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CHEMISTRY AT HIGH TEMPERATURE AND HIGH PRESSURE

The "New" Pressure-Temperature Field

The known steady state, pressure-temperature field available for scientific exploration today is given approximately by Fig. 1. The so-called "new area" was opened for study by the author's design of an apparatus called the "Belt". Using this apparatus, the author succeeded in making diamonds from "carbonaceous material" at GE's Research Laboratory in 1954. Unfortunately (for those of us who are anxious to explore or ask questions about this new area) the apparatus is unavailable. It has been classified "Secret" by the Government because of the importance of industrial diamonds to national defense.

Pressures of 100,000 – 200,000 atmospheres could cause energy changes in condensed systems of the same order of magnitude as those brought about by temperature changes of 1000-2000K; i.e., these are the energies involved in ordinary chemical reactions.

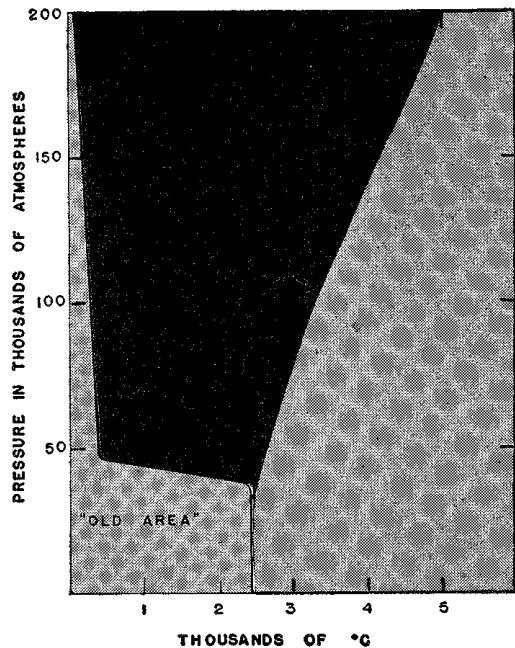


FIG. 1. Comparison of old pressure temperature region with the new region now available.

Thus, the variety of changes produced in matter by these pressures are comparable in number and scope to those produced in matter by these temperatures.

The broad, general effects of pressure and temperatures are diametric opposites.

Application of increasing temperature to a solid system causes an increase in the average distance between atoms. The solid eventually passes through a liquid to a gaseous phase so that the final result of sufficiently high temperature at atmospheric pressure is that the atoms become separated by large distances and occupy only a small portion of the total volume. On the other hand, increasing pressure causes the average distance between atoms to decrease. Pressure (at ordinary temperatures) can cause a gas to condense to a liquid and then become a solid. Further increase in pressure can cause collapse of electronic shells. Eventually (in theory at least) pressures of the order of billions of atmospheres can cause nuclei to be forced within the critical distance of about 10^{-13} cm where nuclear fusion will occur.

Systems of Interest for Study at High Temperature, High Pressure

Almost any system is worthy of investigation in the "new" high-pressure, high-temperature area. The most fruitful field, however, will be found in the investigation of systems with normally "open" structures. This includes crystals whose structures are not closely packed and systems with "open" structures. This includes crystals whose structures are not closely packed and systems with "open" electronic structures such as the elements of the first transition group which have unfilled 3d orbitals. I anticipate continuing work will probably occur in the areas discussed below.

Melting Point as Function of Pressure

The melting points of substances are profoundly affected by pressures of the order of 200,000 atmospheres; for example, the recently reported 600 degrees lowering of the melting point of germanium. Of course, germanium is an exception to the general rule that melting point increases with increasing pressure. The melting point of some refractory materials has been increased by well over 1000C by extremely high pressures. This fact makes it possible to work at higher temperatures at high pressure than would be possible at one atmosphere. As a matter of fact, it is quite possible to work with a "liquid" refractory under high pressure conditions. A liquid can flow only if it contains "holes" into which the molecules can move. At 200,000 atmospheres the number of holes in a molten refractory may be severely reduced and it will be extremely viscous.

Work on the melting points of substances at high pressure has considerable significance in that it should throw some light on the old question as to the nature of the melting point curve as pressure is indefinitely increased. Is there a critical point between liquid and solid analogous to the gas-liquid situation? Is it impossible to melt some substances—like graphite?

Mineral Synthesis

A very interesting result of recent high-pressure, high-temperature work is the synthesis of a new dense silica, "Coesite," not found in nature. I have experimented with sodium silicate solutions at pressures to 100,000 atmospheres at temperatures near 450C in an effort to produce a silica phase even more dense than Coesite. No new phase has been found. The experiments indicate a rather steep threshold pressure for Coesite formation at $32,000 \pm 2000$ atmospheres. Near 60,000 atmospheres the external habit of the Coesite crystals is changed. Below 60,000 atmospheres crystals tend to grow singly with hexagonal outlines. From 60,000 to 100,000 atmospheres, the crystals tend to grow in a planar group containing four hexagons. I have produced Coesite directly from quartz (without catalyst or mineralizer such as water) at pressures in the vicinity of 100,000 atmospheres and temperatures over 2000C. Mineral growth is greatly facilitated by the use of a catalyst (or, as some may prefer, a solvent or mineralizer). At high pressure, high-temperature all the oxides

show sufficient solubility in water that it may be regarded as a universal catalyst for mineral formation. A very wide array of materials are effective in catalyzing mineral synthesis from the oxides. These include urea, ammonium salts, carbonates, phosphates, sulphates, nitrates, borates and of course water.

To synthesize a mineral, the required oxides are placed with the catalyst. The pressure is raised to the desired value followed by application of the desired temperature. Temperature is then lowered followed by pressure reduction. It is not always necessary or desirable to use oxides. Pure metals or their salts will often do. Hydrogen will often be produced if metals are used, but it manages to escape through the hot container. This continuous removal of hydrogen at high-pressure, high-temperature makes it possible to always drive the reaction in the desired direction because of the very favorable volume decreases.

Almost any mineral with a known structure, not in closest packing, presents possibilities for production of a more dense phase at high-pressure, high-temperature. Often the more dense phase with "lock-in" and remain stable when temperature is reduced to normal followed by reduction to normal pressure.

The production of many new minerals with incorporate heavy elements and the less familiar elements of the periodic table presents a particularly fruitful area for research and investigation.

Of course laboratory mineral synthesis has great import in the field of geology. Future work at extreme pressure and temperature will do much to give new information on the interior of the earth and geological processes.

The Synthesis of Hard Materials

Man-made industrial diamonds will in my opinion, be a readily available commercial product within a few years. Diamond is, of course, the hardest material presently known to man. What are the possibilities of making a material harder than diamond? The answers may be found in a consideration of the qualities that make materials macroscopically hard. A necessary condition is high bond energy concentration; that is, high cohesive energy density. A subsidiary requirement is high bond symmetry in three dimensions. Diamond and graphite have the highest cohesive energy densities (ced) of any known substances. Graphite is soft, however, because it fails to meet

the symmetry requirement. Materials with high heats of vaporization and small molar volumes have high cohesive energy density. Compounds with the highest cohesive energy densities are to be found among the borides, carbides, nitrides, oxides and sulfides. Some of these materials do not have high, three dimensional bond symmetry. Since high pressure tends to force atoms into positions that give maximum symmetry, subjection of selected borides, carbides, nitrides, etc. to high-pressure, high-temperature, may give a stable structure of higher hardness. For example, boron-nitride, which has a graphite-like structure and is slippery and soft, might be transformed into a hard, diamond-like material by use of the proper catalyst at high-pressure, high-temperature.

Pressure Effects on Electronic Configurations

It is possible that very high pressures might effect the stability sequence for atomic orbitals. Such effects might most readily be detected in changes of electrical conductivity. Such a situation might exist in the phenomenal increase of electrical resistance of cesium discovered by P. W. Bridgman (Cesium has completely empty 5d orbitals). He found the resistance to rise rapidly to a sharp cusp near 54,000 atmospheres followed by a rapid drop. The resistance at 54,000 atmospheres was 11 times the resistance

at one atmosphere. No volume discontinuity is associated with this sharp cusp. Experiments I have performed with cesium give a much sharper cusp than that obtained by Bridgman. Indeed, it seems that if the necessary pressure could be fixed with enough precision, the peak of the cusp would show a resistance many powers of 10 higher than at one atmosphere. Immediately on passing this sensitive pressure point the electrical resistance drops rapidly to a low value again—a most interesting phenomena. Incidentally, this sharp cusp makes an ideal pressure reference point. I think more of this type phenomena is to be expected at pressures near 200,000 atmospheres and above. The effect of high temperature on these phenomena should be studied. It might be possible to synthesize compounds from elements with empty atomic orbitals in which these elements display unknown and unexpected bonding behavior. Some of these structures may remain stable on return to ordinary conditions of pressure.

The conversion of ammonia to metallic form at pressures somewhat over 200,000 atmospheres will soon become a reality. Hydrogen is expected to become metallic near 500,000 atmospheres and minerals such as olivine near 1,500,000 atmospheres. These phenomena will result from pressure effects on electronic energy levels. END