

### 3. HIGH PRESSURE, HIGH TEMPERATURE

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#### 3.1. Static Pressures and Temperatures Obtainable Today

Within the past five years, laboratory high-pressure, high-temperature apparatus has been developed to the point where pressures of 200,000 atmospheres may simultaneously be obtained with temperatures of 10,000°C. Pressures of this magnitude may be maintained for many hours. Temperatures of 10,000°C, however, may be maintained for only a few seconds. More conservative temperatures, of the order of 2,500°C, may be maintained for many hours as long as means are provided for cooling critical components of the high-pressure device.

#### 3.2. Pressure Media

Since progress in the field of high pressures at high temperature is directly dependent upon the state of the art (in regards to apparatus) a few remarks concerning apparatus development are apropos. First, let us consider the means used to heat a specimen and also the material used to transmit pressure to the specimen. The most satisfactory method for heating a specimen to high temperature is by means of some type of electrical resistance heating element located inside the pressure chamber. With such an arrangement, it becomes necessary to insulate the walls of the confining vessel from the high temperature. Sir Charles Parsons (1888), in his early diamond synthesis studies, utilized a solid refractory medium for this purpose. In his apparatus, this solid material surrounded the electrical resistance furnace and the sample contained therein and also transmitted pressure to the heating element and sample. In the past there has been considerable hesitancy to utilize a solid material to transmit pressure. It is natural to assume that there is considerable frictional "hold-up" in a solid material and therefore poor transmission. At pressures greater than 35,000 atmospheres (at room temperature) all liquids that were liquid at 1 atmosphere and room temperature have become solid. (A 50-50 by volume mixture of n-pentane and iso-pentane remains liquid to 35,000 atmospheres. All other liquids freeze at lower pressures.) Hydrogen and helium would undoubtedly be liquids in the 100,000 atmosphere range of pressure but, at the present time, have not been used as pressure media because of difficulties encountered in confining these elements at very high pressures. Media used to transmit pressures at room temperature, above 35,000 atmospheres, must of necessity, therefore, be solids. Consequently, it has become important to investigate the question as to how well various solid materials transmit, pressure within a confined volume. Some work in this connection has been reported (Bridgman, 1952; Hyde, 1957; Cho, 1958), and experience has shown that frictional holdup is much lower than originally anticipated with many types of solid materials. Fine-grained compacts such as compressed powders of MoS<sub>2</sub>, BN, cornstarch, asbestos, mica or naturally-occurring pyrophyllite and talc have been found to be good media for transmitting pressure. The use of solids to transmit pressure has simplified high-pressures, high-temperature apparatus design and opened up new design possibilities. Frictional hold-up in some designs utilizing solid media have been as low as 3 percent (Boyd, 1958). In any event, frictional hold-up is reproducible and determinable.

At pressures to 35,000 atmospheres and temperatures to 1,500°C, liquids or gases have been used to transmit pressure to a sample contained in a tube furnace (Butuzov, et al., 1953; Birch, et al., 1957). With such systems heat loss is considerably greater than it is in systems that utilize a solid pressure medium and it is necessary to use baffles and reflectors to prevent the walls of the confining vessels from becoming excessively hot.

#### 3.3. Conventional Apparatus

The usual high-pressure apparatus consists of a cylindrical vessel in which one end is fitted with a closure and the other end is fitted with a movable piston. A sample, confined by the walls of the containing vessel, the closure, and the piston, is compressed by the advancing piston. Electrical leads for making measurements and for providing heating power to a furnace confined within the device can be brought in through conical seals. Such devices when properly constructed can reach pressures in the neighborhood of 50,000 atmospheres. Failure of these devices centers around the piston. Cemented tungsten carbides are used for pistons and if materials with compressive strengths higher than those of cemented tungsten carbide

were available, correspondingly higher pressures could be obtained. Troubles connected with piston and cylinder devices are those of closure (gasketing and sealing) and the friction and binding of the piston as it moves in and out of the cylindrical chamber.

Certain "tricks" must be used to reach pressures beyond the 50,000 atmospheres that are obtainable in simple piston and cylinder devices. The strength of a right circular cylinder in compression depends (at least to pressures of several hundred thousand atmospheres) on the difference between the axial pressure and the pressure perpendicular to the axis. Thus, a cylindrical carboloy piston surrounded by a fluid at one atmosphere when subjected to an axial load of about 50,000 atmospheres will fail. However, if the same piston is surrounded by a fluid at one atmosphere when subjected to an axial load of about 50,000 atmospheres it will be able to support an axial load (for per unit cross sectional area) of 100,000 atmospheres. As a matter of fact, some experiments performed by Bridgman (1952) indicated some strengthening of material subjected to such hydrostatic pressure, and this makes it possible for the axial load to be increased even beyond that indicated.

The above consideration shows that it would be possible by "multi-staging" (a process whereby one pressure apparatus is contained inside another pressure apparatus, and so on) to reach extremely high pressure. In practice, a three-stage apparatus has never been built because of mechanical complications. Bridgman, however, has successfully operated a two-stage apparatus at room temperature at pressures of 100,000 atmospheres and has made many useful measurements in such a device. The mechanical complications in this device are rather formidable, however, and it has not been possible to insert electrical leads into the inner chamber. There are also disconcerting factors such as the fact that piston-wall friction in the inner chamber may make up 40 percent of the load exerted on the piston.

### **3.4. Massive Support Principle**

Some types of apparatus, other than two-stage design, capable of reaching 100,000 atmospheres are based on the idea of obtaining a multi-stage effect in a single stage. They are based on the so called "massive support" principle of Bridgman's. The massive support principle is the principle operating when the small faces of two broad truncated cones (called anvils) are forced together along their line of centers. The force per unit area load withstood by the truncated portion of these cones before failure is much greater than the force per unit area load that could be sustained by a right circular cylinder of the same cross section area. This is possible because the anvil faces have mechanical ties fanning out behind the surface of the truncated cone into the broad base behind the cone. This is the principle of massive support. Thin wafers of material may be subjected to pressures between the faces of such truncated cone-type anvils and may be prevented from extruding laterally by a ring-type gasket usually constructed of a fine-grained stony material such as pyrophyllite. Besides preventing lateral extrusion of the wafer-like sample, the gasket material compresses with the advancing anvils thus permitting the sample to be compressed.

### **3.5. Pseudo-Multistaging**

In addition to obtaining higher pressures by virtue of "massive support" it is possible to obtain a pseudo-multistaging effect by compressing solid materials between the sloping shoulders of the anvils. In such designs the space between the faces of the anvils is subjected to the highest pressure while the materials located between the sloping shoulders of the anvils provide a pressure gradient such that pressure decreases in going away from the anvil faces. This additional support given to truncated cone-type anvils makes such anvils useful at still higher pressures. A design embodying this principle has been described by Fitch, Slykhous and Drickamer (1957). This particular device is suitable for optical studies at room temperatures at pressures to 200,000 atmospheres.

### **3.6. Belt Apparatus**

A high-pressures, high-temperature device known as the Belt apparatus that was devised by Hall in 1953, is capable of reaching pressures in the neighborhood of 200,000 atmospheres simultaneously with temperatures above 3,000°C (Hall, 1960). Another apparatus, the Tetrahedral Anvil Apparatus, developed by Hall (1958a, 1958b; Hall and Kistler, 1958) at Brigham Young University, has been successfully used at pressures of 130,000 atmospheres and temperatures of 3,000°C. This device utilizes the principles of massive support and motion via a compressible gasket introduced by Bridgman.

### 3.7. Possibilities of Higher Pressures for the Future

The number of runs that can be made in a high-pressure device before failure is set by the pressure of operation. Several dozen runs may be possible before apparatus failure at 100,000 atmospheres, about six runs may be possible at 150,000 atmospheres and an average of only one run before failure at 200,000 atmospheres. The upper limit of pressure obtainable in a device is that pressure at which failure will occur on the average on each run. The upper limit of pressure of any given device is set by the materials of construction. The materials with the highest compressive strengths available today (in large sizes) are the cemented tungsten carbides. When materials of higher compressive strengths become available the pressure obtainable in any device will increase in direct proportion to the increased compressive strength. Diamonds have the highest compressive strength of any known material. Although the cost and availability of massive single crystals of diamond prohibits their use in most high-pressure apparatus, fine diamond powder is readily available and the cost is low enough that it could be used if it were possible to make a cemented diamond composite analogous to the cemented tungsten carbides. There has been a small amount of effort to make such a material. Certainly, additional effort in this direction would be worthwhile.

The principles of massive support and of motion via compressible gaskets have been the prime factors responsible for the attainment of the pressures available today. Maximum use of these principles seems to have been achieved in the Tetrahedral Anvil device. The principle of pseudo-multistaging as used in Drickamer's device (Fitch, et al., 1957) has, however, not been fully exploited and it is believed that experiments with this principle in connection with the Tetrahedral Anvil device would eventually allow pressures as high as 300,000 to 400,000 atmospheres to be obtained. If an engineering material such as a cemented diamond powder with a compressive strength of 1,250,000 pounds per square inch could be made it would seem reasonable to expect that pressures of 500,000 to 600,000 atmospheres could be obtained in a pseudo-multistaged Tetrahedral Anvil apparatus.

All of the above methods of obtaining static high pressures are based on mechanical principles; i.e., the movement of pistons or anvils. It is possible to generate static high pressures by means of (a) phase changes, (b) chemical reactions, (c) thermal expansions, or (d) the pull of gravity on a long column of liquid. These methods have not had widespread use because the theoretical maximum pressures are not very high in a, b, and c and because the mechanical problems in d are difficult to resolve. For example, the maximum theoretically obtainable pressure generated by freezing water is about 2,000 atmospheres, and that obtained by freezing bismuth about 18,000 atmospheres. However, the maximum theoretically obtainable pressure generated by the freezing of germanium is at least 180,000 atmospheres and the use of this material in this manner would be worth further investigation.

### 3.8. Effects to be Expected at High Pressure

In many respects the effects of pressure are diametrically opposite to the effects of temperature. For example, when a solid material is heated it may pass through certain phase changes, it will then melt, and then become a gas. At still higher temperature a molecular gas will dissociate into atoms which will at still higher temperatures become ions. This entire process is one in which the system "opens up" and the entropy is increased. On the other hand if pressure is applied to a gaseous system, atoms may be forced to collapse to molecules, additional pressure may liquefy the gas which may later become a solid and which then may go through phase changes until a close-packed configuration is obtained. This process is one in which the system is continually "closed up" and the entropy is decreased. As an example, the entropy of potassium metal decreases by about 30 percent on compression to only 12,000 atmospheres. When systems in closest-packed metallic arrangements are compressed, it is possible to obtain a discontinuous decrease in the volume without achieving a new atomic arrangement. This occurs because the pressure is affecting the electronic structure. Important examples of this are to be found in the elements cesium and cerium. The transition in cerium has been studied as a function of pressure and temperature. At room temperature the lattice constant  $a$  of the face-centered cubic cerium lattice is 5.14Å. At a pressure of about 7,000 atmospheres,  $a$  decreases rather abruptly to 4.84Å. This corresponds to a decrease in volume of about 17 percent. As the temperature decreases below room temperature the pressure required to cause this transition decreases until at 109°K the transition occurs spontaneously at one atmosphere with an accompanying volume decrease of 10 percent. This transition is thought to be caused by a shift of  $4f$

electron to the *5d* level. This type of behavior—rare at pressures below 100,000 atmospheres—is expected to become common at pressure above 200,000 atmospheres and may become the most exciting aspect of high pressure work in the future. Since these extremely high pressures are capable of influencing electronic configurations, and since chemistry depends upon these configurations, it is possible that new and hitherto unsuspected types of chemical bonding might be obtained under very high pressure conditions. The hope that some of these new arrangements might show a degree of metastability when pressure is released is encouraged by the fact that the cerium transition is stable at one atmosphere at a sufficiently low temperature.

At a sufficiently high pressure all nonmetals could be made to pass through a metallic phase. This would happen when the kinetic energy of the electrons is raised sufficiently to allow them to escape from the electric fields of their nuclei. Calculations in the connection show that ammonia should become metallic at a pressure of about 250,000 atmospheres and that hydrogen should become metallic at pressures of about 450,000 atmospheres. At still higher pressures inner electrons as well as valence electrons would become detached from their nuclei, the individual identity of atoms would be destroyed and the material would become a homogeneous mass of nuclei and electrons. At the density of material existing in the centers of the white dwarf stars ( $10^{16}$  atms) these systems would be completely degenerate. Only the lowest accessible energy states would be occupied and in these circumstances the temperature would be effectively zero. At extremely high pressures the uncertainty principle becomes important because as matter is compressed into a smaller volume the position of individual particles is known with greater certainty. This must be offset by an increased uncertainty in the momenta of the particles and this can be accomplished only by an increase in their average kinetic energy.

### 3.9. Melting Phenomena

A pressure of 100,000 atmospheres can change the melting point of some substance by as much as 1,000°C. Pressure is probably the most important tool available for the study of melting phenomena and for the elucidation of the nature of the phenomena. There should be increased emphasis placed on studies of melting at extreme pressure with the aim of improving theories of melting.

### 3.10. Synthesis of New Materials

Just as an increase in temperature generally increases the rate of a chemical reaction, an increase in pressure generally retards the rate of a reaction because the diffusion of atoms is suppressed. In order for a chemical reaction to proceed at a measurable rate at pressures of 100,000 atmospheres, then, it is almost always necessary that the system be heated. In most instances temperatures above 1000°C are necessary to counteract the effect of high pressure in retarding reaction rates. This is the reason that it is so very important to have high pressure and high temperature at the same time.

The following new materials (stable or metastable under room conditions) have all been produced under high pressure, high temperature conditions: black phosphorus, black solid carbon disulfide, dense silica (coesite), diamond, cubic boron nitride, all five naturally occurring garnets and several new garnets not found in nature, dense boron phosphate, dense boron arsenate, and many others. Research directed at obtaining new materials by utilization of high pressure at high temperature is certainly a worthwhile program for the future.

### 3.11. Geology

A pressure of 200,000 atmospheres corresponds to that existing at a depth in the earth of about 400 miles. Temperatures existing at that depth at though to be lower than those obtainable in the laboratory. We now have a tool of obvious geological importance and certainly much will be learned in the near future concerning the nature of the interior of the earth by laboratory high-pressure, high temperature studies. Additional emphasis placed on such work would be very worthwhile.

### 3.12. Metallurgical Applications

High pressure can greatly influence solubilities, phases, voids and crystallite sizes in metal systems. It is possible to obtain metallic phases by application of high pressure that can be obtained in no other way.

The use of pressure as a variable, in addition to the variables of composition and temperature which have been extensively utilized in metallurgy, requires additional emphasis.

### 3.13. Conclusions

Temperatures of 1,000°C introduce energy into condensed systems that may be comparable to the energy associated with chemical bonds. Since ordinary flames readily produce temperatures of 1,000°C, temperatures sufficient to cause chemical changes to take place have been available for many thousands of years. The pressure required to introduce energy into condensed systems comparable to that introduced by temperatures of 1,000°C is of the order of 100,000 atmospheres. Although pressure is one of the oldest of the natural variables, such pressures have become available in the laboratory only within the past 15 years, and have been available simultaneously with high temperatures for only about five years. Consequently, research under such conditions is just getting started and it seems safe to predict that much will be learned in the near future from work in this field. It is evident that there will be contributions to most branches of the physical science (including geology and astronomy).

### 3.14. References

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