HIGH PRESSURE PHENOMENA

By
F. Dachille And Rustum Roy

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.

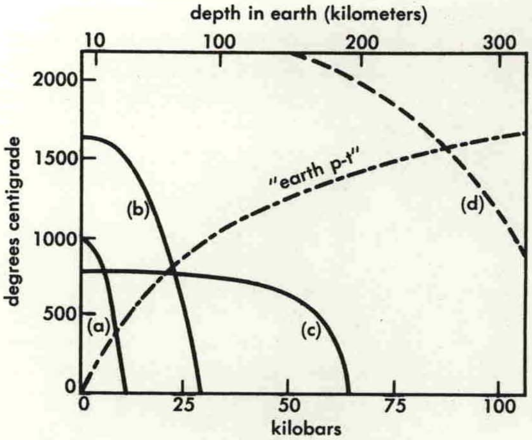

Fig. 1. Experimental limits of various types of apparatus and a generalized pressure-temperature relation of a portion of the earth. (*a*) Simple, externally heated test-tube or cold seal vessels. (*b*) Internally heated, hydrostatic pressure vessels. (*c*) Externally heated, uniaxial pressure devices.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

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 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