

Mind

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BARRY

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Chemistry at very high pressures

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Insulators can become metals and new compounds with unusual properties can be formed at pressures in the 100,000 atmosphere range. The prospect of new materials, and of a better understanding of the forces holding atoms together, are leading to a rapid expansion of research in this field

Man emerged from the Stone Age when he learned to control temperature—fire gave him metals, ceramics and glass, and led eventually to modern technology. But pressure also exerts profound effects: under its action electrical insulators become conductors, soft carbon becomes ultrahard diamond, brittle materials become ductile, sugar becomes a high explosive.

The pressures required to bring about such changes are of the order of 100,000 atmospheres or 1½ million pounds per square inch: this would be roughly equivalent to the weight of a motor car resting on the area of the full stop at the end of this sentence. These pressures do occur naturally in everyday life—they probably produce wear in bearings and on concrete roads—but they are often unsuspected and usually short-lived. To produce them under control in the laboratory, however, is a major technical problem, particularly if they are to act over a volume large enough to be of practical use. So far this has prevented the establishment of a pressure technology comparable with our temperature technology. The industrial processes which use pressure—such as the polymerisation of ethylene—are confined to the range below 10,000 atmospheres: the notable exception is the production of synthetic diamond from graphite at about 60,000 atmospheres.

Since very high pressures can lead to appreciable changes in the bonding of solids, research in this field should improve

our still very limited understanding of the forces holding solids together. With this will come knowledge of how to use existing materials to the best advantage and, eventually, of how to make new and better materials to replace them.

Temperature versus pressure

The atoms in a solid are held together by attractive forces, but since materials do not collapse in on themselves repulsive forces must also be present. These attractive and repulsive forces balance at a position of minimum energy, which corresponds to the inter-atomic distance normally observed. If a material can exist in different forms, with different crystal structures, then each of these forms has a characteristic position of minimum energy.

At the zero pressure and temperature the stable structure has the lowest lying energy minimum, but the effect of temperature or pressure on the energy of a material can be to stabilise one of the other structures. Qualitatively pressure stabilises dense ordered structures relative to open or disordered structures, and temperature has the opposite effect. Quantitatively 1,000°C and 100,000 atmospheres are

roughly equivalent in terms of the energy they introduce (about 2½ kilocalories per gram molecule). This energy is still fairly small compared with the binding energy of most solids (10-150 kilocalories per gram molecule) but is enough to produce structural changes in favourable cases. With still higher pressures the chance of bringing about structural changes is progressively increased.

In pressure-induced changes of structure there is always an increase in density. This is brought about by a closer packing together of the atoms in which each atom increases its number of near neighbours, its 'co-ordination.' Thus the form of carbon stable at low pressures (and high temperatures), graphite, has a density of 2.5 grams per c.c. and a co-ordination of three; in the high-pressure form, diamond, the density is increased to 3.5 and the co-ordination to four.

Silica, SiO₂, provides an example of the high pressure behaviour of a compound. In ordinary quartz (see Fig. 1) each silicon atom has four oxygen neighbours, each oxygen two silicon; thus there is 4:2 co-ordination. Near 110,000 atmospheres, SiO₂ assumes 6:3 co-ordination with a dramatic change in properties (see table).

	Density	Hardness	Refractive Index (mean)	Reaction to hydrogen fluoride
Low-Quartz	2.65	300 kg/mm ²	1.55	Rapid
High pressure SiO ₂ (Stishovite)	4.35	1,800 kg/mm ²	1.81	V. Slow