Reprinted from
ANNUAL REVIEW OF PHYSICAL CHEMISTRY
Vol. 9,1958

HIGH PRESSURE DEVELOPMENTS[1]

By H. TRACY HALL
Brigham Young University, Provo, Utah
AND

S. S. KISTLER
University of Utah, Salt Lake City, Utah

Introduction.--Because it seemed impractical to cover the entire field of high-pressure developments, the authors have limited the coverage to subjects of interest to them personally and to those subjects that seem to have significance for future developments. The field of high pressure, particularly at high temperature, has aroused a great deal of interest of late. Work which has not yet been published is under way in a number of laboratories.

The general effect of high pressure is one of closing up systems, thereby reducing their entropy, For example, a pressure of 12,000 atm. reduces the entropy of potassium metal by 30 per cent. Pressure in many respects, then, produces effects akin to low temperature (one cc. kiloatmosphere is equivalent to 12.19ºK.). Thermodynamically, a system is completely characterized if the volume is known as a function of the two intensive properties, pressure and temperature, and if the specific heat at constant pressure is known as a function of temperature (the foregoing statement assumes that E_0 and S_0 are known). Of course if the foregoing thermodynamic quantities are known for the components of interest in a chemical reaction, the intensive quantities, pressure and temperature, could be adjusted to give favorable thermodynamics for the formation of the desired products. Considerable use of temperature has been made to bring about chemical and physical changes in systems since temperatures in the range of 500ºC.-2000ºC. readily supply energies equivalent to those found in most chemical bonds. However, comparatively little use has been made of pressure because experimental techniques for producing pressures of the order of 100,000 atm. are extremely difficult (such pressures are required to provide compressive energies which correspond in magnitude to chemical bond energies).

In addition to thermodynamics, the chemist must be concerned with the problem of reaction rates when he desires to bring about a transformation. In general, experience indicates that low temperature is unfavorable for chemical reactions to proceed at a reasonable rate. Likewise high pressure generally reduces reaction rates considerably. For this reason it is desirable to be able to obtain high temperatures and

---

[1] The survey of literature pertaining to this review was concluded December 7, 1958.

high pressures simultaneously in order that reactions will proceed at a reasonable rate under high-pressure conditions. Many compounds which cannot be synthesized at atmospheric pressure due to instability can be produced with ease under high pressures. By cooling these compounds before releasing the pressure, many of them gain metastability of such an order that they show no tendency to revert. Detailed treatments of the foregoing considerations have been given by Hall (1, 2), Kistler (3) and Hall et al. (4).

High-pressure, high-temperature apparatus.--A major deterrent to the pursuit of experimental work at high pressure and high temperature has been the nonexistence of equipment capable of producing high temperature and pressure simultaneously. A brief review concerning such apparatus, therefore, seems appropriate. The first high-pressure, high-temperature apparatus of note was built by Parsons for his work on diamond synthesis (5). In this apparatus a refractory substance provided thermal and electrical insulation and also transmitted pressure from a moving piston to the specimen. The latter was heated by electrical resistance methods, Bridgman (6) and others have immersed high-pressure systems in a thermostatic bath, but heating accomplished by this method is limited to the neighborhood of 300ºC. for systems constructed of steel.

A double-ended simple piston and cylinder apparatus utilizing internal electrical heating has been described by Coes (7). This apparatus is shown for the first time in an article by Roy and Tuttle (7a). In this apparatus the sample is enclosed in a metallic container that is in turn surrounded, first, by MgO powder and, second, by a graphite cylinder. This assembly is squeezed between two tungsten carbide pistons working in each end of a hot-pressed alumina cylinder. The sample is heated by a low-voltage current passing through the graphite. The alumina cylinder provides necessary electrical and thermal insulation. Although alumina possesses high strength in compression, its tensile strength is relatively low. Consequently the alumina cylinder is supported laterally by a press-fit, hardened steel binding ring. The pressure on the pistons is maintained by a hydraulic press. This apparatus can be used at pressures of 35,000 atm. at temperatures below 900ºC. for sustained periods of time. Runs have been made at 45,000 atm. at lower temperatures by accepting a reduced life for the apparatus. The temperature of the sample in this apparatus cannot be determined very precisely. An approximate calibration of the pressures has been achieved by use of the bismuth I➞II transition.

Butuzov, Gonikberg & Smirnov (8) have briefly described a high-temperature, high-pressure apparatus that has been used at pressures of 33,000 atm. and temperatures of 600ºC. This apparatus is an adaptation for high temperature use of an apparatus originally designed by P. W. Bridgman. The material under study is contained in a small furnace wound with electrical resistance wire. Pressure is transmitted directly into the material in the furnace by a mixture of isopentane and n-pentane. An apparatus very similar to that of Butuzov et al., except that the pressure-transmitting medium is an inert gas, has recently been described by Birch &

Robertson (9). This apparatus has been used at pressures to 34,000 atm. at temperatures of 1000ºC.

Griggs & Kennedy (10) have introduced a simple apparatus, based on the principle of Bridgman's anvil apparatus (11) which provides pressures of 80,000 atm. at 500ºC., 50,000 atm. at 800ºC. and 20,000 atm. at 1000ºC. This apparatus, which is finding widespread use, has come to be known as the "simple squeezer." The specimen to be compressed is contained in a disk-shaped, metal box of inside dimensions approximately one-quarter inch diameter by .005 inches height. The anvils are made of either cemented carbides or Stellites. Heating is accomplished by surrounding the entire anvil assembly with a resistance-heated furnace. Pressure obtained between the anvils is taken as force per unit area on the anvil face. This device has two drawbacks: (a) There is some uncertainty as to the actual pressure transmitted to the specimen and (b) the sample space is very small. The small sample volume is inherent in the design and cannot be increased appreciably by scaling up the apparatus.

A simple piston and cylinder high-pressure, high-temperature device somewhat like that of Coes has been used at Brigham Young University (12). In this design, the specimen is contained in an electrically conducting tube that may be heated by an electrical current. Pressure is transmitted to the sample by a fine-grained refractory solid such as pyrophyllite.[2] This material also serves as thermal and electrical insulation. Pressure generated within the sample tube is determined from a calibration plot that is constructed from measuring the load required to obtain known electrical resistance discontinuities in Bi and Tl [Bridgman has discovered sharp changes in electrical resistance occurring in Bi at 24,800 atm., Tl at 43,500 atm., Cs at 53,200 atm., and Ba at 77,400 atm. (13)]. These transitions serve as very useful reference points for pressure calibrations. This apparatus is satisfactory for use at maximum pressures of 50,000 atm. at temperatures of 5,000ºC. The higher temperatures are obtained when graphite is used as the sample tube. The use of a refractory medium for transmitting the pressure to the sample is, of course, a return to a method (already mentioned) used by Sir Charles Parsons in 1888. This seems to be the only satisfactory solution to the problem of generating extremely high pressures at extremely high temperatures. Although there is frictional hold-up within the refractory medium, it is reproducible, easy to measure and to make allowances for.

The problem of generating pressures above 50,000 atm. is difficult. The main limitation is one imposed by the strength of materials that might be used for

---

[2] This material, a hydrous aluminum silicate, is a naturally occurring substance. In the United States it is mined in the southeast and is available from the American Lava Company, Chattanooga 5, Tennessee, as "Grade A Lava." Catlinite or "Pipestone" a material often used by Bridgman is very similar to pyrophyllite, differing mainly in that it contains Fe_2O_3. "Soapstone" or talc is similar to pyrophyllite, being a hydrous magnesium silicate. All these materials have been utilized in high pressure gasketing applications for many years.

constructing the high-pressure apparatus. Cemented tungsten carbides, the most satisfactory material presently available, has a compressive strength of the order of 50,000 atm. maximum. One of the most satisfactory ways to make this material serviceable at pressures beyond its normal compressive strength is the use of a principle, first recognized by Bridgman, known as the principle of massive support. This is the principle at work in anvil apparatus. Bridgman's anvil apparatus is primarily a two-dimensional device in which the sample to be compressed has appreciable breadth and width but very small depth and, consequently, a small volume, It would be very desirable somehow to preserve in a three-dimensional device the features that make this two-dimensional device operable. In a practical three-dimensional device it would be desirable to have the breadth, width, and depth of the sample of comparable dimensions. The salient features of Bridgman's anvil apparatus have been utilized by Hall in the construction of a three-dimensional device called the *tetrahedral anvil apparatus* (12). At this writing this apparatus has been successfully used at pressures of 100,000 atm. and temperatures of 3,000ºC. Instead of two opposing anvils with circular faces, four anvils with triangular faces have been used in this equipment. The four anvils are driven together by hydraulic rams along lines normal to the triangular faces, said lines intersecting at tetrahedral angles in the center of a regular tetrahedral volume enclosed by the anvils themselves. In this device, a regular pyrophyllite tetrahedron, the edges of which are 25 per cent longer than the corresponding legs on the triangular anvil faces, serves as pressure-transmitting medium, thermal and electrical insulation, and, by extruding between the anvils as they advance, provides the necessary compressible gasket. The sample container, a tube which also serves as electrical resistance heater, is located within the pyrophyllite tetrahedron and runs diagonally from opposite edges. Electrical connections are made to the sample tube through metal tabs which make contact with the anvils. A thermocouple is spot-welded or inserted in the wall of the sample container, and the leads are brought out through edges of the pyrophyllite tetrahedron. Friction of the pyrophyllite on the thermocouple leads is sufficient to hold them in place during high-pressure operation. Pressure transmitted to the contents of the sample tube is measured by noting changes in electrical resistance of Bi, Tl, Cs, and Ba.

A two-stage apparatus for measuring volume as a function of pressure to 100,000 atm. at room temperature has been described by Bridgman (14). A stepped-piston apparatus capable of developing maximum pressures near 200,000 atm. in which P-V relationships may be measured at room temperature has been developed at Brigham Young University (12).

Jamieson (15) has described a technique whereby x-ray diffraction studies may be made of substances at pressures in the neighborhood of 24,000 atm. In his device the pressure vessel is a three-carat single crystal diamond through which a highly polished straight hole .015 inch in diameter and .172 inch in length has been ground. Pistons, which are driven into each end of the hole by a calibrated spring, are air-hardened drill rod .090 inch long. A similar device has been built at the U. S. Bureau of Standards. The diamond they utilized is a large stone confiscated by the U. S. Customs.

A modified form of Bridgman's anvil apparatus has been devised by Chester & Jones (16) for making superconductivity measurements at low temperature. Ferromagnetic materials complicate superconductivity measurements; therefore beryllium copper was used as the material of construction.

Fitch, Slykhouse & Drickamer (16a), at the Department of Chemistry, University of Illinois, have devised an apparatus for measuring the optical properties of solids at pressures as high as 200,000 atm. This apparatus uses an alkali halide (normally sodium chloride) as a pressure-transmitting medium. Sodium chloride windows are used in this apparatus. The salt is fused in a long narrow hole that extends into the region of high pressure. The rate of extrusion of the sodium chloride at the extreme pressures used is sufficiently slow that optical measurements can be made. The specimen on which measurements are to be made is a thin wafer. It is squeezed between anvils which employ Bridgman's massive support principle. In addition, however, another principle is employed: the anvil is tapered on the sides, i.e., the anvil is a truncated cone. Sodium chloride surrounds this tapered region. When pressure is applied a pressure gradient exists along the taper. This pressure gradient gives a "multi-staging" effect and consequently allows a greater pressure to be sustained between the anvil faces. The greater the taper, the higher the gradient, but also the higher the tendency for compressed material to extrude from between the flat anvil faces. Fitch, Slykhouse & Drickamer have found that a single taper of six degrees on each side of the piston was the most advantageous.

The design of high-pressure, high-temperature apparatus for use in the 100,000 to 1,000,000 atmosphere range is an extremely important problem. The upper limit of pressure usefulness of any device is determined by the compressive strength of the materials of construction. A direct approach to the problem of obtaining higher pressures, then, is to be found in the field of materials. Diamond has the highest compressive strength of any known substance (about three times that of cemented tungsten carbides). Its extremely high cost and unavailability in large sections precludes its general use in high-pressure equipment. Diamond powder, however, is available in sufficient quantity and at such a price that a cemented diamond composition analogous to the cemented carbides could be used if such were obtainable. Although nothing has been published concerning such compositions, it is known that some work is being conducted in this area.

Melting point effects.--The study of melting point phenomena under high pressure conditions (particularly above 100,000 atm.) should eventually shed some light on the old question as to the character of the melting curve as pressure is increased indefinitely. Undoubtedly such studies will improve our comprehension of the nature of liquids and solids and the phenomena of melting. Pressure can either increase or decrease a melting point. If the liquid is more dense than the solid, application of pressure will lower the melting point. Conversely, if the solid is more dense than the liquid, the melting point will be raised. For pressures of the order of 100,000 atmospheres the change of melting temperature may be several hundred degrees C. Butuzov, Boksha & Gonikberg (17), utilizing apparatus previously referred to, have measured the melting point of black phosphorus and have found that the melting point rises smoothly with increasing pressure to about 1000ºC. at 18,000 atm.

Butuzov & Ponyatovskii (18) find that the mean increase in the melting point of In under pressure is 4.13 x 10^{-3} degrees per kg./sq. cm. over the range 0 to 3 x 10^{4} kg./sq. cm. (1 kg./sq. cm.=.968 atm.). The change in melting point is almost linear. The Clapeyron equation gives the change in volume of In on melting as 2.93 x 10^{-3} cc./gm. No polymorphic changes were detected.

Butuzov & Ponyatovskii (19) investigated the phase diagram of bismuth at pressures to 30,000 kg./sq. cm. at temperatures between the melting point and room temperature. The â phase melts in the pressure range of 17,300 to 22,400 kg./sq. cm. at a constant temperature of 184ºC. and hence becomes liquid without change in volume. The melting point of the Õ phase increases 0.0072º per kg./sq. cm. The phase changes á=â and â=á take place very rapidly and with marked hysteresis in the temperature range studied (rate of, change of temperature approximately 1º/sec.). At 20º the hysteresis in terms of pressure is approximately 1000 kg./sq. cm. for the á=â transition and approximately 900 kg. /sq. cm. for the â=Õ transition. Butuzov & Gonikberg et al. (8) report the change in melting point of bismuth as a function of pressure to 22,000 kg./sq. cm. The melting point decreases regularly from 270º at one atm. to 187º at 18,700 kg./sq. cm.

Butuzov & Gonikberg (20) have measured the melting temperature of Sn and Pb at a maximum pressure of 33,000 atm. At this pressure the melting point of Sn has increased to 315ºC. and that of Pb to 527ºC. In both cases no new phases are encountered and the melting curve is a smooth function.

Hall (21) has reported the melting point of Ge as a function of pressure to 180,000 atm. The melting point decreases linearly from 936º at one atm. with a slope of -3.27 x $1O^{-2}$ degrees per atm. The linear dependence indicates that no new solid phases form over this pressure range and that the liquid remains the more dense phase. Electrical resistance measurements indicate that the solid remains a semiconductor and the liquid displays metallic conduction over the entire pressure range.

As yet unpublished is some work by Dr. S. P. Clark (21a) of the Geophysical Laboratory, Carnegie Institution of Washington, on the melting points of NaCl, NaBr, NaI and KCl to 25,000 atm. The apparatus used is that of Birch's as previously described. Clark reports the melting point of NaCl increases from 800º to approximately 1150º at 25,000 atm.

Some recent theoretical work concerning melting points at high pressures that may be of interest are those of Valles (22), where the melting point of Fe at 4 x 10^{7}

atm. has been estimated to be 8136ºC., and Gilvarry (23), where fusion curves for the alkali elements have been predicted for high pressures. The question as to the existence of a critical point between liquid and solid at high pressures has been considered from a theoretical standpoint by Ebert (24) and by Zernike (25).

Of considerable significance to high-pressure work, when a fine-grained refractory material is used to serve as the thermally insulating container and also as pressure-transmitting medium, is the fact that extreme pressure can increase a refractory's melting point by several thousand degrees. Thus, with such a system, it is possible to operate under high pressure conditions at higher temperatures than is possible with the same materials at one atm.

Diamonds.--Since the motivating force behind the development of high-pressure, high-temperature techniques over a period of 100 years or so has been the desire to produce man-made diamonds, it seems appropriate to include in this review something concerning this subject. Perhaps the most cogent remark that can be made concerning the present status of man-made diamonds is that the Metallurgical Products Department of the General Electric Company, Detroit, Michigan, is now displaying pictures of a pretty girl with an "ohhh, diamonds!" expression looking at $30,000 worth of synthetic diamond grit. No direct statements or publications have been issued describing the details of work carried out at the General Electric Laboratory at Schenectady or of the developmental work in Detroit. However, a listing of some of the announcements originating with the Company may be helpful to those interested in this subject. The first, which apparently is no longer available, was the most complete and consisted of a large packet of pictures and printed material (26). Subsequent releases include the announcement in Nature (27) and the announcement by Bridgman (28), who became a consultant for the General Electric Research Laboratory shortly after the initial announcement was published. A constant trickle of minor bits of information from General Electric followed. One of the most interesting of these appeared in the "News-scripts" section of Chemical Engineering News (28a). It stated:

Starting materials apparently are not the most critical factor in General Electric's process for using high pressures to make synthetic diamonds from other forms of carbon (C. & E. N., February 21, 1955, page 718). One curious G. E. scientist, realizing that even a 49-cent jar of peanut butter contains a healthy amount of carbon, recently tried to make diamonds out of peanut butter--and succeeded.

A major news release was issued by General Electric on October 22, 1957 (29), announcing that 100,000 carats of industrial diamond grit had been produced to date, that the material was available for sale at $4.25 per carat, and that an expected 3 1/2 million carats were to be produced during 1958.

The General Swedish Electrical Industry (30) has announced the successful synthesis of diamonds. This company reports that its first diamonds were produced on the 15th of February, 1953. To quote Liander, manager of their design department,

> They consisted of about 40 small crystals ... and they were genuine beyond doubt. This was proved in several ways, among them the extremely reliable x-ray method. On the whole they were cube-like and colorless and faintly tinged with green. The experiment has since been repeated several times, again with successful results. The pressure was then calculated to be 80,000 to 90,000 atmospheres, and the maximum temperature was perhaps 5000ºF.

There have been no official announcements concerning the synthesis of diamonds by well established concerns other than those of General Electric and ASEA (Allmänna Svenska Electriska Aktiebolaget, Västerås, Sweden). However, there are current rumors that success in this endeavor has been achieved by several other American and European companies.

Literature pertinent to the problem of diamond synthesis has been summarized to the year 1911 by von Fersmann & Goldschmidt (31). Additional references are given by Mellor (32). Sonic references of interest in this work since the year 1924 are given in references (33 to 42).

In connection with the synthesis of diamonds the question arises as to whether or not synthetic materials with properties superior to those of diamond might be made. Wentorf (43) recently reported the preparation of a cubic form of boron nitride that rivals the diamond in hardness and is more resistant to oxidation at high temperature. Details of the process have not been given, but it is assumed that the process is closely related to that being used for diamond synthesis at General Electric.

There is no doubt that an adequate supply of industrial diamond grit at reasonable price is in the offing. The transformation this may bring to American industry may almost amount to an industrial revolution!

Geology.--The importance of high-pressure, high-temperature research to geology is quite obvious. Pressures of 200,000 atm. correspond approximately to depths of 400 miles within the earth. Although the temperature existing at such depths is not known with certainty, the temperatures that can be generated at high pressures in the laboratory are certainly as large as those which exist at this depth. Laboratory synthesis of high-pressure minerals can give an accurate estimate of the depth at which such minerals are formed within the earth.

The synthesis of a material of density greater than quartz has been reported by Coes (44). Coes found several systems that would produce this material at high pressure and high temperature. The best reaction mixture found consisted of equal parts of dry sodium meta-silicate and diammonium phosphate. This material was heated at a temperature of 750ºC. under a pressure of 35,000 atm. for a period of 15 hours. The yield of coesite (the name now given to the material) was about 30 mg. The density of this material is 3.01 and its refractive index 1.60 compared to a density of 2.66 and a refractive index of 1.55 for quartz. An outstanding property of this new dense silica is that it is not attacked by long heating in hydrofluoric acid. As yet, coesite has not been found in nature. Additional work oil coesite has been reported by Robertson et al. (45).

The synthesis of several high-pressure minerals, including all the garnets found in nature and some new ones not previously known, aluminum silicates, pyroxines, epidote minerals, and others, have also been reported by Coes (46). Wentorf (47) has discussed the formation of Gore Mountain garnet and hornblend at high temperature and pressure. Robertson et al. (45) have determined the stability relations of jadeite at pressures to 25,000 bars and temperatures to 1200ºC. Griggs & Kennedy (10), utilizing apparatus previously referred to, have reported phase boundaries in the region bounded by 40,000 atm. and 1000ºC. for the systems: gibbsite/diaspore + water, aragonite/calcite, jadeite + water/analcite, coesite/quartz, diaspore/corundum + water, pyrophyllite/sillimanite + quartz + water, pyrophyllite/ kyanite + quartz + water, and kyanite/sillimanite. A review of silicate systems, as well as some new experimental work under hydrothermal conditions, has been given by Roy & Tuttle (48).

Undoubtedly high pressure phases exist at great depths within the earth that do not exist on the earth's surface. High pressure laboratory studies should elucidate the nature of these phases and eventually help to explain more clearly some of the seismic phenomena. The possibility of the existence of phases with vastly different properties than the parent material was touched off by a paper of Wigner & Huntington (49) which calculated the approximate minimum pressure that would be required to transform solid hydrogen into a metallic form. This pressure was of the order of 250,000 atm. At the time their paper was written, such pressures were outside the scope of available techniques. However, today such pressures are within the realm of possibility. Papers which have some bearing on the nature of the earth's interior are listed in references (50 to 53).

Superconductivity as a function of pressure.--Superconductivity is a phenomenon of metallic conductors in which electrons, moving through under an applied emf. at very low temperatures, instead of meeting resistance due to obstruction of their paths by the metallic atoms, move as a wave function harmonically linked to the vibrations of the atoms in such a way as to reduce the resistance to flow to an immeasurably small value (54). The ability of a metal to assume the superconducting state depends upon several factors, including what might be termed its coupling coefficient to the electron, the free volume in the crystals, the natural frequency of the atoms, and the valence, which must be odd and preferably 3, 5 or 7. Among these determinants, pressure may have an influence on three of them, i.e., the free space between the atoms, their natural frequency, and their valence.

In general, if there are polymorphic transitions induced in a metal, by pressure the higher pressure forms will have greater density and therefore less free volume than those at lower pressures, so that pressure should reduce the temperature of transition to the superconducting state and in some cases eliminate it. When no crystal transformation occurs the compression of the lattice may not necessarily reduce the transition temperature.

It has been observed that it is more difficult for heavy atoms to assume the superconducting state than for light, probably because of the low natural frequency of the heavy atoms. Because of the asymmetry of the pressure-density curve it would be anticipated that pressure on heavy metals should increase the temperature of transition by increasing the frequency of vibration of the atoms.

The third possible influence of pressure is to force a valence electron into an unsaturated inner orbital, thus changing the valence from an unfavorable to a favorable number.

Concerning the influence of pressure on the natural frequency of the atoms, and consequently on the temperature at which a metal becomes superconducting, Mase (55) has discussed the observations of Kamerlingh Onnes that pressure decreases the temperature of transition and concludes that in these cases the lowering of the temperature is consequent upon a change in lattice vibrations in an unfavorable direction. A study by Fisk (56) shows good agreement between observation and theory for tin but poor for thallium. However, the pressures used were very small, viz., only up to 1.15 atm. Gaber and Mapother (57), in a more detailed study of the influence of pressure on the transition temperature for tin, found that $dT_c/dP=4.40\pm.20 \times 10^{-5}$ degree/atm. up to 100 atm., which indicates that the tin atom has a natural frequency on the low side of the most favorable, and consequently a rise in pressure raises T_c. Chester and Jones (16) observed that T_c for tin varies approximately linearly with pressure up to 17,500 atm. They show a negative influence of pressure on T_c for thallium. In addition, they observed that bismuth can become superconducting under high pressures.

It is known that where a metal may have an unfavorable crystal structure or unfavorable valence for superconductivity, by alloying it with another element that gives a favorable average valence or a more open crystal structure, it may become superconducting, and to date alloys have been found that become superconducting at higher temperatures than any of the pure metals. Alekseevskii and co-workers (58 to 58c), in addition to studying pure bismuth and cadmium, have given attention to alloys, especially those of gold and bismuth, bismuth and potassium, and bismuth and lithium. In the case of Au_2Bi and Bi_2K, which have monotypical lattices, T_c increases with pressure for the Bi_2K but decreases for Au_2Bi. Since this difference cannot be attributed to changes in the lattice, it is explained as due to a change in the electron concentration. If this is true, alloys deficient in bismuth should have a negative value for dT_c/dP, which was found to be true for BiLi. For Bi_3Ni they found that the transition temperature rises with pressure according to the equation $dT_c/dP=5.4 \times 10^{-5}$ degree $atm.^{-1}$.

No case involving electronic allotropy has yet been studied. It has been proved that the large transition in bismuth is due to a change in lattice structure (59).

Electrical resistance of conducting materials under Pressure.--Relatively few papers on electrical conductivity of materials under pressure or on the theoretical explanation of observed results have appeared since the extensive review of recent work in the field of high pressures by Bridgman (60) and the more recent edition of his book (6, 14). Several theoretical attempts to explain the influence of pressure on resistance were covered in the 1946 review, some of which showed qualitative agreement with segments of the experimental data, but no one of which can be regarded as entirely satisfactory. In general, electrical resistance decreases with increase in pressure, but there are striking exceptions, specifically, calcium, strontium and lithium, which give trouble to the theories.

As an extension of former measurements to higher pressures and in preparation for planned subsequent measurement to 100,000 kg./cm.^{2}, Bridgman measured the electrical resistances of 29 metals and intermetallic compounds to 30,000 kg./cm.^{2} (61). The resistances decrease with pressure for all except the intermetallic compound Ag_2Al. Most of the elements show a decreasing reduction in resistance as the pressure increases to higher values, but eleven showed virtually constant decrease with increasing pressure.

In 1952 Bridgman (13) published resistances of 72 elements, compounds, and alloys to 100,000 kg,/cm.^{2}, following this in the next year by measurements on numerous elements to the same pressure but at temperatures up to 200º (62). His third paper in this series was confined to 20 compositions of bismuth and tin and 5 of bismuth and cadmium (63). This study was followed in 1954 by measurements on 13 binary alloys (64). In the same year he published resistance and compression measurements on 7 rare earth metals unavailable at the time of earlier studies. The metals in this group were samarium, dysprosium, holmium, erbium, thullium, ytterbium and lutecium. To use Bridgman's words (65), the rare earth metals show "an unusual constellation of anomalies." Numerous first-order transitions have been observed with these metals, but most of the transitions are observable only by electrical resistance measurements and these appear to be associated, at least in part, with movement of electrons from the conduction band down into lower unsaturated orbitals of higher energy. This has been most clearly demonstrated with cerium where there is a large volume and resistance break between 7 and 12,000 kg., and where it has been shown that there is no change in the crystal structure. Two other elements, viz., gadolinium and ytterbium show an irreversible change in both resistance and volume. The literature does not reveal that this increase in density has been studied by mechanical or electrical means. If the irreversibility should involve a transfer of outer electrons to inner orbitals, it would be of great scientific interest. The purposes of this review would not be served by detailing the numerous anomalies observed, but it should be mentioned that in all of the rare earths sluggish changes are characteristic and sometimes, as in the case of erbium, a first-order transition is smeared out all the way from 20,000 to 100,000 kg. There will be work for theoreticians in this field for years to come.

Kapustinskii (53) has discussed this electronic allotropy, which he has termed electronic isomerization, and particularly has applied it to geophysical problems. He divides the influence of pressure on the electronic shells into two regions. In the first, extending up to about 120,000 atm., electrons are forced from outer orbitals into unfilled higher energy positions. At much higher pressures, in accord with modern thinking, he postulates that the orbitals become completely "crushed" and the atoms lose their chemical identity. On the basis of this thinking he divides the earth into three zones: zone (a), the geosphere, extends to about 100 km. depth where the periodic laws are obeyed and the normal chemical properties are retained. In zone (b) the lower limit of which is not clearly definable, chemical properties are changed by electronic allotropy but reactions occur and compounds exist much as at the earth's surface. On the other hand, on zone (c), the centrosphere, all of the atoms have lost their chemical identity and exist only in the "universal metallic state." Kapustinskii supports his hypothesis with thermodynamic, quantum mechanical, and seismological data.

In view of Bardeen's (66) success in explaining the six hundredfold decrease in electrical resistance of single crystal tellurium with increase of pressure to 30,000 kg., where it was shown that tellurium is a typical semiconductor in which the normal energy gap between the filled band and the conduction band is 0.29 ev. and decreases with pressure to 0.015 at a pressure of 30,000 kg., Bridgman undertook a study of the effect of pressure on 7 semiconducting oxides plus germanium and silicon in both the n and p conditions (67). Measurements were made to 50,000 kg. using silver sulfate as the "hydrostatic," pressure-distributing material. The oxides studied were ZnO, Mn_3O_4, NiO, TiO_2, V_2O_5, U_3O_8, Fe_2O_3, $NiTiO_3$. No common type of behavior was observed and reproducible data were hard to obtain. Bridgman feels that all that can be hoped for is a qualitative picture which may help in establishing a working hypothesis. The electrical resistance may change in either direction by a factor of 10 or even more. Usually, however, resistance decreases at room temperature and at 200°, with the exception of Mn_3O_4. The decrease in resistance at 200° is generally smaller than that at room temperature. Theoreticians can find data here to fit almost any hypothesis!

One of the most comprehensive studies on the electrical resistance of metals to date is that by Lawson (68) who has analyzed the data extant in an effort to find scientific bases for the various types of behavior observed.

Germanium has been subjected to intensive study for a number of years due to its theoretical and industrial importance, and there are three papers within recent years devoted to the influence of pressure. Hall, Bardeen & Pearson (69) studied the electrical resistance of *p-n* junctions of germanium and applied Shockley's theory of the resistance of such a junction, in which the resistance is regarded as proportional to $\exp(E_g/kT)$ where E_g is the energy gap between the valency and conduction bands. The measurements over a range of 10,000 lb./sq. in. show a $ÄR_0/R_0$ of 12.5 per cent which corresponds to a change ÄE_g of approximately 3.1 x 10^{-3} ev. Also, measurements made at different temperatures yield an energy gap of about 0.72 ev.

Taylor (70) measured the electrical resistance of germanium between 297-475ºK and at pressures up to 4500 lb./sq. in. Over this small range of pressure the resistance varies linearly with pressure and at 300ºK. Ä*R/R*=10.2 ±.04 x 10^{-5}/atm.

Three years later Paul & Brooks (71) raised the upper pressure in similar measurements to 30,000 kg./cm.^{2} at 25º-76ºC., and also measured the influence of pressure on resistance up to 7000 kg. at -195ºC. The results indicate an increase in the total energy gap up to 15,000 kg. at a rate in good agreement with earlier experiments. Above 15,000 kg. the *n*-type germanium shows a rapid rise in resistance regardless of purity. The explanations were based on a decrease of electron mobility with increase in pressure and a concomitant deionization of impurities. In the following year Paul & Pearson (72) made similar measurements on pure single crystal silicon and found that, in contrast to germanium, the energy gap between the conduction and the valence bands decreases with increase in pressure.

Ionic conduction of crystals has received attention from Mennonöh & Jost (73, 74), from Kurnick (75), and from Yanagimoto (76). In the first reference the object was to study the influence of the transition from a pure crystal to a mixed crystal on the pressure coefficient of the electrical conductivity. Both silver chloride and silver bromide were used as the pure crystal and increasing amounts of $PbCl_2$ were added. As was predicted, the pressure coefficient decreases as the amount of lead chloride is increased. Mennonöh & Jost (74) made similar studies at 250º to 300º and up to 10,000 atm. but using solid solutions of silver chloride and lead chloride on the one hand, and silver bromide and lead bromide on the other. For the silver chloride solid solutions, the conductivity decreases with increase in lead chloride toward a limiting value, while with the silver bromide-lead bromide solid solutions, the conductivity increases to a maximum and then decreases as lead bromide is added.

Kurnick studied the concentration of defects in the silver bromide lattice by treating it with cadmium bromide to block the vacancies. The temperature was maintained at 300º and the influence of pressure was studied up to 8000 kg./cm.$_2$ By observing the mobilities of the Ag ions and of the vacancies, it was concluded that the molal volume, ÄV, of imperfections at this temperature amounts to 16 cc./mole. The free volumes associated with these motions were found to be reduced by 2.7 and 7.4 cc./mole, respectively, The ÄV is uninfluenced by the Frenkel disorder type.

The ionic conductivity of $K_4Fe(CN)_6$ was measured by Yanagimoto who found that as the pressure is increased a minimum of conductivity occurs at 1410 kg./cm.$_2$

Karpov (77) prepared 99.4-99.8 per cent pure diamagnetic AgO and measured electrical resistance at pressures up to 12,000 kg./cm.$_2$ at 20º. At the maximum pressure and 20º the specific resistance was found to be 7 x 10^{-2} ± 15 per cent. It was concluded from the fact that the temperature coefficient between -40º and +20º is positive that this compound is an electronic semiconductor.

Magnetic effects of pressure.--In his 1946 review, Bridgman (60) cited nine papers on the interaction of pressure and magnetic properties of ferromagnetic materials. In general the effect of applying pressure at constant field is to decrease the flux, often by very large amounts. A 30 per cent nickel alloy was reported to be rendered nearly nonmagnetic by pressure of 12,000 kg./cm.^{2} Evidence was cited that the Curie temperature for ferromagnetic materials is independent of pressure while other data lead to the conclusion that this point can be displaced by measurable amounts.

Bader (78) in 1953 published a discussion of the influence of pressure on the Curie point for iron and nickel as interpreted from Heisenberg's Exchange Integral. In the following year Sawaguchi (79) published a study of the two-dimensional influence of pressure on the Curie point with barium titanate, in which he observed that the Curie point may be expressed as a function of pressure according to the equation $T_c=120 + 3.1 \times 10^{-5}P^2$. His interpretation of the results was that the influence of one- and three-dimensional pressure on T_c can be accounted for satisfactorily by the Clausius-Clapeyron equation, but for the two-dimensional application of pressure this equation is inadequate. He concludes that there might have been some secondary effects in Forsberg's experimental results other than pure two-dimensional pressure (80).

In the same year Patrick (81) made a very extensive study of pressure and the Curie point, using iron, cobalt, nickel, gadolinium, a 96:4 ferrosilicon, 90:10 ferrosilicon, the alloys compensator, invar, permalloy, monel, alumel, and a manganese-zinc ($Mn_{.5}Zn_{.5}Fe_2O_3$) and a lanthanum-strontium ferrite ($La_{.75}Sr_{.25}MnO_3$). In these materials the Curie point ranged between 16° for gadolinium and 1120° for cobalt. The results disagree with two common forms of interaction curves, and those for iron do not agree with Kornetzki's predictions based on measurements of volumetric magnetostriction. In the same issue of *The Physical Review*, Smoluchowski (82) reviews the experiments of Patrick and finds a fair agreement between them and theory based on a Brillouin function.

The affect of pressure on ferroelectric phenomena in sintered barium and strontium titanates was studied by Michels & van Meurs (83). In this case the dielectric constant of sintered $(Ba,Sr)TiO_3$ was determined at 1000 cycles and between 25° and 150° at pressures up to 3000 atm. In each case studied the dielectric constant, when measured as a function of temperature, rises rapidly to a maximum and then falls off hyperbolically as if following a Curie-Weiss law, $e=c/(T-T_p)$. The influence of pressure was found to be a broadening of the maximum, a reduction of its height and a displacement toward lower temperatures. For example, when the pressure was atmospheric the maximum was found to be at 57° while at a pressure of 3000 atm. the maximum was attained at 45°. Empirical qualitative conclusions on the height and the position of the maximum are drawn.

The saturation magnetization of nickel as a function of pressure was studied by Jones & Stacey (84), who used pressures up to 10,000 atm. and fields to 12,000 oersteds. In addition they tested the hypothesis that some nonferromagnetic materials under sufficient pressure might become ferromagnetic. No evidence for such a transformation was found with palladium, platinum, molybdenum, tungsten, copper, silver, or gold. In no case did the volumetric susceptibility exceed 0.0006 at low-field intensities or 0.0003 at the highest field intensities.

An interesting paper by Benedek & Purcell (85) reports on the nuclear magnetic resonance observed in liquids by the "spin-echo" or free-precession technique using pressures up to 10,000 atm. and studying solutions in water, pentane, hexane, toluene, ethyl iodide, and methyl iodide as the solvents. In all of the solvents the proton relaxation time was found to decrease with increasing pressure, a behavior which was explained by the assumption that the dominant relaxation mechanism involves a coupling between the nuclei and the intramolecular fields and therefore the relaxation time is at least partially determined by the rotational freedom of the molecule, which obviously would be reduced by increasing pressures. A study on the influence of pressure on the Curie point of barium titanate single crystals (86) led Merz to the conclusion that the lowering of the Curie point by pressure gives the same results as shrinking the lattice would through the substitution of strontium for barium. Up to 25,000 atm. $dT_c/dP = -5.8 \times 10^{-3}$ degree/atm.

The first-order transition point near 0ºC. decreases with pressure up to 1500 atm. and subsequently rises again.

Miscellaneous electrical phenomena.--Some miscellaneous electrical phenomena associated with pressure have been studied during recent years. For example, Michels & Perez (87) observed the displacement of the Piezoelectric frequency of quartz by pressure. Two quartz plates were used of 942 and 6040 kilohertz. For these the rate of change of frequency with pressure was 8.03×10^{-6} $cm.^2/kg.$ and -2.03×10^{-6} $cm.^2/kg.$, respectively. It was suggested that oscillating quartz plates might be used for the determination of pressure inside closed vessels. Wall & Gill (88) investigated the influence of pressure on transference numbers for electrolytes and found that 1000 bars produce a slight increase in the transference number for hydrogen ion in N/10 HCl but approximately a 2 per cent decrease for K ion in N/10 KCl and a still larger decrease for NaCl.

Considerable interest has been shown in the effect of pressure on the dielectric constant. For earlier literature the reader is referred to Bridgman's 1946 review. Recently Reitzel (89) has determined the effect of pressure on the dielectric constant of vitreous silica between 25º and 138º and at pressures to 4000 $kg./cm.^2$ The molecular polarization was found to decrease linearly with pressure with a slope that is independent of temperature. The relative decrease in polarization was found to be -1.6×10^{-6} $kg./cm.^2$

Alekseevskii & Brandt (58b) have studied the effect of pressure on the Hall effect. With bismuth of purity 99.9996 per cent, no influence of pressure on the Hall effect was observed, but with bismuth containing 0.02 per cent lead, a maximum in the curve of Hall effect vs. temperature was found between 30º and 40ºK. They speculated that this maximum is due to a dependence of the concentration of conducting electrons on the pressure.

It was observed by Braun (90) that a pressure of oxygen has no effect on phosphors, at least up to 150 kg./cm.^{2} However, large mechanical pressure does change the behavior of phosphors, an influence that has been ascribed by Braun to rupture of the phosphor crystals.

Pressure induced by shock, waves or by a detonating explosive.--In general, pressures that can be attained in the advancing front of a shock wave in a gas do not run higher than the source and therefore shock waves are not a promising source of pressures for scientific study. On the other hand, temperatures in shock waves may exceed 10^{4}ºK. and when combined with the pressure make a unique region for study even though phenomena are exceedingly transient. More rewarding for the study of simultaneous high temperature and high pressure is the detonation of explosives where indications are that pressures of the order of several hundred thousand atmospheres concomitant with temperatures of several thousand degrees may be attained. Here, also, the time interval is extremely short and yet some molecular processes are so rapid as to go virtually to completion in the time available. Only detonations of solid or liquid explosives provide pressures in the high range.

In 1952 Hikita (91) published a useful review of detonation covering theory of mechanisms, equations of state, internal energy, and compositions of the products.

The measurement or calculation of Chapman-Jouguet pressures in detonation of numerous experimenters, a selected list of which is:

Sakurai (92) who described a method of measuring the velocity of the wave front in trinitrotoluene and found a pressure of approximately 60,000 kg./cm.^{2}, in good agreement with theory. Duff & Houston (93), who measured the pressure and reaction zone in a detonating explosive; Nahmani & Manheimer (94), who observed a velocity of 6000 meters per second, a temperature of 4000ºK., and a pressure of 89,000 atm. in detonating nitromethane; Hikita & Kihara (95), who have calculated pressures and other properties of detonating explosives by use of an equation of state of their own devising. Temperatures and pressures for trinitrotoluene, tetryl, pentrite-NaCl, pentrite-NH_4NO_3, TNT-NH_4NO_3, $Hg(ONC)_2$ and $Hg(ONC)_2$-$KClO_3Pb(N_3)_2$.

In 1956 Noddack & Grosch (96) reviewed methods of measuring explosives and temperatures and gave seven tables of data. By the relatively recent method of maximum surface pressure using one-gram compressed charges they found surface pressures between 11,400 and 14,300 kg./cm.$_2$ for four metallic triazides and mercuric fulminate. Cook & Keyes (97) measured the pressures in detonating granulated trinitrotoluene by means of the acceleration of a metal slug. Peak pressures observed ran to about 4500 atm. The last of this series is an important paper on detonation pressure measurement by Schall (98) who concludes that an upper limit to the Chapman-Jouguet pressure can be assigned for any explosive. He avers that the real pressures during detonation come to within 20 to 30 per cent of this tipper limit, which for nitropenta is 310,000 atm. and for hexolite 300,000 atm.

Newer measurements by the method of free surface yield approximately 40 per cent higher pressure; therefore the maximum pressure in the detonating wave front goes up to 400,000 atm. The actual peak pressure is reported as approximately two times the Chapman-Jouguet pressure. On the other hand, Schall concludes that the peak pressure in solids has little significance. He reports that an Abel-type equation of state serves qualitatively very well.

Other than one industrial process making use of a detonated explosive for compacting powdered metals prior to sintering, no recent use of explosives for the study of high pressure effects has been made except in studies of explosives themselves. Nevertheless, the substantial progress in the understanding of phenomena in a detonating explosive within the past decade has made a real contribution to the science of high pressures, especially through attention given to the equation of state. It would seem that electronic allotropy might well be studied in a detonating explosive through its probable effect on the velocity of detonation and through density changes observable by means of high-speed x-rays. Accepting Schall's conclusion that a detonating wave front may go to 400,000 atm., such a technique would make available a new region of pressure at, as yet, unattained temperatures.

Equation of state.--Customarily, the starting point for the determination of an equation of state serviceable in connection with the detonation velocity of an explosive, at least for a solid explosive, has been one of the three equations derived by Fürth (99), by Pack, Evans & James (100), or by Murnaghan (101). Fürth's equation is complicated and difficult to use but satisfactorily fits extant data for solids at very high pressures.

Pack, Evans, & James' equation was suggested by quantum mechanical considerations and is relatively simple, involving only two assignable constants. Murnaghan's equation, derived from elasticity theory for solids, is the simplest of all with but one arbitrary constant, though the sum of the two measurable elastic constants may be used as an arbitrary value for fitting data.

For equations of state for gases under extreme pressure, reference should be made to Kihara & Hikita (102), and a later paper by Hikita (103), who have applied their equation of state to the calculation of the velocity of shock waves in air, iron and lead. A critical review of the classical theory of detonation waves is presented, giving theories for detonation in finite charges, the time dependence of detonation, detonation failures, etc.

In 1954 F. Cramer (104) published an empirical equation for extremely high pressure and applied it to several gases. He gave derivations of the thermodynamic quantities: potential, free energy, internal energy, enthalpy, entropy, and the two specific heats. The equation contains only three arbitrary constants and is said to be in error at 3000 atm. by less than 1 per cent. In the same year Murgai (105) derived an equation for the detonation velocity as a function of loading density.

As pointed out by Cook (106), who also derived an equation of state for extreme pressures from hydrodynamic theory of detonation, nearly any reasonable equation can be satisfactory for condensed explosives due to the inaccuracy in the measurements of detonation velocities.

An entropic equation of state applicable to shock waves was published by Duvall & Zwolinski (107) in 1955.

Perhaps the most important work going on at present in an effort to establish the pressure-volume-temperature relations in a gas is that of Saurel & Vodar (108), who are attempting high precision measurements to 10,000 atm. and 1000ºC.

The influence of pressure on radioactive decay.--It is probable that pressures of any magnitude so far attained in the laboratory will have little or no influence upon radioactive decay involving only intranuclear reactions. On the other hand, a large number of artificially radioactive isotopes are known in which decay may occur through the capture of an orbital electron and the subsequent emission of a neutrino. In such cases of radioactive decay any external influence that affects the electronic configuration of the orbitals surrounding the nucleus or the number of electrons in these orbitals should have an influence upon the rate of radioactive decay. This radioactive decay, called K capture, because the K electrons are closest to the nucleus and are therefore the most frequently captured, should be proportional to the density of electrons near the nucleus, which in turn should be influenced by pressure.

The chemical transformation of an atom to an ion should make sufficient difference in the electronic density, especially for light atoms, to be observable in rate of radioactive decay. The lightest element showing K capture is beryllium, and in 1949 Segré & Wiegand (109) demonstrated that BeO decays more slowly than metallic beryllium. Bauchez et al. (110) demonstrated that beryllium fluoride decays more slowly than beryllium. Subsequently, Bainbridge (111) made a very careful comparison between the rates of radioactive decay of beryllium metal, beryllium oxide and beryllium fluoride, and found that the metal decays 0.13 per cent faster than the oxide and 0.74 per cent faster than the fluoride. This means that the oxide will decay 0.61 per cent faster than the fluoride, which is consistent with what we know about the separation of charge in these two compounds. In addition they found that T_c^{99m} decays more rapidly as potassium tecnetate than as tecnetium sulfide. The pure metal electroplated onto nickel and reduced in hydrogen also decays more rapidly than the sulfide.

To date no paper has been published giving experimental data on the influence of pressure on K capture. However, a private communication from Bainbridge (112) states that he has been working on this problem. Mr. Barney Gogarty, at the University of Utah (113) has found a demonstrable effect of pressure on the decay of beryllium 7 in beryllium chloride and at present is working on the influence of pressure on K capture by gallium.

LITERATURE CITED

1. Hall, H. T., in Proceedings of Symposium, High Temperature--A Tool for the Future, 161-66 (Stanford Research Institute, Menlo Park, California, 218 pp., 1956)
2. Hall, H. T., J. Wash. Acad. Sci., 47, 300-4 (1957)
3. Kistler, S. S., in Proceedings of Symposium, High Temperature-A Tool for the Future, 151-58 (Stanford Research Institute, Menlo Park, California, 218 pp., 1956)
4. Hall, H. T., Brown, B., Nelson, B., and Compton, L.A., J. Phys. Chem. (In press)
5. Parsons, Sir Chas., Proc. Roy. Soc. (London), 44, 320-23 (1888)
6. Bridgman, P. W., The Physics of High Pressure, Plate I facing p. 44 (G. Bell & Sons, London, England, 445 pp., 1949)
7. Coes, L., Jr., A New Dense Silica (Presented at 7th Symposium on Crystal Chemistry, Rutgers University, New Brunswick, New Jersey, June, 1954)

   7a. Roy R., and Tuttle, O. F., Physics and Chemistry of the Earth, 1, 144 (Pergamon Press, London, England, and New York, N. Y., 1956)
8. S. Butuzov, V. P., Gonikberg, M. G., and Smirnov, S. P., Doklady Akad. Nauk S.S.S.R., 89, 651-53 (1913); National Science Foundation Translation No. 76 (September, 1953)
9. Birch, F., and Robertson, E. C., Office of Naval Research, Final Rept., Contract N5-ori-07644, Task No. NR-032400 (March, 1957)
10. Griggs, D. T., and Kennedy, G. C., Am. J. Sci., 254, 720-35 (1956)
11. Bridgman, P. W., Proc. Roy. Soc. (London), A203, 1-17 (1950)
12. Hall, H. T. (In press)
13. Bridgman, P. W., Proc. Am. Acad. Arts Sci., 81, 165-251 (1952)
14. Bridgman, P. W., The Physics of High Pressure, (G. Bell & Sons, London, England, 445 pp., 1949)
15. Jamieson, J. C., J. Geol., 65, 334-43 (1957)
16. Chester, P. F., and Jones, G. 0., Phil. Mag., 44, 1281 (1953)

    16a. Fitch, R. A., Slykhouse, T. E., and Drickhamer, H. G. (Personal communication)
17. Butuzov, V. P., Boksha, S. S., and Gonikberg, M. G., Doklady Akad. Nauk S.S.S.R., 109, 837-40 (1956)
18. Butuzov, V. P., and Ponyatovskii, E. G., Kristoallgrafiya, 1, 736-37 (1956)
19. Butuzov, V. P., and Ponyatovskii, E. G., Kristallografiya, 1, 572-76 (1956)
20. Butuzov, V. P., and Gonikberg, M. G., Doklady Akad. Nauk S.S.S.R., 91, 1083-84 (1953); National Science Foundation Translation No. 144 (December, 1953)
21. Hall, H. T., J. Phys. & Colloid Chem., 54, 1144-46 (1955)

    21a. Clark, S. P., Jr. (Personal communication)
22. Valles, P. E., Ann. geofis. (English summary), 8, 189-200 (1955)
23. Gilvarry, J. J., Phys. Rev., 102, 317-25 (1956)
24. Ebert, L., Ost. Chem-Zeit., 55, 1-11 (1954)

25. Zernike, J., Chemical Phase Theory, 39-46 (Kluwer's Publishing Company, Ltd., Deventer, The Netherlands, 494 pp., 1955)
26. Press Release, Man-made Diamonds (Public Information, Research Information Services, General Electric Research Laboratory, Schenectady, New York, February 15, 1955)
27. Bundy, F. P., Hall, H. T., Strong, H. M., and Wentorf, R. H., Jr., Nature, 176, 51 (1955)
28. Bridgman, P. W., Sci. American, 193, 42-46 (1955)
    28a. Chem. Eng. News, 100 (July 22, 1957)
29. Press Release, Man-Made Diamonds (Press Relations Department, Metallurgical Products Department, General Electric Company, Detroit, Michigan, October 22, 1957)
30. Liander, H., ASEA Journal, 28, 97-98 (1955)
31. Fersmann, A. von, and Goldschmidt, V., Der Diamont (Winter, C., Heidelberg, Germany, 274 pp., 1911)
32. Mellor, J. W., Comprehensive Treatise on Inorganic and Theoretical Chemistry (Longmons Green & Co. Ltd., London, England, 1924)
33. Jessup, R. S., and Rossini, F. D., J. Research Natl. Bur. Standards, 21, 491 (1938)
34. Gunther, P. L., Geselle, P., and Rebentisch, W., Ind. Diamond Rev., 6, 42-46 (1946)
35. Bridgman, P. W., J. Chem. Phys., 15, 92-98 (1947)
36. Eyring, H., and Cagle, F. W., Jr., Zeit. fur Elektrochem., 56, 480-83 (1952)
37. Neuhaus, A., Angew. Chem., 66, 525-36 (1954)
38. Lloyd, S. G., J. Alabama Acad. Sci., 26, 28-32 (1954)
39. Berman, R., and Simon, F., Z. Elektrochem., 59, 333-38 (1955)
40. Liljeblad, R., Arkiv Kemi, 8, 423-32 (1955)
41. Berman, R., and Thewlis, J., Nature, 176, 834-36 (1955)
42. Ruzicka, P., Ind. Diamond Rev., 16, 189-216 (1956)
43. Wentorf, R. H., Jr., J. Chem. Phys., 26, 956 (1957)
44. Coes, L., Jr., Science, 118, 131-32 (1953)
45. Robertson, E. C., Birch, F., and MacDonald, G. J. F., Am. J. Sci., 255, 115-37 (1957)
46. Coes, L., Jr., J. Am. Ceram. Soc., 38, 298 (1955)
47. Wentorf, R. H., Jr., Am. J. Sci., 254, 314-19 (1956)
48. Roy, R., and Tuttle, 0. F., Physics and Chemistry of the Earth, 1, 138-80 (Pergamon Press, Ltd., London, England, and New York, N. Y. (1956)
49. Wigner, E., and Huntington, H. B., J. Chem. Phys., 3, 764-70 (1953)
50. Ryabinin, Y. N., Doklady Akad. Nauk S.S.S.R., 104, 721-24 (1955)
51. Knopoff, L., and Uffen, R. J., J. Geophys. Research, 59, 471-84 (1954)
52. Bernal, M. J. M., and Massey, H. S. W., Monthly Notices Royal Astron. Soc., 114, 172-79 (1954)

53. Kapustinskii, A. F., Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk, 4, 427-34 (1956)
54. Bardeen, J., Cooper, L. N., and Schrieffar, J. R., Phys. Rev., 106, 162 (1957); Matthias, B. T., Sci. American, Nov. 1957, 92.
55. Mase, S., Busseiron Kenyu, 53, 10-15 (1952)
56. Fisk M. D., Phys. Rev., 94, 495-96 (1954)
57. Gaber, M., and Mapother, D. E., Phys. Rev., 94, 1065 (1954)
58. Alekseevskii, N. E., Zhur Eksptl. i Teoret. Fiz., 19, 358-60 (1949)
    58a. Alekseevskii, N. E., Brandt, N. B., and Kostina, T. I., Izvest. Akad. Nauk S.S.S.R. Ser. Fiz., 16, 233-63 (193-2)
    58b. Alekseevskii, N. E., and Brandt, N. B., Zhur. Eksptl. i Teoret. Fiz., 22, 200-03 (1952)
    58c. Alekseevskii, N. E., and Gaidukov, Yu. P., Soviet Phys. JETP, 2, 762-64 (1956)
59. Vershchagin, L. F., and Brandt, I. V., Doklady Akad. Nauk S.S.S.R., 108, 423 (1936)
60. Bridgman, P. W., Rev. Modern Phys., 18, 1 (1946
61. Bridgman, P. W., Proc. Am. Acad. Arts Sci., 79, 149-79 (1951)
62. Bridgman, P. W., Proc. Am. Acad. Arts Sci., 82, 83-100 (1953)
63. Bridgman, P. W., Proc. Am. Acad. Arts Sci., 82, 101-56 (1953); Bridgman, P. W., Proc. Am. Acad, Arts Sci., 84, 1, 111 (1955)
64. Bridgman, P. W., Proc, Am. Acad. Arts Sci., 83, 151 (1954)
65. Bridgman, P. W., Proc. Am.. Acad. Arts Sci., 76, 63 (1948); 81, 211 (1952); 82, 97 (1953); 83, 1 (1954)
66. Bardeen, J., Phys. Rev., 75, 1777 (1949)
67. Bridgman, P. W., Proc. Am. Acad. Arts Sci., 79,127-48 (1951)
68. Lawson, A. W., Seventh Annual Report to ONR on High Pressure Research, 1953-54 (Institute for the Study of Metals, University of Chicago, Chicago, I11.)
69. Hall, H. H., Bardeen, J., and Pearson, G. L., Phys. Rev., 84, 129-32 (1951)
70. Taylor, J. H., Phys. Rev., 80,919-20 (1950)
71. Paul, W., and Brooks, H, Phys. Rev., 94, 1128-33 (1954)
72. Paul, W., and Pearson, G. L., Phys. Rev., 98, 1755-57 (1955)
73. Mennonöh, S., Z. Electrochem., 64, 433-36 (1950)
74. Jost, W., and Mennenöh, S., Z. physik. Chem. (Leipzig), 196, 188-95 (1950)
75. Kurnick, S. W., J. Chem. Phys., 20, 218-28 (1952)
76. Yanagimoto, T., Rev. Phys. Chem. Japan, 23, 30-34 (1953)
77. Karpov, L. Ya., Doklady Akad. Nauk U.S.S.R., 78, 713-16 (1951)
78. Bader, F., Z. Naturforsch., 8a, 675-76 (1953)
79. Sawaguchi, E., Busseiron Kenkyu, 74, 27-30 (1954)
80. Forsberg, P. W., Phys. Rev., 93, 686 (1951)
81. Patrick, L., Phys. Rev., 93, 384-92 (1954)
82. Smoluchowski, R., Phys. Rev., 93, 392-93 (1954)

83. Michels, A., and Meurs, P. van., Compt. rend., 315-16 (1952)
84. Jones, G. 0., and Stacey, F. D., Proc. Phys. Soc. (London), 66B, 255-56 (1953)
85. 85. Benedek, G. B., and Purcell, E. M., J. Chem. Phys., 22, 2003-12 (1954)
86. Merz, W. J., Mass. Inst. Technol. Lab. Insulation Research Tech. Rept., 29, 1-8 (1950)
87. Michels, A., and Perez, J. P., Physica, 17, 563-564 (1951)
88. Wall, F. T., and Gill, S. J., J. Phys. Chem., 59, 278-83 (1955)
89. Reitzel, J., Nature, 178, 940 (1956)
90. Braun, E. A., Bull. Research Council Israel, 4, 219-21 (1954)
91. Hikita, T., J. Ind. Explosives Soc. Japan, 13, 3-8, 77-85 (1952)
92. Sakurai, T., J. 1nd. Explosives Soc. Japan, 15, 8-11 (1954)
93. Duff R. E., and Houston, E., J. Chem. Phys., 23, 1268-73 (1955)
94. Nahmani, G., and Manheimer, Y., J. Chem. Phys., 24, 1074-77 (1956)
95. Hikita, T., and Kihara, T., J. Industrial Explosive Soc. Japan 17, 261-70 (1956)
96. Noddack, W., and Grosch, E., Explosivestoffe, 4, 69-78 (1956)
97. Cook, M. A., and Keyes, R. T., J. Chem. Phys., 24, 191-201 (1956)
98. Schall, R., Z. Elektrochem., 61, 629-05 (1957)
99. Fürth, R., Proc. Roy. Soc. (London), A183, 87 (1944)
100. Pack, D. C., Evans, W. Al., and James, H. J., Proc. Phys. Soc. (London), 60, 1 (1948)
101. Murnaghan, F. D., Finite Deformation of an Elastic Solid, 68, (Wiley, New York, N. Y., 140 pp., 1951)
102. Kihara, T., and Hikita, T., 4th Symposium on Combustion, Cambridge, Mass., 1953, 458-64 (1953)
103. Hikita, T., J. Ind. Explosives Soc. Japan, 15, 250-57 (1954)
104. Cramer, F., Chem. Tech. (Berlin), 6, 450-51, 590-95 (1954)
105. Murgai, M. P., Proc. Natl. Inst. Sci. India, 20, 548-56 (1954)
106. Cook, M. A., J. Chem. Phys., 15, 518 (1947)
107. Duvall, G. E., and Zwolinski, B. J., Chem. Eng. News, 47, 1182 (1955)
108. Saurel, J., and Vodar, B., J. recherches centre natl. recherche sci., Labs. Bellevue, (Paris), 6, 386-92 (1955)
109. Segré, E., and Wiegand, C., Phys. Rev., 75) 39 (1949); 81, 284 (1951)
110. Bauchez, R., Daudel, P., Daudel, R., Muxart, R., and Rogozinski, A., J. phys. radium, 10, 201 (1949).
111. Bainbridge, K. T., Phys. Rev., 90, 430, 610 (1953)
112. Bainbridge, K. T. (Personal communication)
113. Gogarty, B. (Personal communication)