

Ultrahigh Pressures

Laboratory apparatus is now capable of maintaining steady pressures of more than two million pounds per square inch. Under such extreme conditions matter exhibits new properties

By H. Tracy Hall

There is a nice symbolism in the fact that man was able to hit the moon before he could sink a three-mile shaft through the earth's crust. Standing on the threshold of space he has even anticipated by his experiments much of what he will find there. The light, the heat, the nuclear reactions of the stars themselves have been duplicated in miniature. But man has barely begun to approach in his laboratories the outstanding characteristic of the nether world—its enormous static pressure.

The highest steady pressure yet attained in the laboratory is 200,000 atmospheres, almost three million pounds per square inch. (One atmosphere is 14.7 pounds per square inch, the average atmospheric pressure at sea level.) At the center of the earth the pressure is three million atmospheres; at the center of the sun, 100 billion; in white-dwarf stars, something like 10 million billion. On such a scale our efforts seem puny indeed. Viewed in other ways, however, they are nothing to sneeze at. Two hundred thousand atmospheres is the pressure exerted by a column of granite 400 hundred miles high, or a stack of 4,000 Washington Monuments. It is more than enough to manufacture diamonds and other minerals, and it can force matter into entirely new forms never before seen on earth.

This is just a beginning. In the past not nearly so much effort has gone into high-pressure work as into attempts to produce other extreme conditions, such as high temperature and

high voltage. Now the pace is quickening and important discoveries can be expected.

Like temperature and voltage, pressure is a component of energy: mechanical energy is associated with matter under pressure just as heat energy is associated with temperature or electrical energy with voltage. Variations in these components cause changes in the behavior of matter: melting, boiling, ionization and so on. When the range of variation for pressure is extended as far as it has been for other components, important new phenomena will surely come to light.

In a general way we know what sort of structural changes pressure induces in matter, but the important details can only be discovered by experiment. If we start with a sample of matter in its least compressed, or gaseous, state, the application of pressure eventually liquefies it (unless its temperature is too high). Further increase in the pressure squeezes out the holes in the complex but not completely disordered arrangements of atoms or molecules in the liquid, decreasing its fluidity. Still higher pressures force the molecules into the highly ordered lattice-structure of a crystalline solid. In many such solids several types of arrangement are possible, and increasing pressure pushes the material into a succession of different "phases" in which the molecules fall into different geometrical patterns as they are packed closer and closer together. After the closest possible packing has been achieved, the atoms themselves

begin to deform, their electrons being forced into abnormal quantum orbits. With still higher pressure some electrons will actually be squeezed out of their usual molecular orbits and freed to move through the material. At this point the substance has become a metal. Within the range of laboratory pressures now attainable, samples of all these effects can be observed.

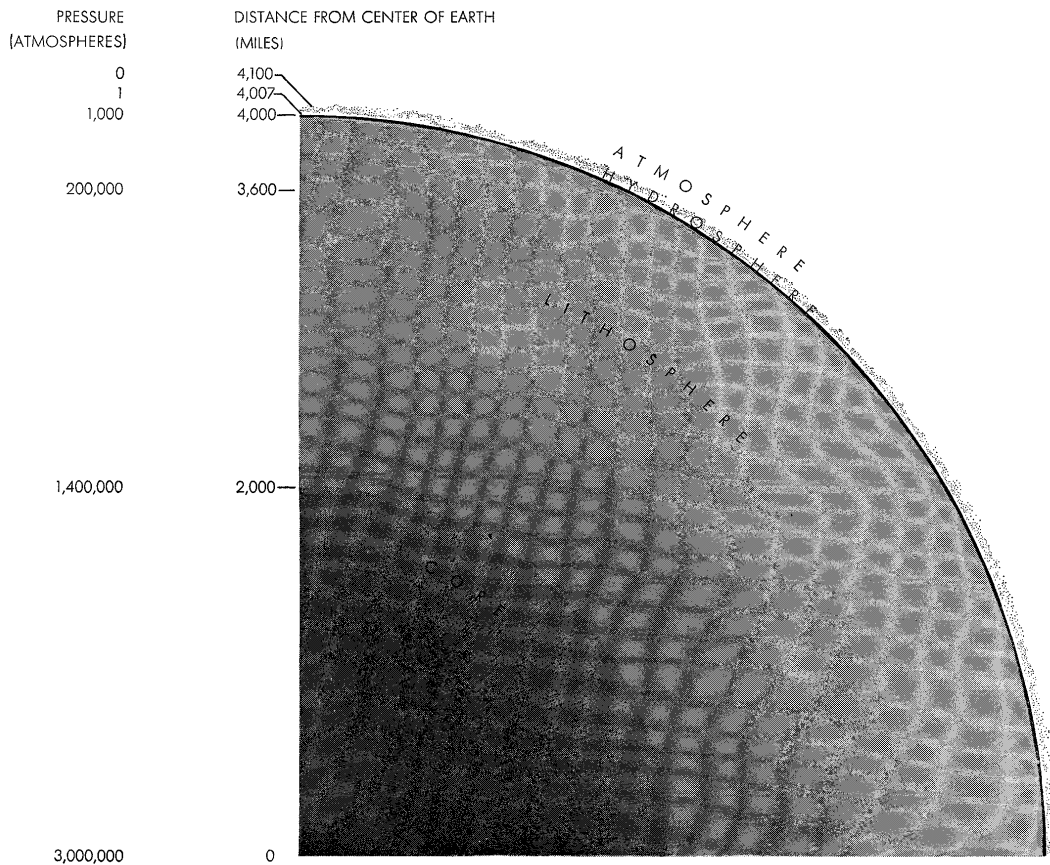
At tremendous pressures, beyond anything that can be imagined in the laboratory but existing in the interiors of stars, matter becomes completely “degenerate.” All the electrons have been stripped from their nuclei. Conceivably still higher pressure could bring the nuclei so close together that they would begin to fuse.

Another way of looking at pressure effects is from the viewpoint of thermodynamics and reaction rate. Thermodynamics is the science of the possible. It specifies the conditions—temperature, pressure, electromagnetic-field strength and so on—under which a given reaction can occur. A rise in pressure may transform an impossible change into a possible

one.

But to say that something *can* happen is not to say that it will happen in a finite length of time. It is the province of reaction-rate theory to predict how fast reactions will go and to tell how to speed them up or slow them down. In their effects on reaction rates (and on many other properties of matter) pressure and temperature are opposites. Increasing temperature tends to loosed matter, shaking up its atoms and making them react faster. Increasing pressure makes matter more dense, diminishing the mobility of the atoms and slowing down reaction rates.

Thermal energy has been widely used to control thermodynamic conditions and reaction rates ever since man started playing with fire. Pressure has been rarely exploited for these purposes, although it can be equally effective. Furthermore, the combined action of pressure and temperature as levers for manipulating a reacting system offers far greater possibilities than does either alone, as we shall see. In fact, many transformations (*e.g.*, graphite into diamond) become possible only under conditions of both high pressure and high temperature.



TERRESTRIAL PRESSURES range from zero at the top of the atmosphere to three million atmospheres (44 million pounds per square inch) at the center of the earth. Discontinuities, as between

air and water or water and solid earth, are marked by abrupt changes in pressure. The transition from lithosphere to core may be a change in crystal structure, not a change from stone to iron.

How are high pressures produced in the laboratory? Basically by the application of principles that have been well known since the time of Archimedes. Pressure is the force exerted per unit area of surface. To make the pressure large, use a large force or a small area. The typical high-pressure device does both. A comparatively small force is applied to a piston in a narrow-bored cylinder filled with liquid. Suppose that the force is 500 pounds and the area of the piston half a square inch. Then the pressure exerted by the piston on the liquid ahead of it will be 1,000 pounds per square inch.

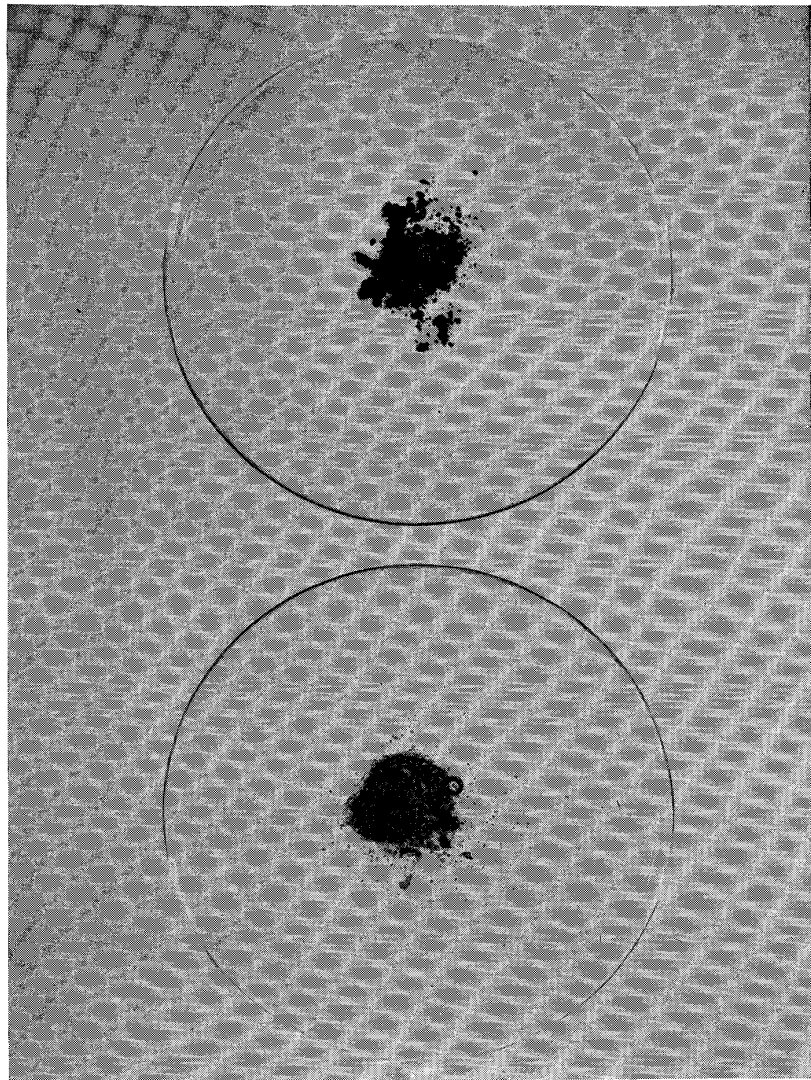
The narrow cylinder connects with a wider one, also filled with liquid. According to an elementary law of physics the pressure is transmitted undiminished through all of the liquid and against the walls of the cylinder. Thus against every square inch of the large cylinder and its piston there is a force of 1,000 pounds. Let us say that the large piston has an area of 200 square inches. The total force pushing it must then be 200 times 1,000 or 200,000 pounds.

Now let the large piston push against a thin rod, say a third of a square inch (about 40,000 atmospheres). Ahead of the rod, and receiving this pressure, is the sample to be studied.

Theoretically there is no limit to the pressure that such an arrangement could produce. In practice the limit is set by the strength of the materials of which the apparatus is made. Eventually the cylinders will burst of the pistons and connecting rods crumble under the huge forces. Of the materials now available cemented tungsten-carbide has the greatest compressive strength. In simple piston-and-cylinder devices it withstands pressures up to 50,000 atmospheres. Although it has a high

resistance to crushing, its tensile strength is rather low. Consequently tungsten-carbide cylinders must be supported by massive alloy-steel binding-rings to prevent them from bursting. When the cylinder is adequately reinforced, the pressure can be increased until the piston fails.

One conceivable way to increase the effective strength of construction materials is to "cascade" piston-and-cylinder combinations, nesting one inside the other. Failure results differential, not absolute, pressure; thus a



CONVERSION of graphite (*top*) to diamond (*bottom*) is accomplished by applying high pressure and high temperature, and then lowering temperature before pressure.

cylinder containing a pressure of 100,000 atmospheres, but located inside a second cylinder where the pressure is 50,000 atmospheres, is subject to a net pressure of only 50,000 atmospheres. By linking the nesting units so that the large piston of one stage activates the small

piston of the next, tremendous pressures could be attained. However, mechanical difficulties have thus far restricted cascading to two stages, and the presses that have been built in this way afford no method of heating the compressed sample.

The most successful and versatile devices now operating above 50,000 atmospheres stem from the apparatus originally developed by Percy W. Bridgman of Harvard University, a lifelong pioneer in high-pressure research. Obviously the weakest link in the pressure chain of the hydraulic arrangement described above is the thin rod that concentrates the thrust of a large piston into a small area. Bridgman replaced the rod by a thick cylindrical "anvil" bluntly tapered at one end. The tapering cone does not extend to a point but is cut off to expose a circular face about a fifth of a square inch in area. This is the working surface, where the total force is finally concentrated. The tremendous load on the face fans out through the mass of material behind it and is thus dispersed. Some of the dispersed force tends to make the anvil explode laterally, and is counterbalanced by steel binding-rings.

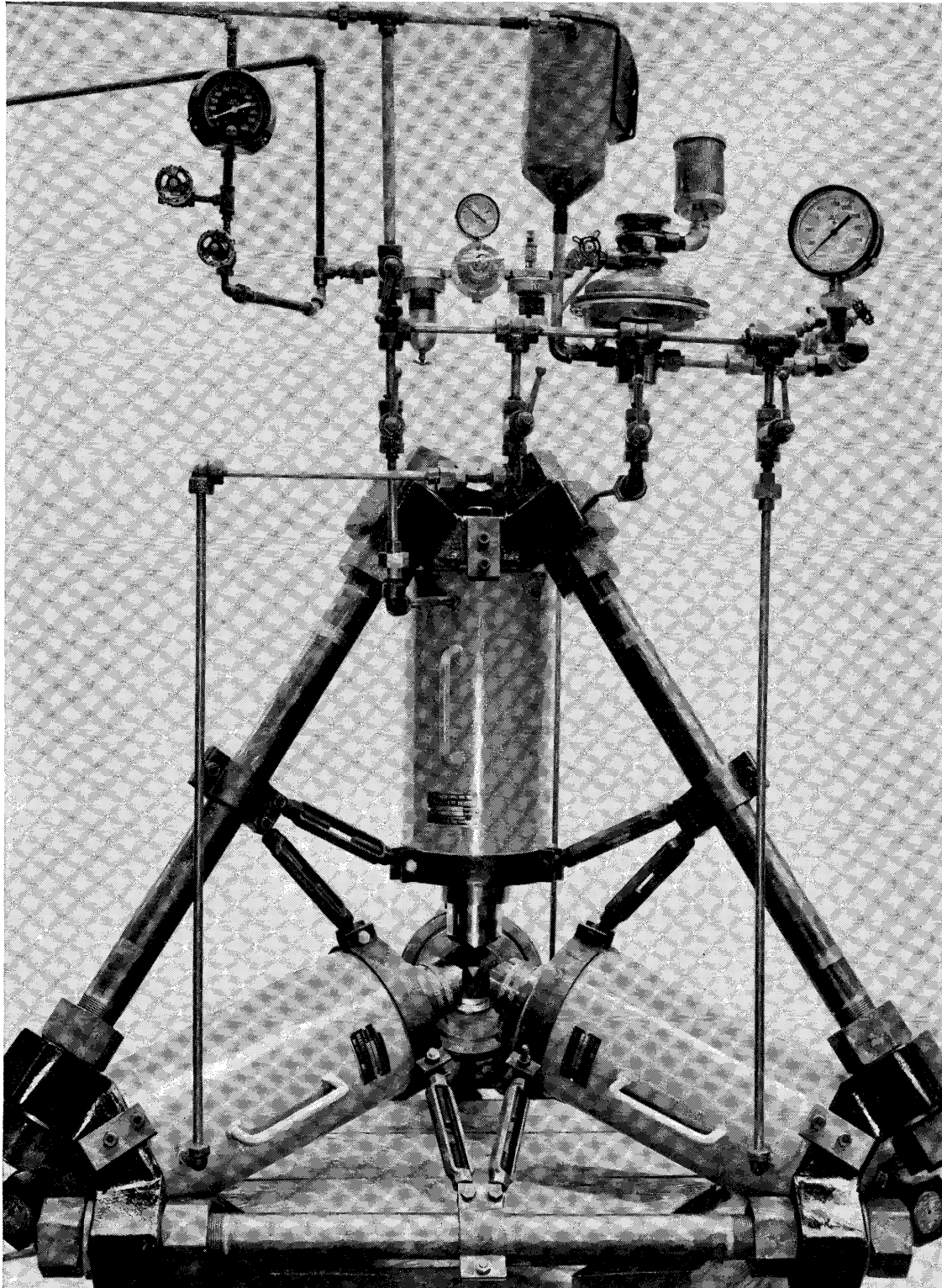
The complete assembly consists of a pair of opposed anvils, each impelled by a piston-and-cylinder device. The sample to be compressed is prepared in the form of a disk about .01 inch thick and a diameter slightly less than that of the anvil faces. To prevent the sample from being squeezed out from between the anvils Bridgman surrounded it with a thin circular gasket made of catlinite, or pipestone. This fine-grained silicate mineral is easily compressible. Furthermore, its surface friction is high under large forces, and in thin sections it has considerable strength in directions perpendicular to the force. Thus the gasket can be compressed without being extruded, and it holds the sample in place.

Bridgman's anvils can operate at pressures up to 200,000 atmospheres. One of their major applications has been to determine how the electrical resistance of many substances varies with pressure. They have also been used to study the formation of minerals. This process requires high temperatures as well as pressures, so the anvils must be placed in a furnace. Heating weakens them, however. At 1,000 degrees centigrade they can develop only about 20,000 atmospheres before failing. At this temperature and pressure the carbide begins to yield or flow. Another drawback of the Bridgman anvils is the small size of the samples they can handle.

Both these difficulties have been considerably reduced in a device known as the tetrahedral-anvil apparatus. It employs four tungsten-carbide anvils, tapered to end in triangular rather circular faces [*see illustration on page 65*]. The anvils are arranged symmetrically around a central point and are forced together by a hydraulic mechanism. If they came into contact, they would enclose a volume in the shape of a regular tetrahedron, or pyramid. Instead they press against the faces of a slightly larger pyramid made of pyrophyllite, a mineral closely related to catlinite. This solid tetrahedron serves as a pressure-transmitting medium, a thermal and electrical insulator and a gasket. The sample is placed in a tunnel drilled through the pyrophyllite [*see top illustration on page 66*]. Around the sample is a carbon or metal sleeve that heats up when an electric current passes through it. Metal tabs run from the ends of the heater tube out to the faces of the tetrahedron, where they pick up current supplied through the anvils themselves. As the anvils move together, the edges of the pyrophyllite are squeezed out and form a gasket.

Tetrahedral anvils have worked at pressures as high as 130,000 atmospheres simultaneously with temperatures up to 3,000 degrees C. During an experiment the sample is of course completely enclosed. The effects of pressure are determined by noting changes in its electrical resistance and by measuring its temperature with a thermocouple. Soon it may be possible to make X-ray diffraction pictures during an experimental run so that structural changes can be followed in greater detail.

With the pressures and temperatures now available it is possible to duplicate some of the geologic processes that have taken place tens of miles below the earth's surface. Many of the earth's minerals have been synthesized, including all the natural garnets (cubic silicate-crystals), some aluminum silicates and other substances known as pyroxenes and epidote-group minerals. Knowing the temperature and pressure required to make these substances, we can deduce the conditions of their natural formation. For example, phase-stability studies on the constituents of so-called eclogite rock show that it could not have been made at a pressure less than 30,000 atmospheres. This means that it originated at least 72 miles below the earth's surface. As these studies continue, the geological history of the earth will become clearer.



TETRAHEDRAL-ANVIL APPARATUS consists of four high-pressure cylinders whose pistons actuate the anvils. Three of the

At this point experiments can throw only an indirect light on conditions in the deep interior of the earth, where pressures far exceed the

cylinders are seen in side view; the fourth, head-on at bottom center. The anvils themselves protrude from the ends of the cylinders.

capacity of laboratory equipment. As is well known, the density of matter in the earth increases abruptly from the mantle to the core. It

has been generally supposed that this sharp increase represents a change in composition from olivine (an iron-magnesium silicate) in the mantle to iron in the core. Recently, however, some geophysicists have suggested that the core too is composed of olivine. The sudden jump in density is explained by assuming that the tremendous pressure at the bottom of the mantle (1.4 million atmospheres) is just enough to convert the material from its normal state, with a density of 3.3 grams per cubic centimeter, to a metallic substance with a density of 10 grams per c.c. Assuming that all the planets have the same average composition, this idea gains support from the fact that the smallest ones, Mars and Mercury, appear not to have a core. Their interior pressure is presumably not high enough to force olivine into the metallic phases.

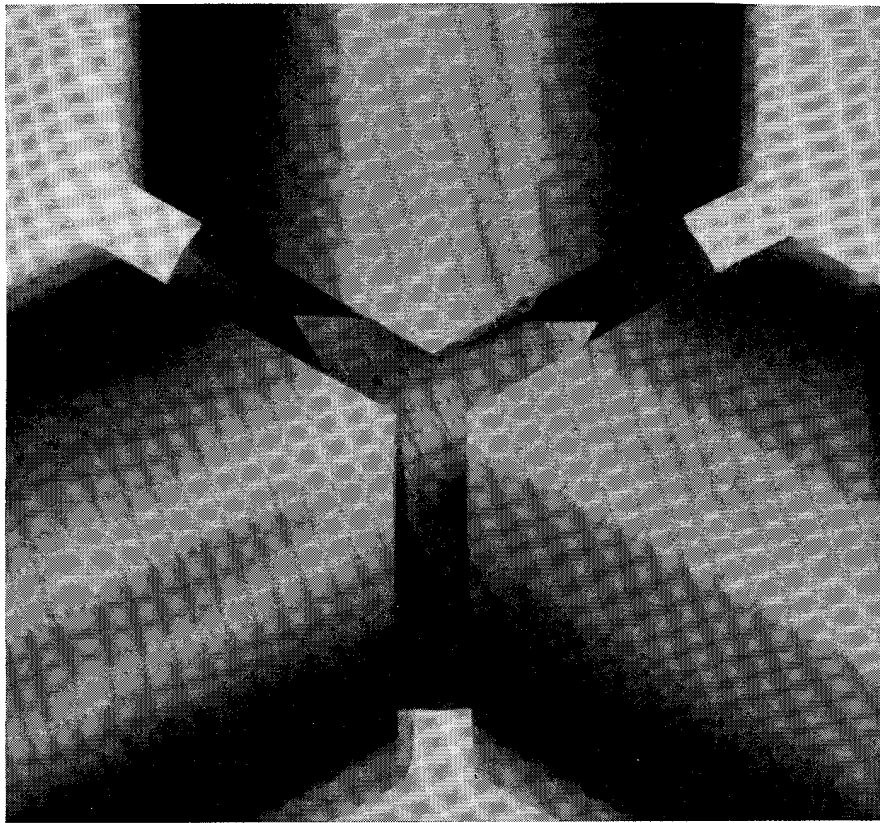
Nor, by a long shot, is the pressure attainable in the laboratory. However, similar transitions can be observed. Tin exists in a nonmetallic gray form with a density of 5.75 grams per c.c. Pressure converts it to metallic white tin with a density of 7.28 grams per c.c. Arsenic and phosphorus are other examples of two-phase elements.

In this connection it is interesting to note that according to theoretical calculations ammonia should change to a metal at something over 200,000 atmospheres, and hydrogen at about 400,000. Such pressures do not seem very far out of reach. Soon it may be possible to create, in effect, a whole new periodic table of the elements!

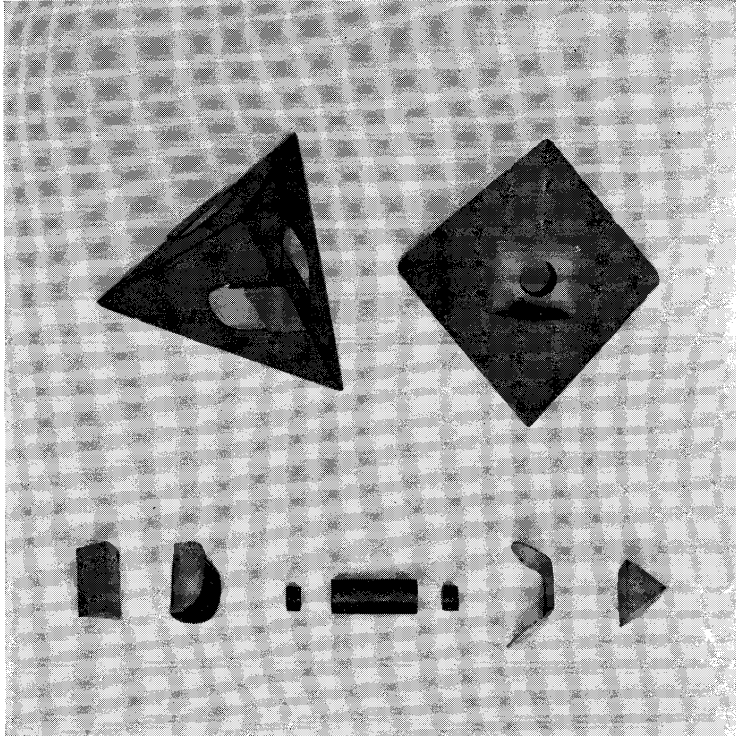
Of all the naturally occurring substances to be synthesized by high pressures, diamond is undoubtedly the most glamorous [see "Synthetic Diamonds," by P.W. Bridgman; Scientific American,

November, 1955]. Thousands of carats of man-made industrial diamonds have been produced since their synthesis was announced four years ago. Although these diamonds still cost somewhat more than natural ones, their superior performance in certain grinding processes makes them worth the difference. As far as is known no one has yet made diamonds of gem quality and size, but it will surely be done.

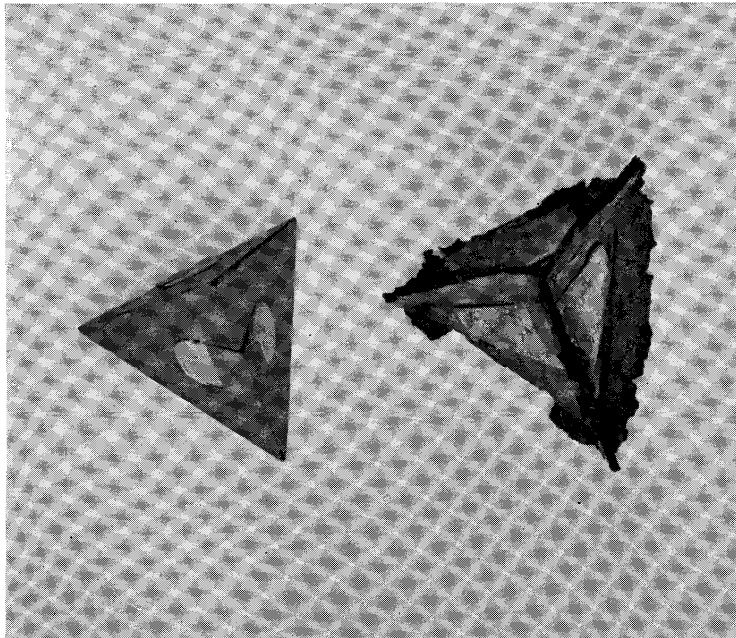
With its separate control over temperature and pressure the tetrahedral-anvil device is a more versatile creator than the earth itself. By means of a four-step operation it can make materials that are not found in nature. The steps are: (1) raise the pressure to a point where a desired transition becomes thermodynamically possible; (2) raise the temperature, increasing the reaction rate enough to make the transition proceed at a reasonable speed; (3) after the reaction is complete, lower the temperature, decreasing the reaction rate; (4) lower the pressure. The newly formed material may now be in a metastable state. According to thermodynamics it should revert to its original condition. This sequence does not usually occur in nature. When a



ANVILS, made of cemented tungsten-carbide, taper to triangular faces about .25 square inch in area. When the four anvils are pushed together, they enclose a tetrahedral volume.



TETRAHEDRAL GASKET on which anvils exert pressure is made of a mineral called pyrophyllite. At top left is an assembled gasket. At top right a gasket is stripped to show hole in which sample is placed. At bottom, from the center out, are the tube which contains the sample, plugs to close the tube, conducting metal tabs and pieces to cover the tabs.



GASKET IS DEFORMED (right) by pressure of anvils. The pyramidal structure holds the sample in place, transmits pressure and serves as an electrical and thermal insulator. substance is heaved up toward the surface from a deep region where the temperature and pressure are high, the two variables generally decrease simultaneously. Hence a metastable material

will have a chance to change back to its stable low-pressure form. Diamonds are metastable at atmospheric pressure. Rare as they are it is almost a miracle that they are found in nature at all. Created under conditions of high pressure and high temperature deep in the earth, they should change to graphite as they are brought toward the surface.

Among the most interesting laboratory creations are the new "materials" coesite and borazon. The former is composed of silicon dioxide (SiO_2), as is quartz. Its density is three grams per c.c., as compared with 2.7 for quartz. Coesite has the remarkable property of resisting attack by hot hydrofluoric acid, which makes it an ideal material for special laboratory apparatus.

Borazon is a crystal of boron nitride (BN) in which atoms of boron and nitrogen form a cubic array. In its normal, low-pressure form the atoms of boron nitride form a hexagonal array like that of graphite; it is similar to graphite in being a slippery solid, although it is white instead of black. Borazon, the high-pressure form, is completely analogous to diamond. It is about as hard, and apparently more resistant to heat. Very likely it will take a place alongside diamond as an industrial abrasive.

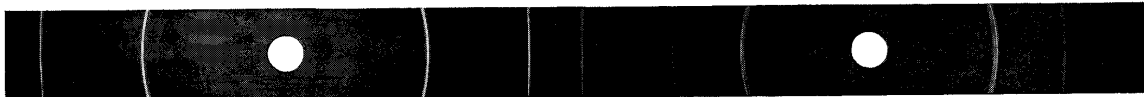
Also like diamond, borazon has enormous compressive strength, greater than that of tungsten carbide. It may eventually be used to make cylinders, pistons and anvils which will make possible higher pressures than can now be achieved. Thus high-pressure research may hoist itself by its own bootstraps, manufacturing materials that will carry it into new regions.

The melting point of solids is strikingly sensitive to pressure. Most substances expand upon melting, the liquid being less dense than the solid. As might be expected, increasing



GRAPHITE has an X-ray diffraction pattern that reveals its hexagonal crystal structure. The sharp luminous bands around the hole

at left were formed by X-rays scattered in a forward direction; the faint bands surrounding hole at right, by X-rays scattered backward.



DIAMOND diffraction pattern indicates a cubic crystal. X-ray beam passed through holes in strip of film which surrounded the pressure raises the melting point of such solids. A higher pressure makes it harder for them to expand, so to speak; therefore they must be heated to a higher temperature in order to melt. Under a pressure of 100,000 atmospheres the melting point of some silicates increases more than 1,000 degrees! Again we have a bootstrap effect. Silicates used as gaskets in the anvil apparatus become increasingly resistant to heat as the pressure goes up, so that experiments can be carried out at higher temperatures than might have been expected.

As a matter of fact, it is quite possible to work with "liquid" refractories under high pressure. A liquid can flow only if it contains holes into which molecules can move. At pressures of the order of 100,000 atmospheres the number of holes is greatly reduced, and the material becomes extremely viscous. It maintains its position and shape even though nominally liquid, continuing to serve as a useful container.

There are a few solids, among them ice, bismuth and germanium, that contract upon melting, the liquid having a higher density than the solid. In these abnormal materials pressure lowers the melting point. The melting point of ice decreases uniformly with increasing pressure, from zero degrees C. at one atmosphere to -22 degrees at 2,045 atmospheres. At this point a new ice forms which is denser than water. Hence a further rise in pressure now raises the melting point in the normal way. In fact, as pressure goes higher and higher, ice passes through several different phases, all of them normal with respect to melting point. The same thing happens with bismuth. Its melting point decreases from 271 degrees C. at one atmosphere to 186 degrees at 16,900. Between 16,900 and 120,000 atmospheres seven additional solid phases of bismuth have been discovered, all normal. Germanium's melting point, 936

degrees at one atmosphere, goes down to 360 degrees at 180,000. No new phases have been encountered.

Abnormal solids offer another way of producing high pressures. By enclosing water in a strong, inexpandible vessel and then freezing it, a pressure of 2,045 atmospheres could be attained. Using germanium it should be possible to go higher than 100,000. So far these possibilities have not been exploited in a practical way.

sample. These X-ray photographs were made by I. Fankuchen and A. Amendola of the Polytechnic Institute of Brooklyn.

As in the case of melting, the transition between liquid and gas is also related to pressure. The condensation point of a gas or vapor, i.e., the pressure at which it condenses to a liquid, increases with temperature. Every gas has a so-called critical point—a temperature above which no pressure can liquefy it. Do normal liquids have a similar point for freezing? Physicists have debated the question for years. It has not yet been answered, but with the help of apparatus to produce high temperature and pressure, it may be soon.

Other intriguing questions suggest themselves. Electrical conductivity increases with pressure. At 100,000 atmospheres the increase is about 20 percent for most metals, but in a few cases it is as much as 400 percent. What would happen at still higher pressures? Would some metals become superconducting?

Almost anywhere that physical or chemical change occurs, high pressure has potential applications. As a final example, let us consider the field of metallurgy. Many metals are hardened by heat treatment: they are raised to a high temperature then plunged into a bath to cool off as fast as possible. Since pressure and temperature are opposites, one wonders whether the same effect might not be obtained in another way: Instead of rapidly lowering the

temperature, suddenly raise the pressure. It works. A quick application of high pressure does harden steel and other metals. Furthermore, the hardening extends throughout the mass of the material. In cooling, a hot metal unavoidably loses heat faster from the surface than from the inside. This produces a hardened skin and a softer interior. Pressure, on the other hand, is spread throughout the material almost instantaneously and all parts are equally affected.

When a molten metal solidifies, the process also takes place from the outside in. Again application of high pressure could make all parts solidify simultaneously, giving a product with different properties.

It is common knowledge that metals are not nearly so strong as they might be. Imperfections in the crystal lattices (missing or misplaced atoms and faulty arrangements, or "dislocations") make actual crystals much weaker than perfect ones would be. Furthermore, practically every sizeable piece of metal is an agglomeration of small crystals that does not have nearly the strength of a single large one. All lattice imperfections, and the grain boundaries between small crystals take up space. The metal occupies a larger volume than if its atoms were all in place in an ideal lattice. High pressure could literally squeeze out imperfections, forcing the metal to become more nearly a perfect single crystal and thus make it stronger.

A new era in high-pressure work, both in the laboratory and on the production line, is clearly on the way. It should be a fascinating and rewarding sweepstakes.