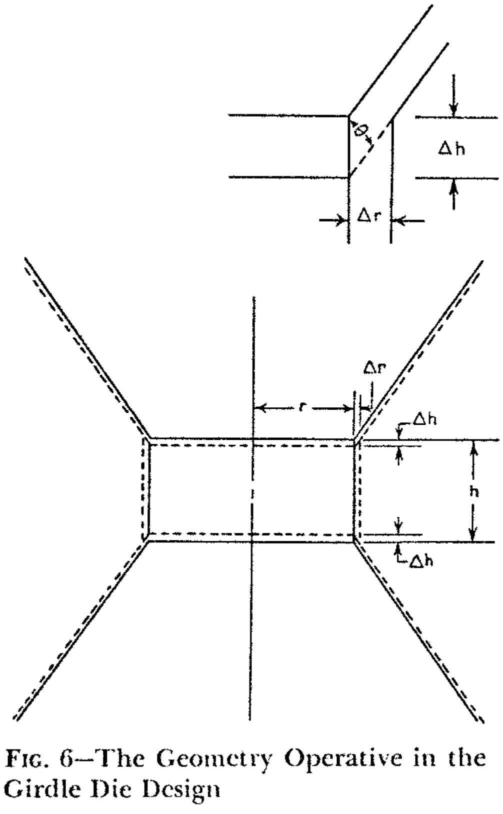

FIG. 6—The Geometry Operative in the Girdle Die Design

The production of high pressure in a device using a conical piston and chamber has also been described by Vereshchagin et al.[14] However, their main concern was not the obtaining of increased pressure by use of the massive support principle, but rather the development of a device that would not require any sealing gaskets. By proper selection of angles and contact areas they managed to maintain a slightly higher pressure on the contacting surfaces of the cone shaped piston and cylinder than existed in the pressure chamber proper. Under these conditions there was no leak.

In the Bridgman anvil design there is a rather sharp line of demarcation between the extremely high pressure existing in the gasket and sample and the ambient pressure immediately adjacent to the gasket. It seems likely that this apparatus might be improved by a judicious redesigning of the gasket arrangement. This might be accomplished by selection of various materials with different compressibilities and internal frictions and by using concentric rings of gaskets rather than a single gasket. In these arrangements a multistage effect would be achieved in a single stage. This would avoid the mechanical and other complications encountered in multistage devices.

This very effect has been obtained in a device of Drickamer and his associates.[15] This ingenuous equipment permits the observation of the effect of pressure on optical phenomena to 200,000 atmospheres. An alkali halide (normally sodium chloride) is utilized as pressure transmitting medium and also as windows (Fig. 7). Although sodium chloride has a relatively low shear strength and is effectively a fluid at very high pressure, it is a very viscous fluid. When fused in a long narrow hole by the repeated application of pressures of about 40,000 atmospheres, it is not extruded for a very long time even under the action of much higher pressures. The chamber *A* is constructed of hardened steel (Rc = 60) and is surrounded by a steel binding ring *B*. In a typical design, the piston (*C* and *C´*) diameter is ½ inch. The sodium chloride window *G* consists of holes of sizes .188 inch at the largest diameter to .082 inch at the smallest diameter which have been filled with fused salt under high pressure as previously mentioned. The carbide pistons *C* and *C´* are surrounded with shrunk-on steel rings *D* and *D´*. Proper alignment of the piston assemblies is provided by rings *E* and *E´*. Ring *E´* is threaded and serves to hold piston *C´* in a fixed position. Piston *C* is the movable piston. The pistons are tapered away from the flat tip. A tip diameter consistent with the other dimensions referred to is .093 inches. The threaded arrangement *F* serves as a support to help prevent extrusion of the sodium chloride windows.

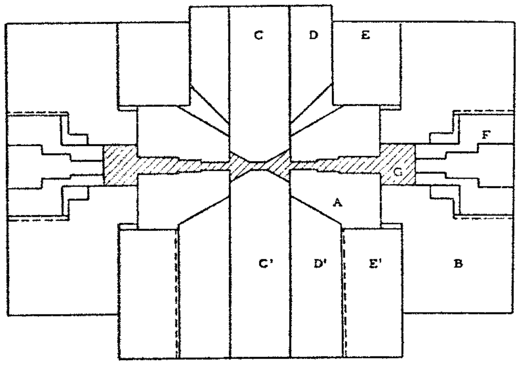

FIG. 7—Drickamer Apparatus

When the space between the pistons is filled with a material such as sodium chloride and a load is applied to the movable piston, the sodium chloride located between the flat tips of the piston will be compressed by a greater amount than the sodium chloride between the sloping sides of the piston. This results in a pressure gradient existing within the sodium chloride from the edge of the flat to the outside of the piston. The greater the piston taper the higher the gradient, but then there will also be a higher tendency for sodium chloride to extrude from between the flat piston tips. After trying a wide variety of tapers Drickamer and his associates found that a single taper of 6° on each piston was the most advantageous. The very high pressure is only on the central piston flat. It does not break under loads exceeding the normal compressive strength of the carbide because of the principle of massive support. The salt also supports the piston along the taper. The salt from the edge of the flat outward is under a continuously decreasing pressure and acts as a series of cells within a cell. This produces, in a single stage, a multistage effect. At extremely high pressure the thickness of the wafer between the flat faces of the piston may be only a few thousandths of an inch. Despite this, however, it is possible to pass a beam of light through the windows, between the anvil and out of the opposite window of sufficient intensity to make spectral or other optical measurements. To perform an experiment, the central disk of NaCl is replaced by a disk of the sample of interest. The pressure obtained in the device as a function of load on the piston was determined by observing phase transitions previously observed by Bridgman in bismuth at 24,800 atmospheres, in tellurium at 43,500 atmospheres, in silver bromide at 83,200 atmospheres and in silver chloride at 87,100 atmospheres. Additional details of calibration are available in the referenced article.

The obtaining of a multi-stage effect by proper use of solid materials offers hope of great simplification over the usual procedure of applying external support by use of a hydrostatic fluid. It will be recalled that the protruding portion of the piston in a simple piston and cylinder apparatus is the vulnerable part subject to failure. There have been some attempts to provide support to the protruding portion of the piston by means of a solid pressure transmitting material that is subjected to a load by a secondary piston. A successful design embodying this idea, capable of working to pressures of about 65,000 atmospheres at temperatures above 1000°C, has been described by F. R. Boyd and J. L. England.[16]

Solid pressure media were used to transmit pressure as long ago as 1888 by Sir Charles Parsons.[17] There has until quite recently, however, been considerable suspicion as to the results obtained by using solids to transmit pressure. Recent work, however, has proved that for most purposes solid materials can be used very effectively to transmit pressure. It may not be generally recognized that most materials that are normally liquids at room temperature and pressure become solids at pressures below 10,000 atmospheres. The best known composition for maintaining its liquid nature at high pressures is a 50-50 (by volume) mixture of normal and iso-pentane. This material does not become solid at room temperature until a pressure of 35,000 atmospheres is reached. At room temperature it is quite likely that the only true fluid available for use at pressures of 100,000 atmospheres and higher is hydrogen. All other materials would be solid at such a pressure. The difficulties to be encountered in attempting to use hydrogen as a high pressure medium are formidable if not impossible to overcome (hydrogen makes steel “rotten” at 9000 atmospheres[18]). The mixture of iso-pentane and normal pentane which is quite satisfactory for transmitting pressure up to the vicinity of 35,000 atmospheres is a very unsatisfactory pressure transmitting material after it has solidified. The logical question then arises, might it not be possible that some materials normally solid under ambient conditions would be better pressure transmitters at pressures beyond 35,000 atmospheres than materials originally liquids? The answer to this question is yes. In addition solid materials are easier to handle. Also, some solids possess much better thermal-insulating qualities than any liquid and hence are much to be preferred where internal furnaces are to be used. Bridgman considered this problem and discovered that silver chloride and silver sulfate in particular were very good pressure transmitters at all pressures above a few hundred atmospheres.

Recognizing the advantages to be gained by the utilization of solids to transmit pressure, some research in this connection has been conducted at Brigham Young University.[19] In these studies the effectiveness of pressure transmission by such materials as powdered boron, boron nitride, mica, molybdenum disulfide, ferric oxide, corn starch, zinc oxide, compressed cotton, block talk, pyrophyllite and other materials has been measured. In general, it was found, that materials with low internal friction made very good pressure transmitting substances. For most purposes materials with a coefficient of friction lower than 0.35 are quite satisfactory. A study of the effect of pressure on the friction of several materials has also recently been made in our laboratory.[20] Block pyrophyllite and talc are currently receiving considerable attention as pressure transmitting materials. In addition to transmitting pressure very satisfactorily, these materials are also very good thermo-insulators, are readily machinable, and, in thin sections, have sufficient friction to be used as gaskets in anvil applications. The effectiveness of solids as pressure transmitters depends to a considerable extent upon the geometry of the high pressure system. It is difficult to transmit pressure effectively with solids over long distances down a narrow tube, or into the apex of a conical cavity. This fact has already been utilized in the pressure apparatus of Drickamer where, in this instance, the pressure transmitting material was sodium chloride which has the relatively low coefficient of friction of 0.10.

As ordinarily used in high pressure apparatus, a fine-grained powdery material with a coefficient of friction of .45 is a rather good pressure transmitter. For example: Consider a simple piston and cylinder device in which the chamber and pistons have a diameter of ½ inch and where the distance between the piston tips within the chamber is initially ¾ inch. (In this instance each piston protrudes from the cylindrical cavity and both pistons will be driven to a center point within the chamber. Such a device is referred to as a double-ended apparatus.). The cell assembly consists of a pyrophyllite cylinder ¾ inch long and ½ inch in diameter. The specimen to be compressed consists of a cylinder 1/16 inch in diameter and ½ inch long located symmetrically along the cylindrical axis within the pyrophyllite. External surfaces of the pyrophyllite and piston and cylinder are coated with a dry film lubricant such as molybdenum disulfide. Piston fit to cylinder is very good so that there will be no extrusion of pyrophyllite between the sliding surfaces. Under such circumstances the actual pressure found to exist within the 1/16 inch diameter by ½ inch long specimen (providing the specimen is of a reasonably hydrostatic material such as silver chloride) is no less than 10% smaller than the calculated pressure obtained by dividing the force applied to the piston by the piston's cross sectional area. The diameter of 1/16 inch for the specimen is rather a lower limit considering the other set dimensions and geometry. If the diameter is decreased beyond this point it will be found that higher forces must be applied to the piston in order to obtain the same pressure. A device utilizing solid pressure transmitting media, massive support and "motion via compressible gasket" capable of reaching sustained pressures of at least 135,000 atmospheres simultaneously with sustained temperatures of 2000°C has recently been described.[21] This device is available commercially from the Engineering Supervision Company, 787 United Nations Plaza, New York 17, New York, under license from Research Corporation. This device is essentially a three-dimensional version of Bridgman's anvil apparatus. Instead of using two opposing anvils with circular faces, it utilizes four anvils with triangular faces. These anvils (shown in Fig. 8) are driven together by hydraulic rams along lines normal to the triangular faces. The anvil center lines intersect at tetrahedral angles in the center of a regular tetrahedral volume enclosed by the anvil faces. As used in the apparatus, each anvil is surrounded by a shrunk-on or press fit steel binding ring. This binding ring is designed to absorb the tensive loads developed as has previously been described. In this device a regular pyrophyllite tetrahedron (Fig. 9), the legs of which are 25% longer than the corresponding legs on the triangular anvil faces, serves as pressure transmitting medium, thermal and electrical insulation and also provides the necessary compressible gasket.

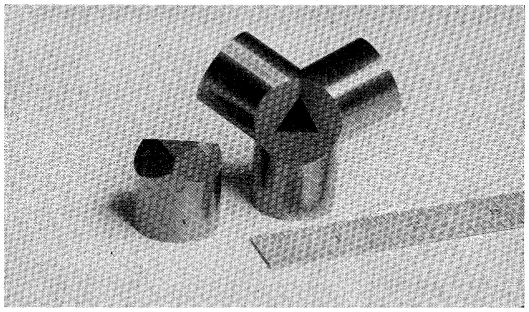

Fig. 8—Tetrahedral Anvils

The sample container, a tube which also serves as electrical resistance heater, is located within the pyrophyllite tetrahedron and runs diagonally from opposite edges as is shown. Electrical connections are made to the sample tube through metal tabs shapes as shown in cross-section in the figure. These tabs make electrical contact to the end of the tube and also make contact with the sloping faces of a pair of adjacent anvils through which the heating current passes. Prisms of pyrophyllite located at the ends of the sample tube provide thermal insulation in this region. A thermocouple spot-welded to the sample container is used to measure temperature.

The thermocouple leads are brought out through the edges of the tetrahedron in the space between the anvils. Friction of the pyrophyllite gasket on the fine wires is sufficient to hold them in place during high pressure operation. Several electrical leads may be inserted into the sample area without difficulty. It is helpful to sandwich the thermocouple wires between two wafers of

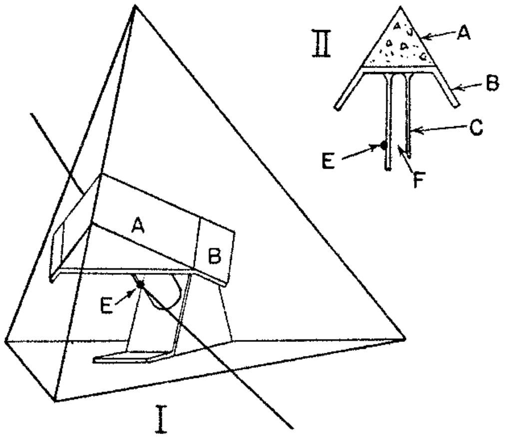

Fig. 9—I. Detail of Pyrophyllite Tetrahedron with Diagonal Edge-to-Edge Heater-Sample Tube
II. Detail of Heater-Sample Tube

pyrophyllite whose total thickness is initially equal to the distance between the sloping sides of adjacent anvils. This serves to provide a gasket in the region where the thermocouple wires emerge from the tetrahedron before a gasket is formed by extrusion of the tetrahedron edges as the anvils advance. If this is not done, there is some difficulty with the initial lava extrusion tearing the thermocouple wires in two as the lava advances to form the gasket.

To operate the tetrahedral anvil device, the pyrophyllite tetrahedron assembly is centered on the anvil faces, the anvils are then simultaneously forced together by hydraulic rams. Prior to centering the pyrophyllite tetrahedron on the anvil faces, the exposed pyrophyllite surfaces are painted with red iron-oxide to increase the surface friction (Coefficient of friction of Fe_2O_3 powder is about 0.7). Since the triangular faces of the pyrophyllite tetrahedron are larger than the triangular anvil faces, some pyrophyllite is forced between the sloping sides of the anvils, and a gasket is automatically formed. Continued motion of the anvils compresses the gasket and tetrahedron and consequently the sample.

At this point it would be well to mention the relative compression of this device. Relative compression is the ratio of the volume swept out by the advance of the anvil faces compared to the initial volume of the pyrophyllite tetrahedron. If this ratio is too small the relative compression will not be great enough to generate a high pressure within the sample space. Before the first tetrahedral anvil device was built ant tested, this was a question of some concern because the volume to be compressed was considerably larger than the volume to be compressed in the case of Bridgman's anvils. Experience with the tetrahedral device has shown, however, that the volume decrease caused by advance of the anvils is sufficient to reach pressures of at least 135,000 atmospheres within the diagonal cylindrical volume inside the tetrahedron when the ration of tetrahedron volume to the volume of the cylindrical hole is of the order of 16 to 1. With this volume ration the pressure generated in a hydrostatic specimen does not depend upon the compressibility of the specimen.

Pressure calibration of the tetrahedral anvil device is made by substituting a silver-chloride rod containing a pressure sensing wire for the specimen. The pressure sensing wire makes electrical contact with the metal tabs. The resistance of the pressure sensing wire is then measured as a function of the force applied to the anvils. Certain materials such as bismuth, thallium, cesium, and barium undergo abrupt changes in electrical resistance at pressure previously determined by P. W. Bridgman. When these transitions are observed to occur, the corresponding force on the anvils is recorded, and a calibration plot of pressure versus force of the anvils is established. This plot is found to be linear for the tetrahedral anvil device, and, when once established, the force of the anvils can be taken as a measure of the pressure being exerted by the pyrophyllite on the walls of the cylindrical sample chamber.

The question often arises as to the effect of sample heating on increasing the pressure within the sample chamber. Calculation shows that at pressures above 10,000 atmospheres heating of most materials to temperatures as high as 2000°C causes a rise in pressure that is less than the estimated error by which the pressure is know. A conservative estimate indicates that pressure in the tetrahedral anvil device is known within plus or minus 5% at pressures above 10,000 atmospheres.

In making a pressure calibration, it is found that the transitions in bismuth, thallium, cesium, and barium occur at a much lower loading on release of load than on increasing load. This is due to the hysteretic properties of the pyrophyllite. Normally, pressure calibration is based on measurements made with increasing load. Consequently, during experiments in which the pressure is to be varied, measurements are taken in one direction only; namely, on increasing load. Relative resistance changes occurring in the calibration materials are shown in Fig. 10. The transition in Bismuth at 121,000 atmospheres is a new transition recently discovered by F. P. Bundy.[22]

Questions are often asked as to the relative merits of tetrahedral anvils as compared to cubic anvils. In a cubic system, six anvils with square faces would surround a pyrophyllite cube. Such an arrangement might offer some advantages because of the simpler geometry. While a cubic anvil system is satisfactory for many purposes, tetrahedral anvils provide optimum conditions in regard to the maximum pressure obtainable, and the maximum lifetime of apparatus. For anvils with equal face areas each cubic anvil must advance a distance 61% greater than each tetrahedral anvil in order to obtain the same relative compression. Since total anvil advance is quite limited in compressible gasket systems, this is an important consideration. Furthermore, the principle of massive support achieves its maximum value (when regular geometric solids are considered) in the tetrahedral anvil apparatus.

Conclusion

The devices that have been discussed, illustrate six ideas that have been useful in obtaining pressures greater than are possible with ordinary simple piston and cylinder apparatus. They are: (1) the principle of massive support, (2) the obtaining of relative motion by means of a compressible gasket, (3) the obtaining of relative motion by elastic distortion, (4) the obtaining of relative motion by means of new mechanical designs, (5) the obtaining of a multistage effect within a single stage, (6) the use of solids to transmit pressure. A seventh means of obtaining higher pressures, applicable to any apparatus, would be the development of materials with improved compressive strength; i.e., materials with compressive strength greater than that of commercial cemented tungsten carbide. The use of the massive support principle has been illustrated in the Bridgman Anvil, Tetrahedral Anvil, Stepped-Piston, Blackhawk Special, Girdle, and Drickamer designs. Motion by means of compressible gasket is necessary in the Bridgman, Tetrahedral Anvil, and Drickamer apparatus. Motion is obtained by means of elastic distortion and proper geometrical proportions in the Girdle design of Wilson. Motion is obtained by means of new mechanical designs in the Stepped Piston and Blackhawk Special devices. Multi-staging within a single stage is utilized in the Drickamer design and is partially evident in the Tetrahedral and Girdle equipment. In the tetrahedral design, each of the anvils tend to support other anvils, and in the Girdle design, the tapered piston tends to support the tapered chamber and vice versa. More effective utilization of the principles just enumerated, coupled with the use of new engineering materials, possessing improved compressive strengths, suggests that static pressures as high as 500,000 atmospheres are foreseeable in the not-too-distant future.

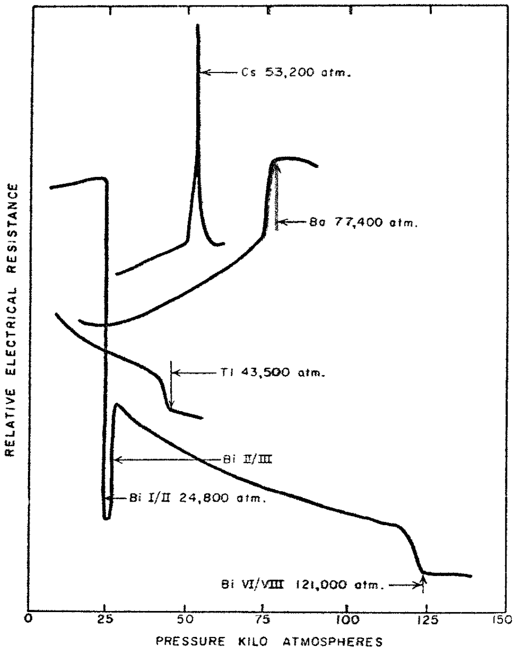

Fig. 10—Phase Transformations Used in Apparatus Calibration

Acknowledgments

The author gratefully acknowledges financial grants made to the high pressure research program at Brigham Young University by the National Science Foundation, the Carnegie Institution of Washington, the du Pont Company, and the Alfred P. Sloan Foundation.

References

[1] W. Paul and D. M. Warschauer, Rev. Sci. Inst. *27* 418-419 (1956).

[2] "The Physics of High Pressure," G. Bell & Sons, Ltd. (London) (1958).

[3] F. Birch, E. C. Robertson & S. P. Clark, Jr., Ind. and Eng. Chem. *49* 1965-6 (1957).

[4] Described by R. Roy and O. F. Tuttle, "Physics and Chemistry of the Earth," *1* 144 Pergamon Press, London & New York (1956).

[5] H. T. Hall, Rev. Sci. Inst. *29* 267-275 (1958).

[6] J. C. Jamieson, J. of Geol. *65* 334-343 (1957).

[7] Reference 2 page 401-403.

[8] Proc. Roy. Soc. (London) *A203* 1 (1950).

[9] Proc. Am. Acad. Arts Sci. *81* 165-251 (1952).

[10] D. T. Griggs and G. C. Kennedy, Am. J. Sci. *254* 722-735 (1956).

[11] H. T. Hall, Rev. Sci. Inst. *29* 267-275 (1958).

[12] Reference 2, page 91.

[13] Battelle Memorial Institute Report No. BMI-1328, UC-25 Metallurgy and Ceramics (TID-4500, 14th Edition) (March 18, 1959).

[14] L. F. Vereshchagin, A. I. Likhter, and V. I. Ivanov, Zhur. Tekh. Fiz. *26* 874-7 (1956).

[15] R. A. Fitch, T. E. Slykhouse, H. G. Drickamer, J. Opt. Soc. Am. *74* 1015 (1957).

[16] Annual Report of the Director of the Geophysical Laboratory for 1957-58, pages 170-173. (Washington, D.C.)

[17] Proc. Roy. Soc. (London) *A44* 320-323 (1888).

[18] Reference 2, page 96-97.

---

[19] Yang Lai Cho, unpublished thesis Brigham Young University, “Propagation of High Pressure in the Solid State,” (1958).

[20] Gerald R. Hyde, unpublished thesis Brigham Young University, “Friction at Very High Pressure,” (1958).

[21] H. T. Hall, Rev. Sci. Inst. *29* 267-275 (1958); Science *128* 225-229 (1958). Sci. American *201* (5) 61-67 (1959).

[22] Phys. Rev. *110* 314-318 (1958).