

apparatus will be both massive and costly, but since diamond is valuable, money is fairly readily available for its production. Clearly, high-pressure technology will benefit from engineering developments brought about by the demand for synthetic diamond, and in the more distant future, from the development of continuous as opposed to batch processes (even though at present there is no obvious means of achieving this). But the key to pressure chemistry lies in developing apparatus to reach still higher pressures than those required for diamond synthesis, in a volume large enough to house a high-temperature cell and its thermal insulation. A good short-range target is continuous operation at 200,000 atmospheres and 2,000°C with a specimen at least one millimetre in diameter and two millimetres long. This increased pressure would greatly broaden the range of reactions and transformations open to study, and the high temperature would enable us to investigate a wide variety of solvent-catalysts.

The metallurgical implications of high-pressure treatment are already being explored. New alloys and intermetallic compounds have been found, while the marked effects of pressure on diffusion and precipitation may have important practical consequences. The influence of pressure on diffusionless transformations is also of considerable metallurgical interest. For example, the martensitic transformation, which is of great technical importance in connection with the tempering of steels, is considerably affected by high pressures and is now being studied in a number of laboratories.

Most high-pressure chemical research has been inorganic, probably because organic compounds appear relatively unstable by comparison. What high-pressure organic chemistry has been done, however, suggests that important effects will be found in this field. As a simple example, sugar, a carbohydrate, decomposes explosively to carbon and water at about 50,000 atmospheres. This can be interpreted in terms of  $-OH$  groups being forced closer together and suggests that high pressures could be used to bring about new types of condensation or polymerisation reactions.

Pressure tends to bring about ordering and an increase in density even with relatively disordered material like glasses and polymers. With these it has the general

effect of causing a permanent reduction in free volume—the random networks become more tightly packed. The properties and structure of such 'densified' materials should be of considerable interest, but as yet have been little studied.

One particularly interesting possibility has not yet been mentioned. We have described the ways in which very high pressures can stabilise forms which under normal conditions of pressure and temperature would be theoretically unstable. However, it is possible that the normally observed forms of certain materials, perhaps even familiar materials, may turn out to be metastable. In such a case pressure could be used to bring about a transformation to a form which is thermodynamically more stable. The element phosphorus is the only example so far known. Normally phosphorus exists in two forms, red and white, both of them insulators. At pressures above about 10,000 atmospheres, however, both transform to a black semiconductor which appears to be the thermodynamically stable form. This is not found normally because phosphorus, whether it is in liquid or gaseous form, or dissolved in solvents, exists as  $P_4$  molecules. These are incorporated unchanged in red or white phosphorus, but they must be broken up before the black phosphorus lattice can form. Thus there is an energy barrier to the formation of the stable material. Such energy barriers are likely to be encountered in cases where highly stable molecules are formed.

An extreme example could be the gas carbon dioxide, which by analogy with silica might exist in a quartz-like structure—"carba." However, our preliminary calculations suggest that very high pressures indeed would be needed to stabilise it—probably several hundred thousand atmospheres. And if the molecular form is metastable, the stable form is more likely to have a structure in which carbon has a co-ordination less than four.

Any such predictions are based on very crude theoretical models, largely because no better methods have yet been developed. Chemistry at high pressures is still essentially in the observational and data-collecting stage, but with the rapid increase in effort devoted to it, the 'take-off point' will very soon be reached when pressure-chemistry will emerge as one of the significant areas of scientific advance.

ENDS



Fig 5 In the tetrahedral anvil apparatus high pressures are generated by four triangularly shaped anvils (middle) pushing against the faces of the tetrahedral test cell of pyrophyllite (top). Specimen is contained within the cell. Force is applied to one anvil, remaining three 'nest' inside the tapered steel cone shown, and are powered by wedging reactions