

PRESSURE AND TEMPERATURE REQUIREMENTS FOR MAKING DIAMOND

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I. INTRODUCTION

Two simple facts suggest that the most favorable conditions for the synthesis of diamond would be high pressure and high temperature. These facts are that carbon is a very refractory element, and that diamond is the most dense form of carbon. However, before launching an extensive research program, the actual magnitudes of the required pressure and temperature had to be established as accurately as possible for two reasons: first, to find whether the physical conditions required would be within the realm of possibility; and second, to get an indication of the equipment that would have to be obtained or developed.

II. SUGGESTIONS FROM THERMODYNAMICS

You have seen from the carbon phase diagram, which Dr. Suits presented earlier, that the diamond phase of carbon is thermodynamically stable only at very high pressures. I should like to present a more elaborate carbon phase diagram (Slide I), and discuss it in more detail.

Pressure is plotted logarithmically on the vertical axis, and temperature linearly on the horizontal axis. Note the temperatures with which you are familiar: absolute zero, room temperature, melting iron, carbon-arc temperature, and sun's surface temperature. Only parts of this diagram are established accurately by experimental measurements. The boundary between

graphite and vapor at low pressures is quite well established. The boundaries at higher pressures between graphite, vapor, and liquid are based on the work of Basset, a French scientist, and are not fully accepted.

The location of the boundary between the graphite and diamond stable regions has very little direct experimental basis at present. The position of the lower-temperature end of it has been calculated by thermodynamic methods using available data on the densities, compressibilities, expansion coefficients, etc. of graphite and of diamond. The band outlined by the two solid lines includes the amount of uncertainty resulting from known lack of accuracy of the physical data used in the calculations. Rossini and Jessup, of the U.S. National Bureau of Standards, screened the available data and carried out the details of this calculation with great thoroughness in the late 1930's. The higher-temperature part of the boundary, shown by dashed lines, is purely extrapolated from the other part as the physical data required have never been taken.

The dotted line running across the diagram shows the upper limits of pressure and temperature that scientists are known to have reached in controlled experiments (this excludes atomic bombs). Professor Bridgman, of Harvard University, is the outstanding investigator in this field at room temperature, and at temperatures up to 5000°F for very short intervals of time. Basset, of Paris, has been the most active worker in the high-temperature region. The interval of time that pressure and temperature can be sustained simultaneously is important because all reactions and transitions are time-temperature dependent.

You undoubtedly noticed from the diagram that Bridgman has operated well up into the diamond-stable region, and you may wonder if he has ever tried diamond synthesis. He has tried many times, but without success. The reason for the lack of success, as he has stated in several of his papers, is that, at the relatively low temperatures at which his experiments were run, the thermal agitation of the carbon atoms in the graphite crystal lattice was not energetic enough to shake them loose to make them available for regrouping in the more stable diamond crystal lattice form. In other words, the reaction rate was negligible. He recognized the necessity of going to higher temperatures, but he had not developed apparatus capable of operating at these high pressures and temperatures simultaneously. His best effort in this direction was 450,000 lbs/sq. in. and 3500°F to 5000°F for periods of one or two seconds.

Conversely, diamond exists quite well in the graphite-stable region at temperatures below 2250°F to 3150°F. However, when diamond is heated to temperatures above about 3150°F at low pressure it rapidly changes to graphite because the thermal agitation of the atoms becomes energetic enough to swing them loose from the diamond lattice and they regroup in the more stable graphite lattice form.

The observations we have just made about the thermodynamic stability and reaction rate of diamond and graphite lead to the conclusion that diamond might be formed at those pressures which lie within the diamond-stable region, provided the temperature is high enough to cause a reasonable reaction rate.

The possibility of making diamonds in the region of 600,000 to 1,500,000 lbs/sq. in. and 1350°F to 5000°F seemed good enough to justify a vigorous attempt to develop apparatus capable of operating at these levels for extended periods of time.

III. PRESSURE VESSELS

Practically all ultra-high-pressure generators are based on the principle of pushing a piston into a cylinder that encloses the substance to be subjected to the pressure. If the gaskets or cylinder do not leak, the application of more force on the piston results in greater pressure in the cylinder until some part of the enclosure yields or breaks. The upper limit of attainable pressures is set by breakage of the cylinder or piston and not by the force available to push the piston. Hydraulic presses are usually used to exert the force on the piston, but the size of the press, or the force it is capable of exerting, has very little to do with the maximum pressure that can be generated; the pressure vessel is the limiting factor.

The main factor which limits the maximum pressures that can be reached within vessels is the strength of materials. The strongest steels in the most favorable form and size (piano wire, for example) have ultimate tensile strengths of the order of 200,000 to 300,000 lbs/sq. in. Sintered carbides, such as carboloy, have compressive strengths of the order of 700,000 or more lbs/sq. in. The pressure we were aiming for is about 1,500,000 lbs/sq. in. Merely making the walls thicker on a pressure vessel contributes very little to its pressure holding ability after a certain wall thickness is reached.

By using multiple shrink bands on the cylinder part (a technique used years ago in making large gun barrels), and special sealing gasket devices between the piston and cylinder, Bridgman had developed single-stage pressure vessels good for 735,000 lbs/sq. in. at room temperatures. At higher temperatures, materials get weaker and in general the attainable pressures are lower.

By making use of some of the known design methods of Bridgman and by developing some new ways of distributing stress and giving additional support to critical parts, our research group has succeeded in developing pressure vessels that can be operated at pressures up to at least 1,500,000 lbs/sq. in. and temperatures up to about 5000°F for long periods of time.

IV. CALIBRATION OF PRESSURES AND TEMPERATURES

An obvious question is, "How are pressures of this tremendous magnitude determined, and how are temperatures inside such vessels measured?" It isn't easy, but fortunately certain substances undergo sharp phase transitions at definite pressures. In some metals these transitions are accompanied by abrupt changes in electrical resistance. Slide 2 shows four examples of this type of behavior discovered by Bridgman. The resistance of bismuth metal rises slowly with pressure until 365,000 lbs/sq. in. is reached, then it abruptly drops as the bismuth changes to its second phase; then at about 397,000 lbs/sq. in. the bismuth changes to a third phase and the resistance suddenly increases to a third value. To calibrate a pressure chamber a bismuth wire is incorporated in it with suitable electrical connections. The pressure required to cause the bismuth transition then corresponds to 365,000 lbs/sq. in. in the pressure

chamber. Other calibration points make use of the phase transitions in thallium at 640,000 lbs/sq.in., cesium at 785,000 lbs/sq.in., and barium at 1,140,000 lbs/sq.in. Beyond this other methods must be used, and we have developed at least one.

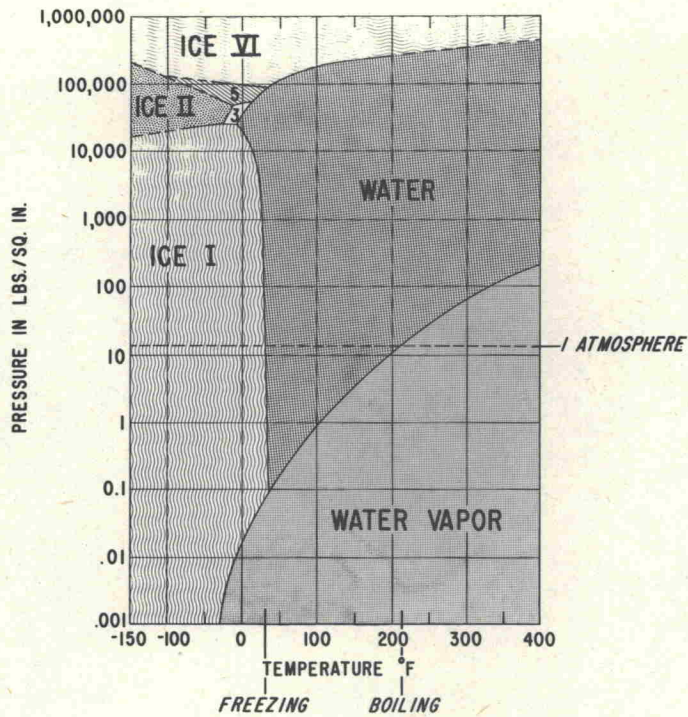
Temperatures inside the pressure cells are measured by use of thermocouples, melting points of materials, change of electrical resistance of wires, Curie points of magnetic materials, thermocolor paints, etc.

V. REGION NOW AVAILABLE FOR RESEARCH

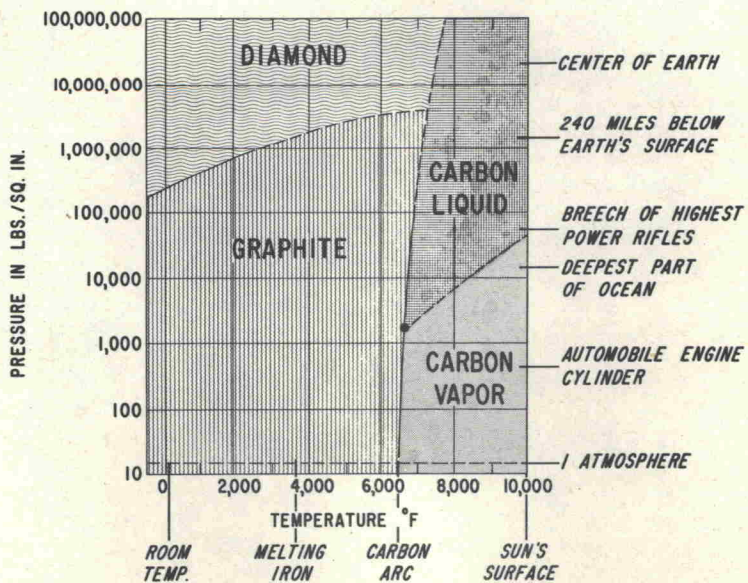
In closing, I should like to present on Slide 3 a pressure-temperature diagram, using linear scales on both axes this time, showing the new region of exploratory research which has been opened up by the development of our new high-pressure and high-temperature techniques. Note that the newly available region covers about as much area as does all the old region.

We have succeeded in attaining both our parallel goals of high pressure and of the synthesis of diamond. As usual in science, the achievement of such goals brings into focus more goals which are still farther on. You can be sure that as this new area is explored many interesting, and perhaps useful, discoveries about nature will be made.

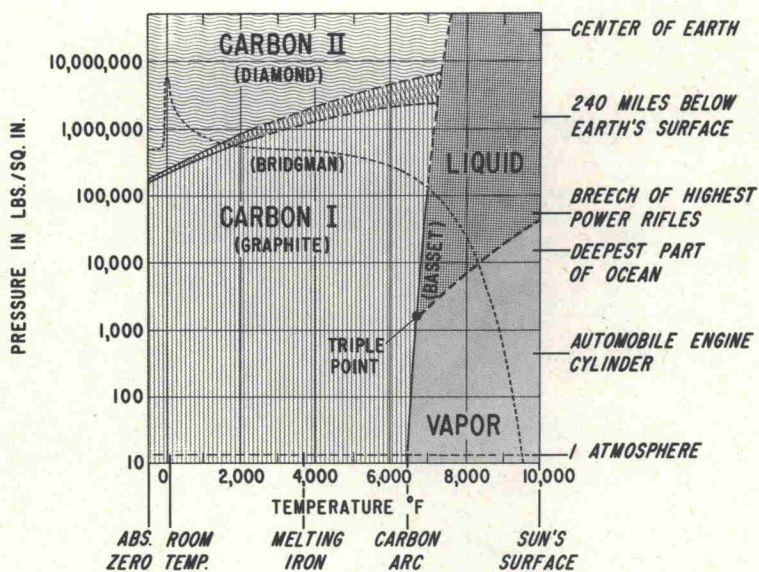
PHASE DIAGRAM FOR WATER



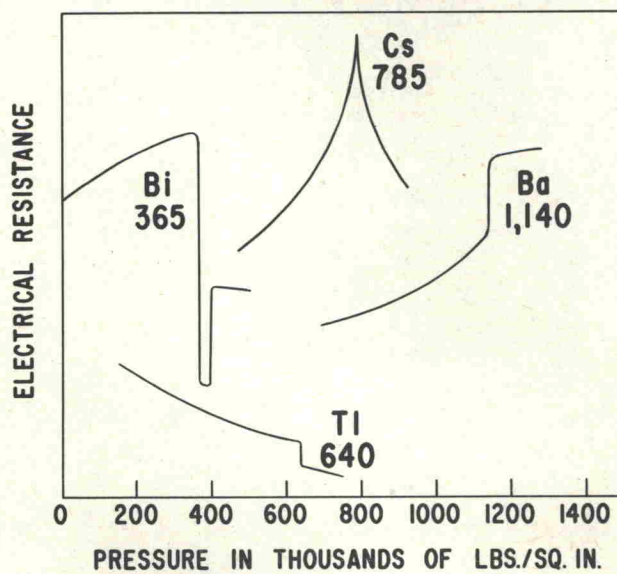
PHASE DIAGRAM FOR CARBON



PHASE DIAGRAM FOR CARBON



CHANGES OF RESISTANCE OF Bi, Tl, Cs AND Ba WITH PRESSURE



NEW PRESSURE TEMPERATURE REGION

