Chapter **II**
HIGH-PRESSURE TECHNIQUES
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1   INTRODUCTION

This chapter is written, primarily for the nonspecialist, out of 25 years of experience in designing and constructing all types of high-pressure equipment. During this period there have been only brief intervals in which I have not had a piece of apparatus under construction. My notebooks record about 250 ideas on apparatus design and at least 32 different devices valued at around $2 million have been built under my direction. I have been personally involved in all aspects of the work, including conception, design, drafting, and machining. In the latter I have tried to emulate that pioneer in the field of high pressure of whom it has been said, "there was only one person at Harvard who was a better machinist than Charlie Chase and that was Percy Bridgman." Mr. Charles Chase was Physics Professor Percy W. Bridgman's unusually skilled machinist and craftsman. In this work I too believe in getting my hands dirty. But it has not been work. For me it has been love.

The modern-day interest in high-pressure technology was most certainly sparked by the announcement on February 15, 1955, by the General Electric Company, that diamonds had, at long last, been made by man. Indeed, this had been one of the most intriguing, unsolved problems of science, attempts to synthesize diamond by the conversion of its polymorph graphite having been instigated in 1792. That was the year Lavoisier discovered that diamond consisted only of the element carbon.

Considerable excitement surrounded the General Electric announcement as journalists from around the world assembled to hear the news. There was also disappointment. For while there was a discussion of the unsuccessful attempts of others to synthesize diamond, and the tiny diamonds that had been made were displayed, the details of how these diamonds were made and the details of the equipment that was used were not revealed. Several months later, additional secrecy beyond company interest was revealed by the United States Government. Abatement of the secrecy did not come until five years later.

You can well imagine my anguish, anxiety, and dismay when, having invented (January 2, 1953) the belt apparatus in which the synthesis was achieved and having accomplished the world's first reproducible synthesis of Diamond (December 16, 1954), I was not able to publish or claim recognition for an accomplishment that had been sought by eminent scientists, including Nobel laureates, for much more than 100 years; and further, of watching my accomplishments being diluted through various means as the years went by, including leaks of information from company and government sources that allowed others, not hampered by proprietary or governmental interest, to come ever closer to the process and to the design that were original to me. A sampling of some of these problems is found elsewhere[1]. These difficulties, however, led to the development of other high-pressure equipment, specifically the multianvil presses, of which the most important members are the tetrahedral and cubic presses. These are discussed later.

Practical diamond synthesis requires pressures of the order of 50,000 atmospheres (atm) and higher. Having mentioned a practical unit of pressure measurement, I might diverge for a moment. Through the years many units have been used to measure pressure. Harvard Professor P. W. Bridgman, who received the Nobel Prize in 1948 for his work in the field of high pressure, measured pressure in kilograms per square centimeter. Bridgman's first paper on high pressure was published in 1908, and his last, in 1958. Chemists commonly use the atmosphere, or the kiloatmosphere, while geologists and others prefer the bar or the kilobar. Recently the National Bureau of Standards began encouraging the use of the newton per square meter (now called the pascal, abbreviated Pa). Fortunately, these units are closely related: 1 atm = 1.0133 bar = 1.0332 kg/cm^2 = 14.696 $lb/in.^2$ = 760 torr (mm Hg) = 1.0133 X 10^5 N/m^2 or Pa.

The rapid growth and apparent decline of high-pressure research since 1950 is graphically represented in Fig. 2.1. This figure shows the number of papers published in the field through 1974. Only paper reporting work above 5000 atm are included in the count.

The United States Bureau of Standards maintains a high-pressure data center at Brigham Young University. This center has the function of evaluating certain aspects of data found in the high-pressure literature. It compiles a "Bibliography on High Pressure Research," a curre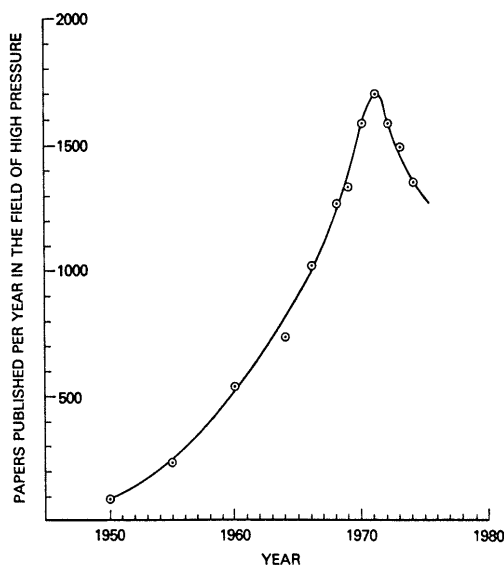nt-awareness bulletin, published in six issues annually, on a subscription basis. The center cooperates with foreign countries, notably Japan and Russia, which compile like information for their countries. The center attempts to obtain and file one copy of every article on high pressure published anywhere in the world. Another publication of the center is "The International Directory of workers in the Field of High Pressure Research," compiled by John F. Cannon and Leo Merrill, April 1971 (a directory was also issued in April 1968). There is also a high-pressure bibliography covering the period from 1900 to 1968. Volume I includes a bibliography and author index and Volume II, a subject index, published in April 1970 under the direction of Leo Merrill, Associate Director of the center. Another publication of note from the center is "Behavior of the Elements at High Pressures," by John Francis Cannon, which is reprint number 55 from *J. Phys. Chem. Ref. Data*, 1974. Reprint number 12, from *J. Phys. Chem. Ref. Data*, by D. L. Decker, W. A. Bassett, L. Merrill, H. T. Hall, and J. D. Barnett, is entitled "High Pressure Calibration, a Critical Review." This is a good source of information concerning the calibration of high-pressure equipment. *The International Directory of Workers in the Field of High Pressure* includes the names of researchers, their affiliation, and the pressure range covered by their research. It also indicates the temperature range and the type of apparatus used, such as the belt, Bridgman Anvils, cubic press, diamond anvils, gas apparatus, liquid systems, shock techniques, piston-cylinder devices, and so on. Also , if the workers have interests in calibration and equipment design, this is indicated. There is also a key to the type of interest that the particular laboratory or investigator has. For example, if the person is interested in crystal chemistry, that is so indicated. Other subject headings are crystal structure, equilibrium studies, inorganic synthesis, lattice defects, organic chemistry, polymorphism, electronic and quantum properties, geological and geophysical properties, magnetic properties, amorphous solids, diamond research, mechanical properties, metallography and metallurgy, method of analysis, infrared, Mossbauer, neutron diffraction, optical properties, thermodynamics, and so on. This publication, then, can be the new interested researcher's entrée into the field of high pressure.

Most high-pressure apparatus used for research is constructed in university shops and laboratories to suit some particular interest of the

Fig. 2.1. Number of papers in the field of high pressure, 1950–1974.

investigator. Consequently, when considered in specific detail, there are nearly as many high-pressure devices as there are high-pressure researchers. However, when considered in broad perspective, there are a limited number of basic devices. In order of their development, they are (1) piston-cylinder, (2) Bridgman anvil, (3) the belt, and (4) multiple anvils, the principal multianvil types being the tetrahedral press and the cubic press. These are landmark devices, and all other devices, by whatever name they may be called, are derivatives of these. The origins of the piston-cylinder apparatus are lost in antiquity, but some important adaptations of it for high-pressure, high-temperature use are due to Parsons and Coes, whose work will soon be discussed. Bridgman anvil devices are the invention of Percy W. Bridgman; the belt and multiple-anvil types are the inventions of this author.

The chemical changes that can be induced in a system by perfusing a substance with energy are qualitatively related to the intensity factor (pressure, temperature, volts, etc.) of the energy. As far as chemistry is concerned, the most important energy introduced into the chemical substances of concern is heat. Heat of sufficient potency to bring about changes in chemical bonding has been available for a long time, from fires, flames, torches, and Bunsen burners. Readily obtainable temperatures of a few hundred degrees Celsius cause many chemical changes to occur. In terms of "ideal" energy equivalence, one cubic centimeter kiloatmosphere is equivalent to a $12.19°K$ change in temperature.

Of course the atomic and molecular effects of temperature and pressure on substances are not the same. However, pressure and temperature diametric opposites in some ways. For example, as temperature is increased, solids transform to liquids, which in turn become gases. Systems then proceed to products of molecular dissociation, and at sufficiently high temperature the atomic nuclei will be separated from the electrons, and so on. With increased pressure, on the other hand, substances originally gaseous become liquids, which in turn transform to solids; and with ever increasing pressure, the collapse of electronic shells will occur. At pressures of billions of atmospheres nuclear fusion occurs. Simultaneous high temperature with pressure is important in the field of chemistry because of the general effect of high pressure on reaction rates. High pressure tends to reduce the rate of a chemical reaction.

Therefore, in order to have a chemical reaction take place under high-pressure conditions in a reasonable length of time, it is almost always desirable to use elevated temperature. Some of the thermodynamic and kinetic problems have been considered elsewhere[2].

Tens of thousands of atmospheres are required to produce changes in solids and liquid substances qualitatively equivalent to the changes that can be produced in these same substances by means of heat energy. Temperature can be controlled easily and cheaply. Pressure has been controlled only with recent technology and at great cost. Also, not until recent years has high-pressure equipment been available for purchase. Researchers have has to devise their own. Consequently heat has been much more universally applied to studying chemical change than has pressure.

Pressure is ordinarily defined as a force being exerted upon a unit of area. Within the universe, the range of natural pressures that exists is enormous. The vast reaches of space between the galaxies contain such as small amount of matter that the vacuum existing there is more nearly perfect than any that can be obtained in the laboratory. The distance between atoms in this space is so great that it does not make sense to talk of gaseous pressures as existing at all.

All pressures of any magnitude occurring in nature on a macroscopic scale are due to gravitational forces. The earth's gravitational field attracts the air molecules that form our atmosphere. The average pressure of this blanket of air at sea level is 14.70 lb/in.^{2} (the normal atmosphere). The pressure existing at the greatest ocean depth is ~1000 atm. Interestingly some of the early pressure experiments were performed by lowering liquid-filled, corked bottles into the sea. Halfway between the earth's surface and its center, at the core boundary, the pressure is about 1.4×10^6 atm, and at the earth's center the pressure is estimated to be 3×10^6 atm. The pressure at the center of the sun is estimated at about 10^{11} atm, and the pressures found at the center of white dwarf stars may be 10^{16} atm. Matter at 10^{16} atm will completely degenerate. It will have an effective temperature of absolute zero and a density of one million grams per cubic centimeter.

Man and his machines are indeed puny with regard to any discussion in galactic dimensions. Other comparisons, however, can place man's accomplishments in flattering light. For example, the laboratory-attained pressure of

200,000 atm is equivalent to that present at the base of a column of granite 400 miles high—4000 Washington Monuments stacked on top of each other.

A point has been reached in the field of scientific endeavor where results can often be achieved if vast sums of money can be spent. There are two aspects to this development. The first aspect concerns the increasing complexity of science. At the turn of the century a particle accelerator in the form of a glow-discharge tube might have cost $100. In 1934 the first cyclotron cost approximately $50,000. Today, a multibillion-volt particle accelerator may cost hundreds of millions of dollars. The second aspect involves expendability. Institutional accounting procedures have for years categorized expenditures into areas of supplies, equipment, travel, and so on, and the category of equipment has usually been defined in terms of cost. That is, anything valued at $100 to $500 or more has arbitrarily been defined as a major item of equipment. Such property must be given an inventory number and thereafter be properly accounted for, and there have been some difficulties between the scientists and the accountants over this matter. Before the accountants have placed an inventory tag on a certain "equipment item," set up as maintenance procedure, and so on, the scientist may have already destroyed the item in his experiments. The ultimate example of today's willingness to expend is exemplified by the billion-dollar rockets being shot into space. High-pressure research, when probing at the highest pressures, requires a modest willingness to spend and expend. The expendable equipment lost to an active investigator working in the field of high pressure is of the order of $2000 to $20,000 per year. Most of this loss occurs from the breakage of cemented tungsten carbide pistons, anvils, and so on.

The highest pressures attainable by man are attained by explosive means. Pressure and temperature are simultaneously generated by explosions, but the period for which the pressure and temperature exist is of the order of micro- or at the most milliseconds. Much of the apparatus used in these experiments is literally "blown up," and the cost of the expendable materials can be much greater than the tungsten carbide broken in static-pressure apparatus (apparatus that can hold pressure for at least several minutes, but more usually for hours or days). While the generation of pressure by explosive means is not discussed in detail in this treatise, there are some interesting aspects of it that will be mentioned. Pressure as high as 10 million atmospheres have been claimed by some investigators. However most of the literature deals with pressure of the order of a few hundred thousand atmospheres or even less. In most chemical (synthesis) experiments, the sequence of events is as follows. Pressure is applied at room temperature to the substance in which chemical change is wanted. This is followed by increasing the temperature to the point where reaction will occur. Next, the temperature is reduced to room temperature to prevent reversion, and this is turn is followed by reducing the pressure to atmospheric. These events are easily controlled in static-pressure apparatus but are not so readily controlled in an explosion.

The use of explosions to generate pressure was considered at the General Electric Company during the same time that static high-pressure apparatus was being used in attempts to synthesize diamond. It was concluded, however, that the pressure and temperature sequence could not be properly controlled to convert graphite to diamond. In 1961, approximately six years after I had synthesized diamond in static-pressure apparatus, John C. Jamieson, Professor at the University of Chicago, and P. S. DeCarli of the Stanford Research Institute collaborated in an attempt to make diamond by explosive means and succeeded[3]. Their experiment was eminently elegant. They used a 55-gallon drum half-filled with water, open at the top, with a board across it on which was placed a block of graphite. This in turn had on top of it an explosive device. The explosive was fired from a safe distance, and after a settling time, the powder in the bottom of the drum was recovered, dried, and enriched by density separation. They obtained a definite X-ray diffraction pattern, although the lines were very broad, for diamond. The diamond was up to 10μm is size, and the yield in the process was something of the order of 2%. This work was financed by Allied Chemical Corporation. Improvements were made in the process, and for a time it was possible to purchase a dark-gray diamond powder from that company. This diamond was not pure and apparently contained around 12% oxygen, which may be the reason that the material is no longer available. The function of the water in Jamieson and DeCarli's experiment was to cool the newly formed diamond so fast that is did not convert back to graphite.

Subsequent to DeCarli and Jamieson's development, personnel at the du Pont Company

developed a process in which iron was the coolant[4]. They compressed, by explosive means, a material known as ductile or malleable iron. This iron contains a high proportion of carbon dispersed as graphitic spheroids. If a shaped charge of explosive is applied to ductile iron, a shock wave passes through it (explosive techniques are also called shock wave techniques). A shock wave passing through a solid is like a sound wave. There is a pressure front, followed by a trough in which the pressure falls. The rate at which the pressure front travels through a solid depends on the nature of the material, and there are other things that occur, such as reflections and absorptions, which complicate matters. Temperature also rises and falls in a pattern that depends on several variables. The advance of a front through nonhomogeneous material, such as ductile iron, will be complicated, but the net result of a proper experiment is that part of the graphite in the spheroids is transformed to diamond. The iron, which immediately surrounds the spheroids, serves to take away the heat and quench the diamond rapidly enough that it does not all revert to graphite.

There is a wonderful story, perhaps apocryphal, concerning the du Pont development. There was an abandoned mine tunnel somewhere in one of the north central states, I think Minnesota, in which a large quantity of ductile iron was placed. This was surrounded with appropriate charges of dynamite that were later detonated, resulting in the formation of several tons of impure diamond powder. After the explosion subsided, a front-end loader removed some material and deposited it in a digester where dilute sulfuric acid dissolved the iron, leaving a pasty residue. This residue was dried and subsequently dissolved in one or more oxides of lead, which selectively oxidized the graphite, leaving most of the diamond untouched. Further minor cleaning operations yielded a pure diamond powder of submicron size that under the microscope had a spongy appearance. When most of this batch had been sold, the front-end loader again went into the man-made diamond mine, retrieved more material, and so on. Supposedly there is enough diamond in this mine to last the world for many years!

But there are now improvements in the process, and the mine has been abandoned. A rather complicated device is now used onto which appropriately shaped charges are fastened. Rather than ductile iron being used as a charge,

graphite containing copper particles is used. The purpose of the copper is to appropriately absorb the heat to prevent reversion of the newly formed diamond. Recovery of the diamond in an explosion could of course be a problem, but there is a momentum-absorbing plug at the end of the cylindrical device which gives away at the appropriate time, allowing the charge to be less violently blown into a retrieval container. Apparently the submicron diamond powder after retrieval and purification is again placed into an explosive device and reshocked, whereupon an agglomerization of the diamond takes place, producing particles of up to 40 or 50μm. These larger are more in demand than the original submicron sizes.

2 METHOD FOR GENERATING STATIC PRESSURES

In the introduction to this volume, I gave three general methods for obtaining high values of intensive properties such as pressure, temperature, voltage, and the like. They were disproportionation, gathering or focusing, and in situ energy transformation. At the present time the use of disproportionation to obtain high pressure has given the most satisfactory result. However there are energy-transformation processes that have also been used, some of which are attractive for further development. It is possible to generate pressure by increasing the temperature of a material which fills a confined space, for example, the heating of a liquid in a metal tube. Chemical energy may also be utilized to generate pressure by employing a chemical reaction or a phase change in which the products of the reaction or the new phases formed will tend to occupy a larger volume than that to which they are confined. The freezing of water in a confined space is a common example of this principle, as many know who have frozen radiators or pipes in the wintertime. The freezing of water in a confined space can generate a theoretical maximum pressure of about 2000 atm. The solidification of liquid bismuth in a confined volume can generate a theoretical maximum pressure of about 17,000 atm. Likewise, the freezing of molten germanium can generate a theoretical pressure of the order of 100,000 atm. These theoretical pressures can be approached providing the container volume increases only slightly as the freezing liquid presses against it. It is also necessary that the volume of the germanium, bismuth, or water is large compared to the

volume of the material being subjected to compression by the expansion process. At the present time, germanium has been demonstrated to be capable of generating higher pressures by a freezing process than any other known substance. However, its use in a pressure-generating device has not yet been fully exploited.

As mentioned, disproportionation provides the most satisfactory means of obtaining high pressures at the present time. The most obvious form taken by a high-pressure device is that of a piston and cylinder. In such a device, a sample confined by the cylinder drives the smaller piston into its cylinder, this being the disproportionation principle (see Fig. 2.2). In the field of hydraulics this type of device is called an intensifier.

3   PISTON-CYLINDER DEVICES

Today's piston-cylinder devices are operable to pressures around 50,000 atm with solid media[5]. In these devices both the piston and the cylinder are constructed of cemented tungsten carbide. The cemented tungsten carbide used is made of pure, virgin, material, formula WC, cemented together with approximately 3 to 12% cobalt. For general-purpose use, a tungsten carbide containing 6 to 8% cobalt is the most

desirable. Tungsten carbides have the highest compressive strength of any engineering material readily available at this present time. Although cemented carbides possess tremendous compressive strengths, they have rather low tensile strengths and are brittle. Their tensile strength increases with increasing cobalt content. However, the compressive strength decreases with increasing cobalt content. Compressive strengths for 3 weight-percent cement tungsten carbide cylinders of 60,000 atm have been reported by some manufacturers. However, the usual commercial product has a compressive strength of only 35,000 atm. These figures are for solid "rounds" in which the length equals the diameter, the round being compressed between carbide blocks. Longer rounds will have lower compressive strengths (the so-called column effect). Because of the low tensile strength, cylinders constructed of this material must be supported in such a manner that the carbide is not subjected to a damaging tensile load. This can be accomplished by surrounding the carbide cylinder with massive alloy-steel binding rings.

The upper pressure limit of a piston-cylinder device so constructed is set by failure of the pistons. When materials with compressive strengths greater than those of the cemented carbides become available, the upper pressure limits obtainable in a piston and cylinder device, as well as in other types of devices, will be increased. Sintered diamond, a newly available material, will eventually make it possible to obtain higher pressures[6].

Tremendous pressure could be theoretically obtained by a cascade process wherein one piston-and-cylinder device would be placed inside another, and so on. The failure of high-pressure components is not caused by the absolute pressure to which they are subjected, but rather the differential pressure. Thus a cylinder in which the internal pressure is 100,000 atm and the surrounding external pressure is 50,000 atm is in no more danger of failure than a cylinder wherein the internal pressure is 50,000 atm and the external pressure is zero. There is some indication that tungsten carbide increases in strength under high pressure and can therefore under these conditions withstand a greater differential pressure. At the present time, the experimental problems connected with cascading have made it impossible to utilize this principle beyond two stages. As a matter of fact, the only use of a two-stage device that has been reported in the literature is due to Bridgman[7]. The working volume of Bridgman's apparatus was
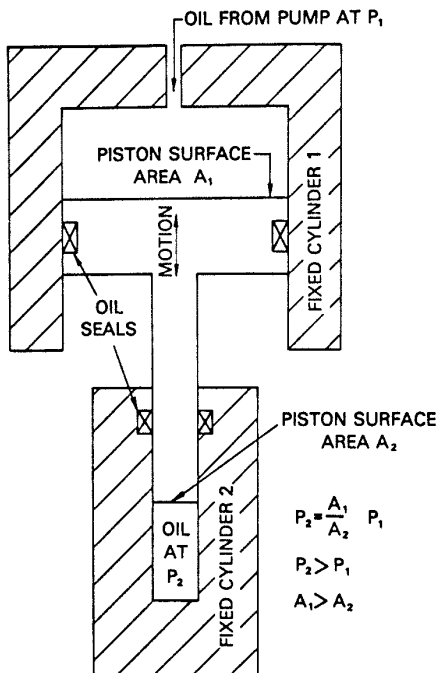

Fig. 2.2. Generation of pressure by disproportionation.

$$P_2 = \frac{A_1}{A_2} \, P_1$$

$$P_2 > P_1$$

$$A_1 > A_2$$

very small. The final piston had a diameter of approximately 1.5 mm, and the sample length was also about 1.5 mm. This device is complicated and difficult to use. Electrical leads could not be taken into the sample area. A double-ram hydraulic press was required for its operation. The double-ram press has two coaxial thrust generators. The initial program at the General Electric Company for equipment to synthesize diamonds called for the construction of a Bridgman two-stage piston cylinder device of greatly enlarge size. It was hoped that the larger size would make it possible to introduce electrical leads into the inner chamber to provide current for electrical resistance heating of the sample and also to make temperature and other kinds of measurements. However the invention of the belt apparatus, which is infinitely simpler and easier to use, resulted in abandonment of this approach.

The High Pressure Institute in Moscow, Russia, has been constructing a monumental high-pressure apparatus for a number of years. It has been reported that the total investment in this unfinished device is around $20 million. It is expected to be a piston-and-cylinder apparatus of five stages. Drawings of the contemplated apparatus are not available, but the problems of providing thrust from the outside through all five stages and of providing electrical communication to the innermost stage for measurement and to supply heating current are formidable, if not impossible.

Let us now return to providing further details of single-stage piston-cylinder apparatus. Emphasis will be on modern devices that use solids or a combination of solid plus liquid to transmit pressure, since there is a plethora of literature available on fluid pressure apparatus. Pressure transmission by solids allows much higher pressures to be achieved and also allows high temperature simultaneously with high pressure. This is important in chemistry.

Sir Charles Parsons was the first to attack the problem of generating high pressure simultaneously with high temperature[8]. He began a diamond synthesis program about 1880 and ended it about 1928. From his studies he concluded that neither he nor anyone else had, up to that point, succeeded in making diamond. Parsons had excellent laboratory and machine shop facilities and conducted experiments on a grand scale for that period. His pressure apparatus consisted of piston-cylinder devices that used internal electrical resistance heating (see Fig. 2.3). He used a solid pressure-
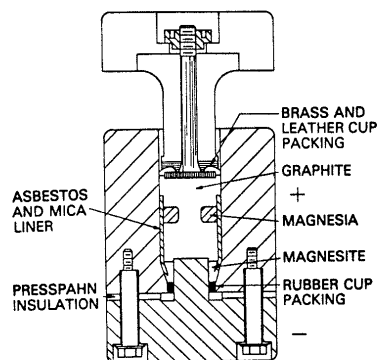

Fig. 2.3. One of Parson's high-pressure, high-temperature devices.

transmitting material which also served as thermal and electrical insulation. He seems to have been the first person to utilize such a combination in a high-pressure, high-temperature device. His cylindrical chambers ranged in diameter from 1 to 15 cm. The maximum pressure at the temperature he reported was of the order of 15,000 atm at 3000°C.

Loring L. Coes, Jr., of the Norton Co., was the first person to develop a piston-cylinder device with capabilities substantially beyond those of the Parsons device. In July 1953, Coes reported the synthesis of a new dense silica which has since been called coesite[9]. Coesite has a density of 3.01, whereas the density of quartz is only 2.65. The refractive index of quartz in 1.50; the refractive index of coesite is 1.60. This material was discovered during a synthesis study of the minerals with which diamonds are associated in the diamond-bearing pipes of South Africa. Although man-made "minerals" are not usually named in honor of their discoverer, this new SiO_2 substance was unique and so interesting that researchers immediately began to call it coesite. Coesite was later found to be present in some meteorite craters and constitutes the first instance in which a mineral was produced in the laboratory before it was discovered in nature. Coes reported that the material was made at a pressure near 35,000 atm at a temperature between 500° and 800°C. Incidentally, another SiO_2 material, called stishovite, more dense than coesite, was synthesized by S. M. Stishov and S. V. Popova in 1961 at a reported pressure of about 115 kilobars and a temperature of about 1300°C. This material has the remarkable density of 4.35 and a refractive index of 1.81[10]. Stishovite has also been found in meteorite craters.

Coes' first apparatus was not described in the 1953 *Science* article. On April 21, 1954, at the American Ceramic Society Meeting in Chicago, Coes presented a paper entitled "High Pressure Minerals." This paper described a number of garnets and other materials that he had synthesized during the course of his research on the synthesis of diamond. Again, he did not discuss the nature of the equipment used. However at the 7th Symposium on Crystal Chemistry as applied to ceramics at Rutgers university, New Brunswick, New Jersey, on June 4, 1954, Coes described his apparatus. He did not personally publish a description of this equipment, however, until 1962[11]. A diagram of the apparatus and of the sample chamber is given in Fig. 2.4. The key feature of the device is the use of a hot, molded alumina liner or cylinder. The apparatus is double ended, pressure being generated by pushing a tungsten carbide piston into each end of the alumina cylinder. Because the alumina cylinder is electrically insulating, heating is accomplished, very simply, by passing an electric current from one piston through a sample heating tube and out through the opposite piston. The apparatus was used at pressures as high as 45,000 atm simultaneously with a temperature of 800°C. A temperature of 1000°C could be obtained at a lower pressure of 30,000 atm. Temperature was measured by means of a thermocouple located in a well, as shown in the figure. Although the temperature at this point is lower than the temperature in the sample, comparisons of temperatures measured here were made with a thermocouple inserted in the sample at 1000 atm. From these measurements it was possible to correct the temperature reading of the thermocouple in the well to the approximate temperature of the sample in the chamber.

At 45,000 atm and 800°C, only one run is obtained in this device, the pistons and the alumina cylinder both being expendable. Even at 30,000 atm the alumina cylinder is only useful for a few runs, as is also the case for the tungsten carbide pistons. The expense of using such a device is great, and while it was used extensively at the Norton Co., I am unaware of any use of the device elsewhere except for some limited use of the equipment at Brigham Young University. Coes was kind enough to give a number of alumina cylinders to me sometime around 1957, at which time I experimented briefly with their use. Coes once related to me that they had barrels of broken alumina cylinders around the lab. In fact, they had so many they wondered if a use could be found for them. Consequently, the
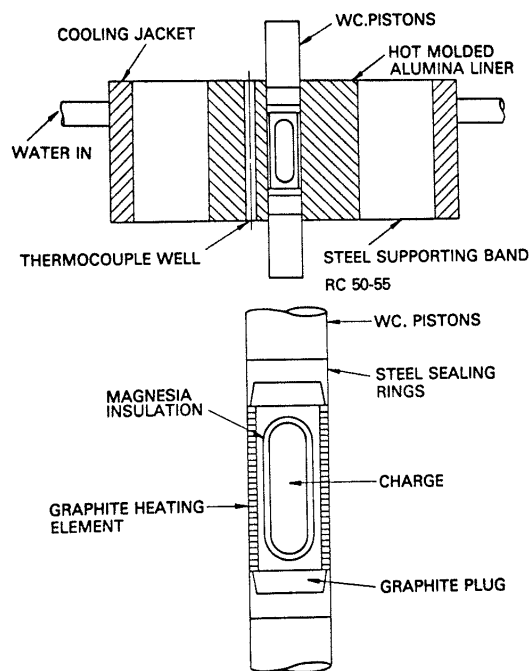

Fig. 2.4. Coes apparatus.

broken cylinders were crushed to provide mesh-size abrasive particles which were subsequently made into grinding wheels. These wheels performed better than the wheels they were then manufacturing. Consequently, this serendipitous discovery led to an important change in the method of manufacture of aluminum oxide grain for use in grinding wheels.

Nowadays both the piston and the cylinder are constructed of cemented tungsten carbide, and electrical insulation is provided in a different manner than in the device of Coes. For the highest pressure the cobalt content should be only 3%. Such a tungsten carbide is very brittle. Therefore the alignment of the piston and the cylinder and the hydraulic ram providing the thrust must be nearly perfect to prevent off-axis loading. The tungsten carbide should be fine grained. The industry code number in the United States for this carbide is C-4.

The outside diameter of the cylinder should be about six times its inside diameter. When solid materials are used for transmitting the pressure, the sample cell length should be less than twice the piston diameter. With the cylinder in place in its binding rings, the fit between the piston and the cylinder should be as close as possible. A clearance of 0.0025 mm is appropriate. The surface of the cylinder hole should be highly polished, as should also the
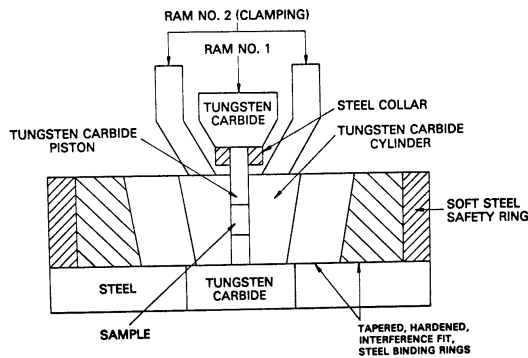
Fig. 2.5. Piston–cylinder device of tungsten carbide using two rams.

outside diameter of the piston; the ends of the piston must be ground absolutely square with the cylindrical axis. A coaxial ram press is used to operate the piston and cylinder device. The inner ram provides thrust to the piston, and the outer ram provides clamping force to the cylinder (Fig. 2.5). The clamping force is necessary to prevent the tungsten carbide cylinder from splitting in two in a plane perpendicular to the cylindrical axis. Such splitting will usually occur in a plane that coincides with the surface of the tip of the piston. The surface roughness values (standard machining practice) of the inside diameter of the cylinder and the outside diameter of the piston should be about 1 μm. The remaining surfaces of the piston and the cylinder may have a higher roughness value of about 4μm. The smooth surfaces of these components reduce breakage. Fracture under high stress begins on irregularities in the materials, often at surface scratches. In addition, the friction between the piston and the bore of the cylinder as the piston moves within the bore is reduced when the surfaces are smooth. In experiments where it is not necessary to have electrical leads into the sample region, it is best to make the piston-and-cylinder device double-ended, as Coes did. A double-ended piston-and-cylinder device requires extraspecial care in the alignment and in the parallelism of the various components with the moving elements of the hydraulic press.

The piston should be as short as possible and should protrude as little as possible from the bore of the cylinder. The protruding part of the piston is the weak part, and fracture will usually occur there. A tight-fitting collar, as shown in Fig. 2.5, around a portion of the protruding part of the piston is very helpful in preventing breakage on the exposed piston ends. This collar is of low alloy steel such as SAE Number 4340 hardened to Rockwell C55. The interference fit between the collar and the piston should be about 0.003 cm/cm of piston diameter. That is, the inside diameter (I.D.) of the collar is smaller than the outside diameter (O.D.) of the piston by 0.003 cm for each cm of piston diameter. In addition, the I. D. of the collar should be tapered about 0.050 cm/cm length. A matching taper is placed at one end of the piston so that when the collar is pushed over the piston with a forcing press, the interference of about 0.003 cm/cm is developed when the small end of the collar is flush with the small end of the tapered portion of the piston. Molybdenum disulfide paste (such as Molykote G) is used as a lubricant between the mating surfaces as they are forced together.

A fully annealed (dead soft) steel safety ring surrounds the hardened steel collar. This must be in place at all times during and after the forcing operation. Highly hardened steels can break capriciously when under heavy tension, and precautions must be taken. The O.D. of the collar should be about three times the piston diameter and its thickness should about equal the piston diameter. The safety ring I.D. should be the same as the O.D. of the collar. There is no taper here. The O.D. of the safety ring should be about five times the piston diameter. All these parts are built to precision tolerances, the hardened steels and carbides being ground to final dimensions.

At maximum compression of the sample the portion of the piston "exposed to air" should be as small as possible so that all portions of the piston are receiving some kind of "support"; that is, the cylinder supports that portion of the piston within the bore (in compression the piston expands), the reaction of the sample against the tip of the piston within the bore supports the tip, the driving force of the press on the top side of the piston supports the top, and the tight-fitting collar around the piston supports the portion it surrounds. Thus, the only part of the piston unsupported is the small exposed portion that has not entered the cylinder bore.

When operating at the highest pressures, even with the aforementioned support precautions, the piston's lifetime is usually only one or two runs, and those using simple-piston and cylinder devices at the highest pressures must have a large supply of pistons.

After each run the cylinder bore and the outside diameter of the piston are carefully cleaned and coated lightly with molybdenum disulfide powder, a very good dry lubricant. This powder is best applied by dipping the finger into it and then rubbing the coated finger onto the parts.

The steel platens of a commercial press will usually be a rather soft steel with Rockwell C hardness around 20. Consequently the tungsten carbide piston cannot push directly against these platens. Hardened steel, preferably of Rockwell C55, must be placed on top of the platens, and then tungsten carbide must be placed on top of the hardened steel. This tungsten carbide in turn bears on the end of the piston. All of these components must be square and parallel, including the platens of the press, for the slightest cocking of the brittle pistons will cause them to break. The tungsten carbide backing block, which bears on the end of the piston, should also be of grade C4. Its area should be about three to five times that of the area of the end of the piston, and this backing block must be supported by a steel binding ring to keep it under radial compression. In this application, a single binding ring is usually satisfactory. A low-alloy steel forging, such as SAE Number 4340 heat treated to Rc40-43 with a 0.0015 cm/cm diameter interference fit is commonly used. The sides need not be tapered but may be straight at this relatively low interference. The edges of the carbide backing block are rounded and polished, and the steel ring is pushed over the carbide with a forcing press. Molybdenum disulfide paste is again used as a lubricant between the mating parts. The outside diameter of the binding ring is usually about twice the diameter of the carbide backing block. The thickness of the backing block should be about two thirds of its diameter.

In electrical resistance heating of samples under high pressure, the resistance heater is usually of very low electrical resistance. Consequently a high current at low voltage is required. High currents require large electrical conductors. It is difficult to use a double-ended piston cylinder device, where pistons and cylinders are electrical conductors, if electrical resistance heating is required. In this instance it is best to have a closure on one end of the cylinder bore to serve as one electrical contact and the moving piston at the other end of the cylinder serving as the second electrical contact. The closure must be insulated from the cylinder bore, or there will be a short circuit. It is also desirable to place thermocouples and other electrical leads inside the higher-pressure chamber. The closure can also serve this purpose. A suitable closure is shown in Fig. 2.6. This closure is made about 0.13 mm smaller in diameter than the bore and is wrapped with a strip of electrically insulating paper about 0.05 mm thick. Thermocouple or other electrical leads

S=CLOSURE
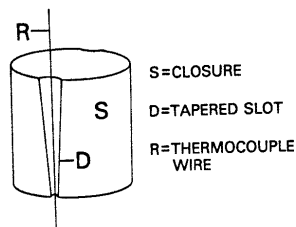D=TAPERED SLOT
R=THERMOCOUPLE WIRE

Fig. 2.6. Cylinder closure.

can gain entrance to the interior of the cylinder, as is shown in Fig. 2.6, where there are two tapered slots (more could be used). The taper is not critical. A taper of about 0.1 cm/cm on a diameter is satisfactory. Electrical leads of about 0.1 to 0.2 mm in diameter are satisfactory for most purposes. The narrow part of the tapered slot should be about 1 mm in diameter. A piece of pyrophyllite is machined to fit the slot, and a tiny hole is drilled along its length to accommodate a wire. This hole can be considerably larger than the wire without causing problems. For example, if a 0.2-mm wire is used, a 0.4-mm hole is satisfactory.

Under high-pressure operation the pyrophyllite is compressed and driven into the taper, and forms a strong frictional grip around the wire. The frictional properties of the pyrophyllite can be increased by painting the surface with a water suspension of red iron oxide and allowing this to dry. Instead of using slots on the exterior surface of the closure, it is possible to put tapered holes within the closure. For example, a tapered axial hole along the center line of the closure would appropriately do the same job. However, such a tapered hole is usually more expensive to make than the ground tapered slots on the surface. The thermocouple wires or electrical leads so introduced into the sample should be covered with an electrical insulating enamel. Provision should be made to prevent these electrical leads from being pinched or cut at places where they emerge from the closure. This requires holes or slots to be formed or ground in the carbide backing block to accommodate their passage. The bottom side of the cylinder and binding ring must be insulated with a sheet of electrical insulation (usually fiber glass epoxy) to prevent contact with the backing block. However the closure must make electrical contact with the backing block. The backing block and steel assemblies must be electrically insulated from the platens of the press in order to prevent short circuiting through the hydraulic press.
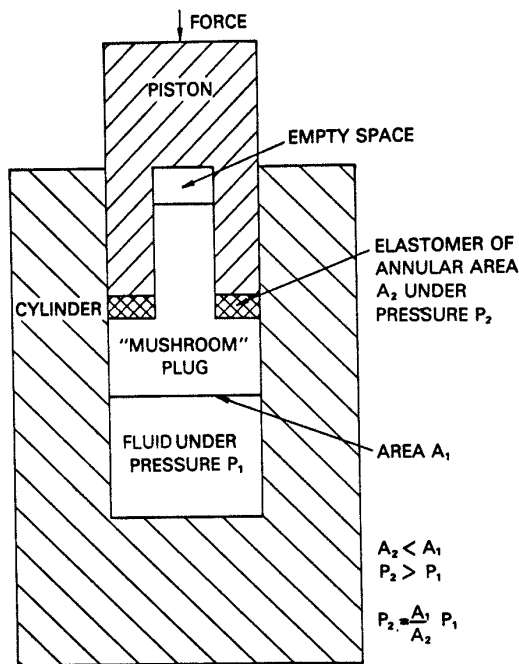
Fig. 2.7. Bridgman seal.

A = METAL WASHER (TOP)

B = PLUG OF THERMAL INSULATION

C = CYLINDER OF THERMAL INSULATION

D = SAMPLE END CLOSURE DISK

E = ELECTRICALLY CONDUCTING TUBE

F = SAMPLE SPACE

G = METAL WASHER (BOTTOM)

Fig. 2.8. Cell assembly for internal resistance heating.

An assembly for internal resistance heating of the sample to high temperatures is shown in Fig. 2.8. The entire assembly of Fig. 2.8 is compressed by the piston. Heating current passes from the piston through the metal washer A which it contacts to the electrically conducting heater sample tube E, then out through the metal washer G, the contacting cylinder closure, and the carbide backing block. The electrically conducting tube may be a high-temperature metal such as tantalum or molybdenum or it may be made of graphite. The metal washers should be made of a refractory metal. The solid cylinder C surrounding the heater sample tube must transmit pressure quasi-hydrostatically to the tube and must be electrically and thermally insulating. It must also withstand high temperature. A common material used for this purpose is the naturally occurring mineral pyrophyllite, sometimes called Grade A Lava, or Wonderstone. This material is a hydrous aluminum silicate which will lose water at high temperature and which under high-temperature, high-pressure conditions will transform into other materials of higher density. Pyrophyllite is related to talc. Talc is a hydrous magnesium silicate and is softer than pyrophyllite. Often a liner made of hexagonal boron nitride is used to surround the heater sample tube. This material will of course not give off water. Water from pyrophyllite sometimes penetrates through the
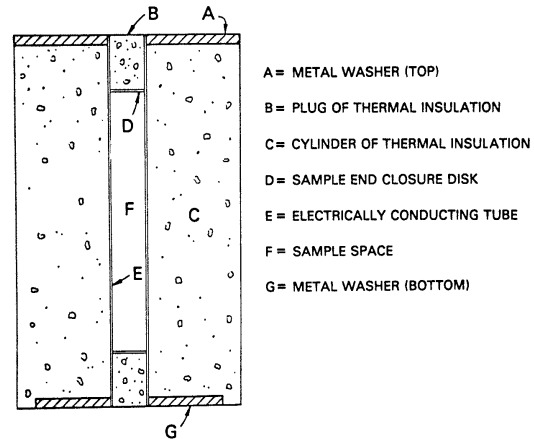
heating tube into the sample, or else hydrogen and oxygen will be given off at the high-temperature, high-pressure conditions. As a result, undesired reactions may occur. The BN, at sufficiently high pressures and temperatures, will convert to cubic boron nitride, a high-density polymorph analogous to diamond, and may not transmit the pressure as desired.

There is considerable leeway in the design parameters for the insertion of electrical leads into high-pressure apparatus, and workers in the field tend to develop their own particular preferences. In general, an electrical lead can be inserted by having the wire pass through an unfired ceramic material in a tapered slot or hole and, in some instances, even in a slot or hole with parallel sides. The frictional properties of the ceramic material cause bind-up in the hole or slot and prevent the extrusion of the thermocouple wire. In some instances thermocouple wires are pinched off in passing through the slot if the slot is too short but changing the slope of the taper or the diameter of the hole or the particular frictional material used can, with trial and error, eliminate the difficulty. Pyrophyllite is the most commonly used material. However commercially available unfired or partially sintered alumina, magnesia, and other substances will also serve for this purpose. Also it is possible to merely compact a powder into the hole through which the thermocouple passes. Red iron oxide has higher frictional properties against tungsten carbide surfaces than any material that has been studied and is often used in this application as well as to coat pyrophyllite to increase surface friction where pyrophyllite contacts tungsten carbide. Sheathed pairs of thermocouple wires (or other wires) are readily available today and can be

used advantageously in high-pressure high-temperature research for insertion into the sample cell. The sheath is usually stainless steel but may be made of more refractory metals such as tantalum. The two wires (it is also possible to obtain material with more wires) are imbedded in a ceramic powder, usually MgO or Al_2O_3, within the sheath. The total diameter of the assembly is often only 0.25 mm.

Piston-and-cylinder devices were first used in the compression of gases, and the piston usually had a leather cup packing, exactly like the hand-operated air pump used for inflating a bicycle or automobile tire. Pressures attainable in such devices, of course, are small. More sophisticated seals are needed for higher pressures. O-rings serve admirably in many applications, but if pressures cause extrusion of the O-ring, the "Bridgman seal" can be used[12]. The Bridgman seal is shown in Fig. 2.7. A plastic or elastomeric substance, in the form of a washer, goes between the hardened steel mushroom head and the piston tip which has a central hole to accept the stem of the mushroom plug. Gas or liquid pressure is exerted against the mushroom head of the seal. The area of the mushroom plug head exceeds the area of the flexible washer. Consequently, the pressure against the washer will always exceed the pressure of the fluid under pressure. This being the case, there is no way that this seal can leak. The washer will just push harder and harder against the walls of the cylinder as oil pressure increases. Professor Bridgman has told the amusing story of applying for a patent on this seal. The idea was original and unique to him, but in applying for the patent he found that the same principle had been used in a patented sausage grinder. Consequently he was not able to obtain a patent. Yet workers in the field of high pressure invariably refer to the seal as the Bridgman seal, the sausage grinder inventor having been lost to history.

The direct heating of gases and liquids in apparatus where solid pressure-transmitting media are not employed can only be achieved by external heating of the entire chamber. Temperatures of about 300°C are obtainable in externally heated piston-cylinder devices. Higher temperatures are precluded by loss of strength of steel and tungsten carbide above 300°C.

In any experiment at pressure it would be desirable to have the specimen that is the object of the research subjected to what is termed hydrostatic pressure; that is, pressure impinges on the macroscopic object of study from every direction on a microscopic scale. This occurs when a true fluid surrounds the specimen under test. In the high-pressure devices invented to date, the pressure-transmitting medium must be a solid to obtain the highest static pressure. Thus the pressure on the specimen is not truly hydrostatic, but with proper design the pressures can be reasonably hydrostatic. This is often referred to as a quasi-hydrostatic pressure. The highest hydrostatic pressures are obtained using a solid pressure-transmitting substance that presses on a thin-walled metal tube in which liquid is contained. This liquid, in turn, may be exercising its pressure on a sample contained within itself[13]. There is a problem as to the choice of a suitable liquid because most liquid reagents found on the laboratory shelf become solid (freeze) at room temperature at pressures less than 10,000 atm. Liquids that will remain liquid at high pressure are usually mixtures of molecules that do not fit together well and consequently have difficulty in crystallizing. A mixture of 4:1 by volume methanol/ethanol remains hydrostatic to almost 100,000 atm at room temperature[14] and 1:1 by volume pentane/isopentane to about 70,000 atm. The viscosity of liquids increases with pressure, and no doubt the above mixtures have the consistency of heavy molasses as their hydrostatic limit is approached.

There are some solid substances that transmit pressure rather well. Notable among them is indium metal. Among nonconductors, silver chloride transmits pressure effectively. Whether a substance will be a good pressure-transmitting medium (will approach hydrostaticity) or not can be inferred from shear friction measurements made under pressure in Bridgman anvils[15]. Indium and silver chloride have low shear friction at high pressure.

A little philosophy concerning hydrostaticity might be in order at this point. If the object of study at high pressure is a solid material, one might indeed have a true fluid pressing in on this solid specimen from all directions, and one would be inclined to say that the specimen is being subjected to hydrostatic pressure. Well, of course it is on its exterior surface. However the question could be asked, "What about the pressure at some point deep within this solid substance?" The pressure at this point would have to be transmitted by the solid specimen that surrounds that point, and this in turn would depend on the characteristics of the solid and also on its shape. If the specimen is a metal, it would also depend on the particular physical

treatment or heat treatment the metal might have had. One would expect that the pressure at the center of a sphere of steel would be higher than at the center of a tungsten carbide sphere of the same size (the modulus of elasticity of tungsten carbide is three times that of steel). Geometrical effects have been observed in such materials as bismuth since this material is often used as a fixed point for the calibration of high-pressure apparatus. With a true hydrostatic liquid surrounding bismuth metal, the transition point will be obtained at a different press loading when the bismuth is used in the form of a thin ribbon than when the bismuth is used as a round wire. Can one really perform "hydrostatic" experiments on solid substances?

When the cell assembly (Fig. 2.8) for a piston-cylinder device is compressed, there is a certain amount of "frictional holdup"; that is, a certain percentage of the pressure at the piston tip is not transmitted to the sample. This frictional holdup is due to two things. There is frictional holdup within the pyrophyllite because it is a solid. There is also frictional holdup at the interface between the cylinder of pyrophyllite and the bore of the tungsten carbide cylinder. The friction I at this interface can be reduced by painting the outside of the pyrophyllite with a suspension of molybdenum disulfide or by sheathing the pyrophyllite with In, BN, AgCl, or NaCl. Silver chloride and sodium chloride are corrosive to most metal parts and should not be allowed to remain in contact with them for long periods of time. Substances other than pyrophyllite may be used for the solid portion of the cell in piston-cylinder devices. They have their advantages and disadvantages. For example, boron nitride would have a lower internal friction, but it is much more expensive and has a much higher thermal conductivity, thus requiring higher electrical power to maintain the high temperature inside. Sodium chloride is a rather good substance to use, since its thermal conductivity under pressure seems to be nearly the same as that of pyrophyllite and its pressure-transmitting characteristics are better. However the fabrication of sodium chloride cylinders is difficult.

When polycrystalline refractory, substances are used as pressure-transmitting media, a hysteresis exists in which, with increasing pressure external to the solid, the pressure within the solid is less than that outside. Upon reduction of external pressure, however, the pressure inside is higher than that on the outside. A typical hysteresis loop is shown in Fig. 2.9 for a cell
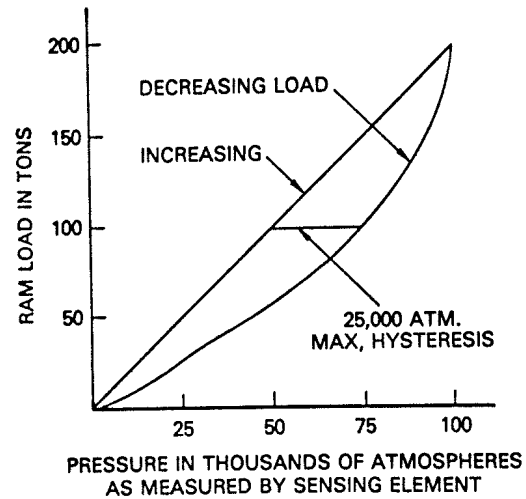

Fig. 2.9. Hysteresis loop for pyrophyllite.

assembly such as that of Fig. 2.8, in which pyrophyllite is the pressure-transmitting medium. It is possible to utilize this phenomenon to reduce the load on the pistons or other elements of a high-pressure device and therefore increase the useful life of expensive carbide components. It works in this manner (refer to Fig. 2.9): The press load, that is, the load on the piston, would be increased to a certain value whereupon there would be a given value of pressure at the surface of the sample and a lesser pressure at the center of the sample. The pressure on the piston tip could then be reduced by reducing the pressure on the hydraulic ram that activates the piston. This would result in a reduction of the pressure on the exterior of the pyrophyllite, while the higher pressure would be maintained at its center. Hysteretic phenomena have been observed in which a differential pressure of 25,000 atm has been maintained; that is, the piston would be retracted to the point where the pressure at its tip was 25,000 atm lower than the pressure being maintained by frictional hysteresis in the center of a pyrophyllite cylinder.

Because of the hysteresis in solid pressure-transmitting substances (apparatus friction also enters in), calibration of pressure apparatus is usually made on a basis of ascending (increasing) pressure only. Calibration is usually made in the following fashion: a cylinder of silver chloride is substituted for components B, D, E, and F of Fig. 2.8 and a wire of fixed point calibration material such as bismuth, thallium, or

barium is placed through an axial hole in the silver chloride. The pressure-sensing wire

Table 2.1 Fixed-Point Transitions

Hg	7470 ± 2 atm at 0°C
Bi I-II	25.16 ± 0.06 katm at 25°C
Tl II-III	36.2 ± 0.3 katm
Cs II-III	41.9 ± 1 katm (up only)
Cs III-IV	42.4 ± 1 katm (up only)
Ba I-II	54.3 ± 2 katm
Bi III-V	76.0 ± 3 katm
Sn 1-11	99 ± 6 atm
Ba	~138 (up only)

makes contact with metal disks (substituted for washers A and G), which in turn make electrical contact with the piston, the closure, the backing blocks, and so on, and thence to an instrument that accurately measures electrical resistance. The accepted fixed-point transition pressures for a number of calibrants, including Bi, Tl, and Ba, are given in Table 2.1[16]. The shapes of some of the electrical resistance curves are shown in Fig. 2.10.
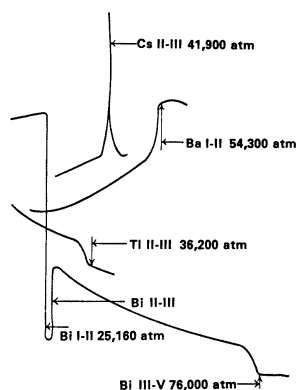

Fig. 2.10. Electrical resistance curves of some fixed-point pressure calibration metals.

The determination of the pressure at which these electrical discontinuities occur is difficult. Briefly, there is a device called the free piston gauge that can be used to determine fixed points up to about 25,000 atm. Beyond this pressure, techniques become more complicated, but in the main the higher pressure fixed-point transitions are determined against in situ X-ray diffraction measurements in which the electrical resistance of a substance, such as barium, is measured simultaneously with the measurement of the change in the crystal lattice spacings of a substance such as sodium chloride. In some experiments, the detailed nature of the phase change of the fixed-point material (Sn, Ba, etc.) has been determined at the identical place where

the corresponding electrical discontinuity occurs and simultaneously with a determination of the lattice spacing in NaCl which surrounds the fixed-point material[17]. The continuous change in lattice parameter of sodium chloride as a function of pressure (semiempirically determined by D. L. Decker) is the currently accepted standard used to determine the value of the fixed points[18].

There is some hysteresis in the metal wire itself as it undergoes transformation on increasing pressure, as compared to undergoing the reverse transformation on decreasing pressure. These hysteretic effects, however, are much smaller than is observed in such substances as pyrophyllite. The silver chloride cylinder in which the fixed-point wire is enclosed is made by compressing powdered silver chloride in a hardened steel die to the required shape. The central hole is made by a tiny spade drill. Care must be exercised to avoid breaking the drill, inasmuch as the silver chloride has a gummy, tough consistency. The bismuth, barium, and tin wires are usually prepared by extrusion through a die. The best die has a conical entrance angle, the exact dimensions of this cone not being too important, and an abrupt 90° exit angle. The usual diameter of the wire is around 0.1 to 0.4 mm. A slug of the metal to be extruded is placed in the die, and a piston pushes on it to cause extrusion. Bismuth and tin are readily extruded into the air. Since heat is generated in extrusion through the die, care must be used in the case of barium. Barium wire is difficult to make because it tends to hold up in the die and then, at a certain pressure, extrudes violently emitting fire and poisonous smoke. It should be extruded with care into paraffin oil. Thallium can be extruded well but, like barium, is poisonous! Barium and thallium oxidize in air and need to be kept under oil.

Another way of obtaining a "wire" of these substances is to simply place a slug of the material between two tungsten carbide blocks and press the material into a flat sheet. A flat wire can then be obtained by cutting it from the sheet with a razor blade. Connecting fixed-point calibrant wires to metal components of the cell can be a problem. Thallium and barium wires must be scraped free of oxide just before use. Barium is quite brittle. Bismuth is very stable in air, but is also brittle. Soldered connections have been used, and it is possible to use bismuth itself as a solder to bismuth wire, but I prefer to make mechanical connections to all calibrant wires. They are made along the lines indicated in Fig.
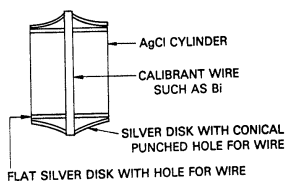
AgCl CYLINDER

CALIBRANT WIRE
SUCH AS Bi

SILVER DISK WITH CONICAL
PUNCHED HOLE FOR WIRE

FLAT SILVER DISK WITH HOLE FOR WIRE

Fig. 2.11. Method for obtaining electrical contact with calibrant metals.

2.11. A cleanly drilled hole is made in one disk of metal, and a hole is punched with a sharp awl in another disk. The disk is usually made of copper or silver sheet; then a piece of bismuth wire or other wire is placed in this assembly as shown in the figure. When the assembly comes under pressure, the conical hole punched in the copper sheet with the awl is forced to collapse on the wire and make a good connection. A great deal of art is involved in this procedure, and each researcher tends to develop his own methods to overcome the problems. Cesium is a very reactive liquid metal at room temperature, but a "wire" of it can be made by filling a small polyethylene tube with it from a hypodermic needle under paraffin oil. Solid wires of copper or other metal just slightly larger than the inside diameter of the tubing are inserted in each end of the polyethylene tube to make electrical connection to the cesium and to protect it from the atmosphere.

Equipment that utilizes solid pressure-transmitting media is calibrated by noting the hydraulic ram oil pressure required to cause each of the fixed-point transitions to occur. The transitions are made only with increasing pressure, and pressure is increased very slowly over as much as an entire day. A person has to become familiar with his own particular apparatus and cell design by making several calibration runs in order to obtain a useful calibration curve. The hydraulic oil pressure to the hydraulic system, read on a sensitive gauge, is plotted as a function of the accepted fixed-point pressures of the calibrants, and a line is drawn to best fit the points. This is all done at room temperature. Even so, this is often used as the pressure calibration when the press is used at high temperature.

There will certainly be some uncertainty in knowing what the pressure is when the device is used at high temperature. Pressure studies at high temperature (say at 800°C and above) have been few because the problem is so difficult. At high temperature, changes take place in the pyrophyllite or other pressure media that generally increase the density of the pressure-transmitting material and tend to lower the

pressure. On the other hand, the elevated temperature will cause expansion and tend to increase pressure. About the best that can be done at present is to assume that these effects approximately cancel each other. Another problem, although minor to the aforementioned problems, is that the reading of a thermocouple is affected by pressure. These difficulties make it imperative that a high-pressure apparatus be described in great detail, listing pertinent dimensions, materials of construction, and procedures in order that others will be able to make sound judgments on the research. Pressure values without this information are not meaningful.

The most common thermocouple used at temperatures above 1000°C in high-pressure work is Pt, Pt-10% Rh. Such a thermocouple will behave well to about 1700°C. With a given cell design and physical arrangement in a given apparatus, a temperature calibration curve can be obtained by plotting thermocouple temperature versus the electrical power in watts. This plot can subsequently be used to indicate the approximate temperature of a sample simply by measuring the current and the voltage imposed upon the heater sample tube. Additional confirmation and extension of the plot may be obtained by observing the wattage required to melt fine wires of tungsten or other high-melting metals. These wires are inserted in the sample in the same manner as the thermocouple leads, melting being detected by the occurrence of an open circuit. When more accurate temperature information is needed than that afforded by the watts-versus-temperature plot, thermocouple leads should be inserted and individual measurements made for the experiment concerned.

Pyrophyllite melts incongruently to a glassy substance at temperatures near 1500°C at pressures of a few thousand atmospheres. Its melting point is increased considerably at higher pressure, but the pyrophyllite does form a hard, white mixture of substances, as has been previously mentioned. This white, hard substance is observable only on removing the cell after an experiment. The exact nature of this material is not known at the high pressure and temperature involved in its formation, and whether or not it seriously hinders transmission of pressure to the sample is also not known.

When the sample located between the moving piston and the closure is subjected to high pressure, the tungsten carbide cylinder in this region is caused to expand (its diameter increases). The maximum increase in diameter

occurs at a plane midway between the ends of the sample and tapers off toward the ends of the sample. However the clearance, which initially may only be 0.004 mm on a diameter between the piston and the cylinder bore in the piston tip region, increases sufficiently to allow cell material to extrude between the piston and cylinder. This causes severe binding of the piston, making the piston difficult to remove, and much piston breakage ensues. This is particularly true if it is pyrophyllite that extrudes. This problem can be reduced by placing an outer sleeve around the pyrophyllite that is made of polycrystalline hexagonal boron nitride. Boron nitride tends to be slippery and partially overcomes the problem. Whatever the material, when load on the piston is removed, the trapped material between the piston and the cylinder becomes more tightly wedged because the pressure on the cylinder is now relieved and it contracts. This is a major difficulty with piston-and-cylinder devices at high pressure. Sometimes a hardened steel ring with an outside diameter that fits snugly against the cylinder wall and that has a tapering inside diameter (Fig. 2.12) is placed against the tip of the piston to hinder extrusion[19]. Breaking the piston every single run is to be expected at 50,000 atm.

The belt device, to be described later, does not cost any more than a piston and cylinder device; in fact, the costs are comparable. Furthermore the belt does not require a clamping cylinder. In spite of this, the piston-and-cylinder device is used by many workers in the high-pressure field. Ordinarily, though, the device is used at pressures below 40,000 atm. The difficulties mentioned above are not as important at these pressures, but at 50,000 atm and above, the problems are vexatious.

Many of the items discussed for piston-cylinder apparatus are applicable to other types of apparatus to be considered later.
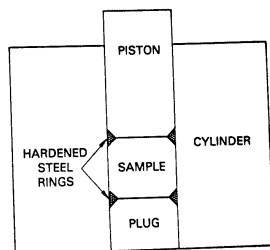

Fig. 2.12. Hardened steel ring to prevent extrusion of material between piston and cylinder wall.

4   BINDING RINGS

Piston-cylinder and belt devices require binding rings to give lateral support to a tungsten carbide cylinder or die. The support required is substantial and is usually provided by a set of compound binding rings, that is, two or more binding rings nested together. There are theories for the construction of these sets[20], but most sets are the result of trial and error. The idea of the compound binding ring set is to squeeze the carbide as strongly as possible but at the same time keep the size of the rings relatively small. In research, the binding ring set is usually lifted in and out of the hydraulic press by hand--often at arm's reach. Not only that, but (as I well remember from my earliest research with the belt) at arm's reach on tiptoe. Thus it is important to keep the weight of the set manageable.

A practical set is shown in Fig. 2.13. This set employs two tension rings, a split shim, and a safety ring. Note the tapers and the interference fits. The smaller diameter given at an interface is the I.D. of the outer ring, and the larger diameter is the O.D. of the inner ring. Assembly begins by placing the outer tension ring within the dead soft, low-carbon safety ring. Next, the inner tension ring is forced into the outer tension ring. Molybdenum disulfide paste lubricant is used on all sliding surfaces during the assembly. At this stage the I.D. of the inner tension ring is taper ground to the dimensions shown. The shim which consists of four equal segments is equispaced around the carbide cylinder or die (there are gaps between the shim segments), and this subassembly is then forced into the inner tension ring. It may require 200 tons of thrust for this final assembly operation.

The design is such that the assembled tension rings are stressed near their ultimate practical capabilities, and occasionally one or both rings will break. I have seen this happen on several occasions, once while holding a newly assembled set in my hands. However the safety ring absorbed the stored energy and prevented mishap in this and in the other instances. If there is going to be breakage, it usually occurs during the first 24 hr after assembly. Ring sets surviving a week will be good for many years.

The primary purpose of the shim is to save the inner tension ring from being scored or damaged from breakage of the tungsten carbide die. Tungsten carbide, being harder than steel, will readily scratch, scuff, and gall at a carbide-steel interface upon breaking but more particularly and severely when a fractured die is forced out of a press-fit assembly. The shim sustains only modest damage on carbide die
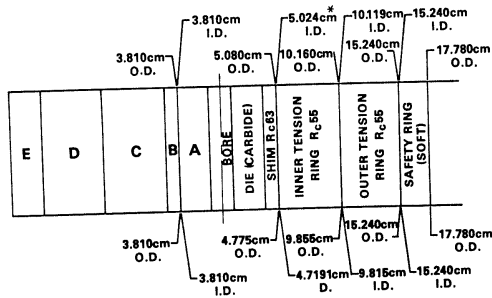
Fig. 2.13. Compound binding ring set. *NOTE—This dimension is ground with ring C in D in E. Other binding-ring and shim diameters are ground with rings disassembled. Shim, after hardening and grinding, is slit longitudinally into four equal sections.

fracture, and the die and shim are pushed out together. The shim, being in sections, can then be readily removed from the broken carbide. A pushing-out operation is not needed. A little touch-up work is usually required on the inner surfaces of the four-piece shim whereupon it is ready to accept a new die and be forced again into the compound binding ring assembly.

For long runs at high temperature, a water cooling jacket is built to surround the safety ring. Hardened, low-alloy steels will lose their strength if heated too hot, and temperature expansion of the steel will decrease the inward thrust on the die. It is best to keep the steel at a temperature below 100° C. Tungsten carbide will also lose strength with increasing temperature.

The tension rings are constructed of AISI-4340 aircraft-quality ring forgings. After being machined to size plus a grind allowance, they are heat treated to Rockwell C-55. Final dimensions are then obtained by grinding. The C-47 to C-53 hardness range in this steel is notch sensitive and should be avoided because parts of such hardness are more likely to fracture. The shim is constructed of an air hardening, nondeforming tool steel. It is ground to size and cut into four equal segments parallel to the cylindrical axis. It is then heat treated to Rockwell C-63 and peened by a steel shot blast primarily to remove scale. Finally, the outer surface is polished to reduce friction during assembly. The taper of the fits is small enough that friction will keep the rings from sliding apart after assembly. The units are rather permanent and stable. I have had some sets for nearly 20 years that are still in good condition. The dimensions of Fig. 2.13 may be used as a base for scaling upward or downward in size.

5 HYDRAULIC PRESSES

Somewhere in a scientific laboratory there is usually a hydraulic press. If so, it can often be inexpensively modified to provide driving thrust for piston-cylinder, belt, and Bridgman anvil apparatus. Such apparatus are consequently popular since a good 300-ton press (a nominal size for research) can cost $25,000 or more.

Presses not specifically designed for high-pressure research usually are not well enough aligned and have too much play in their sliding mechanisms. However this can be overcome by use of a device called a die set. Die sets are used in the precision punch and die stamping of sheep metal and are designed for the very purpose of solving these press problems. The die set is interposed between the platens of the press, and the high-pressure apparatus is placed within the die set.

Ordinary hydraulic presses have only one ram. There is not a second ram for use in clamping the cylinder of a piston-cylinder device. In this event a permanent clamp can be placed on the cylinder. This increases the weight of the cylinder with its compound binding ring assembly and necessitates some changes in design but is satisfactory. The clamp consists of two disks of hardened steel relieved so as to clamp only the carbide cylinder from top to bottom. There is no clamping of the binding rings. A circle of matching holes in these disks just beyond the O.D. of the safety ring accepts a dozen or so high-strength bolts which are heavily but evenly torqued to provide at least 25 tons of clamping load. The central region of the clamp tapers away from its I.D. at a 45° angle to provide room for the piston, its collar, and so on.

If a standard hydraulic press is to be purchased, a *hobbing press* is the least expensive and the best. It has high tonnage in a small size and fairly good alignment. Presses specifically designed for high-pressure use are available from only a few commercial suppliers. The best commercial high-pressure equipment is sold as a completely integrated, turn-key package but is very expensive.

The least expensive hydraulic presses have spring or gravity return cylinders. In the latter case the cylinder pushes upward from the bottom of the press, and gravity pulls it down. The return action of these presses is slow. It is much better to have a press with a double-acting ram (hydraulic cylinder). Oil, under pressure, advances and also returns such a ram.

Pressurized oil for actuating hydraulic presses is usually supplied by an electrically driven two-stage hydraulic pump. This pump automatically supplies a large volume of oil at low pressure- say 35 atm- to move the pressing

elements to the point of contact. Then the high-pressure stage of the pump automatically takes over as resistance to motion is sensed. The second stage supplies high-pressure oil at low volume to move the pistons, or other pressing elements the short distance required to generate a high pressure in an apparatus which utilizes a solid pressure-transmitting medium. Electric pumps capable of operation at 650 atm are readily available and are of modest cost. Electrically driven pumps for higher pressures are very expensive. If higher oil pressures are desired, it costs less to buy air-driven reciprocating pumps. Such pumps, capable of pressurizing fluids (including hydraulic oil) to 4000 atm, are readily available.

If convenience or automatic controls for the hydraulic press are desired, it is best to use oil pressures below 650 atm. Electrically and pneumatically controlled systems are readily available up to this pressure. For experiments lasting more than a few minutes, automatic oil pressure control is highly desirable. Oil pressure will change with temperature and will fall because of seal leakage in the press.

Oil pressure is measured with a precision bourdon tube gauge. For electronic recording, special pressure transducers are commercially obtainable.

6 ELECTRICAL RESISTANCE HEATING EQUIPMENT

The graphite and metal heater sample tubes have an electrical resistance of the order of 0.001 ohm in a cell such as that of Fig. 2.8. It will require about 500 W (a heating current in the neighborhood of 250 A at a potential around 2 V) to reach a temperature of 1500° C in the sample. There are experiments in which a current of 1000 A may be required, but currents of this magnitude should only be used for a few minutes. Longer periods of time will damage the tungsten carbide. Such high currents cause strong local heating where the current leaves the tungsten carbide to flow into the cell. The combination of pressure plus temperature causes much more carbide breakage than does pressure alone.

Alternating current is usually used for heating. The least expensive low-voltage, high-current transformers that I have found are *stacked core* welding transformers (the so-called *wound core* transformers will not do). These transformers have a limited-duty cycle for their intended purpose at their indicated power rating
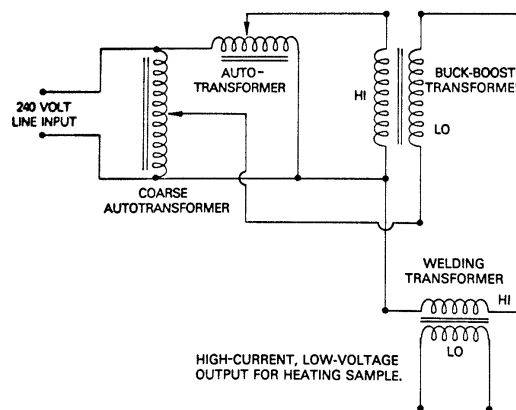

Fig. 2.14. Variable autotransformer control of welding transformer.

but can be used in continuous-duty resistance heating at a lower rating. A 35-kVA, 440-V, 50- or 60-Hz transformer is satisfactory for general research but it should be used only at a 220 V maximum. At 220 V, the voltage of such a transformer is around 4 V with external series arrangement of the output. The transformers are usually water cooled and a 35-kVA unit weighs about 100 kg. They are available from a number of welding transformer manufacturers.

It will be necessary to vary the output of the welding transformer. This may be done by using a variable autotransformer arrangement with coarse and fine controls as shown in figure 2.14. The coarse-control autotransformer should be rated at about 100 A. The output of the fine-control autotransformer should be rated at about 10 A. The bias transformer is a "buck-boost" transformer of 1:10 or 1:20 turns ratio capable of carrying 100 A in its low-voltage output. Buck-boost transformers are available from industrial electrical distributors.

The circuit should contain a voltmeter and an ammeter to determine the voltage across the sample heater tube and the current flowing through it. A current transformer rated at 1000 A will be required in the current-measuring circuit. A wattmeter is also desirable. The product of V X A will not always agree with the wattmeter reading because of power factor considerations.

A less expensive control for the output of the welding transformer is a silicon-controlled rectifier (SCR). I have been unable to locate a standard commercial control of 100-A capacity but have had such controls custom-made by an electrical engineer. SCR controls are light in weight and small in size. However, they have the distinct disadvantage of generating a lot of electrical noise which may affect the operation of

sensitive electronic measuring instruments being used in a high-pressure, experiment.

Direct-current heating of the sample would be desirable for experiments in which measurements would be adversely affected by the presence of the 50- or 60-cycle alternating current. Standard, variable voltage electronic direct-current supplies are commercially available up to 100 A at about 8 V, and these units may be used in parallel. They are however expensive.

7 OPPOSED-ANVIL DEVICES

The highest static pressures obtained in the laboratory are obtained in opposed-anvil devices. Bridgman relates that he conceived this idea while contemplating the pressure that might exist at the contact point of two knife blades pressed together at right angles to each other. One principle, operative in this apparatus is shown in Fig. 2.15. Two truncated tungsten carbide cones pressed together along an axis as shown at (A) will withstand a greater load than two right circular cylinders with the same face area and length as shown at (B). Bridgman called this the massive support principle. In Bridgman's first anvil research, a pinch of powder or a solid disk was placed between the faces of the anvils (Fig. 2.16a), and they were then pressed together. Pressure was computed simply as force per unit area of the faces.

Later, an assembly (cell) as shown in Fig. 2.16b was devised to enable the electrical resistance of metals to be measured as a function of pressure. The outer ring E of the cell is pipestone. Pipestone is an impure pyrophyllite obtained near Pipestone, Minnesota. This substance was used by American Indians in making peace pipes. Within the pipestone ring is a silver chloride disk F in which a metallic ribbon G is embedded, as shown. This ribbon makes contact on the top side with the top anvil face and on the bottom side with the bottom anvil face. If the anvils are electrically isolated from each other, an electrical indicating device can be connected to them to measure electrical resistance as a function of pressure. If the anvil circular faces are approximately 10 mm in diameter, the pipestone ring is made about 0.6 mm thick. The outside diameter of the pipestone ring is 10 mm (same as anvil diameter), and the inside diameter is about 7.5 mm. This in essence is a two-dimensional pressure apparatus, and the components within the cell are tiny indeed. Bridgman measured the electrical resistance of
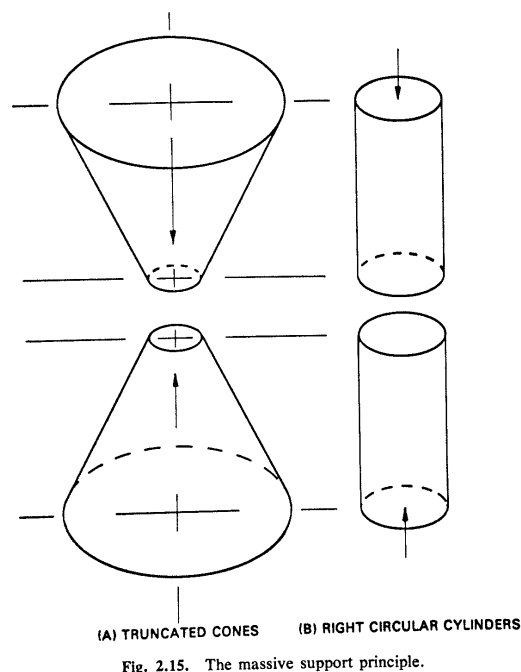

(A) TRUNCATED CONES　　(B) RIGHT CIRCULAR CYLINDERS

Fig. 2.15. The massive support principle.

many substances at pressures up to what were thought to be 100,000 atm[21]. Later work has shown however that the highest pressure obtained in these experiments was only 65,000 atm.

It is a general principle that the smaller the apparatus, the higher the pressure that can be generated. This is particularly true of opposed-anvil apparatus. These devices have been miniaturized to the point where diamonds are used for the anvils and cells are assembled under microscopes. The cell (sample) thickness may be as small as 0.025 mm, and the diameter may only be 0.50 mm. Great care must be used in such miniscule devices to avoid error. Slight dimensional errors in fabricated parts (pipestone rings or silver chloride disks, for example) can cause great changes in the pressure obtained with a given anvil load. Also, samples being X-rayed, a common procedure with diamond anvils, may shift in position and an X-ray diffraction pattern of the wrong material may be taken. A serious
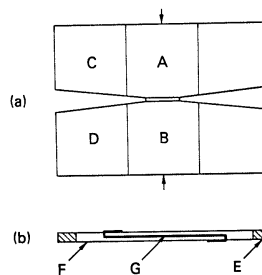

Fig. 2.16. Opposed anvils (a) and electrical resistance cell (b).

extant error of this nature occurred when a researcher published the exciting discovery of a new form of carbon of greater density than diamond. Actually the X-ray diffraction pattern of the "new carbon" was merely that of silver chloride!

Unfortunately much of the work reported in the literature in which tiny samples and opposed-anvil-type devices have been used contains serious errors. The most common error relates to overstating the pressure. Pressures as high as 700,000 atm have been reported. Subsequently the pressure was found to be less than 300,000 atm. Small opposed-anvil devices are capricious and great care should be exercised in their use.

Compression of a gasket to obtain motion is the second principle operative in opposed-anvil devices. This is the means by which a thicker sample is contained and compressed. In the case of ungasketed anvils, the frictional forces of the sample itself come to equilibrium with the applied load at some thickness characteristic of the substance. This thickness would be of the order of 10% of that of a gasketed sample. The pressure obtained at a given anvil load varies with the substance.

It is amazing that a thin ring of pyrophyllite gasket can contain the sample as the pressure builds up. The gasket not only decreases in thickness as the anvils advance but some of it extrudes until an equilibrium situation is reached for a given pressure. On release of pressure blowouts are a common phenomenon. Pyrophyllite elasticity is limited and, having partially extruded during pressure buildup, it cannot return to its initial thickness. Consequently, it loses its frictional hold on the anvil faces, and the compressed sample blows out. Accurate alignment of the anvils, particularly parallelism of the faces, is an important consideration. Slight misalignment can cause premature anvil breakage and blowouts and skew the pressure distribution within the sample.

At pressures of 100,000 atm and beyond, the faces of tungsten carbide anvils are permanently deformed and become concave. Sometimes the deformed anvils are "refigured" (ground flat again with a diamond grinding wheel). After refiguring, anvils are stronger (since they have been cold worked by the deformation) and can be subjected to even higher loads than when new. At the higher pressures, opposed anvils are often used but once, since they usually break on release of pressure.

The sample while under pressure is lens-shaped, being thicker at the center and thinner at the edges. This is due not only to permanent deformation of the anvils but also to the elasticity of the anvils. There is also a pressure gradient in solid samples, the pressure being highest at the center along the anvil axis, trailing off to much smaller pressures at the interface with the gasket. As a matter of fact, this is one of the major disadvantages of the device. Consequently, when measurements of various kinds are to be made, it is necessary to make the measurement in a tiny space as close as possible to the center of the sample. This can be done in X-ray diffraction or optical experiments where a very fine pencil or rays is impinged upon the sample along the centerline axis.

By using a metal, rather than a pipestone or pyrophyllite, gasket, it has been possible to work with liquids to very high pressures, and X-ray diffraction as well as optical observation and measurement of single crystals has been accomplished[22].

Diamond anvils are particularly appealing because they can be used under a microscope, it being most interesting and satisfying to observe directly a phase transformation taking place at a pressure of 100,000 atm. Their use was first described in 1959[22]. The least expensive way to obtain diamonds for use as anvils is to purchase brilliant cut gem diamonds from a major supplier in New York or Amsterdam. These diamonds are purchased with one slight modification: the culets (bottom tips of the diamonds) are ground off to form small flats parallel to the tables (broad top surfaces). These flats are ground to different surface areas to minimize axial alignment problems when they are pressed together. Alternatively a ground-off culet flat is sometimes pressed against the table of another diamond. The diamonds are commonly of about one-tenth carat (0.020 g). The anvil faces are often about 0.5 mm across. The ground-off culet will not be perfectly round but octagonal. If optical properties are of no great concern, yellowish diamonds, which cost less than water-white diamonds, can be used. If transmission in the infrared is needed, type II diamonds should be purchased. Type I diamonds have an intense absorption band at wavelengths from about 7 to 9 #m. Regardless of color or type, though, the diamonds must be physically sound. Major diamond vendors are familiar with these factors and are prepared to supply the needs of diamond anvil users. Although diamond is the strongest substance (in compression) known to man, it is

brittle, and an off-axis load would readily chip it. To assure that the planes of the mating diamond anvils are parallel to each other as they come together, they are mounted in spherical sockets. Alternatively one diamond may be mounted to swivel about the x-axis and the other about the y-axis Cartesian coordinates to accomplish the same purpose. The diamond is commonly set in a metallic mounting (usually stainless steel) by pressing it into the metal to form a seat. It is then held in place by epoxy cement. When the anvils are used in X-ray diffraction work, the metal used is often beryllium because of its relative X-ray transparency.

The area of contact of diamond anvils is so small that it is not necessary to use hydraulic rams to drive them together. Most researchers use either springs, whose tension can be increased or decreased by thumbscrews, or merely the inherent elasticity of steel itself, and clamp the anvils together with socket head capscrews. In spite of the cost of gem-quality diamonds, a diamond anvil apparatus is the least expensive apparatus that a person can acquire. Consequently they are very popular. Some other materials that have been used for opposed anvils are polycrystalline alumina and single-crystal sapphire.

Diamond anvils are so tiny that it would be very difficult to provide internal heating to operate at high temperature simultaneously with high pressure. However Ming and Bassett[23] have used a laser beam to heat samples between the faces of the diamonds and have even converted graphite to diamond by this means. Barnett, Block, and Piermarini[24] have constructed a device for externally heating diamond anvils.

In addition to the pressure gradient problem in opposed anvils, there is the very real problem of accurately determining the pressure. Simultaneous X-ray diffraction of NaCl and a substance embedded therein has been used in diamond anvils[25]. The lattice spacing of the NaCl is used to indicate the pressure on the embedded substance. A drawback of the system is the exposure time required-up to 300 hr.

In some respects the ultimate diamond anvil apparatus is that of Barnett, Block, and Piermarini[24]. They have described an optical system for rapid routine pressure measurement which utilizes a pressure shift in the sharp R-line fluorescence of ruby. A metal gasket (simply a relatively large square of Inconel about 0.13 mm thick in which a hole of about 0.20 mm in diameter has been drilled) is centered between the diamond anvils and a 4:1 mix of methanol
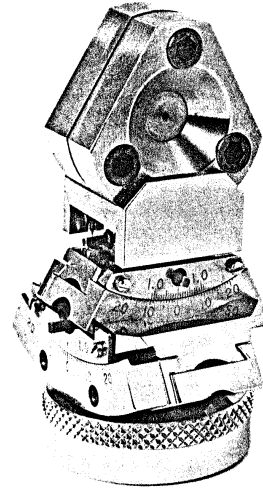

Fig. 2.17. Diamond anvil apparatus for single-crystal X-ray diffraction studies. From Merrill and Bassett [26].

and ethanol is placed in the hole. A speck of ruby is added as well as a speck of whatever else is desired, and the anvils are closed on the gasket. Whatever is inside is trapped, and further advance of the anvils subjects the contents to hydrostatic pressure all the way to 100,000 atm. And the pressure is known by the fluorescence of the speck of ruby!

A recent miniature diamond anvil pressure apparatus for single-crystal X-ray diffraction studies[26] is shown in Fig. 2.17. This device also uses the method of encasing liquids within a small-diameter hole in the metal foil, a technique first used by Van Valkenburg[27]. Beryllium foil is used because of its X-ray transparency. This apparatus is mounted on a standard goniometer head which may be attached to a standard X-ray precession camera or to a single-crystal orienter. The single crystal to be studied is immersed in a true liquid. This device has been used in the study of two high-pressure phases of calcium carbonate, $CaCO_3$ (II) and $CaCO_3$ (III).

8 BELT APPARATUS

Figure 2.19 shows an exploded view of the belt high-temperature high-pressure apparatus[28]. I invented this device in January of 1953 while employed at the General Electric Research Laboratory in Schenectady, New York. At first the device was not taken too seriously by my colleagues or the management. Consequently it was not protected with company secrecy as one might have expected. For example, on September 16, 1953, a prominent high-pressure researcher, Professor A. Michels of the Van der
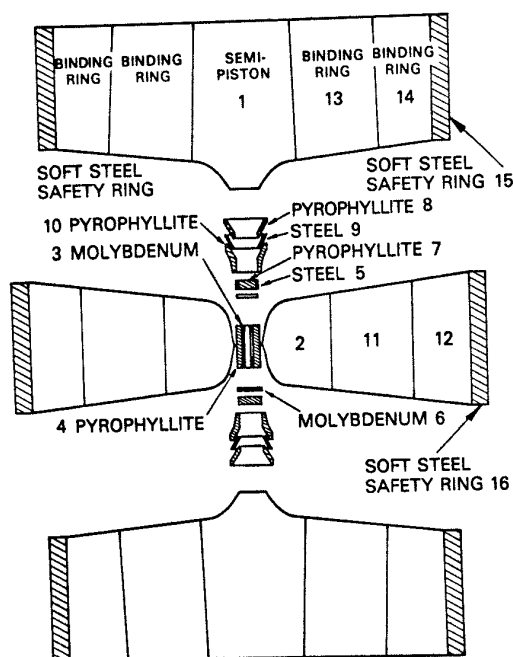
Fig. 2.18. Exploded view of belt apparatus.

Waals Laboratory, Amsterdam, visited the G.E. research laboratory as the guest of a G.E. official. Professor Michels' wife accompanied him on this visit. I was told to show them the details of the belt, and while I explained and demonstrated, Mrs. Michels took notes, took measurements, and made detailed sketches. Many people at G.E. who were not connected with the diamond synthesis project knew about the belt, and one young G.E. researcher conveyed the details of the device to his former professor, who was working in the field of high-pressure at a Midwest university.

The first written report within G.E. on the belt was the usual patent disclosure letter to the Director of Research. There were subsequent follow-up letters on additional details and miscellaneous memorandum reports that were circulated to about a dozen persons within the company. The most formal company report that I wrote was No. RL-1064 of March 1954 entitled "The Belt Ultra High Pressure, High Temperature Apparatus," This document was labeled "class 4," under which this statement appeared: "This document contains information of importance to G.E. Its distribution is rigidly limited." This report was circulated within the laboratory and also to G.E. personnel elsewhere. It not only contained the general details of the belt and its operation, but included scale drawings and dimensions. This 1954 report,

stripped of its detailed drawings and dimensions, became the Review of Scientific Instruments article published in February of 1960[28].

It was not until I had made diamonds in December of 1954 that company secrecy on the belt began to firm up. You can imagine my eagerness as a young scientist to make my mark, upon accomplishing the twin task of developing a high-pressure, high-temperature apparatus capable of synthesizing diamonds and then making them. You can further imagine my anxiety on being unable to have my work published for six years. This anxiety was heightened by the fact that information concerning the belt was at large in the world and that others might publish on this or related devices before I would have the opportunity. The knowledge that the belt existed and the knowledge that diamonds had been synthesized gave others a tremendous advantage in trying to accomplish the same things. There were some other leaks of vital information. After several hundred copies of one of the earliest press releases was distributed in 1955, it was decided that the details and photographs of the belt in this brochure were too revealing. Distribution of this particular brochure was then stopped, and one that was less explicit was substituted. Also, persons in government laboratories professing "need to know" obtained copies of the patent applications.

Although I have not published the full details of the human side of the development of the belt apparatus and the first synthesis of diamonds, I have given some personal glimpses into the events that transpired[29].

The belt was the first apparatus capable of operating simultaneously at high pressure and high temperature at pressures of 100,000 atm. Maximum pressures of the order of 150,000 atm simultaneously with temperatures in excess of 2000°C have been maintained for long periods of time in this device. Referring to Fig. 2.18, the functions of the various parts are as follows: two tapered tungsten carbide pistons (1) push into each side of a tapered tungsten carbide chamber (2). Pressure is transmitted to the sample contained in a molybdenum tube (3). This tube not only serves as an electrical resistance heating element but also contains the sample and is often referred to as the heater sample tube. Graphite and tantalum tubes are also used. Pressure is transmitted to the sample contained in the tube (3) by pyrophyllite (4). The pyrophyllite also serves as thermal and electrical insulation. Electricity passing through the tube (3) serves to
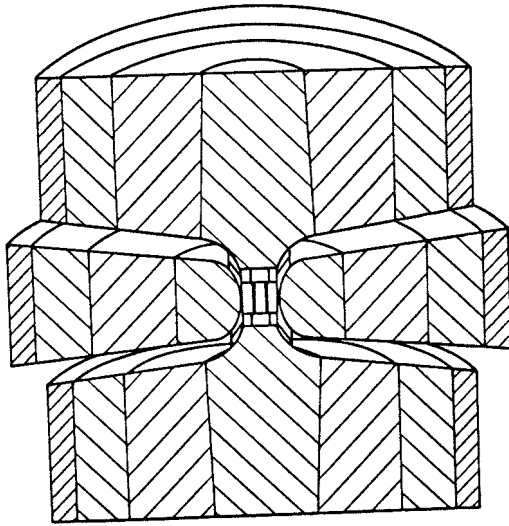
Fig. 2.19. The belt in closed position.

heat the sample. Current enters this tube through a molybdenum disk (6), which in turn touches a steel ring (5), which in turn touches the tip of the piston. The short, pyrophyllite cylinders (7) provide thermal insulation at the ends of the sample tube. A sandwich gasket, composed of pyrophyllite (8 and 10) and steel (9), maintains the pressure in the chamber.

The hardened steel compound binding rings (11) and (12) provide lateral thrust to the chamber. Binding rings (13) and (14) do the same for the conical pistons. Rings (15) and (16) are made of dead soft low-carbon steel and are intended to absorb the energy released should the inner binding rings fail. These binding ring sets are similar to those already discussed for piston-
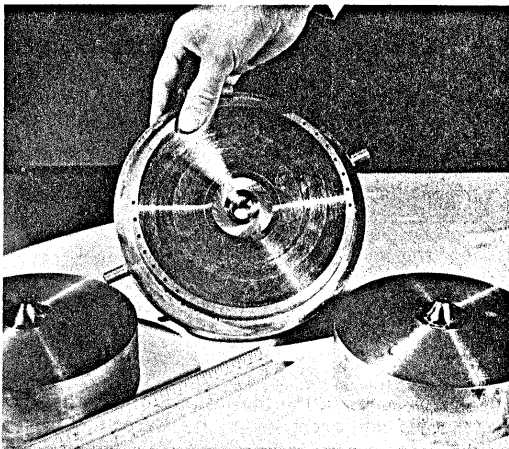

Fig. 2.20. The first belt apparatus.

cylinder apparatus. The chamber (2) and binding rings (11) and (12) form a "torroidal belt" around the sample, and from this I took the code name "belt" for the apparatus. For sustained operation at high temperature, the conical pistons and the corresponding chamber must be cooled. Figure 2.19 shows the belt assembly in closed position. Figure 2.20 shows a photograph of the first belt apparatus.

The belt uses a compressible gasket in a manner akin to that used in Bridgman anvils, but there are some differences. In Bridgman anvils the gasket is a flat ring in a plane 90° from the axis of compression. The motion of the anvils is determined by the amount that the gasket can be compressed. For more compression, one would use a thicker gasket. However there is a limit to the possible thickness of the gasket. If it is too thick, chunks will break from it allowing the sample to escape, and the gasket will not compress symmetrically or evenly. The maximum permissible thickness of the gasket is determined by trial and error. For opposed anvils with 1 cm-diameter faces, the maximum thickness for a pyrophyllite gasket is about 0.25 mm. It would be more for anvils with larger-diameter faces if the gasket width were correspondingly increased.

In the belt the gasket is arranged at an angle less than 90° to the direction of compression, as is shown in the single-ended device (halfbelt) of Fig. 2.21. In the belt design the thickness t between the two arrows A-A is substantially the same as would be possible to use in a Bridgman anvil device with faces of this diameter. However in the belt, the relative movement of the tapered piston into the tapered cylinder is along the axis given by B-B. This thickness s is given by $s = t/\cos \theta$. The stroke (maximum motion) in the belt is correspondingly increased. The force acting perpendicular to the contact area between the gasket and the tungsten carbide components (A-A) is reduced by $\cos \theta$ over the case where the gasket is perpendicular to the direction of compression. Therefore the friction
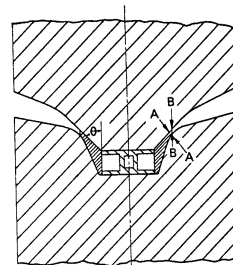

Fig. 2.21. Detail of motion obtained via compressible gasket in the belt.

between the gasket and the tungsten carbide will be reduced by cos θ. The smaller the angle θ is made, the larger s becomes. The limit on the smallness of θ is set in part by the frictional forces along the gasket-tungsten carbide interface. When they become too small, the gasket will be blown out by the pressure.

A conical piston has much greater strength than does the cylindrical piston of a piston-cylinder design. Consequently, if sufficient stroke can be obtained to make the apparatus useful, a device with conical pistons should be able to obtain a much higher pressure than is obtained in piston-and-cylinder devices, and this is indeed the case. The sandwich gasket further increases the stroke, hence the sample size and the ultimate pressure of any system utilizing stone gaskets. For example, it will allow an increase in sample thickness in Bridgman anvils. In the belt the thickness of the gasket can be more than doubled by the insertion of the thin metal cone, which is the "meat between the bread" in this array. The metal reduces gasket crumbling, allowing smooth compression and extrusion. The available stroke of the belt apparatus of Fig. 2.18, which utilizes the combined effects of double-ending, tapered gasket, and the sandwich gasket, is approximately 6 mm, compared to a maximum of about 0.7 mm in a Bridgman anvil device of comparable face diameter. This greatly increased stroke makes it possible to have a tremendously large sample size (compared to that available in opposed anvils) and, of course, offers a size practical for the commercial production of diamond.

There are some other advantages of the belt. Very accurate alignment is required for piston-and-cylinder devices. Good alignment, comparatively speaking, is required in Bridgman anvils. The belt is the least sensitive to misalignment, and slight axial misalignment or cocking of the moving members with respect to each other does not interfere with its operation. For certain purposes a plain pyrophyllite gasket (nonsandwich gasket) is perfectly suitable for use in the belt. In other instances two steel cones can be used in the sandwich gasket to increase the stroke of the belt even more. The distance between the two conical piston tips will determine the pressure that can be reached. To obtain the highest pressure, the conical piston tips are placed only about 1 mm apart. Such devices have been called "high compression belts." In addition to placing the piston tips close together, one would miniaturize the apparatus to take advantage of the effect already mentioned that higher pressure can be obtained in smaller devices than in larger devices. There seem to be two effects that make this so. There is the surface-to-volume ratio, which has often been observed to effect changes in engineering problems. Also, in sintered tungsten carbide parts, a part can be made more free from defects in small sizes than in large sizes. In the usual manufacture of cemented tungsten carbide, cobalt powder and tungsten carbide powder are intimately mixed together and then cold pressed to the approximate shape desired. The preformed part is then sintered at a temperature just below the melting point of cobalt. In large parts, cobalt tends to concentrate in the bottom of the part owing to the forces of gravity. This is not so likely to occur in smaller parts. There is also the statistical situation that a large part has a greater probability of containing a flaw than does a small part. In brittle substances, such as cemented tungsten carbide, breakage usually starts at a flaw within or on the surface of the material.

There is a cooperative phenomenon at work in the belt to allow it to operate at higher pressures. Through the gasket, the tapered piston is supported by the tapered conical chamber, and vice versa. An included angle between 60° and 90° is suitable for the conical piston in the belt apparatus. However in some special belts (unpublished work of the author), the angle has been decreased to as low as 20°. Figure 2.22 shows the central region of the belt and the gasket after a high-pressure run.

Thermocouple wires and other electrical leads are inserted into the sample region of the cell by drilling fine holes through the pyrophyllite in a manner such that the wires do not make contact with the tungsten carbide components. Frictional forces will hold the wires
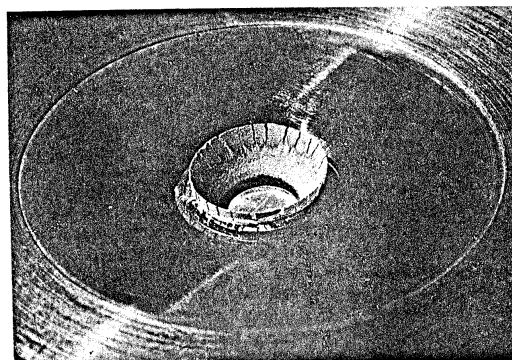

Fig. 2.22. Central region of the belt and the gasket after a run.

in place as pressure is developed within the system. In the belt, the center of the gasket assembly sustains more load than the outer regions, and there is a gradual drop of pressure along the gasket to atmospheric pressure at its outer edge. This is a kind of multistaging effect and is also a factor in making it possible to sustain such very high pressures in a relatively large volume.

9   MULTIANVIL APPARATUS

Opposed-anvil, piston-and-cylinder, and belt apparatus may all be classified as uniaxial devices. That is, the means for mechanically reducing the volume of a substance is accomplished by moving certain apparatus components toward each other along a line. There are some disadvantages to uniaxial devices. When quasi-hydrostatic pressure-transmitting materials are used, pressure gradients will invariably be set up within the cell in a pattern depending on the movement of the compressing members. The Poisson ratio of the material between the pistons or anvils will also influence these pressure gradients. So will the geometry of the cell components.

In the belt apparatus, the heater sample tube is originally a right circular cylinder; but when the high-pressure, high-temperature run is over, it will have been considerably foreshortened and will have a barrel shape. If one were producing a sintered part, for example, a sintered diamond cylinder, it will be distorted in the sintering process. Furthermore the sintered product will tend to delaminate (break into several disks perpendicular to the axis of compression) after pressure is released. Sometimes the strains resulting from the uniaxial compression are so great the material almost explodes as the layers separate from each other. This problem can be overcome to some extent by surrounding the heater sample tube with a material that is more hydrostatic than pyrophyllite, for example, sodium chloride. Indium metal will also serve this purpose well because of its very low internal friction. However it is metallic, has a low melting point, and also has a relatively high thermal conductivity, and these characteristics restrict its use.

Uniaxial hydraulic presses are rather standard equipment in research laboratories and in industry. Consequently they have been used to power the advance of pistons, anvils, and the like in high-pressure devices. Researchers have tended to think in terms of uniaxial machines.

However the problem just ascribed to uniaxial devices can be overcome in apparatus in which compressing members are thrust toward a central region along several axes. The first such device was the tetrahedral anvil press[5]. This was the first high-temperature, high-pressure device capable of synthesizing diamonds that was revealed to the world. It came into being as a matter of necessity, and the reader might be interested in a brief account of these circumstances.

After leaving the General Electric Company in the fall of 1955 to become Director of Research and Professor of Chemistry at Brigham Young University (BYU), I was besieged with requests from scientists everywhere to reveal the details of the belt. Circumstances of company secrecy compounded by a government secrecy order, however, prevented disclosure. In fact, I could not even use the apparatus for research at BYU. It soon became apparent that this problem would not be resolved for some time. Consequently I found myself being encouraged by many persons and institutions to try to develop another apparatus that could be made available to scientists everywhere. Financial support for such an undertaking came first from the Carnegie Institution of Washington. Shortly
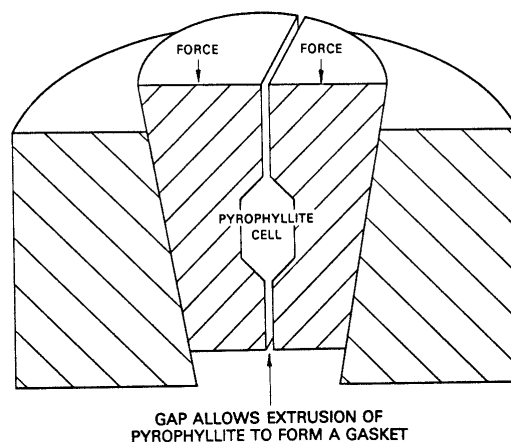
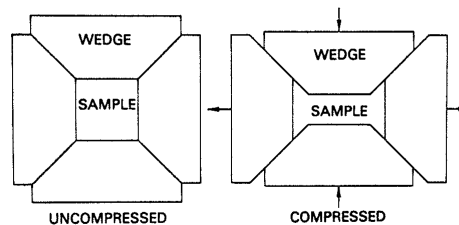

Fig. 2.23.   Tapered wedge press.

Fig. 2.24.   Black Hawk Special.

thereafter, additional financial aid was received from various government agencies, notably the National Science Foundation.

Within two years I had tested several ideas in which pressure was generated by moving "anvils" along several axes. Some of these devices utilized a uniaxial hydraulic press to cause tapered wedges sliding in a cone-shaped ring to move toward each other and thus compress a pyrophyllite cylinder radially inward (Fig. 2.23). Another device was called the "Black Hawk Special." This machine utilizes a number of flat wedges placed between two flat plates. The plates are maintained at a fixed distance corresponding to the thickness of the wedges. Alternate wedges advance or retract, as shown in Fig. 2.24, to reduce the volume and thus increase the pressure. The movement of the wedges is exaggerated in the figure to better illustrate the principle. I also built and tested a variety of uniaxial devices. The most successful device, however, used hydraulic rams built into a special press frame to afford symmetrical action in three-dimensional space. I considered tetrahedral presses, hexahedral (cubic), and higher-order multianvil presses, but calculations and intuition showed that the tetrahedral press would be capable of generating the highest pressures. The original tetrahedral press is shown in Fig. 2.25, and a cluster of tetrahedral anvils is shown in
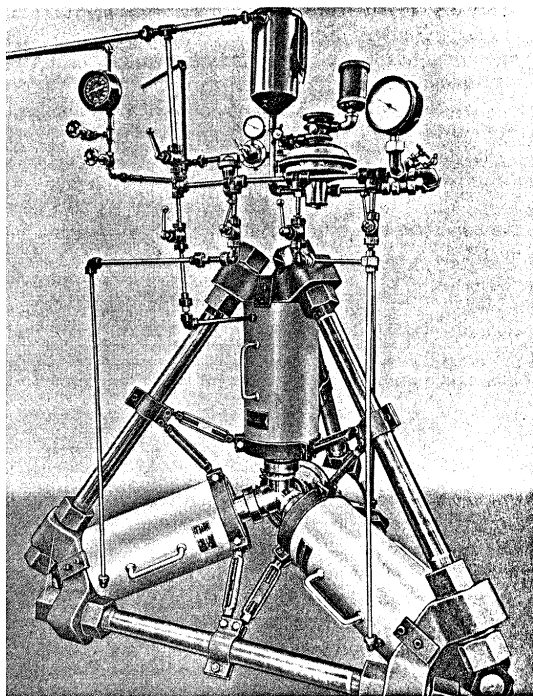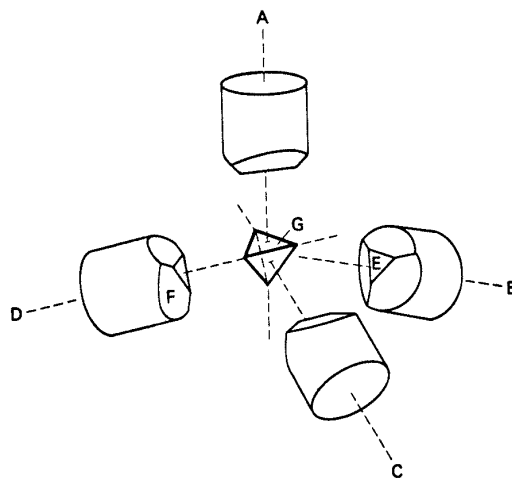

Fig. 2.26. Cluster of tetrahedral anvils.

Fig. 2.26. During the Christmas holidays of 1957 diamonds were made in this apparatus—a test of the device that seemed important at the time. Patents were obtained on it through BYU and Research Corporation, and all claims were quickly granted on the first office action.

The device was described at the Spring 1958 Meeting of the American Chemical Society in San Francisco and was published in the April 1958 *Review of Scientific Instruments*, and many scientists from all over the world visited Provo to see it. Regardless, the U.S. Government (contrary to previous agreement) placed a secrecy order on the tetrahedral press on January 15, 1959. Note that thousands of copies of the *Review of Scientific Instruments*, which fully described it, had been distributed all over the world nine months before this. Fortunately this secrecy was short-lived, having been rescinded within six months.

A tetrahedral press might be considered a three-dimensional extension of the two-dimensional Bridgman anvil concept. The principle of massive support is still at work in the tetrahedral press and other multianvil presses, but to a lesser extent than in Bridgman anvils. In a regular series of multianvil presses, the solid angle subtended by each anvil decreases as the number of anvils increases. This solid angle is largest in the tetrahedral press and is the primary reason why higher pressures can be obtained in this press than are achieved in cubic and higher-order presses. Some articles in the literature claim that the greater the number of anvils in a multianvil device, the higher the pressure that

Fig. 2.25. The original tetrahedral press.

can be achieved. This runs contrary to my experience.

In multianvil devices the anvils support each other through load on the gaskets, and this tends to compensate for the reduction in massive support over that available in opposed anvils. The four anvils of the tetrahedral press (Fig. 2.26) are driven toward a central point by hydraulic rams whose axes lie along lines normal to the triangular anvil faces. The hydraulic rams and collinear anvil axes (A, B, C, D) intersect at the tetrahedral angle of 109.47° at the center of the regular tetrahedral volume enclosed by the anvil faces.

Tungsten carbide is usually used as the material of construction for the anvils. Each anvil is surrounded by a single press-fit steel binding ring which, as usual, absorbs the tensile loads developed within the tungsten carbide. The sloping shoulders of the binding ring break away at a 2° steeper angle on each side than do the corresponding 45° shoulders of the anvils. This provides a widening gap moving outward from the center of the press and decreases the likelihood of binding rings touching each other in case of slight misalignment. Such touching would constitute an electrical short circuit. The tapering gap also lessens the likelihood of pinching off thermocouple wires or other electrical leads that may be inserted into the sample. The cell in which the pressure is

generated consists of a regular pyrophyllite tetrahedron, as is shown in Fig. 2.27.

If the anvils (Fig. 2.26) are advanced symmetrically toward the center of the press until their sloping shoulders F touch, their triangular faces E will define a regular tetrahedron of a given size. The tetrahedral cell G is made larger than this size so that a gasket will be automatically formed by extrusion of excess pyrophyllite as the anvil faces impinge on this larger cell. In practice, the edges of the tetrahedral cell are made about 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 provides the necessary compressing gasket. This cell contains considerably fewer and simpler parts than the corresponding cell and preformed gaskets of the belt. The cell is machined from pyrophyllite by standard machine tools such as lathes and milling machines. Either high-speed steel or tungsten carbide cutting tools may be used. Rough shapes of pyrophyllite are sawed with a bandsaw from commercial blocks which are available up to a 30-cm cube[30]. The material is mined in South Africa.

Referring again to Fig. 2.27, the diagonally disposed heater sample tube is usually made of a high-melting metal, such as molybdenum. The tab is also of molybdenum, and the pyrophyllite prisms provide thermal insulation at the ends. Thermocouple leads may be brought out through edges of the tetrahedron. Four electrically insulated anvils provide four electrical connections to the cell's interior. If only half a tab is used for heating current, two anvils are free for other connections. There are other ways that the heater sample tube and other components may be arranged within the tetrahedron. For example, a heater sample tube could make contact through one triangular face of the tetrahedron with a second tab making contact through an adjacent face, as shown in Fig. 2.28. Several electrical leads for various measuring purposes may then be brought out through an apex as is also shown in the figure. This apex is usually fired in a furnace at 750°C for 12 hr to increase its hardness and strength over that of the natural stone. This helps to prevent pinch-off of the wires passing through the prism. If such fired pyrophyllite is used for the entire tetrahedron, a suitable gasket will not form. There will be crunching sounds and expulsion of large chunks of material as the anvils come together. A smooth, noiseless

TETRAHEDRAL CELL

MOLYBDENUM CURRENT TAB
SPECIMEN CAVITY
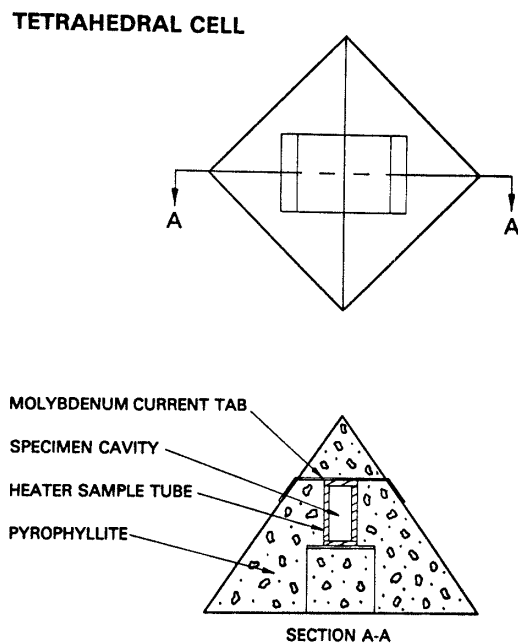HEATER SAMPLE TUBE
PYROPHYLLITE

SECTION A-A

Fig. 2.27. Tetrahedral cell.

extrusion of material is needed for proper gasket formation.

Pressure calibration of the tetrahedral press is made in a manner similar to that described for the piston-cylinder apparatus. A typical edge length for the anvil triangular face for use in research is 2 cm. The corresponding length of the triangular edge of the tetrahedral cell would be 2.5 cm. The highest pressure observed in a tetrahedral press at Brigham Young University (with 6 mm on edge anvil faces) is 120,000 atm, based on X-ray diffraction measurements on NaCl contained therein (Decker's NaCl scale). The everyday working pressure used at BYU with 2 cm on edge anvil faces in tetrahedral presses is 70,000 atm. At this pressure and at

Fig. 2.29. Anvil guide for cubic press.

sample cell was placed apex down in the nest, Next, the upper ram was advanced until the triangular face of its anvil touched the upward-facing triangular base of the pyrophyllite tetrahedron. Each anvil was then individually advanced approximately 0. 1 mm at a time by admitting hydraulic oil under pressure sequentially to the first, second, third, and fourth rams and repeating the process until the desired pressure was built up within the sample. This procedure required skill, and it was difficult and time consuming to teach others to use the press. Consequently I sought means for synchronizing the motion of the anvils so that at any instant the anvil faces would be equidistant from the center of the tetrahedral frame as defined by the tie bars which hold the press together.

Consideration was given to mechanisms that would control the flow of oil to the rams or that would operate from a position-indicating transducer. Such devices were complicated and did not satisfactorily solve the problem. The final solution was simple but took longer to conceive than anticipated. The solution is a mechanical device that I have called an anvil guide[31]. Figure 2.29 shows a cross section of an anvil guide device as applied to a cubic press. It consists of 12 guide rods or guide pins and six guide plates. 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 four guide holes symmetrically arranged at 90° angles to each other. The axis of each hole makes an angle of 45° with respect to the ram axis. When assembled, the guide rods are positioned within
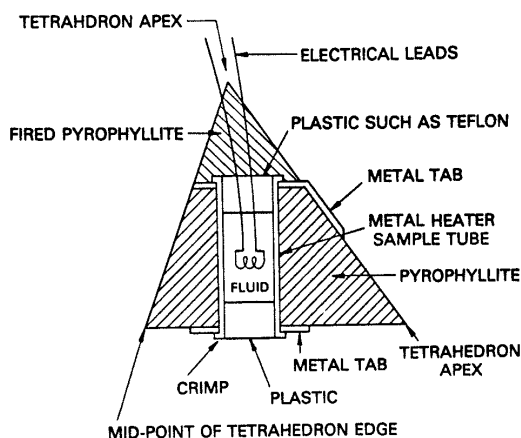

Fig. 2.28. Another version of the tetrahedral cell.

room temperature, tungsten carbide anvils of 8% cobalt content will last indefinitely. High temperature simultaneously used with high pressure, however, causes some breakage. Simultaneous 1500°C at 70,000 atm conditions with the same anvils gives an anvil lifetime of about 2000 runs. This varies with the size of the sample within the tetrahedron and the current flowing through the anvils. To increase lifetime, the sample and the heating current should be small.

The design of the press in multianvil apparatus is important. In the original tetrahedral press, the bases, tie bars, and other appurtenances were not machined to any particular precision. Consequently turnbuckle arrangements as shown in Fig. 2.25 were used to align the tetrahedral axes of the rams. Each of the four hydraulic rams were independently valved. To operate the device, the lower three rams were advanced until the anvils almost touched to form a "nest." Then the pyrophyllite
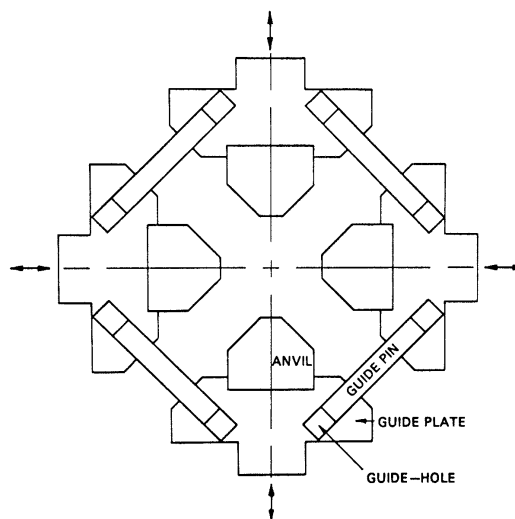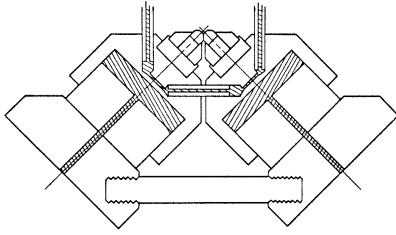
Fig. 2.30. Inverted ram cubic press with anvil-guide retraction system and right/left-hand thread tie bars.

the guide holes in which they are free to slide as the rams advance or retract. All rams, being interconnected by the guide rods and plates, are forced to move synchronously together as hydraulic oil is simultaneously applied to all the rams. In the tetrahedral press, there are six guide rods and four guide plates. The three holes in each guide plate are disposed at 120° angles about the ram axis, and each makes an angle of 35.26° to the ram axis.

The most advanced cubic (or tetrahedral) press built to date[32] incorporates a hollow guide-pin system for retraction of the hydraulic rams, which saves weight and machining costs and improves mechanical proportions (Fig. 2.30). This system unclutters the anvil region (from water-cooling lines) and provides better access. Oil circulating through the guide pin system, when it is not being used to retract the press, provides cooling. The use of inverted hydraulic rams and right/left-hand thread tie bars and bases reduces weight and cost further. Retraction is accomplished by admitting pressurized hydraulic oil to the anvil guide assembly. Le Chatelier's principle requires the interconnected system to increase in volume, and this is accomplished if the cylinders move (retract) toward the bases. Anvil guide mechanisms can also be applied to any other variety of polyhedral press.

The guide pins and holes need not be symmetrically disposed as indicated in Fig. 2.29 but need only to be parallel to the tie bar axes. They may thus be offset to facilitate the admission of beams of matter or radiation such as neutrons and X-rays into the sample. Alternatively one or more pins may be eliminated without adversely affecting the operation of the anvil guide. Two smaller-diameter guide pins that straddle the normal symmetrical position of a single pin have also been used to give access.

The cubic press is the next member in the series of polyhedral presses. Anvil breakage is somewhat higher than that in tetrahedral presses, and the maximum pressure achieved is not as

high. The everyday working pressure for cubic presses is about 5000 atm less than that of tetrahedral presses. Excellent anvil lifetime is obtained in high-pressure, high-temperature runs at 65,000 atm. There are some secrets to obtaining long anvil lifetime in cubic presses. In my first cubic press there were occasions on which all six anvils would break for no apparent reason. This was very puzzling until I finally realized that the anvils were breaking every time that I first used the press after returning from a meeting or speaking engagement away from the university. This caused me to wonder if there could be such a thing as too long a rest period--a period of nonuse of the anvils. So deliberate experiments were performed to test this idea. Two things were learned. First, the anvils should not remain idle for more than 60 hr if they are being routinely used at 65,000 atm. Second, if the anvils are unused for periods longer than 60 hr, they should be "stress relieved" at a pressure of about 25,000 atm (at room temperature) for a period of 12 hr before resuming routine use at 65,000 atm. This breakage phenomenon does not exist for the tetrahedral press, and no such precautions are required.

An advantage of the cubic press is its rectangular coordinate geometry. A typical cubic cell is shown in Fig. 2.31, and a typical cubic press is shown in Fig. 2.32. It is possible with the cubic press to have six independent contacts emanate from within the high-pressure cell and connect to the outside through the six electrically isolated anvil assemblies.

PYROPHYLLITE
SPECIMEN CAVITY
HEATER SAMPLE TUBE
MOLYBDENUM CURRENT DISK
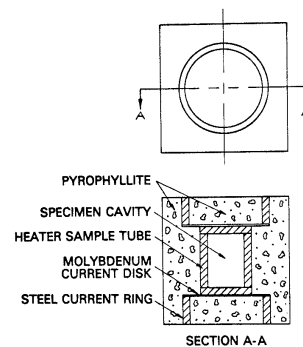STEEL CURRENT RING

SECTION A-A   Fig. 2.31. Typical cubic cell.

Multianvil presses need not be regular as are the tetrahedral and cubic presses so far described. For example, it is possible to have a tetragonal press. Opposite ends of the cell have square faces, and the four sides are rectangular. The anvils for such a press would enclose a tetragon, and the cell assembly would be oversize in order to allow for extrusion of a
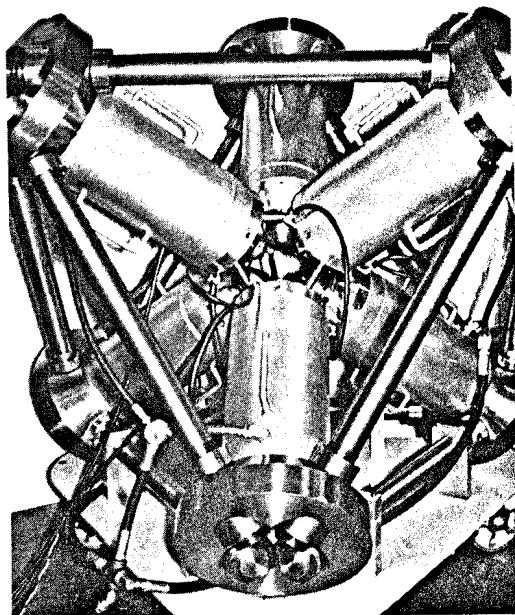
Fig. 2.32. Typical cubic press.

gasket as is the case with the presses already described.

As can be seen, in multianvil press systems the entire system (hydraulic rams, anvils, guide pins, etc.) is engineered as a unit. This contrasts with most situations for belts, Bridgman anvils, and piston-cylinder devices, where the hydraulic press is a separate, standard item of manufacture that is modified to accept the aforementioned devices. Even with uniaxial systems, however, the best apparatus is a totally engineered, integrated unit, press and all.

10 INSTRUMENTATION

The basic high-pressure apparatus that have been described have been instrumented in numerous ways to study a great variety of phenomena. It is not the purpose of this chapter to delve into the details of such instrumentation. Considerable ingenuity has been used by many researchers, and a few references are listed below to sample briefly what has been done.

> Differential thermal analysis (DTA)[33]
> Mössbauer effect[34]
> Diffusion[13]
> Manganin gauge pressure measurement[35]
> Neutron diffraction (time of flight)[36]
> Optical measurements[37]
> X-ray diffraction[38]
> Cryogenic techniques[39]

> Nuclear magnetic resonance[40]
> Electron spin resonance[41]
> Thermal conductivity[42]

Publications of the author dealing with high-pressure apparatus that have not been referenced are cited in Refs. 43 through 53.

11 THE SYNTHESIS OF DIAMOND: AN EXAMPLE OF THE USE OF HIGH-PRESSURE, HIGH-TEMPERATURE APPARATUS

A cubic press with six 20.3 cm-diameter (320 cm^2-area) hydraulic rams and six 1.27 cm on edge square-faced anvils (1.61 cm^2 area) is used. The hydraulic rams are suspended in an octahedral frame consisting of ram bases and tie bars. This frame is mounted with one triangular face of the octahedron parallel to the floor. I prefer this mounting because debris from the cell (crumbled gasket, etc.) falls between the three lower anvils as the press opens and does not, for the most part, get into the sliding mechanisms of the press. Cubic presses are sometimes mounted with a line through opposite apices of the octahedron perpendicular to the floor. This locates one anvil facing upward with its face parallel to the floor, which is convenient for placing the cell. Gravity holds the cell in place as it rides upward while the anvils advance toward the center of the press. However pyrophyllite debris will fall onto the sliding surfaces of four guide pins unless protective shields are used.

The cubic pyrophyllite sample cell is 1.59 cm on edge. It has a central bore of 6.35 mm and a counterbore on each end to accommodate the current ring and its central pyrophyllite disk. The current rings (two each) are made of AISI 1020 cold-finished steel and are 11.07 mm O.D. by 8.46 mm I.D. by 4.22 mm thick. A pyrophyllite disk 8.46 mm in diameter and 4.22 mm thick is placed inside each current ring and provides thermal insulation at each end of the heater sample tube. Two molybdenum disks 10.90 mm in diameter and 0.25 mm thick are used to carry heating current from the current rings to the sample. The sample consists of alternating disks of graphite and nickel with graphite disks touching the molybdenum disks at each end. The nickel disks are 6.22 mm in diameter and 0.36 mm thick, and the graphite disks are 6.22 mm in diameter and 0.76 mm thick. This stack of alternating nickel and graphite disks will serve as its own heating element.

A paper tab about 5 mm wide and 10 cm long is glued to an edge of the assembled cell with a minimum amount of white glue. The external pyrophyllite portions of the cell are painted with a water suspension of red iron oxide (Fe_2O_3) powder. The cell is then dried at 120ºC for 1/2 hr. With the anvils in retracted position, the cell is roughly centered on one of the lower anvils and held in place by placing a piece of adhesive tape across the paper tab onto the face of an anvil binding ring. The current rings should be placed so that they touch (upon anvil closure) the opposed pair of anvils that carry the heating current. Oil pressure is applied to the hydraulic rams until the anvils impinge on the cell and the pressure (room temperature calibration) is built up to about 60,000 atm. This will occur at an oil pressure of about 476 atm.

After the cell is pressurized, heating current is applied. The characteristics of the electrical system will come into play at this point, and a little experimentation may be required in order to determine the correct setting of the electrical controls. Assume that variable autotransformers are used to control the voltage impressed across the sample. They should be set so that the initial current passing through the sample is about 800 A. If the setting is correct for making diamonds from the graphite, the current will start to decrease within 20 sec of its being applied, and as the current falls, the voltage rises. This is the signal that diamonds are forming! The contents of the cell are at a temperature near 1500ºC, and at this temperature graphite dissolves in the molten nickel which acts as a solvent-catalyst for changing graphite to diamond. Diamond is precipitated from the liquid nickel-carbon system, and since diamond is an electrical insulator (it probably conducts some at 1500ºC) it impedes the flow of electricity as it is formed. Thus the current falls and the voltage rises.

I noticed this phenomenon in the first synthesis of diamond; in fact, I have a patent on it (U.S. pat. 2,947,608 assigned to General Electric). One can easily find the heating power required to make diamond by this means without actually knowing the temperature inside the cell.

The current may fall to about 200 A as the diamond forms. After 60 sec of heating, the power is disconnected. The sample will cool to near room temperature in about 5 sec. About 20 sec after the heating power is disconnected, the pressure may be released and the anvils retracted. This brief delay is intended to allow adjustments to take place in the cell and anvils following the drastic change in temperature of the sample. This helps to preserve the life of the anvils.

The cell is removed from the press and split open with a mallet blow to a sharp knife set to bisect a square face of the pyrophyllite cube parallel to the sample axis. One or two blows will usually expose the core, which now consists of tiny diamond crystals intermingled with nickel and graphite. The entire mass tends to be a monolithic unit but can usually be cleaved with a knife and mallet along the original nickel-graphite boundaries. The diamond crystals at this point will be covered with a film of nickel metal.

The nickel and graphite may be separated from the diamond by first treating the sample very carefully with hot concentrated H_2SO_4 + $NaNO_3$. The sample is placed in a beaker to which is added the concentrated H_2SO_4 and then about 10% by weight $NaNO_3$. The mixture is heated strongly on a hot plate. Clouds of graphite particles will be seen to rise from the sample. Heating is continued for perhaps an hour until most of the graphite is oxidized and disappears. After the liquid is decanted, the residue is treated with concentrated HCl but is heated only lightly on the hot plate or let stand overnight at room temperature. The diamonds will be reasonably clean at this stage, and their morphological features can be readily observed at 10x magnification. For further cleaning, the H_2SO_4 + $NaNO_3$ and the HCl steps are repeated as many times as necessary to remove all the graphite and nickel. There will still be some residue from the pyrophyllite. This can only be removed by a long-term treatment with concentrated HF (perhaps a week) or by a fusion with NH_4F. The yield of diamond should be about 1 carat (0.20 g).

The diamond obtained is called diamond grit in the trade and could be used in some grades of resinoid-bonded diamond grinding wheels. The diamonds may be black. Transparent, slightly greenish or yellowish diamonds can be formed by lowering the temperature and pressure to a point where diamond is still the thermodynamically stable phase (with respect to graphite) but where the diamonds are grown more slowly. Under these conditions the yield will decrease.

For information concerning the thermodynamics and Kinetics of diamond synthesis, see the *Journal of Chemical Education* article of Ref. (29).

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