

HIGH-PRESSURE INORGANIC CHEMISTRY

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EDITED BY  
**F. ALBERT COTTON**  
DEPARTMENT OF CHEMISTRY,  
MASSACHUSETTS INSTITUTE  
OF TECHNOLOGY, CAMBRIDGE,  
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## High-Pressure Inorganic -Chemistry

By H. TRACY HALL

*Brigham Young University, Provo, Utah*

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### I. Introduction

High pressure (beyond 10,000 atm.) is a relatively new tool in chemistry. Beyond 10,000 atm. the chemist deals primarily with liquids or solids since most gases transform to a condensed phase at such pressures unless the temperature is rather high. As a matter of fact, most ordinary liquids transform to solids at a pressure of 10,000 atm. The most resistant liquid to solidification presently known is a 50-50 mixture of normal pentane and isopentane. This mixture solidifies somewhere in the vicinity of 35,000 atm. at room temperature.

Some information concerning the pressure properties of the elements would serve as a starting point for later consideration of the properties of heteroatomic systems. If the one atmosphere compressibilities ( $1/V$ )  $(dv/dP)_T$  of the condensed elements are plotted as a function of atomic number, some interesting periodicities are observed. In the first row of the periodic table a minimum is observed at carbon (in the form of diamond). Diamond is the most incompressible substance known. Proceeding through the periodic table, definite minima are observed at silicon, chromium, nickel, germanium, rhodium, tin, lanthanum, iridium and lead. Maxima in compressibility are observed experimentally for helium and are predicted for neon, argon, and xenon. Closest to the "inert gas" maxima are lithium, sodium, potassium, and cesium. Next in line are the alkaline earth metals. Cesium has the highest compressibility of the alkali metals, and is some 400 times more compressible than diamond at one atmosphere.

As pressure is increased the compressibility of the elements decreases. However, the elements with high compressibilities at one atmosphere show a much greater decrease in compressibility than the more incompressible elements. Therefore, at a pressure of 100,000 atm. (the compressibilities of about 30 elements have been measured to this pressure) the range of compressibilities has been considerably leveled. In addition, there have been some shifts to higher atomic number in relative compressibilities. Calcium, strontium, and barium at 100,000 atm. are more compressible than potassium, rubidium, and cesium.

These considerations are of general interest because the same electrons that are responsible for chemical bonding primarily determine the compressibility and, of course, the atomic size at a given pressure. Tables of atom sizes have always been useful in visualizing possible chemical compounds, probable structures, and properties of multiatom systems. The Campbell periodic table is a familiar item in this connection. As an aid to judging atomic size relationships at elevated pressures, the author has constructed the periodic table shown in Figure 1. Superimposed on the standard (one atmosphere) Campbell chart is a chart (smaller, inner circles) of atom sizes at 100,000 atm. The atomic radii at one atmosphere (upper value) and at 100,000 atm. (lower value) are enclosed within the eccentric circles which indicate the relative sizes of the atoms and ions at the two pressures. The values of radii enclosed by parentheses have been estimated by the author. All other values are based on experimental measurements taken from the literature.

### II. Effects of Pressure on the Elements

In some respects, the simplest type of chemical reaction is that in which only one kind of atom is involved as, for example, is the case in an allotropic transformation. The classic reaction of this type is the

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transformation of graphite to diamond. High pressure research and diamond synthesis attempts have been intimately connected for at least eighty years. Diamonds themselves have been the object of synthesis ever since Antoine Lavoisier in 1792 discovered (by burning diamonds in oxygen and identifying the resultant carbon dioxide) that, chemically, diamond is nothing but carbon. Attempts to make diamond have always been cloaked in secrecy, surrounded with mystery and steeped in alchemy. Through the years, chicanery,

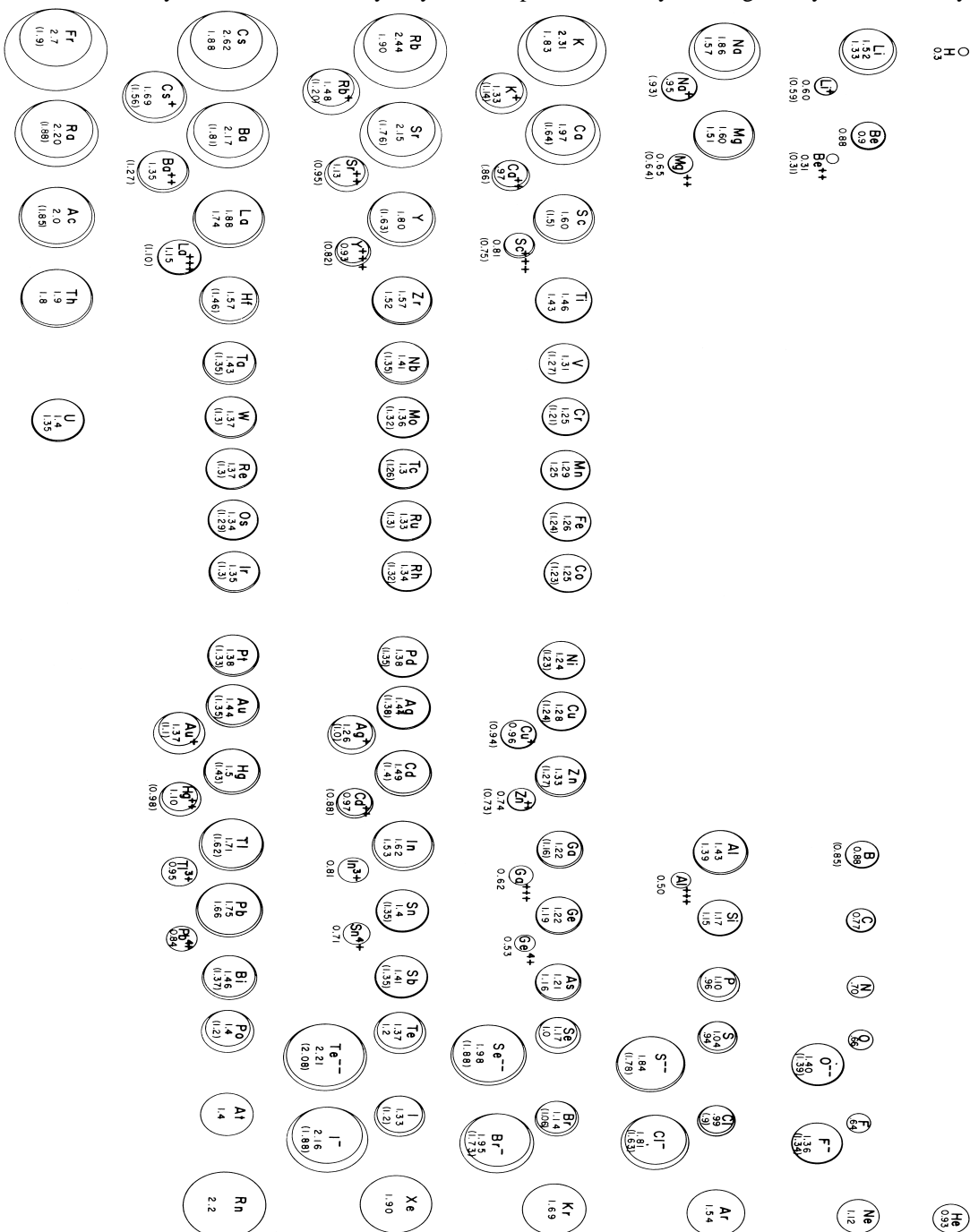


Fig. 1. Periodic chart of the elements showing relative atomic sizes at 1 and 100,000 atm. pressure. The upper numbers within the eccentric circles give the atom or ion radii (in angstroms) at 1 atm., the lower numbers give the radii at 100,000. Values in parentheses are estimated.

suspicion, jealousy, pretention, and dishonesty have lined the elusive trail to the synthesis of this most precious of diadems. When synthesis was finally accomplished, "official releases" artfully framed in corporate image, disclosed no scientific details and obscured the human aspects of the achievement. With the passing of time and the lifting of secrecy, however, it became possible to partially penetrate the obscuring screen (1,2).

The graphite-diamond transformation is a reconstructive transformation; that is, the transformation involves the breakdown of one crystal lattice and the reorganization of another. This is to be contrasted with a displacive transition which occurs with a relatively minor shift of atoms. Reconstructive transitions, unless catalyzed in some manner, usually have an appreciable activation energy compared to displacive transitions and, therefore, often proceed sluggishly. The diamond-graphite reaction proceeds readily in the presence of molten transition metal catalysts at minimum pressures of about 48,000 atm. Minimum temperatures possible are in the vicinity of 1250°C. and are made possible by the use of various alloys of iron and nickel. Pure nickel is a very effective metal to use in diamond synthesis but requires a somewhat higher pressure and temperature than the alloys (3,4). A transition metal seems to act as both "solvent" and "catalyst" in the synthesis of diamond from graphite or carbon. As a solvent, it breaks down the graphite lattice, thus freeing carbon atoms for possible reorganization into the diamond lattice. However, this does not seem to be sufficient because it has not been possible, at present, to form diamond from some inorganic compounds (5) and some metals in which carbon is soluble (6). It is likely that the transition metal is effective as a catalyst because it forms a loosely bonded carbon-metal complex in which carbon atom electrons are properly positioned to form the tetrahedral bond.

Diamond, at 25°C. and one atmosphere, is unstable with respect to graphite by 692 cal. The activation energy required for reconstructive transformation to graphite, however, is so high that this metastable material is "stable" for all practical purposes. Diamond can, however, be readily transformed to graphite at one atmosphere merely by heating it to the neighborhood of 1500°C. Under the pressure-temperature conditions where diamond is synthesized, diamond is stable with respect to graphite. In order to bring the newly formed diamond to room temperature and pressure without having it transform to graphite, it is only necessary to reduce the temperature before lowering the pressure.

Many of the elements have now been converted to new polymorphic forms by high pressure. Most of these transitions are readily reversible. In some instances, however, they are sluggish and display a hysteresis. For example, a sluggish crystal structure change from face-centered cubic to body-centered cubic occurs in the element ytterbium at 40,000 atm. As pressure is reduced, however, the high-pressure body-centered cubic phase persists until about 20,000 atm. where a sluggish transition to the normal face-centered cubic phase begins to take place (7,8). This particular transformation is unusual in that a close-packed structure is transformed into a more loosely packed structure by the action of pressure. Since a decrease in macroscopic volume accompanies this transformation, individual atoms, on the basis of a hard sphere model, must decrease in volume a proportionate amount to allow for the looser packing.

An unusual reversible transition occurs in the element cerium at about 7000 atm. (9). The volume decreases by 13% but the crystal structure which is face-centered cubic under normal conditions remains unchanged! A sharp decrease in electrical resistance accompanies the volume change (this was also true in the ytterbium transition). The elements ytterbium and cerium display anomalous valence properties, and the present theory on the pressure-induced transformations in these elements suggests that the transformations are "electronic" in nature; that is, pressure induces the transfer of electrons between nearby quantum states.

A sufficiently high pressure should induce electronic transitions in all the elements. The effect of pressure on electronic states is such that all nonmetals should ultimately become metals. This has already been observed for the elements carbon (10), silicon (11), germanium (11), phosphorus (12), sulfur (13), selenium (14), and iodine (14) and has also been observed for several compounds. Chemistry, of course, is primarily concerned with the behavior of the outermost electrons in atoms. When these electrons are grossly influenced by pressure, the ordinary chemistry of an element or compound can be expected to change considerably.

As pressure is increased beyond the point where all substances become metallic, ordinary chemistry begins to lose its meaning. A "soup" of nuclei and electrons should be obtained in the billion atmosphere range. At trillions of atmospheres, nuclei should be forced together within the critical distance of  $10^{-13}$  cm., where nuclear reactions begin to take place. Such conditions seem to exist within the interiors of some stars.

Pressure is a more effective tool than temperature for inducing polymorphic change. Fifty-three metals have been studied as a function of temperature at one atmosphere and also as a function of pressure at 25°C. In these metals, a total of 40 transitions have been induced by pressure as against only 21 induced by temperature. However, pressure and temperature properly combined are much more effective than either agent used alone. For example, when water is subjected to low or high temperature at one atmosphere, no new solids are found. If, on the other hand, water is subjected to increasing pressure at 25°C., two new

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solids are obtained. However, when the pressure-temperature field from -50 to 100°C. and 1 to 25,000 atm. is explored, five new, solid phases of ice are produced.

White phosphorus, when subjected to 12,000 atm. at 200°C., is irreversibly transformed into a black, crystalline form of density 2.69 g./cm.<sup>3</sup> (the density of white phosphorus is 1.83) (15,16). Black phosphorus has been found to have a slightly lower free energy than the white and red forms at ordinary conditions. Although it is the stable isotope, it transforms to the white form on sublimation or crystallization from a solvent. Kinetics apparently take precedence over thermodynamics in these instances. When black phosphorus, which is a semiconductor with a layer-lattice structure, is subjected to about 85,000 atm., it is reversibly transformed to an arsenic-type structure (A7, rhombohedral cell) with a calculated density of 3.56 g./cm.<sup>3</sup>. This material is a poor metal-probably like antimony or bismuth. At about 110,000 atm., the arsenic type structure transforms to a simple cubic structure with  $a = 2.377$  A. and a calculated density of 3.83. This polymorph is definitely a metal (12).

Carbon (graphite), silicon, and germanium when subjected to pressures of about 150,000, 160,000, and 120,000 atm., respectively, followed by release of pressure can be irreversibly transformed into new structures. The new carbon phase can be indexed as a cubic structure with  $a = 5.545$  A., density (estimated) = 2.80 g./cm.<sup>3</sup>, and with 24 atoms per unit cell (17). The recovered silicon phase is body-centered cubic with  $a = 6.64$  A. and 16 atoms per unit cell. The density is 2.55 and the resulting structure consists of a novel arrangement of distorted tetrahedra (18). The new germanium phase is tetragonal with  $a = 5.93$  A. and  $c = 6.98$  A. There are 12 atoms per unit cell and the theoretical density is 5.91. It is a semiconductor and readily reverts to the normal form at temperatures above 200°C. (19).

Much more could be said concerning pressure-induced phase transformations in the elements. However, the examples given above will serve to illustrate the range and complexity of the changes that occur.

### III. Effects of Pressure on Compounds

#### A. COMPOUNDS ISOELECTRONIC WITH GROUP IV ELEMENTS

Turning now to transformations and syntheses involving compounds, let us consider some analogs of carbon. Boron nitride is isoelectronic with carbon. A hexagonal form with crystal structure, density, and properties similar to graphite has been known for some time and it has long been speculated that a diamond-like form of the material ought to exist. The hoped for diamond form was synthesized by Wentorf about 1957 (20). Alkali and alkaline earth metals and their nitrides serve as catalysts for converting the hexagonal boron nitride into a diamond-like form. The minimum pressures and temperatures required are about 45,000 atm. and 1500°C. In this material, boron and nitrogen atoms alternate throughout a tetrahedrally bonded network. The density and hardness are comparable to that of diamond while the resistance of the material to oxidation at high temperatures is superior to that of diamond. It is contemplated that this substance will find use as an abrasive or semiconductor.

The list of possible binary compounds (composed of elements with principal quantum number  $n = 2$ ) that are isoelectronic with carbon is given in Table 1. Adjacent to each compound is a number giving the absolute difference in electronegativity,  $\Delta x$ , between the two elements in the compound.

TABLE I  
Binary Compounds, Isoelectronic with Carbon and with  $n = 2$ , Listed with  $\Delta x$  Values

BN	(1)	BeN <sub>2</sub>	(1.5)	LiN <sub>3</sub>	(2)
B <sub>2</sub> O	(1.5)	BeO	(2)	Li <sub>2</sub> O <sub>3</sub>	(2.5)
B <sub>3</sub> F	(2)	Be <sub>3</sub> F <sub>2</sub>	(2.5)	LiF	(3)

Elements with  $n = 2$  have the ability to form tetrahedral bonds providing the electronegativity difference between the combining atoms is not too great. In the above list, the greatest electronegativity difference is shown in the compound LiF which normally crystallizes in the NaCl (rock salt) structure with octahedral coordination. BeO, with an electronegativity difference of 2, commonly crystallizes in the hexagonal ZnO type structure where tetrahedral coordination prevails. BN, which has already been discussed, shows an electronegativity difference of 1 and exists in both a graphite-like and diamond-like form. The compound

B<sub>2</sub>O, with an electronegativity difference of 1.5, has, in recent years, been synthesized in a graphite-like form at high pressure and temperature (21). The unit cell is hexagonal with  $a = 7.981$  and  $c = 9.091$ . The calculated density is 2.24 g./cm.<sup>3</sup> which closely approximates the density of graphite. The  $a$  axis dimension is 8% greater than  $3a$  for graphite while the  $c$  axis dimension is 10% smaller than  $c$  for graphite. The synthesis of the diamond-like form of B<sub>2</sub>O by high pressure and temperature techniques has not yet been fully confirmed, but the evidence at hand foreshadows final proof of its preparation (21). From this work, the eventual synthesis of the symmetrical (with respect to B<sub>2</sub>O) compound BeN<sub>2</sub> in both graphite and diamond-like polymorphs is predicted. The diamond-like forms of B<sub>2</sub>O and BeN<sub>2</sub> should both compare favorably with diamond in hardness and should find uses as abrasives and semiconductors. It is likely that tetrahedral bonding will also be possible in the proposed compounds B<sub>3</sub>F and LiN<sub>3</sub> (electronegativity differences of 2) and these compounds should eventually be synthesized by high pressure and temperature means. The proposed compounds Be<sub>3</sub>F<sub>2</sub> and Li<sub>2</sub>O<sub>3</sub> with electronegativity differences of 2.5 are probably borderline cases with respect to forming tetrahedral bonds. In these compounds, however, it may be possible to have tetrahedral bonding while the compounds are under pressure because of the attendant decrease in  $\Delta x$ . This might be more than offset, however, by an increase in "metallicity" accompanying the increase in pressure. If tetrahedrally bonded structures did form, they would probably transform to nondirectionally bonded structures on release of pressure.

A set of nine compounds, analogous to the above, that are isoelectronic with Si can be selected from the next row of the periodic table where  $n = 3$ . They are listed, along with  $\Delta x$ , in Table II.

TABLE II  
Binary Compounds, Isoelectronic with Silicon and with  $n = 3$ , Listed with  $\Delta X$  Values

AIP	(0.6)	MgP <sub>2</sub>	(0.9)	NaP <sub>3</sub>	(1.3)
Al <sub>2</sub> S	(1.0)	MgS	(1.3)	Na <sub>2</sub> S <sub>3</sub>	(1.6)
Al <sub>3</sub> Cl	(1.5)	Mg <sub>3</sub> Cl <sub>2</sub>	(1.8)	NaCl	(2.1)

The only compounds presently known in this series are AIP with a tetrahedrally bonded zincblende structure, MgS with a rocksalt structure, and NaCl (rocksalt). With the increased metallicity of the  $n = 3$  period, the tendency to form strong directed bonds probably ceases when  $\Delta x$  exceeds 1.3. It is likely that MgS is a borderline case and could under certain conditions exist in a tetrahedrally bonded structure. This compounds Al<sub>2</sub>S and MgP<sub>3</sub> should display tetrahedral bonding and could probably be prepared under high pressure, high temperature conditions from appropriate mixtures of the elements. These compounds would be of interest as semiconductors. The remaining compounds, Al<sub>3</sub>Cl, Mg<sub>3</sub>Cl<sub>2</sub>, and Na<sub>2</sub>S<sub>3</sub> might exist in a tetrahedrally bonded state at a sufficiently high pressure, but it is questionable that this state would survive a return to atmospheric pressure.

There is, of course, a possible series of isoelectronic "cross-compounds" between the elements with  $n = 2$  and  $n = 3$  that is analogous to the above series. An average principal quantum number  $\bar{o}$  for  $A_iX_j$  compounds can be assigned as follows:

$$\bar{o} = \sum c_i n_i / \sum c_i$$

where  $n_i$  is the principal quantum number of the valence electron of the atom of kind  $i$  and  $c_i$  is the number, per formula unit, of atoms of this kind (22). The possible cross-compounds together with  $\bar{o}$  and  $\Delta x$  are listed in Table III.

TABLE III  
Binary Cross-Compounds, Composed of Elements with  $\bar{o} = 2$  and  $\bar{o} = 3$ , Averaging Four Valence Electrons per Atom, Together with  $\bar{o}$  and  $\Delta x$

Compound	$\Delta X$	$\bar{o}$	Compound	$\Delta X$	$\bar{o}$
BP	0.1	2.5	AlN	1.5	2.5
B <sub>2</sub> S	0.5	2.3	Al <sub>2</sub> O	2.0	2.7
B <sub>3</sub> Cl	1.0	2.2	Al <sub>3</sub> F	2.5	2.8
BeP <sub>2</sub>	0.6	2.7	MgN <sub>2</sub>	1.8	2.3
BeS	1.0	2.5	MgO	2.3	2.5
Be <sub>3</sub> Cl <sub>2</sub>	1.5	2.4	Mg <sub>3</sub> F <sub>2</sub>	2.8	2.6
LiP <sub>3</sub>	1.1	2.8	NaN <sub>3</sub>	2.1	2.2
Li <sub>2</sub> S <sub>3</sub>	1.5	2.6	Na <sub>2</sub> O <sub>3</sub>	2.6	2.4

LiCl	2.0	2.5	NaF	3.1	2.5
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In the above list, the compounds BP, AlN, BeS, and NaN<sub>3</sub> are known in structures possessing tetrahedral bonding. These compounds are usually prepared at approximately one atmosphere pressure. However, those who have high-pressure, high-temperature equipment will find it convenient to synthesize crystalline BP from the intimately mixed elements at about 10,000 atm. and 1800°C. The compounds MgO, LiCl, and NaF are, of course, well known substances crystallizing in the rocksalt structure. Gaging the interplay of  $\delta$  and  $Dx$  in determining the directional character of bonds, it is likely that the following compounds (from the above list) would possess tetrahedral bonding: B<sub>2</sub>S, B<sub>3</sub>Cl, and BeP<sub>2</sub>. The following would be borderline candidates for forming tetrahedral structures: Be<sub>3</sub>Cl<sub>2</sub>, LiP<sub>3</sub>, Al<sub>2</sub>O, and MgN<sub>2</sub>. The remaining compounds, Li<sub>2</sub>S<sub>3</sub>, Al<sub>3</sub>F, Mg<sub>3</sub>F<sub>2</sub>, and Na<sub>2</sub>O<sub>3</sub> would not be expected to form tetrahedral bonds.

The proposed tetrahedrally bonded materials discussed in the paragraphs would have relatively high melting or sublimation temperature, high hardness, high thermal conductivity and semiconducting properties. Consequently, these compounds are of practical as well as scientific interest.

In the wonderful world of chemistry it is possible to extend the above concepts to compounds containing more than two kinds of atoms. This, of course, greatly increases the number of possible isoelectronic types, increases the system complexity, and certainly increases the uncertainties in predicting which compounds might be formed. Lists of ternary compounds have been prepared and have been found to be useful in high-pressure synthesis research.

## B. OTHER COMPOUNDS

The above discussion has centered around compounds isoelectronic with carbon; that is, compounds in which the average number of bonding electrons per atom equals four. This is an unnecessary restriction. Compounds isoelectronic with boron (average of three valence electrons per atom), with nitrogen (five valence electrons per atom), etc., are also of interest. To illustrate, the binary compounds (with  $n = 2$ ) that are isoelectronic with nitrogen are: CO (1), C<sub>2</sub>F (1.5), BO<sub>2</sub> (1.5), BF (2.0), BeO<sub>3</sub> (2.0), Be<sub>2</sub>F<sub>3</sub> (2.5), LiO<sub>4</sub> (2.5), and LiF<sub>2</sub> (3.0). The number in parentheses following the compound is  $\Delta x$ . Where  $\Delta x$  is not too large, such compounds approximate the properties of the element with which they are isoelectronic. These kinds of compounds are of interest to the high-pressure researcher for several reasons: (1) Most of them have not yet been synthesized by other means. Consequently, it would seem prudent to try the newly available tool of high pressure. High pressure is the "brute force" method of bringing atoms into close proximity for the formation of bonds. (2) Diamond and cubic BN, and probably hexagonal B<sub>2</sub>O, are thermodynamically stable only under high pressure conditions. Consequently, high pressure is nominally required for their synthesis. It is suspected that many of the proposed compounds will also be stable only under high pressure conditions. High temperature is also required because the appropriate transformations or syntheses involve reconstructive changes where strong, directed valence bonds are broken and formed. Temperature is necessary to loosen these bonds. When strongly directed bonds are involved, the activation energy for reorganization is usually high. Consequently, once the compound has been synthesized in its thermodynamically stable high-pressure, high-temperature environment, it can usually be "captured" in a metastable form at room conditions by reducing the temperature to 25°C. before the pressure is reduced to atmospheric. (3) Regardless of the thermodynamic situation, since high temperatures are likely to be required, and, since some of the ingredients in the proposed reactions are quite volatile, high pressure is required to contain them.

Silica (SiO<sub>2</sub>) is an important inorganic compound, particularly because of its widespread occurrence in the rocks of which the earth is constituted. Silica exhibits a high degree of polymorphism over the pressure-temperature field. The most common polymorph is known as quartz. When quartz is slowly heated at atmospheric pressure, polymorphs known as high quartz, tridymite, and cristobalite are successively produced before melting occurs at about 1710°C.

In 1953 Coes (23) reported the synthesis of a new dense silica that he had encountered in the course of research directed towards the synthesis of diamond. The new form was retrieved at room conditions by the usual procedure of reducing the synthesis temperature before reducing the pressure. This new silica, coesite, can readily be made from a number of starting materials containing SiO<sub>2</sub>. Convenient conditions are 35,000 atm. and 750°C. Mineralizers (solventcatalysts) such as water, boric acid,

$\text{NH}_4\text{Cl}, (\text{NH}_4)_2 \text{HPO}_4$ , and other salts expedite the reaction. Silica gel, quartz powder, or sodium silicate solutions are good sources of  $\text{SiO}_2$ . At higher pressures and temperatures coesite can be readily formed from dry quartz. Coesite has a density of  $3.00 \text{ g./cm.}^3$  and a refractive index of 1.60 compared to corresponding values of 2.65 and 1.54 for quartz. Coesite, in contrast to quartz, is very resistant to attack by concentrated hydrofluoric acid. When heated to about  $1200^\circ\text{C.}$  at atmospheric pressure, coesite transforms to quartz and thence to cristobalite. Below  $1000^\circ\text{C.}$ , dry coesite probably persists indefinitely (24).

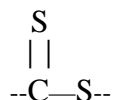
Coesite was probably the first mineral to be synthesized in the laboratory before it was discovered in nature. The first natural occurrence of coesite was reported in 1960. It was identified as an abundant mineral in sheared Coconino sandstone at Meteor Crater, Arizona, and was formed from quartz by the action of pressure and temperature accompanying meteoric impact (25).

A silica, still more dense than coesite, was reported to have been made from quartz at a pressure of about 160,000 atm. (now corrected to about 120,000 atm.) and a temperature of about  $1300^\circ\text{C.}$ , by Stishov and Popova in 1961 (26). This new polymorph is isostructural with rutile (27) and is 47% denser than coesite and 62% denser than quartz! It is the first compound known in which six oxygen atoms are coordinated about a silicon atom rather than the usual four. The new polymorph has been named stishovite. Its mean index of refraction is about 1.81 and its density is about  $4.30 \text{ g./cm.}^3$ . Stishovite has now been found along with coesite in meteorite craters and, like coesite, was formed by the action of transient pressure and temperature generated by impact (28). Stishovite is more resistant to attack by hydrofluoric acid than coesite, but is less resistant to thermal decomposition. At temperatures slightly above  $400^\circ\text{C.}$  stishovite breaks down to an amorphous material (24). The above discoveries concerning the effects of pressure on  $\text{SiO}_2$ , coupled with other discoveries emanating from high-pressure, high-temperature research on silicate materials, have important Implications concerning the nature of things at great depths within the earth.

The abundant effects of high pressure/temperature on  $\text{SiO}_2$  have naturally prompted studies on analogous substances. In the synthesis of isoelectronic analogs of diamond, each atom in the structure, regardless of kind, would be required to approximate the properties of a tetrahedrally bonded carbon atom. In a silica analog, however, the bonding properties of two atoms, namely oxygen and silicon, must be approximated. Furthermore, the ratio of two oxygen-like atoms to one silicon-like atom must be preserved. Silicon can be approximated by such combinations of elements as BP,  $\text{Al}_2\text{S}$ ,  $\text{MgP}_2$ ,  $\text{MgS}$ , etc., as discussed above under the subject of diamond analogs. Combined with oxygen, these would yield the possible silica isotopes of  $\text{BPO}_4$ ,  $\text{Al}_2\text{SO}_6$ ,  $\text{MgPO}_6$ ,  $\text{MgSO}_4$ , etc. Oxygen can be approximated by such combinations as NF,  $\text{CF}_2$ ,  $\text{BF}_3$ , etc. Combined with silicon these would yield the possible silica isotopes of  $\text{SiNF}$ ,  $\text{Si}_3\text{C}_2\text{F}_4$ ,  $\text{Si}_2\text{BF}_3$ , etc. There are, of course, many possible cross-combinations and if the elements with  $n = 2, 4$ , and 5 are brought into the picture, the total number of possibilities increases considerably. There are yet other isoelectronic analogs for silica. For example, consider the compounds in which there are a total of three atoms and 16 valence electrons, such as BOF and  $\text{BeF}_2$ . Taken all together, the total number of possible combinations becomes very large. However, only a very few of the possible combinations have been explored by high-pressure, high-temperature techniques. The compounds  $\text{BeF}_2$ ,  $\text{AlPO}_4$ ,  $\text{AlAsO}_4$ ,  $\text{AlVO}_4$ ,  $\text{MnAsO}_4$ ,  $\text{GaAsO}_4$ ,  $\text{GaSbO}_4$ ,  $\text{BPO}_4$ ,  $\text{BVO}_4$ ,  $\text{BASO}_4$ ,  $\text{FePO}_4$ , and  $\text{FeAsO}_4$  have been studied by Datchile and Roy (29).  $\text{BeF}_2$  was found to transform from a quartz form to a coesite form at about 22,000 atm. at  $500^\circ\text{C.}$  At the same temperature,  $\text{BPO}_4$  transforms from a cristobalite to a quartz form at 46,000 atm. and  $\text{MnPO}_4$ ,  $\text{FePO}_4$ ,  $\text{GaPO}_4$ , and  $\text{AlPO}_4$  all transform to previously unknown forms at about 55,000 atm.  $\text{BASO}_4$  has also been found to transform to a quartz form at about 40,000 atm. and  $500^\circ\text{C.}$  (30,31).

A rutile form of  $\text{AlAsO}_4$  has been prepared at 90,000 atm. and  $900^\circ\text{C.}$  (32). The density is  $5.15 \text{ g./cm.}^3$ , an increase of 54% over the quartz modification. A rutile form of  $\text{CrVO}_3$  has also been made by reacting mixtures of  $\text{Cr}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  at  $750^\circ\text{C.}$  and 60,000 atm. and a new orthorhombic form of  $\text{FeVO}_4$  has been synthesized from  $\text{Fe}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  under the same conditions (33).

In 1941, Bridgman (34) changed liquid  $\text{CS}_2$  into a black, semiconducting solid at  $175^\circ\text{C.}$  and 40,000 atm. The same black solid can be prepared by heating and pressuring a stoichiometric mixture of carbon and sulfur (5). Infrared studies (35) suggest that this material has a linear polymeric structure containing units





Therefore, it differs considerably from the  $\text{SiO}_2$  structures. Attempts to synthesize analogous solid forms of  $\text{CO}_2$  in the Brigham Young University high-pressure laboratory have not yet met with success. It may be that  $\text{COS}$  would be a better candidate for synthesis.  $\text{BeCl}_2$  might also behave similarly to  $\text{CS}_2$ .

An encyclopedic discussion of all the systems that have been investigated at high pressure-temperature does not meet the objectives of this paper. Suffice it to simply mention some additional systems that have been studied: glass, a large variety of minerals, molybdates, carbides, borides, silicides, oxides, sulfides, selenides, rare-earth compounds, II-VI and III-V and related solid-state compounds, carbonates, sulfates, chlorides, hydrides, etc. Many new materials have resulted from these studies. Organic systems, particularly polymerizable substances, have attracted increasing attention at pressures beyond 10,000 atm. Radiation has been used in conjunction with pressure and temperature in some polymerizations. Pressure-temperature has proved useful as an agent to affect isomerization, dehydration, oxidation, hydrogenation, protein denaturation, solvation, solubilization, precipitation, and so forth.

#### IV. Effects of High Pressure on Properties

In addition to syntheses, various types of measurements of interest to the chemist have been made at high pressure. For instance the influence of pressure on the ionization of water has been measured (36). The ionization increases regularly, with pressure, until at  $25^\circ\text{C}$ . and 2000 atm. the ionization constant is four times as great as at 1 atm. and  $25^\circ\text{C}$ . The ionization of weak electrolytes and the dissociation of complex ions also increases considerably with pressure due to the decrease in volume that accompanies ionic solvation (37,38). The ionization constant of dilute ammonia solution is increased by a factor of about 500 at a pressure of 12,000 atm. and  $45^\circ\text{C}$ . (39). The basic ionization constant of piperidine in methanol at  $45^\circ\text{C}$ . increases by a factor of about 1100 at 12,000 atm. This is a greater effect than has been found to occur in aqueous solutions of weak bases and is attributed to the greater increase in the dielectric constant of methanol at high pressure (40).

Melting points are drastically affected by the pressures now available in the laboratory. The fusion curves of many of the elements and several compounds have now been determined at pressures to 60,000 atm. and, in a few instances, beyond. Most melting points increase with pressure in accordance with the fact that the density of the solid phase is usually greater than that of the liquid at the melting point. Tin and indium with normal melting points of  $232$  and  $156^\circ\text{C}$ . melt at  $460$  and  $400^\circ$ , respectively, at 65,000 atm. (41). The first fusion curve to be determined to very high pressures was that of germanium (42). Germanium is a material in which the liquid is denser than the solid at the melting point. Consequently, the fusion curve falls with increasing pressure. The melting point of germanium at one atmosphere is about  $900^\circ\text{C}$ . At about 115,000 atm. the melting point has decreased to about  $375^\circ$ --a melting point lowering of  $525^\circ\text{C}$ .

The rates of chemical reactions in solution at high pressure have been the subject for considerable research. Pressure provides an additional variable, besides the usual variables of temperature and composition, for elucidating the mechanisms of reactions and for understanding rates. Hamann (43) has listed several classes of reactions such as unimolecular dissociations, bimolecular associations, bimolecular exchanges, and double decompositions and has indicated the number of bonds broken or formed, the relative change in the number of ionic charges, the activation volume change of the solvent, and the activation volume change for the reacting molecules. He then gives the expected sign of the overall change in activation volume. If there is an increase of activation volume, pressure will, in general, decrease the rate of the reaction. If, on the other hand, the volume decreases on passing from the initial to the activated state, pressure will accelerate the reaction. Hamann lists a number of reactions for which the experimental results confirm the theoretical conclusions.

In connection with reactions at high pressure, the effects of pressure combined with shear have received attention for some time. Bridgman (44,45) performed the first experiments of this type. He used his opposed flat anvil apparatus (to be described later) to generate the pressure in combination with a rotatable anvil positioned between the opposed anvils. In examining hundreds of substances, he observed various mechanical and chemical effects. Some transitions, decompositions, and syntheses were caused to take place in the presence of shear that would not take place under a purely hydrostatic pressure. More recently, Jamieson and Goldsmith (46) and Datchile and Roy (47) have investigated reactions occurring during grinding in mechanical mixers and mortars. Jamieson and Goldsmith ground various carbonates for periods up to three days. Calcite was partially converted to aragonite. Local pressures involved in mortar

grinding of calcite were estimated to reach 20,000 atm. Several mixtures of pure carbonates reacted to form heterogeneous solid solutions, several pure carbonates were caused to decompose, and in the case of  $\text{MnCO}_3$ , at least two oxidation states were attained after loss of  $\text{CO}_2$ . Dachille and Roy studied the effects of grinding on  $\text{MnF}_2$ ,  $\text{BeF}_2$ ,  $\text{SiO}_2$ ,  $\text{PbO}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ , and  $\text{BaSO}_4$ . These substances have pressure-induced transitions at room temperature (extrapolated from higher temperature results) at pressures of 9500; 15,500; 13,500; 5500; 10,000; 18,500; and 30,000 atm., respectively. Grinding for several hours produced varying amounts of the high-pressure phases of  $\text{MnF}_2$ ,  $\text{BeF}_2$ ,  $\text{PbO}$ , and  $\text{Sb}_2\text{O}_3$ . In addition, high-pressure forms of  $\text{PbO}_2$ ,  $\text{CaCO}_3$ , and other substances were produced. Grinding and shearing were also observed to result in a very marked acceleration of the rates of pressure-induced transformations.

Libby (48) has proposed that ultrarapid rates of reaction may be obtained in polymorphic changes or chemical syntheses by first passing to the metallic state. As has already been mentioned, a sufficiently high pressure should transform all substances to metals. Following compression to the metallic state, release of pressure would present an opportunity for transformation to various nonmetallic states (either stable or metastable) with lower values of free energy. The nondirectional, labile metallic bond, on becoming unstable with reduction of pressure, should reform rapidly to the nonmetallic configuration.

A possible experimental example of the above idea may be the conversion of rhombohedral graphite to diamond by explosive shock as has been demonstrated by DeCarli and Jamieson (49). A paper on the behavior of strongly shocked carbon by Alder and Christian (50) and a paper on the theory of metallic diamond by Libby (51) may be of additional interest to the reader in connection with the above idea. The highest attainable laboratory pressures are produced in explosive shocks which are, of course, of very short duration. Pressures produced in these shocks, however, are high enough to induce the metallic state in many substances. If, as Libby proposes, the metallic state will transform at an ultrarapid rate to nonmetallic states of lower free energy upon release of pressure, practical applications for transforming large amounts of matter with conventional and nuclear explosions may be in the offing.

## V. Equipment and Techniques for High-Pressure Work

It would now seem appropriate to give consideration to the methods used to produce high pressure in the laboratory. Generation of pressure by explosive shock will not be considered. The reader interested in this subject is referred to an article by Duvall and Fowles (52). Considered in broad perspective, there are a limited number of types of high-pressure apparatus that have been developed. They are: (1) piston-cylinder, (2) Bridgman anvil, (3) belt, and (4) multiple anvil devices.

The piston-cylinder was the earliest type of high-pressure device. It consists of a strong cylinder fitted at one end with a sealing plug and at the other end with a movable piston. The sample to be compressed is placed inside the cylinder between the plug and the piston. The piston is then driven into the cylinder, thereby compressing the sample. If the sample is a liquid, it is necessary to provide some kind of a seal on the piston tip and plug. When the sample is a solid, there is usually no trouble with "leak" if the piston fits snugly to the cylinder. Sir Charles Parsons was the first person to use piston-cylinder devices simultaneously with high temperature (53,54). A solid pressure transmitting material inside his piston-cylinder apparatus also served to provide thermal and electrical insulation. An electrically heated resistance furnace, within this solid pressure transmitting material, surrounded the sample and provided the elevated temperatures. Parsons' chamber diameters ranged from 3/8 to 6 in. and his maximum pressures and temperatures were of the order of 15,000 and 3000°C. His work was motivated by a great desire to synthesize diamond. This same desire also motivated most other highpressure, high-temperature experimenters up until the time that diamond was finally synthesized.

In the early piston-cylinder devices, both the piston and cylinder were constructed of high-quality tool steel. The piston was usually made glass hard while the cylinder was somewhat softer. The maximum pressures attainable were somewhere in the neighborhood of 25,000 atm. As piston-cylinder devices were improved, cemented tungsten carbide was substituted for steel. Because cemented tungsten carbides have limited tensile strengths (their tensile strengths are of the order of 1/50th of their compressive strengths), cylinders of this material must be supported by external binding rings. These are designed to keep the tungsten carbide under compression at all times. Piston-cylinder devices, with tungsten carbides, can be routinely used at pressures to 40,000 atm. and can occasionally be taken to the vicinity of 60,000 atm.

As has already been mentioned, Coes reported the synthesis of a new dense silica in July of 1953. He synthesized this substance, as well as a wide variety of garnets and other minerals, in a piston-cylinder device in which the cylinder was constructed of hot-pressed alumina. This apparatus was first described at

the "Seventh Symposium On Crystal Chemistry As Applied to Ceramics," held at Rutgers University, New Brunswick, New Jersey, June 4, 1954. Coes did not, however, publish a description of this apparatus until 1962 (55). The apparatus consists of a special alumina cylinder that is force-fit into a steel binding ring as shown in Figure 2. The apparatus is double-ended, pressure being generated by pushing a tungsten carbide piston into each end of the alumina cylinder. Heating is accomplished by passing an electric current from one piston through a heating tube (in which the sample is centered) and out through the opposite piston. The alumina cylinder insulates the two pistons from each other, thus making such resistance heating possible. The ultimate pressure capabilities of this apparatus are somewhere in the neighborhood of 45,000

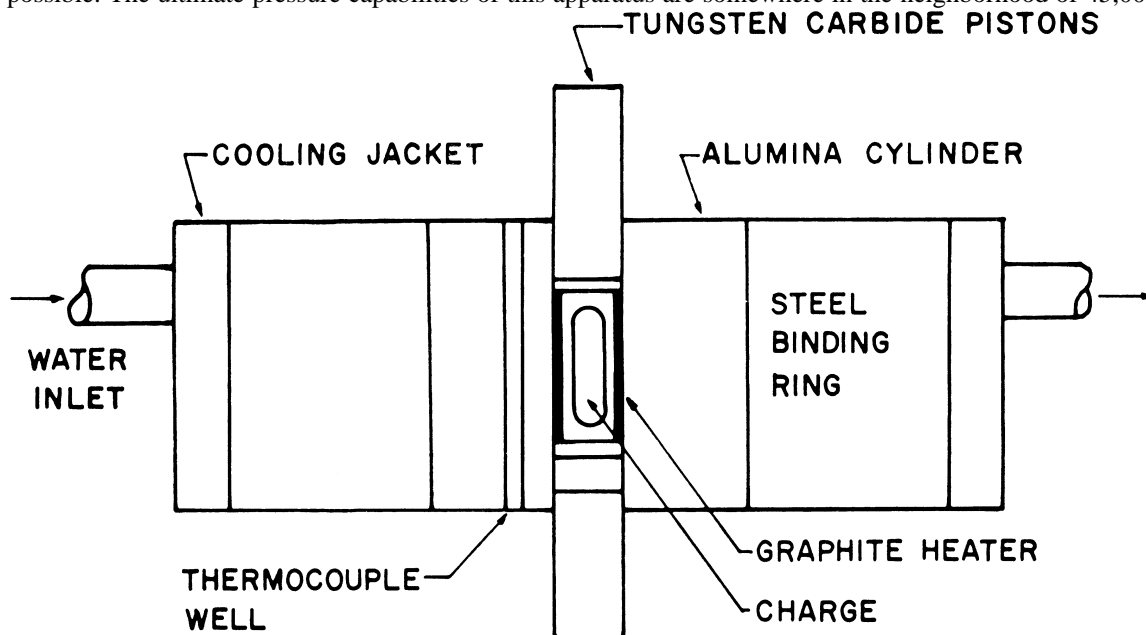


Fig. 2. Coes' piston-cylinder apparatus.

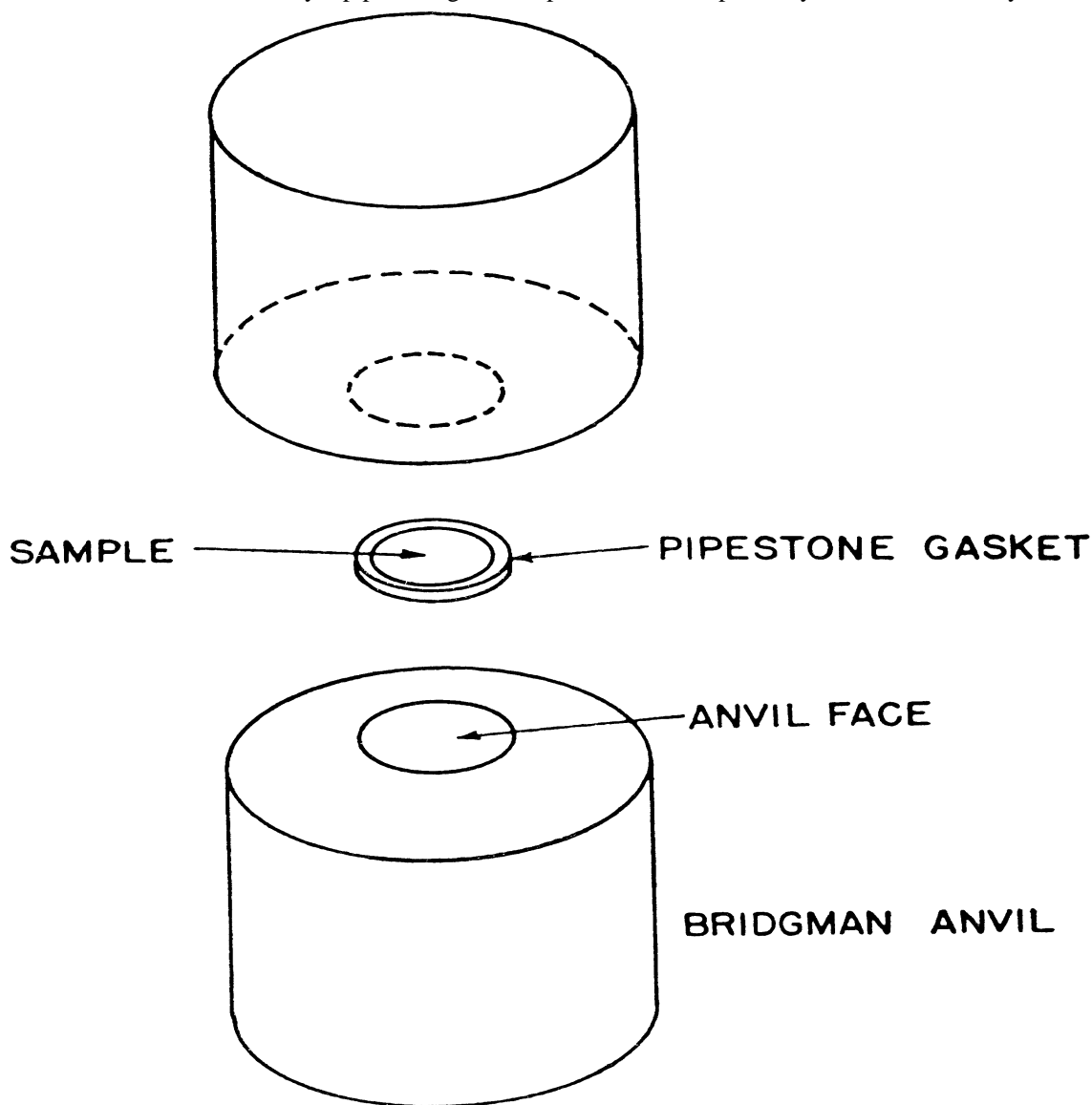
atm. at a temperature of 800°C. At a pressure of 30,000 atm. the temperature can be increased to the neighborhood of 1000°C. Temperature is measured by means of a thermocouple located in a well adjacent to the cylindrical chamber as shown in the drawing. The temperature in this well is lower than the temperature in the sample, but comparisons made with a thermocouple at the sample location at one atmosphere make it possible to correct the temperature reading of the thermocouple located in the well while under pressure. Other variations of the piston-cylinder apparatus for high pressure-temperature use have been described by Birch, Robertson, and Clark (56), Hall (57), and Boyd and England (58).

Theoretically, very high pressures could be developed by a process known as multistaging. In multistaging, one high-pressure apparatus is placed inside the chamber of a larger high-pressure apparatus and so on. True multistaging has not been carried out beyond two stages. Bridgman (59,60) constructed a two-stage piston-cylinder apparatus where the inside piston had a diameter of 1/16 in. With this device he measured the compressibilities of a large number of substances to pressures of 100,000 atm. The theory of a two-stage apparatus is based on the idea that the pressure responsible for breakage of components is a differential pressure; namely, the difference in pressure between the interior and exterior of the apparatus. Therefore, if one apparatus, which, for example, could generate 50,000 atm. as a singlestage device, were placed inside the chamber of a larger apparatus (also capable of generating a pressure of 50,000 atm.), it would be possible to generate 100,000 atm. in the inside apparatus.

In 1935, Bridgman (61-63) began to experiment with what have come to be known as Bridgman anvils (see Fig. 3). Bridgman anvils consist of a pair of cylindrical pieces of tungsten carbide each of which has a small, slightly raised circular face on one end. These faces generate pressure in a thin, circular sample when the anvils are forced together along their line of centers. Bridgman anvils are capable of producing the highest static pressures attainable at the present time. This is possible because of the principle of "massive support." When the faces of a pair of Bridgman anvils bear on each other, any axial thrust imposed on the abutting faces is "fanned out" into the greater circular area behind the faces. Massive support is thereby provided to the faces and they are able to withstand a much greater load than would the

face of a right-circular cylinder of the same area. Note that the mechanical ties to the face of a right-circular cylinder reach back into an area that remains constant with distance.

In order for Bridgman anvils to accommodate a sample and transmit pressure to it in a reasonably hydrostatic fashion, the sample is embedded in a silver chloride disk as is shown in Figure 3. The disk of silver chloride is surrounded by a pipestone gasket. Pipestone consists primarily of micron-sized crystals of



**Fig. 3. Bridgman anvils.**

hydrous aluminum silicates with small amounts of iron oxides and other substances. For centuries this material was used by American Indians in making smoking pipes; hence, the name pipestone. Under load, a thin section of pipestone is very strong. Because of its frictional characteristics, it bites into the periphery of the anvil faces, forms a gasket and effectively prevents extrusion of the silver chloride as pressure develops between the advancing anvil faces. Gaskets of metal and plastic have been found to be more effective than pipestone for some applications (64,65).

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

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Bridgman anvils can be forced together until the force/area pressure is at least 200,000 atm. By immersing the anvils in a fluid at 30,000 atm., Bridgman was able to generate force/area pressures of about 450,000 atm. In more recent times, anvil support has been provided by means of solid media (66,67). The highest pressures are generated when the anvil faces are rather small (of the order of 1/16 in. diameter). With anvil faces this size, the body of the anvil is usually of the order of 3/4 in. in diameter and 3/4 in. long. Apparently, large anvils contain a more than proportionately greater number of flaws or defects than small anvils. Since cracks begin to propagate at these defects, the chances for a crack to start are greater in a large anvil than in a small anvil. Consequently, at the present time, the maximum pressure developed with large tungsten carbide pressure components is always less than that obtained with small components.

It is necessary in achieving the highest pressures to strengthen the anvils or other tungsten carbide components by "cold-work." During cold-working, the anvils are deformed, and, consequently, must be reground to proper dimensions before use.

Samples compressed between Bridgman anvils are most commonly heated by an external furnace around the anvil system (64). Externally heated anvils have been used to temperatures of 300-400°C. at 100,000 atm. When the temperature is raised to 900°C., however, the maximum pressure attainable is

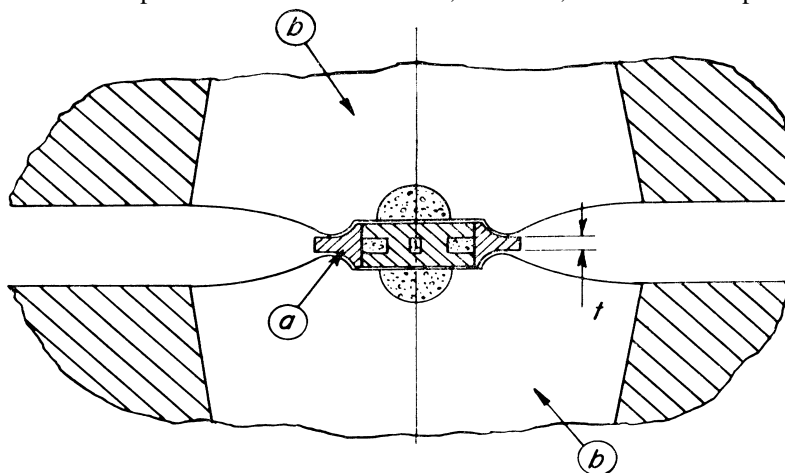


Fig. 4. Bundy's "saucer" anvils.

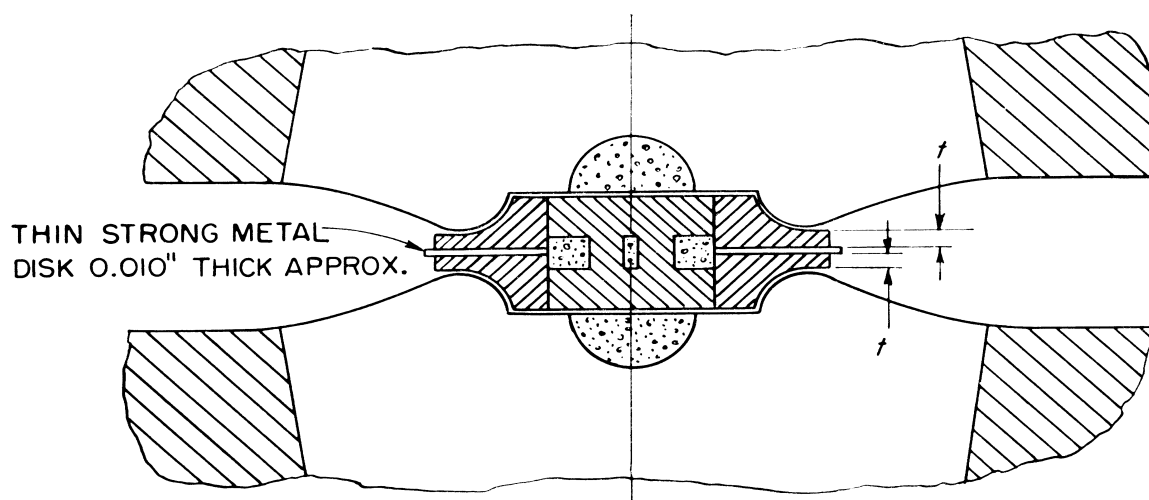
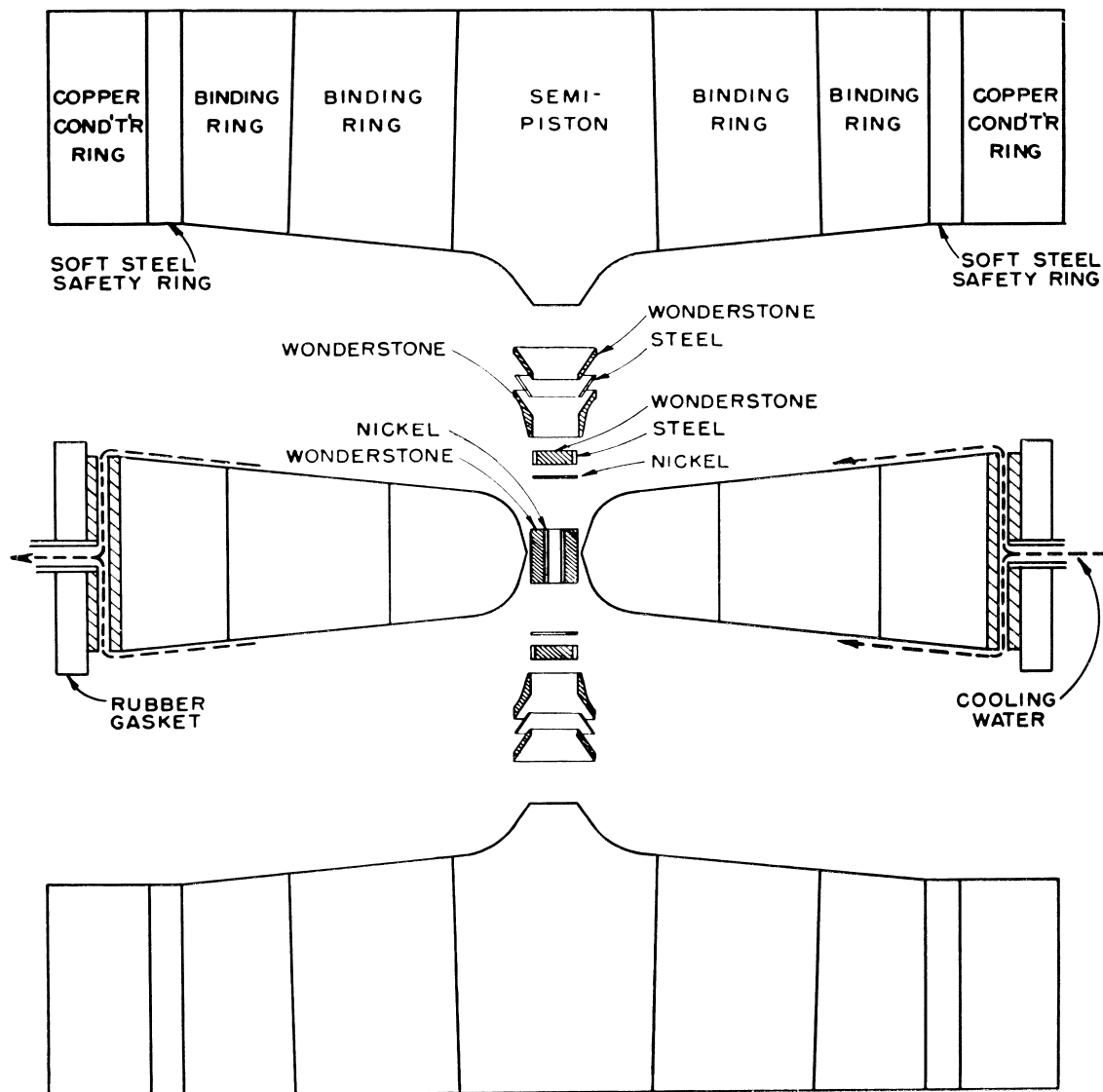


Fig. 5. The Sandwich gasket applied to saucer anvils.

reduced to about 20,000 atm. due to the reduced yield point of cemented carbides at this elevated temperature.

Drickamer and associates at the University of Illinois have effectively utilized Bridgman anvils (with solid support media) in a variety of different experiments to reported pressures of 700,000 atm. (66,67). Infrared, visible, and ultraviolet spectra, electrical resistance, x-ray diffraction, Mössbauer and other experiments have been performed by this productive group. Jamieson and Lawson (68) have pioneered the use of Bridgman anvils in x-ray diffractometry. Lippincott, Weir, and Van Valkenburg (69) have used tiny Bridgman anvils, constructed of single-crystal diamond, in infrared studies. Piermarini and Weir have used tiny diamond anvils for x-ray diffraction experiments (70).

Most of the current high-pressure research utilizes Bridgman anvils. There are two reasons for this: (1) They are relatively inexpensive. (2) They achieve the highest pressures. However, they have



"THE BELT"- HIGH-TEMPERATURE, HIGH-PRESSURE APPARATUS

Fig. 6. The Belt apparatus, "exploded view."

serious drawbacks: (1) The sample is extremely tiny. (2) They cannot be heated to high temperature while maintaining a high pressure. (3) The sample specimen is sheared considerably during the compressing process. (4) A Gaussian-shaped pressure profile exists across the diameter of the sample. Because of this, the "resolution" of Bridgman anvil devices is poor. For example, transitions in cesium occurring 400 atm. apart, in the vicinity of 40,000 atm., are clearly separated in the Tetrahedral anvil press (to be described

later). However, in Bridgman anvils, the two transitions are seen as one and, furthermore, the pressure at which the transition takes place has been reported to occur anywhere between 40,000 and 80,000 atm.

Bridgman made an attempt to increase the thickness of the sample between his flat anvils, thereby increasing the volume, by hollowing the anvils. This severely reduced the pressure that could be achieved because the ratio of available anvil motion (the initial gasket thickness remains unchanged) to sample thickness was greatly increased. In addition, considerable breakage was experienced because of the stress concentration points in his angular design.

Bundy (71) improved considerably on Bridgman's hollowed anvils in a device called the "Saucer" (see Fig. 4). Thermal insulation was provided at the ends of the sample by a hemisphere of hot-pressed alumina embedded in the tungsten anvils (b). A "spool" of graphite contained a tiny cylindrical sample in its center and served as the resistance heating element. A disk of alumina surrounded the small diameter portion of the spool. This, in turn, was surrounded by a contoured pyrophyllite gasket (a). The overall cell

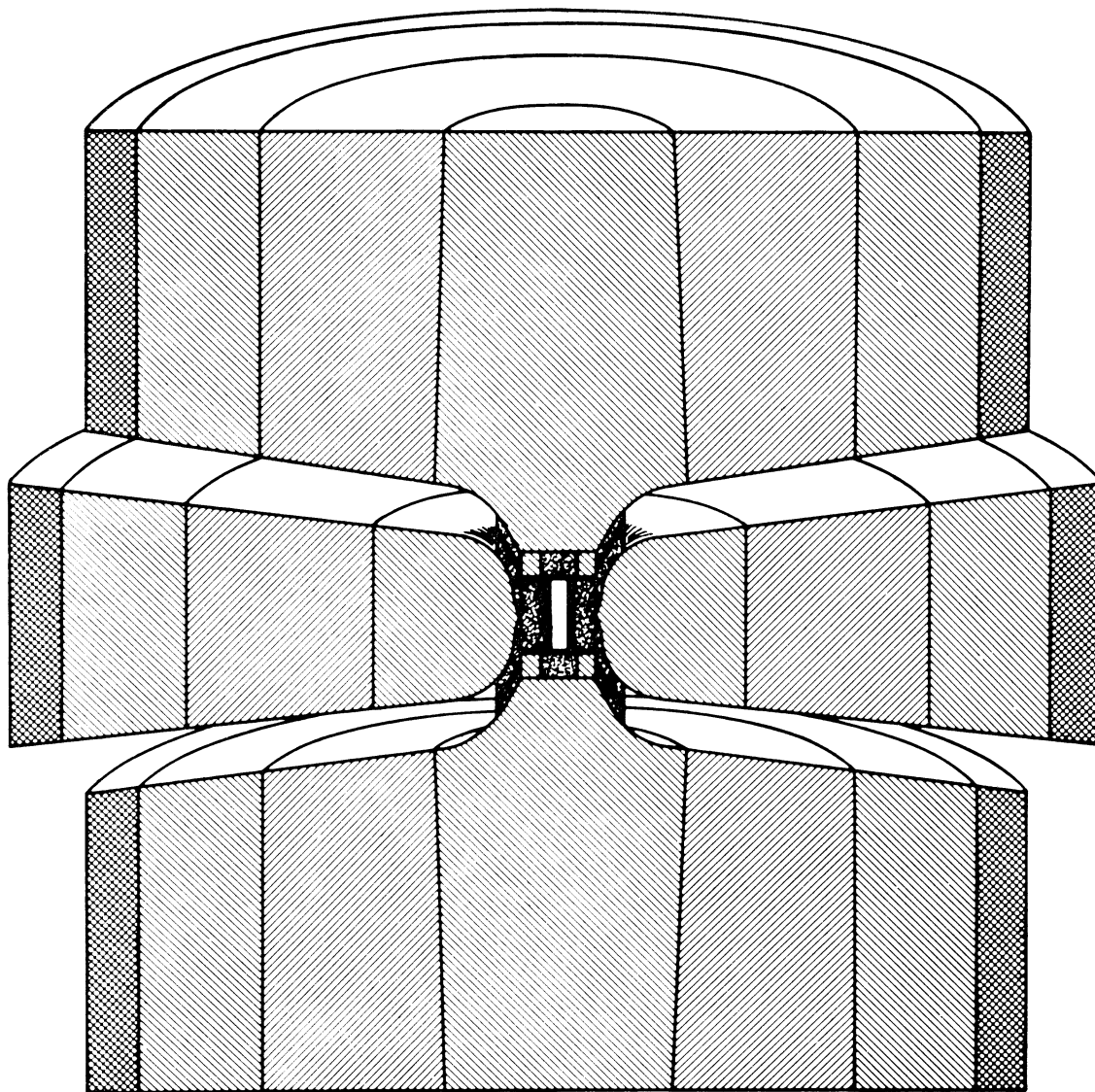
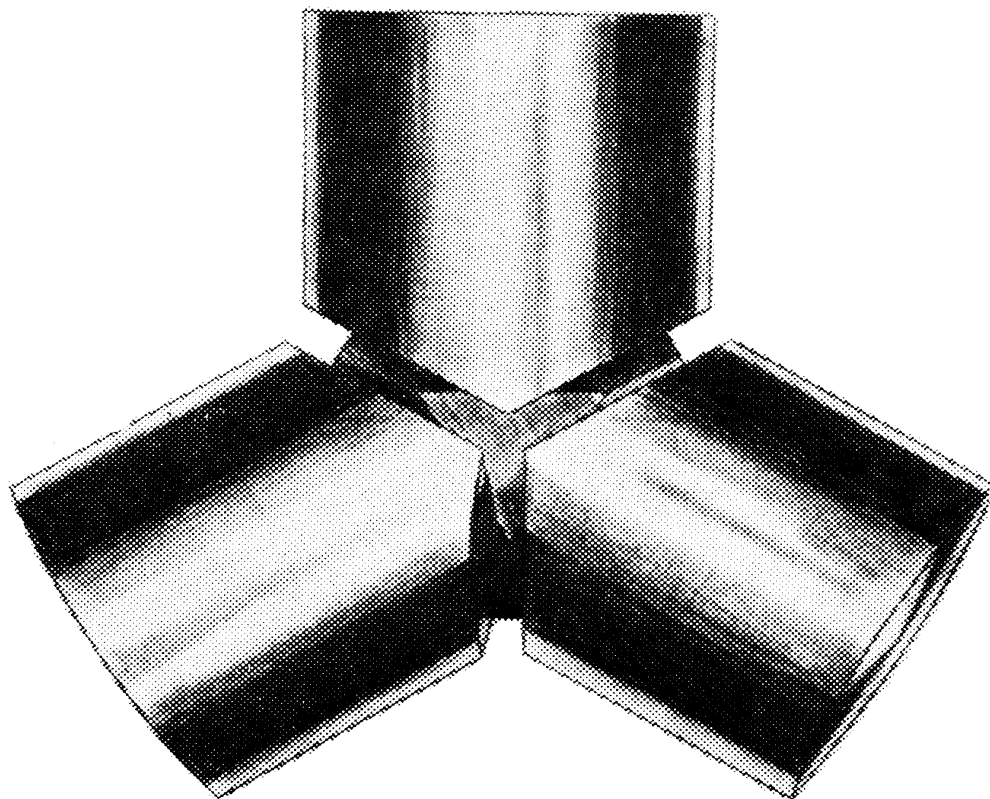


Fig. 7. The Belt apparatus, "closed view."

height and, consequently, the sample volume was limited by the optimum thickness ( $t$ ) of the gasket. Temperatures as high as 2500°C. were obtained simultaneously with pressures in the neighborhood of 35,000 atm. in this device. The pressure range of Bundy's device was extended somewhat and the volume was increased considerably by the author's invention of the "sandwich gasket" composed of steel and

pyrophyllite as shown in Figure 5 (72,73). When stony material such as pyrophyllite is used as gasket material, there is an optimum initial thickness for the gasket. When thicknesses greater than this optimum are used, the pyrophyllite crumbles irregularly as the gasket is compressed and the maximum pressure that can be developed is reduced. Two sections of pyrophyllite with an intermediate section of steel, as in the sandwich gasket, however, more than double the available anvil motion and permit a larger sample to be accommodated. Additional layers in the sandwich gasket are useful in some high-pressure designs.

The idea of using a conical piston and conical-shaped chamber together with a compressible sandwich gasket to generate pressure was conceived and perfected by the author late in 1952 and early 1953. This apparatus came to be called the "Belt" and was first described in a General Electric Research Laboratory Report No. RL-1064, in March of 1954. Distribution of this report, however, was rigidly limited within the company. The report was published six years later as an article in the Review of Scientific Instruments (72,74). Diagrams of the belt apparatus are given in Figures 6 and 7. The function of the various components can be explained by referring to Fig. 6. The semipistons (made of tungsten carbide) are forced into each end of a conically shaped carbide chamber by a hydraulic press. Pressure generated by the advancing semipiston is transmitted to the sample contained in a nickel heater tube by a pyrophyllite cylinder (noted as wonderstone in Fig. 6) or similar material. In addition to transmitting pressure, the



**Fig. 8. Tetrahedral anvils.**

pyrophyllite provides thermal and electrical insulation. The sample is heated by passing an electrical current through the heater-sample tube. Current enters this tube from the pistons by way of hardened steel conducting rings and nickel end disks. Short cylindrical sections of pyrophyllite (which are surrounded by the steel conducting rings) provide thermal insulation at the ends of the heater-sample tube. The sandwich gaskets which consist of two pyrophyllite sections with a steel cone between them compress and extrude under piston load, thus allowing the generation of pressure within the chamber. Hardened steel binding rings maintain a compressive load on the cemented tungsten carbide chamber to prevent it from breaking as pressure is developed. The tapered pistons are strengthened in the same manner by press-fit binding rings.



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Soft steel safety rings surround the press-fit binding rings as a protective measure should the binding rings fail. The carbide chamber and its associated binding rings form a toroidal "belt" around the sample, and it was from this that the apparatus received its name. Graphite or tantalum may be used in place of the nickel sample-heater tube and the nickel end disks for working at the higher temperatures. The belt apparatus is capable of generating pressures (new scale) in the neighborhood of 150,000 atm. simultaneously with

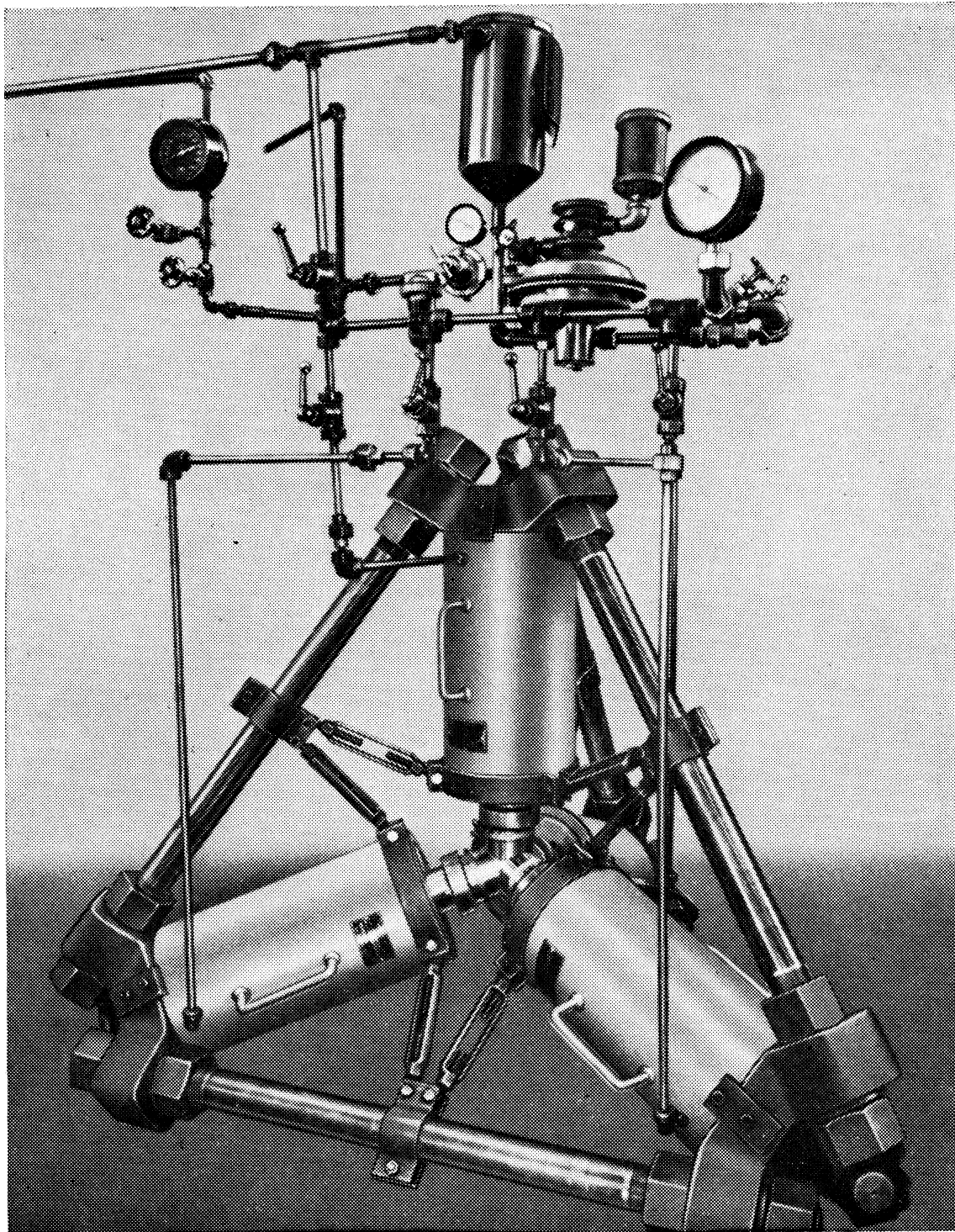
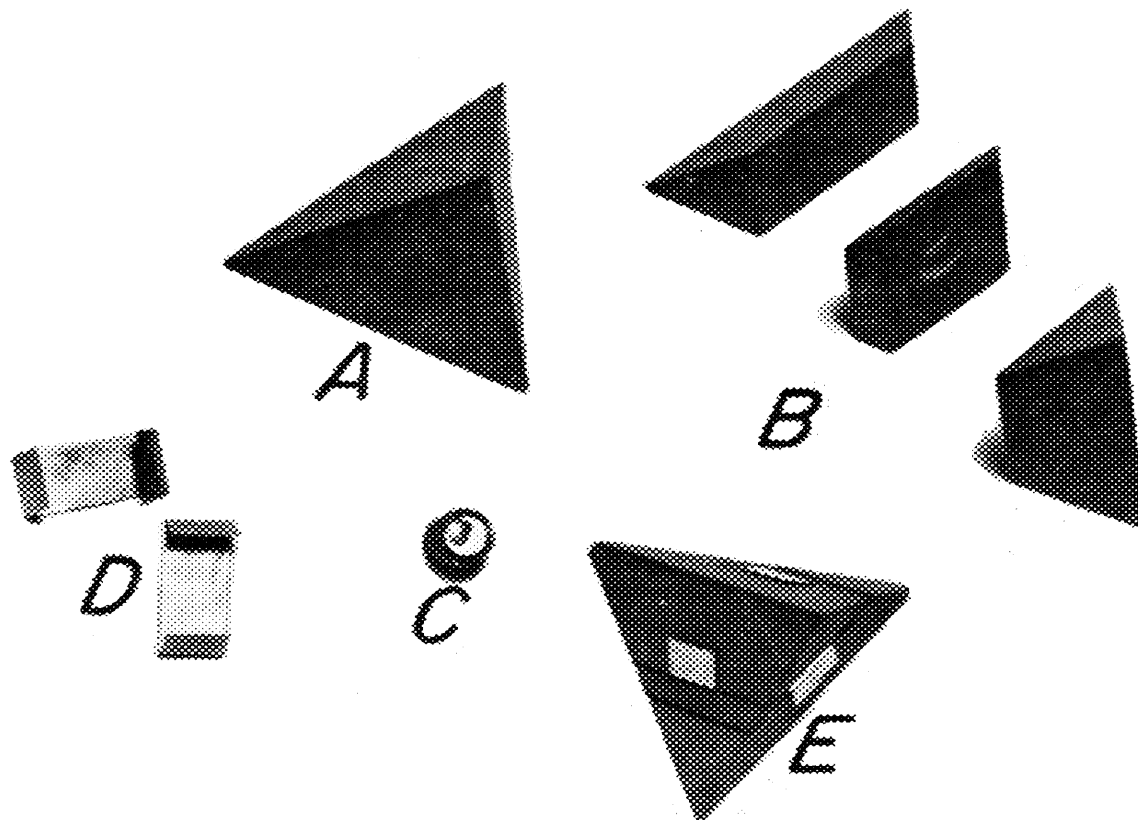


Fig. 9. The original tetrahedral press.

steady-state temperatures of the order of 2000°C. Temperatures of at least 5000°C. can be maintained for millisecond periods. The basic principles of the belt have been utilized by other researchers in constructing similar device (75,76).

Brief mention of the pressure scale would be appropriate at this point. The belt was originally calibrated in terms of sharp electrical resistance changes occurring in bismuth, thallium, cesium, and barium. These resistance transitions, measured by Bridgman in his anvil apparatus, were reported to occur at pressures of 24.9 44, 54, and 78 thousand atmospheres, respectively (77). Calibration based on these fixed points is now referred to as the "old" pressure scale. The new scale is based on fixed points of 25.4, 37, 42, and 59 thousand atmospheres, respectively, for the same transitions (78).

A secondary pressure calibration based on fixed points is necessary in apparatus using compressible gaskets and/or solid pressure transmitting media. Part of the ram load is, of course, absorbed by the gaskets and, in the case where solid pressure transmitting substances are used, is also used in overcoming internal friction in the solid. In calibrating an apparatus, a silver chloride specimen carrying a calibrating wire is substituted for the sample. (Silver chloride, compared to most solids, transmits pressure quite hydrostatically.) The oil pressure to the hydraulic rams which force the pressure generating components together is then slowly increased and recorded simultaneously with the change of electrical resistance of the pressure sensing wire. The oil pressure required to induce each transition is then plotted as



**Fig. 10. Tetrahedral cell construction.**

a function of the accepted pressure value for this fixed point. A smooth curve through these points and the origin then serves as the pressure calibration curve for the apparatus.

The massive support principle is at work in the belt in both the tapered pistons and the chamber. In addition, the piston and chamber support each other through the sandwich gasket. The highest pressures in the belt are achieved when the cell length is short compared to its diameter. (In this situation, the belt approaches a supported Bridgman anvil device.) With a short sample, of course, the sample volume of the belt is reduced. The belt will operate routinely at pressures to 80,000 atm. with a cell length to diameter ratio of about 2:1. The sandwich gasket in the belt provides a pseudomultistaging effect which contributes

to its ability to generate high pressure. This results from the gradual drop of pressure along the gasket from the tip of the piston outward towards the rim of the gasket.

The first member of a regular series of multiple anvil presses is the tetrahedral press (57,79). This press came into being as a matter of necessity when the belt, because of circumstances of secrecy, could no longer be used for research by its inventor. The tetrahedral press is an extension of the "two-dimensional" Bridgman anvil concept to three dimensions. A three-dimensional device is necessary to overcome the problem of the small sample size inherent in Bridgman anvils. Overcoming this problem also makes it possible to utilize internal electrical resistance heating for working at high temperatures. The principle of massive support is still at work in the tetrahedral press and similar multiple anvil devices, but to a lesser extent than in Bridgman anvils. The average solid angle subtended by the sloping shoulders of an anvil must, necessarily, decrease as the number of anvils in the apparatus is increased. However, anvils tend to support each other through the compressible gaskets in multiple anvil devices, and this tends to compensate for the reduction in massive support.

In the tetrahedral press, four anvils with triangular faces (see Figs. 8 and 9) are driven toward a central point by hydraulic rams whose axes lie along lines normal to the triangular anvil faces. The anvil axes intersect at tetrahedral angles ( $109.47^\circ$ ) in the center of a regular tetrahedral volume enclosed by the

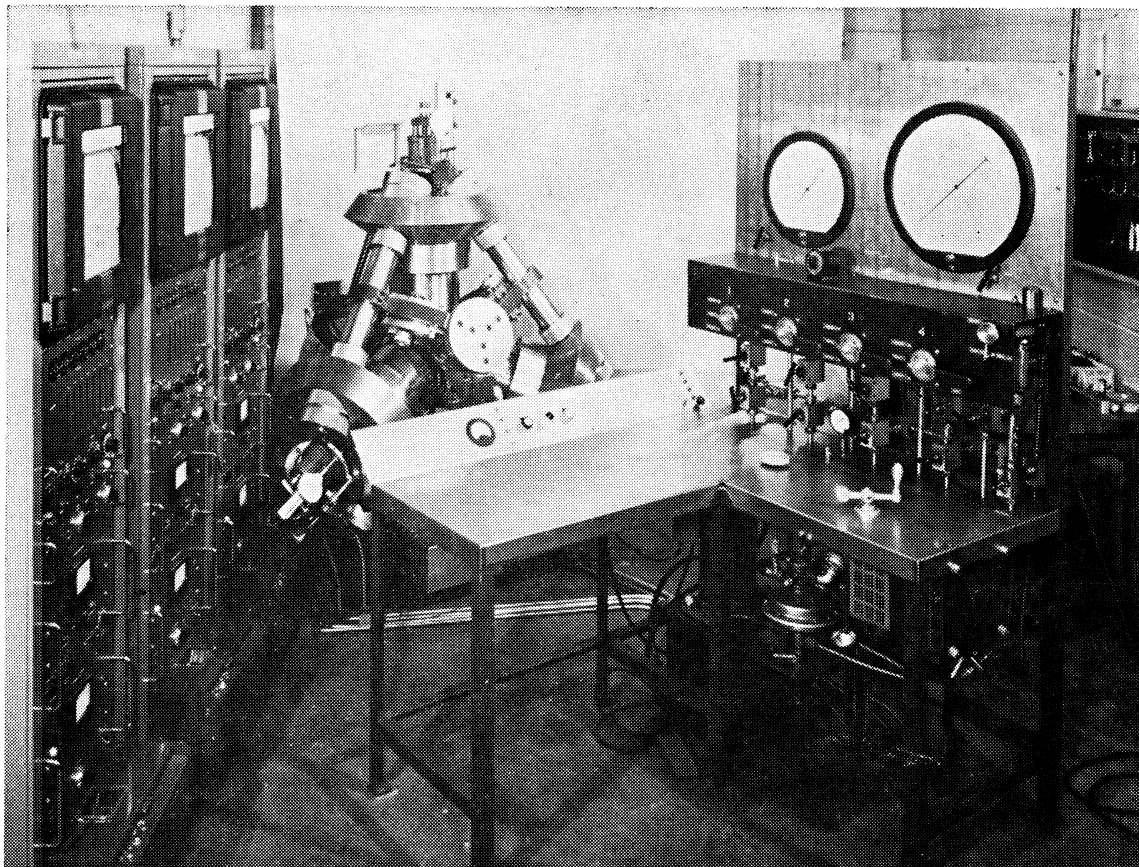


Fig. 11. Tetrahedral x-ray diffraction press.

anvil faces. The anvils are usually constructed of cemented carbides and are surrounded by press-fit binding rings.

The cell in which the pressure is generated consists of a regular pyrophyllite tetrahedron as shown in Figure 10. Sometimes a gasket is preformed along the six edges of the pyrophyllite tetrahedron. In other cases, the edges of the tetrahedron are made approximately 25% longer than the corresponding legs on the triangular anvil faces and a gasket is automatically formed as the anvils advance. When a plain tetrahedral cell is used, it is usually cut from a solid block of pyrophyllite with an abrasive disk or thin metal cutting saw. The typical edge length of a tetrahedral cell used for research is 1 in. (the corresponding edges of the triangular faced anvils are  $3/4$  in- long). In order to place a sample within the pyrophyllite tetrahedron A (see Fig. 10), a central slab, B, 0.100 in. thick is cut from it with thin slitting saws. The faces of the central

slab are parallel to two opposite edges of the tetrahedron. A 0.188-in.-diam. sample hole is then drilled through the center of the slab perpendicular to its faces. Electrical connection to the sample heater tube or to a calibration specimen C is made with 0.005-in.-thick metal connecting tabs, D, which, in turn, make electrical contact with the anvils. The completed cell, E, is assembled and held together with water soluble glue. The surface of the tetrahedron is then painted with rouge (thick ethanol suspension) and dried at 95°C. for about 1/2 hr. and is then kept in a desiccator until used. The rouge is used to increase the surface friction of the pyrophyllite. This increases the efficiency of the apparatus.

The working volume of the cell just described is rather small being only 2.3% of the initial tetrahedron volume and 5.6% of the volume of a tetrahedron defined by the completely closed anvils. This small volume is used in most research applications in order that the average pressure exerted over the surface of the sample will, for a given ram thrust, be the same regardless of the sample's compressibility. Also, in this small working volume a rather uniform pressure is distributed over the sample surface and sample distortion is minimized. When the above considerations are not important, much larger working volumes may be used.

Temperature inside the cell can be measured by locating a thermocouple in the immediate vicinity of the sample under study. Thermocouple leads are brought out through the edges of the tetrahedron in the space between the sloping anvil shoulders where the gasket is located. Friction of the pyrophyllite gaskets on the fine wires (usually 0.005 or 0.010 in. diameter) is sufficient to hold them in place during high-pressure operation. Thermocouple wires can similarly be inserted in the sample volume of the belt apparatus.

An anvil guide device, which simultaneously and synchronously advances the anvils toward the center of the sample tetrahedron, has been used in recent years to increase the efficiency of the tetrahedral press (80). In the original device, the anvils were brought together by independent valves which controlled each ram. The position of each anvil was indicated by a dial gage. With an anvil guide, all the rams are controlled from one central valve. Indicators of anvil position are not needed since each anvil is always located in its proper position relative to the other anvils.

Routine pressures of 110,000 atm. (combined with high temperature) are possible with 1/2 in. (length of triangular face) tetrahedral anvils. Higher pressures are available at a sacrifice in anvil lifetime.

Following the tetrahedral press in the regular series of polyhedral presses is the cubic press. In this press, six hydraulic rams advance six anvils, with square faces and 45° sloping shoulders, toward the center of a cube. The octahedral press follows the cubic press in the sequence, and so on.

The weak point in piston-cylinder devices, as they are used today, is the piston. This supported piston apparatus is designed to give additional support to the piston and approaches a two-stage piston-cylinder device in its design and operation. The first equipment of this type to be described was that of

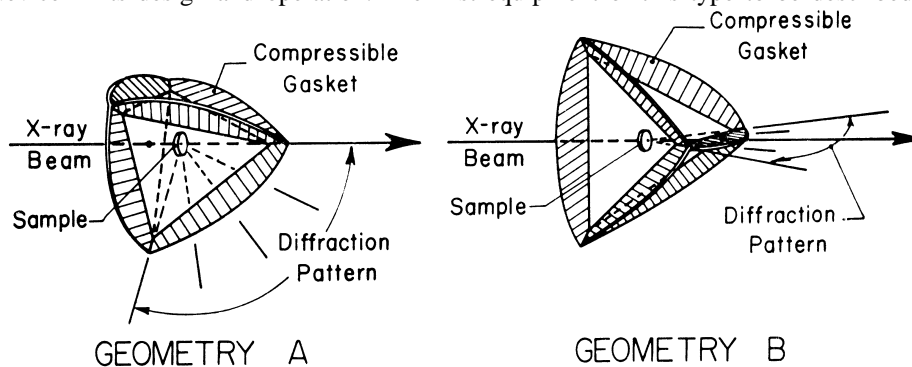


Fig. 12. Tetrahedral sample chamber showing the two possible x-ray geometries using the compressible gasket as the exit pupil.

Boyd and England (81). In this apparatus the carbide chamber is supported radially by binding rings and axially by bolted end plates. The protruding portion of the piston is supported radially by a compressible annular ring of solid material, such as potassium bromide, which is compressed by a piston which also drives the smaller, high-pressure piston. The binding rings, the loaded end plates, and the potassium bromide, then, are used to give support in this apparatus that was supplied by a hydraulic fluid under pressure in Bridgman's two-stage apparatus.

A device similar to that of Boyd and England above has been described by Giardini, Tydings, and Levin (82). Maximum pressures of about 80,000 atm. have been reported for supported piston devices.

Mention has already been made of the fact that Bridgman anvils are being utilized in x-ray diffraction research at high pressure. The tetrahedral anvil press has also been equipped for x-ray diffraction studies (83). The apparatus (see Fig. 11) consists of a tetrahedral press to which three geared scanning tracks have been attached. The tracks are mounted on the press so that diffracted x-rays exiting from spaces between the sloping anvil shoulders (through the gaskets) will be intercepted over about a  $100^\circ$  sector (see Figs. 12 and 13). One of the hydraulic rams has an opening to accommodate an x-ray tube. This tube directs a primary beam of x-rays through a hole along the ram axis and thence through a 0.030-in.-diam. collimating hole located in one tetrahedral anvil. The 0.030-in. hole is terminated on the triangular face of the anvil by a  $90^\circ$  hollow cone. A solid beryllium cone is placed in the hollow cone to prevent extrusion of cell material into the 0.030 in. hole. Tetrahedral cells made of pyrophyllite cannot be used in x-ray diffraction work because they are not sufficiently transparent to x-rays. Satisfactory cells have been constructed of lithium hydride, boron, mixtures of lithium hydride and boron, and boron-filled phenol-

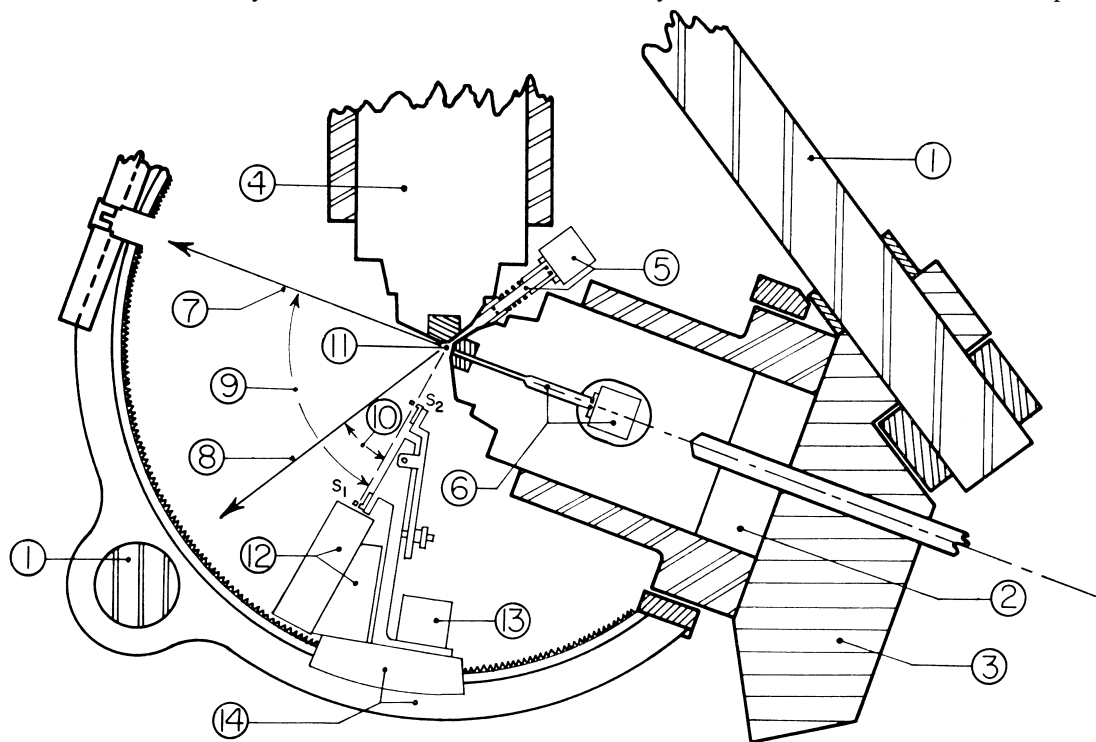


Fig. 13. Cross section of the apparatus showing the x-ray tube mounted in each position and the detector scanning mechanism as they relate to the high-pressure system: (1) tiebar, (2) hydraulic oil, (3) ram base, (4) piston assembly, (5) x-ray tube and collimator in position B, (6) x-ray tube and collimator in position A, (7) undeviated x-ray beam, position A, (8) undeviated x-ray beam, position B, (9) diffraction angle ( $2\theta$ ), position A, (10) diffraction angle ( $2\theta$ ), position B, (11) sample, (12) scintillation counter and preamp, (13) scanning motor, (14) scanning carriage and track.

formaldehyde plastics. Powders of these materials are compressed into dense tetrahedrons by a die designed for the purpose. These tetrahedrons are then drilled or sawed in the same manner as pyrophyllite in order to provide openings for the sample, etc. The specimen to be studied is located in the center of the tetrahedral cell. If the specimen is an electrical conductor it may be utilized in the form of a thin sheet that can be heated directly by an electric current. Nonconductors can be heated indirectly by placement inside a graphite or beryllium heater. These materials, because of their relative transparency to x-rays, will not usually interfere with the desired diffraction patterns. Often it is possible to arrange an open-ended

cylindrical heater or strip-type heater which does not intercept the primary or exit x-ray beams. In this case, the heater may be made of any material.

A synchronous motor drives a carriage (on which slits, counter tube and cathode follower are mounted) along each x-ray track. Signals from the cathode follower are amplified by a preamplifier located

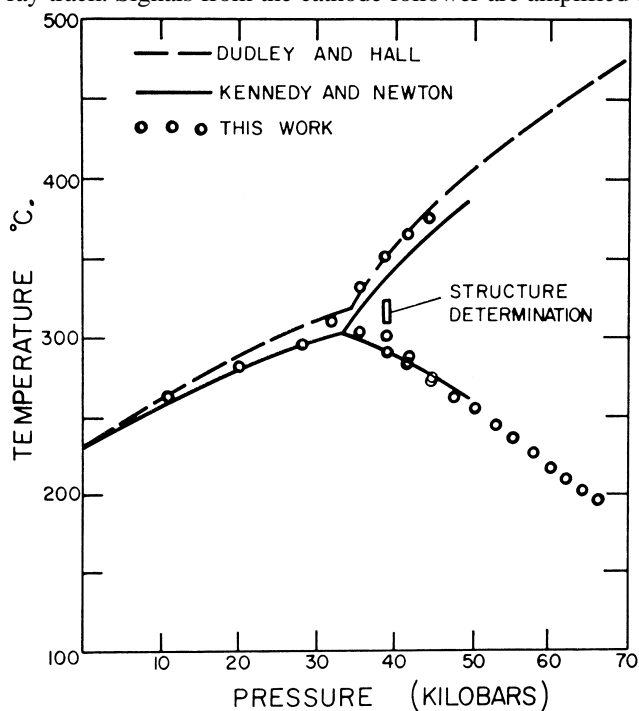


Fig. 14. Phase diagram of tin as measured by x-ray diffraction techniques.

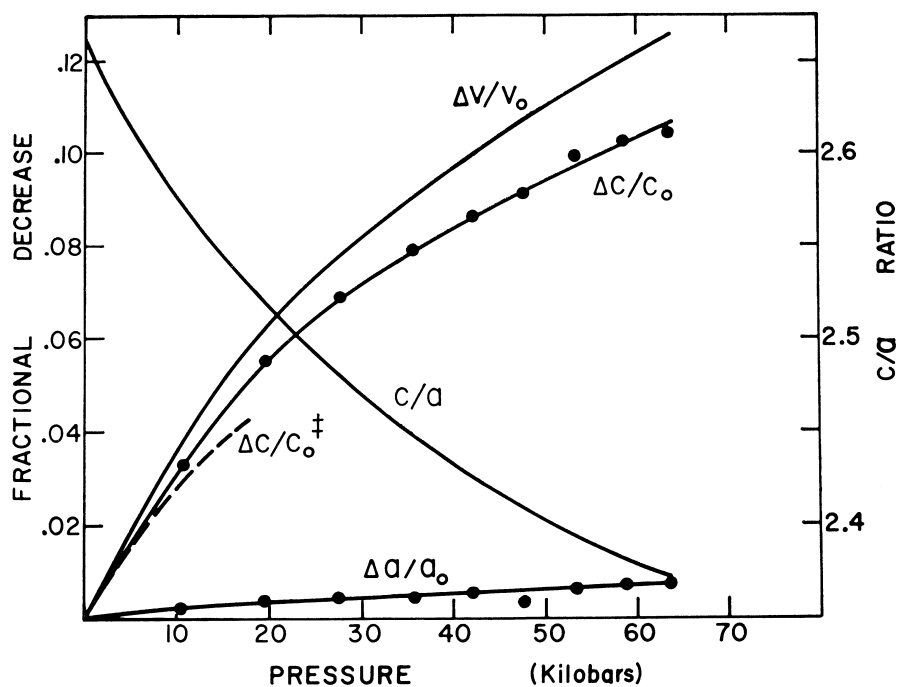


Fig. 15. Lattice parameters of hexagonal BN as a function of pressure to 65 kbar. The dashed curve is data reported by Kabalkina and Vereshchagin.

nearby and are then conducted to the electronic sensing and recording equipment. With the three identical track systems it is possible to monitor the disappearance of one phase simultaneously with the appearance of another and, at the same time, monitor the pressure within the cell by observing the change in  $d$  spacing of a calibrating substance. In addition to mounting the x-ray tube inside one of the rams, it is possible to mount the tube so that it directs a primary beam of x-rays through the center of one edge of a gasket (see Figs. 12 and 13). With this mounting, the diffraction pattern exits through only one gasket but gives a pattern covering a  $50^\circ$  angle each side of the primary beam. The first geometry (A) gives a pattern on only one side of the primary beam. This device makes it possible to examine reversible phase transformations at the pressures and temperatures where they occur. With 1/16-in. anvils, x-ray diffraction measurements have been made at pressures to 120,000 atm. Maximum temperatures of  $1000^\circ\text{C}$ . have been sustained for a few minutes and temperatures of  $500^\circ\text{C}$ . have been sustained for many hours. As an example of the kind of information that can be obtained with this device, the phase diagram of tin is given in Figure 14. In Figure 15, the lattice parameters of hexagonal boron nitride as a function of pressure to 65,000 atm. are given. Notice that the compressibility of anisotropic crystals along different crystallographic axes may be determined in this device. Previous compressibility measurements made in piston-cylinder devices will, of course, give only the average compressibility of the crystal.

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