HIGH PRESSURE PHENOMENA

By

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High-pressure phenomena

Of those variables which have the largest effect on the free energy, or chemical activity of any system (defined as a portion of the universe isolated for study) the most important are composition, temperature, and pressure. The vast majority of relevant research in chemistry and physics has been concerned with variations in the first two parameters. There has been a good reason for this; it has been experimentally difficult to change the pressure enough to make an appreciable difference on

a system. It can easily be calculated that to cause the equivalent change in an average, or typical, substance it is possible either to cool it by 1°C or to subject it to a pressure of 100 atmospheres (atm). (A bar equals 0.987 atm, and can be considered to be roughly equal to 15 psi.) Every science laboratory equipped with a bunsen burner can heat a substance to about 1000°C; to achieve the same effect with pressure one would need 100,-000 atm, or the equivalent of close to 1,500,000 pounds per square inch (psi). An orientation in the magnitude of high pressures is important. Atmospheric pressures on or above the surface of the earth range from 0 to 14.7 psi. Certainly 99.99% of the chemical reactions studied have been studied at or just below atmospheric pressure. However, high pressures are not uncommon. They range from the 2–5 atm in automobile tires and pressure cookers, through 100 or so atm in the boilers of ships and power plants, to perhaps 100,-000 atm at the point of impact of a high-speed rifle bullet and a hard wall. High pressures up to 100,000 atm can be generated nowadays in a very simple apparatus using automotive truck jacks. In the laboratories of chemists and earth scientists the pressures and temperatures attainable for studying chemical reactions have increased from about 10,000 atm in 1900 to 25,000 atm in 1940 and to 100,000 atm in 1960. *See* HIGH-PRESSURE PHYSICS.

Areas of high-pressure research. The earth itself is a giant laboratory in which pressures up to about 3,000,000 atm are generated with increasing depth; moreover, in the earth the temperature and pressure increase together (Fig. 1). It is generally agreed, however, that of the rocks actually observed on the surface of the earth, none has been subjected to pressure greater than 10–100,000 atm. A possible exception may be some meteorites which could have originated in the interior of a large disintegrated planet. *See* METEORITE.

The interest of the earth scientist, especially the geochemist, in high-pressure inorganic reactions is therefore natural, since in attempting to understand natural processes leading to the formation of various rocks, it is essential to duplicate the conditions existing in the earth. The science of interpretive petrology rests today on the accumulation of data obtained at high temperatures, high pressures, or both. Theories concerning the composition and properties of the different layers deep within the earth which may explain seismic discontinuities, the magnetism of the earth, possible slippage of one layer over another, and other natural phenomena can be checked only by research of high-temperature and high-pressure processes and reactions.

An additional impetus to research in this field is the ability to produce, under pressure, previously unsynthesized minerals, as well as quite new materials which may be expected to be especially dense and hard. Other phases which contain volatile
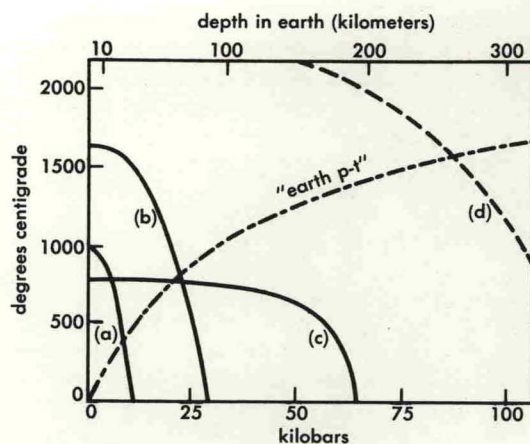

Fig. 1. Experimental limits of various types of apparatus and a generalized pressure-temperature relation of a portion of the earth. (a) Simple, externally heated test-tube or cold seal vessels. (b) Internally heated, hydrostatic pressure vessels. (c) Externally heated, uniaxial pressure devices. (d) Internally heated, piston and cylinder devices.

components, such as water or carbon dioxide, can only be prepared under high pressures of these volatiles. Finally, there is considerable evidence that fluids such as water are excellent catalysts for many inorganic reactions occurring under high pressure.

Apparatus in high-pressure research. Much of the recent significant research in this field has been made possible by new apparatus. This in turn owes its origin in large measure to the new materials, such as hard alloys and carbides, produced by an advancing technology. Below are described three or four major families of apparatus with which the majority of high-pressure chemical research is carried on today. In each of these a sample is subjected to fluid or mechanical pressure for a period of time, from minutes up to days or months, at some desired temperature. The reaction is stopped abruptly, or quenched, by rapid cooling and more or less rapid removal of pressure. The resultant products, often in a metastable condition in the laboratory, are examined by using x-ray techniques, the petrographic microscope, differential thermal analysis, infrared absorption spectroscopy, and other more common or more specialized techniques.

The starting materials used in these reactions are often of great importance. The use of amorphous materials such as glasses and gels or other metastable phases is often a decisive factor in the chemical kinetics problem encountered, since time is usually an important limitation with respect to the strength of the equipment.

The types of apparatus commonly used today can be divided into four categories, depending on whether or not the pressure is hydrostatic and

whether the heating is external or internal. The range of pressure and temperature which each of these types can cover is shown in Fig. 1. Also shown are the estimated pressure and temperature within a portion of the earth. The complexity and ease of operation are not inversely related to the pressures attainable, both the externally heated devices being quite simple.

In Fig. 2 more detail is given on the first type, the cold seal test-tube pressure vessel which is the workhorse of much high-pressure research today in the range up to 5000 atm and 1000°C. This extremely simple device can be used to react a very wide range of materials, whether solid or liquid. The materials, whether simple silicates or concentrated HF or NaOH solutions, are sealed into platinum or gold capsules which transmit the hydrostatic pressure actually supplied by an inert
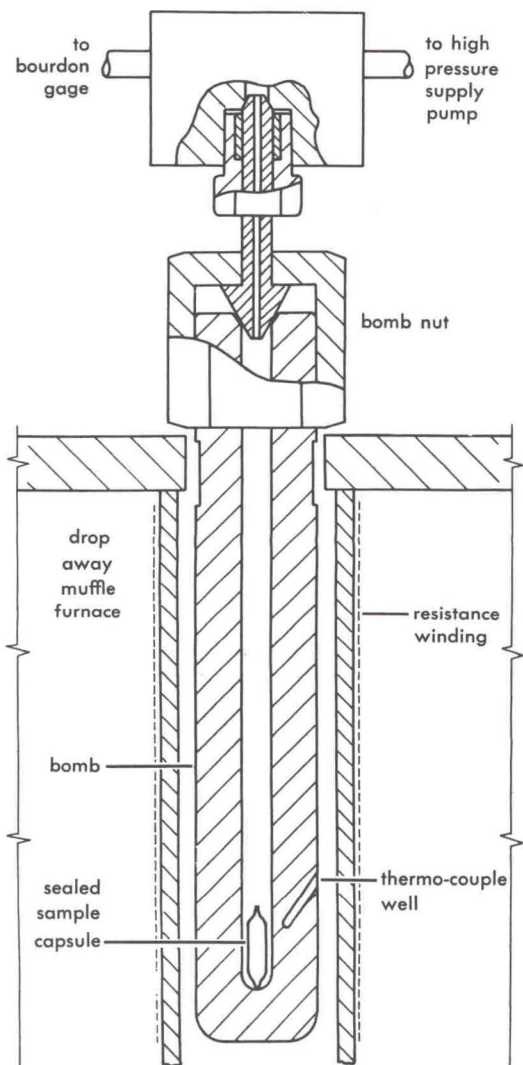
fluid outside the capsule. These vessels are heated by an external furnace as illustrated. A related device, which also uses fluid pressure, has the furnace inside the vessel, which is cooled by flowing water. Such devices are ultimately limited by the fact that virtually all gases are frozen at room temperature when the pressure reaches 25,000–30,000 atm. The pressure-temperature (p-t) working range of these types of vessels can be compared by making reference to curves a and b respectively in Fig. 1.

The second and simpler type has been evolved from designs by P. W. Bridgman, a pioneer in high-pressure research. As shown in Fig. 3, it uses a hydraulic ram to apply a directed or uniaxial pressure on a small wafer of sample surrounded by a nickel ring and platinum foil pressed between appropriate small-area piston faces. Pressures up to 60,000 bars are possible with this setup, heated externally to temperatures approaching 650°C or slightly higher (conditions schematically shown in c of Fig. 1), depending on the material and design of the pistons. Complex mechanical buttressing of the pistons has been used in some modifications to raise the operating pressures to almost 200,000 atm.

The third type, the prototype of which was first described fully by L. Coes, is shown in Fig. 4. It is essentially an internally heated chamber of a piston and cylinder arrangement with the cylinder walls buttressed and cooled to support internal pressures of 60,000 atm at sample temperatures up to 2000°C. A number of variants of this type of apparatus as well as of the second type are being tried in the effort to reach higher pressures. Some use support from four pistons at tetrahedral angles; others use different ways of supplying the supporting pressure. At this time little systematic work has been reported on experiments with such apparatus, but it is apparent that temperatures of about 2000°C can be sustained for at least a few minutes at a pressure of 100,000 atm.

Another type of apparatus uses the energy of a shock wave to produce the high experimental pressures. Explosive charges or the impact of a rapidly moving column of gas is utilized to produce pressures of the order of 400,000 atm. The coincident temperatures and pressures are difficult to measure or calculate. The duration of these conditions is in microseconds, much too short to allow rearrangements of atoms or ions in crystalline structures and therefore of less interest to the geochemist. For example, although coesite, the dense form of silica, is made quite readily in hours at 20,000 atm and at 400–500°C, shock pressures of 200,000–400,000 atm have failed to accomplish this.

Synthesis of minerals and new materials. A good measure of the success of the earth scientist in the high-pressure field is the fact that since the synthesis of diamonds, it can now be claimed that any material which has been observed in nature can be made in the laboratory. To be sure, there

Fig. 2. Cold seal test-tube pressure vessel. Basic overall size of the test tube is 8 in. in length by 1 in. diameter.
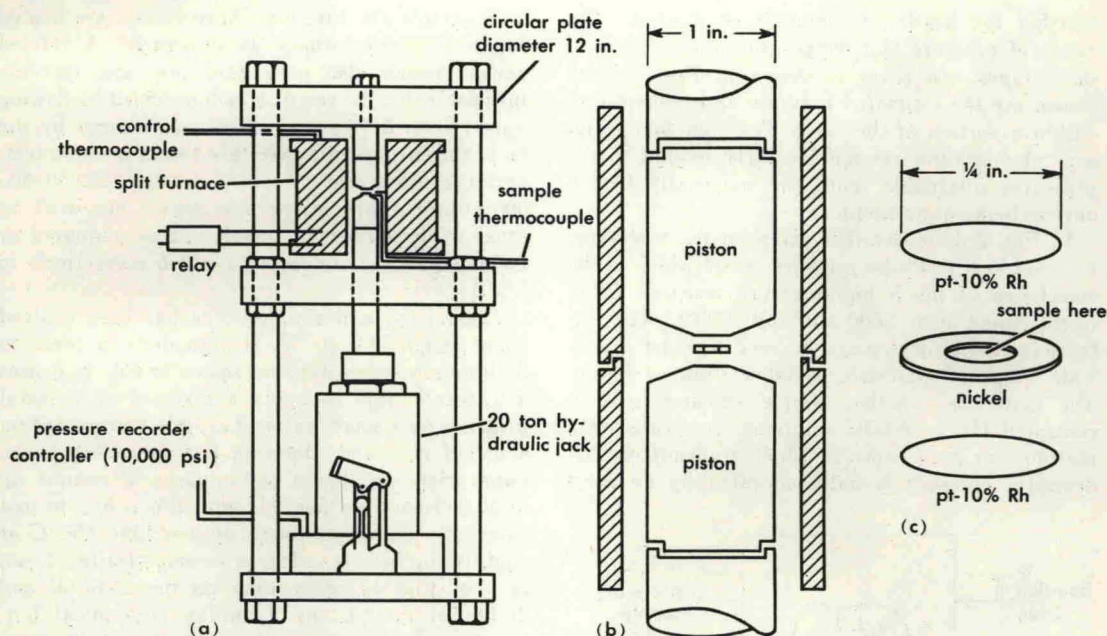
Fig. 3. (a) Schematic layout of uniaxial high-pressure apparatus with accessories. (b) Details of high-pressure pistons. (c) Sample assembly.

are many which have not been tried, but there is no reason to doubt that in every case the laboratory can duplicate the efforts of nature. See DIAMOND; GEM, MANUFACTURED.

First, one may mention the synthesis of the hard, dense phases which have presumably been thrust up rapidly from great depth. The most spectacular of the recent successes is the synthesis of diamonds in a few laboratories. Perhaps more important to the mineralogist has been the synthesis of the minerals jadeite, lawsonite, sillimanite, kyanite, and garnets such as pyrope, almandine, and andradite. All these phases were first synthesized in a dramatic breakthrough by Coes, using the apparatus shown in Fig. 4. Next is the extensive and
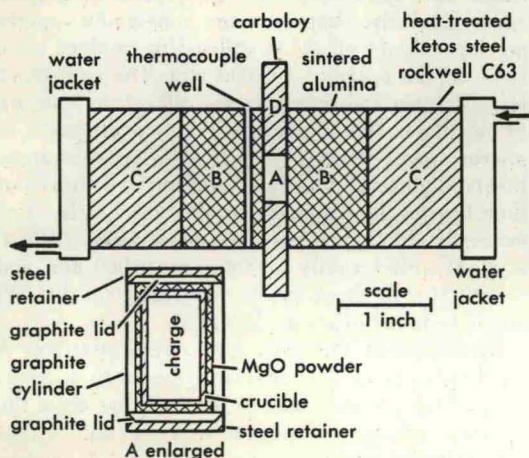

Fig. 4. Coes-type high-temperature–high-pressure apparatus.

systematic work on volatile-containing phases such as micas, clays, and complex carbonates. Under high water pressures all pure or end-member phases have been prepared and their properties studied and defined. Moreover, the extent of the systematic replacement of one ion by another has been studied. Isotopic fractionation effects in minerals have likewise been examined in the laboratory, using deuterium for hydrogen and O^{18} for O^{16}.

Many of the most interesting syntheses achieved have yielded phases which do not occur in nature and have never before been prepared. In some cases a long-expected phase was finally prepared, such as the hard cubic form of BN, analogous to diamond. In others, unexpected phases were found; thus, silica, SiO_2, itself the most abundant substance on earth, gives a new form called coesite, some 10% denser than the usual form, quartz. New high-pressure forms of a large number of substances have been found. They cover the periodic table from B_2O_3 and BeF_2 through $MnPO_4$, MnF_2, and $FePO_4$ to PbO_2 and U_3O_8. It must be remembered that these changes include only those transformations which involve such a major rearrangement of strong bonds that, when the high pressure is removed rapidly, the reverse reaction is prevented and the high-pressure form is preserved metastable to ambient conditions. So far only simple compounds of monovalent cations have failed to yield new phases of this type.

Melting under volatile pressure. It is well known that the addition of one substance to another lowers the freezing point of the latter. This is true of the vast majority of substances; the addition of salt to
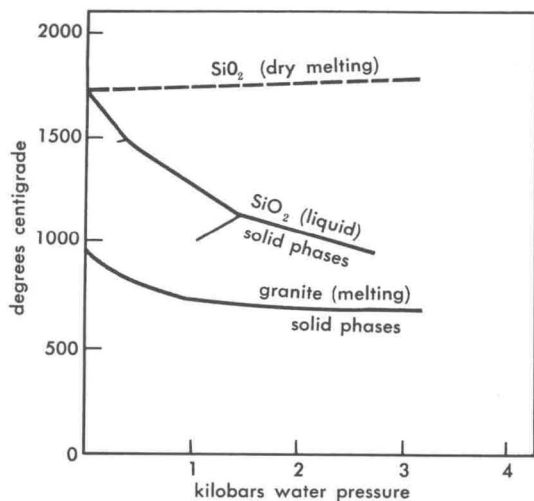
Fig. 5. Effect of water pressure on melting of silica, SiO_2, and granite, with water entering the liquids. The melting behavior of SiO_2 under inert pressure is shown for comparison.

water is one of the commonest in experience. For many decades it had intrigued geologists to consider what influence water or other volatile materials would have on the melting behavior of rocks. Naturally, to carry out such an experiment the entire assembly of rock and volatile addition would have to be confined under pressure at or near the melting points of the rocks which are of the order of 1000–1500°C. In Fig. 5 two examples are shown of the influence of water pressure on common rocks and minerals. The lowering of the melting point of SiO_2 from 1730 to 1250°C under only 1000 atm of water pressure is quite dramatic. The water in this case dissolves in the siliceous liquid. Also shown for comparison is the influence of inert or dry pressure on the melting point of silica. In this case the gas or solid transmitting the pressure does not dissolve in either the liquid or solid silica. The similar dry-pressure curve is also shown later for the important mineral diopside, to illustrate the fact that in general the melting point is raised slowly with pressure. The distinction between melting in an inert atmosphere and one in which the volatile phase under pressure dissolves in the liquid should be borne in mind. In deeply buried rocks it can be assumed that much of the water is effectively sealed in the system and may enter the liquid phase. The results of the study of melting the assemblage of minerals which form granite are also shown in Fig. 5. The fact that a granite can be melted as low as 660°C at a pressure of 4000 atm (corresponding to a burial of about 10 miles) with only a few per cent of water in the liquid is one of the most important clues on the origin of many of the commonest igneous rocks in the earth.

Applications in petrology. While the synthesis of new or important compounds has a spectacular aspect, much of the recent effort of physical chemists working with high pressures is concerned only incidentally with synthesis. Instead, the main drive is toward the obtaining of new data on the pressure, temperature, and composition conditions under which certain mineral assemblages are stable. Nature provides several typical assemblages of minerals as characteristic of certain rock types or families. As the conditions under which each particular assemblage is stable are determined, a partial reconstruction can be provided of the conditions which must have existed at any particular place on the earth.

Two different types of reactions may be studied in this connection. The first type involves reactions such as decarbonation or dehydration. Two simple reactions of this type are used in the pressure-temperature diagram of Fig. 6, to illustrate the principle of the application of such data. The general form of such curves is seen to be convex toward the high-temperature and low-pressure side, with very steep slopes at pressures above a few thousand atmospheres, with an asymptotic approach to the temperature axis at very low pressures. On the low-temperature side of such curves, the hydrates such as mica, or carbonates such as magnesite, are stable. Thus, if the pressure from the depth of burial can be estimated by studying the minerals present, it is possible to determine whether or not the rock has been heated to temperatures above the curve. Thus it is possible to explain why the dark micas occur in some high-temperature extrusive rocks (lavas) while the white or muscovite micas do not. The dehydration-decomposition curve for the latter, not shown in Fig. 6, lies some 350°C lower than the dark-mica curve shown, while the temperatures of these rocks are intermediate.

In Fig. 7 is shown a compilation on one diagram of several p-t curves for assorted yet common compositions. Each curve represents a transformation reaction, where the composition of the condensed phases on either side of the p-t curve is the same. It may be noted that these curves are quite different from those of Fig. 6. They are all essentially straight lines in the pressure range shown. The
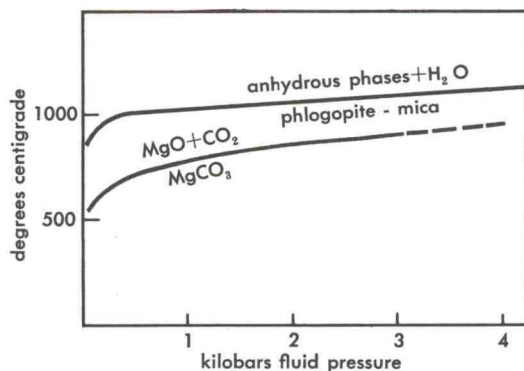

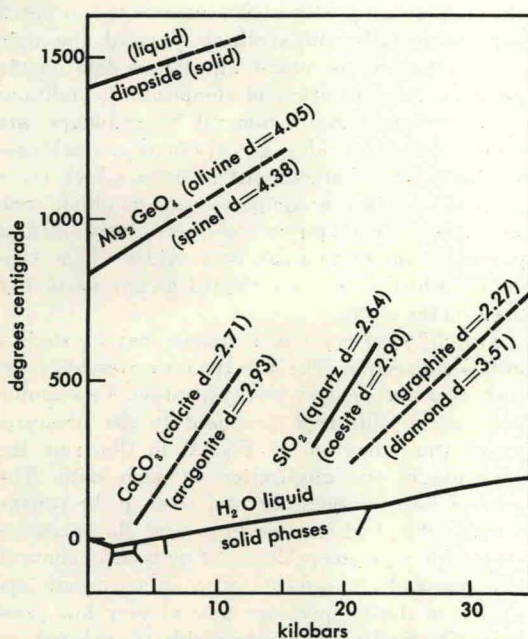Fig. 6. Typical stability curves for minerals which lose CO_2 or H_2O on heating.

Fig. 7. Curves showing pressure-temperature dependence of typical solid-solid and solid-liquid transformations for single substances.

(eds.), *Physics and Chemistry of the Earth*, vol. 1, 1956.

dense form is favored by high pressure. The pressure theoretically required to make diamonds is actually quite modest. Transformations that require twice the pressure to give the dense forms have been studied quantitatively.

In general, Fig. 7 illustrates how solid-liquid transformations such as the melting of ice do not differ basically from solid-solid transitions. These curves may of course be used in a manner similar to that described for Fig. 6 to suggest whether or not a particular rock was exposed to a certain set of *p-t* conditions. In practice, curves of both types are used to refine as far as possible the petrologic predictions which can be made.

Application to geophysical problems. From the same studies on the changes in phase (from less dense to more dense forms) in those minerals which geologists believe make up most of the mantle of the earth, it is possible to explain some of the variations in the velocities of seismic pulses at different depths in the earth. The present results do in fact suggest the possibility that the layering in the earth may not reflect changes in composition at all. Indeed, refined and sophisticated measurements of color changes in important minerals such as olivine at pressures up to 150,000 atm indicate that such a mineral may become metallic at pressures of less than 1,000,000 atm. In such phases the neutron and proton cores may eventually be stripped of their extra nuclear electrons to become a sort of metallic plasma. This may well represent the real conditions at the core of the earth. *See* EARTH INTERIOR. [F.DA.; R.R.]

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