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*Copy for
Tracy Hall*

12-minute talk for APS, San Diego

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THE THERMODYNAMICS AND PHASE REACTIONS OF CARBON
AND OF BORON NITRIDE

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At the time our project on reactions and transformations at high pressures and temperatures was started early in 1952 the P, T thermodynamic phase diagram of carbon was rather sketchy. The vapor pressure line was known quite well and the triple point for graphite/vapor/liquid had been established at about 0.1 kbar, 4000°K. It was fairly obvious that diamond was the stable form at higher pressures. In 1938 Rossini and Jessup, at our National Bureau of Standards, had established the heats of formation of graphite and of diamond with sufficient accuracy so that with the known values of specific heats, compressibilities, etc., of the two forms, they were able to calculate the P, T locus of the line of equal free energy from 0 to 900°K. (Slide 1). This is shown in Slide 1 running from 17 kbar, 0°K to about 30 kbar, 900°K.

In a 1947 paper on attempted diamond synthesis Bridgman discussed briefly how the line of Rossini and Jessup might be expected to extend to higher pressures and temperatures. He presented arguments that the pressure would increase less than linearly with temperature. In 1955 Berman and Simon, on the basis of some newer specific heat and compressibility data, concluded

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that the pressure along the equilibrium line should increase about linearly with temperature. Also in 1955 Liljeblad published data and an argument that the pressure along the equilibrium line would reach a flat maximum of about 65 kbar at about 2500 - 3000°K.

At the beginning of 1955 when we had learned to do reproducible diamond synthesis in our laboratory it became possible to establish experimentally the location of the diamond/graphite equilibrium line by doing large numbers of experiments at different pressures and temperatures and observing whether synthesis or graphitization of diamond occurred. Slide 2 shows the raw data of such a series of experiments carried out in a "belt" high pressure apparatus using molten nickel as the catalyst/solvent for aiding the phase transition process. It is seen that a certain minimum heating power (i.e. temperature) was required, and that as the heating power was increased a greater press force on the apparatus was needed. The area on the chart in which diamond synthesis could be accomplished was V-shaped, the low temperature side corresponding to the melting temperature of Ni in the presence of carbon at the pressure, - and the high temperature side corresponding to thermodynamic equilibrium conditions.

(Slide 3). By doing several such series of experiments using different catalyst/solvent metals of a considerable range of melting points data of the type shown in this slide were generated. Of course the conversion of loading force and heating power applied to the apparatus to pressure and temperature numbers required extensive and careful work on calibration of the

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apparatus. It can be seen from the slide that the high temperature sides of the "notches" define reasonably well the P, T thermodynamic equilibrium line between the graphite and diamond phases of carbon. This experimentally determined line agreed quite well with the extrapolation proposed by Berman and Simon, and hence added confidence to the values they had assumed about the specific heats and compressibilities of graphite and diamond at the very high pressures and temperatures.

(Slide 4). As the pressure capability of the apparatus was increased on up to over 150 kbar, and as high temperature techniques were developed, the melting line of graphite was established, and the pressure-temperature conditions for the fast, direct, transition from graphite to diamond were found. According to the experiments the melting temperature of graphite increases with pressure to a broad maximum of about 4500°K at 60 kbar, and then decreases with further increase in pressure. The triple point for graphite/diamond/liquid according to that study is at about 130 kbar, 4000°K.

In respect to transformation kinetics, one of the most interesting observations from that set of experiments is that the threshold temperature for the fast (i.e. millisecond) transformation of graphite to diamond is just a couple hundred degrees or so below the melting point of metastable graphite at the ambient pressure, - and cubic type diamond is formed. The analogous fast transition of small diamond crystals to graphite by flash-heating also occurs a couple hundred degrees short of the melting temperature of ^{metastable} diamond at the pressure, - as shown on the chart.

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In the studies of the direct transformation of graphite to diamond an unexpected result occurred when the starting material was single crystal graphite. At pressures above about 130 kbar the electrical resistance of the specimen measured in the a, b plane of the graphite would increase by one or two orders of magnitude even at room temperatures. If the specimen was heated to 1000°C or so while in this high resistance state, then cooled and depressurized it would retain its high resistivity, and when examined by xray diffraction proved to be the hexagonal (or wurtzite) form of diamond. Later it was found by duPont researchers that strong shock compression of iron ingots containing highly crystalline graphite inclusions also produces hexagonal diamond. Taking these observations as a hint, a careful re-examination of the black diamond inclusions in the nickel-iron meteorite fragments of the Arizona Meteor Crater proved to be hexagonal type diamond. They were almost certainly produced from crystalline graphite inclusions by shock pressure during impact with the earth, or by a collision somewhere in space earlier.

In a flash heating experiment at pressures above 130 kbar, starting with a specimen of single crystal graphite, hexagonal diamond is formed if the maximum temperature falls in the range of about 1500 to 2500°K. However, if the maximum temperature exceeds 2500°K the product is the usual cubic type diamond. The question arises as to whether the hexagonal type diamond is thermodynamically stable. To date the experimental evidence indicates that it is not, - that it forms only at relatively low temperatures in solid-state to solid-state transformations in which

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steric conditions do not allow the atom movements required to go from graphite to the cubic diamond arrangement. When the temperatures get high enough to provide the necessary activation energy the transformation to the cubic form occurs. In all fluid, or quasi fluid, media reactions the cubic diamond form is always produced.

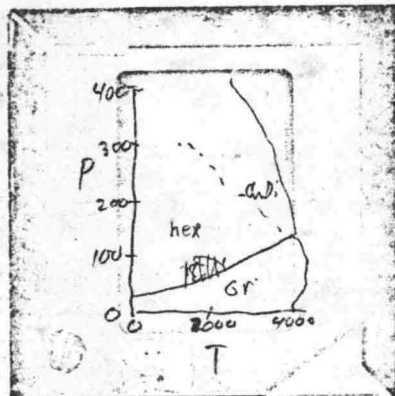
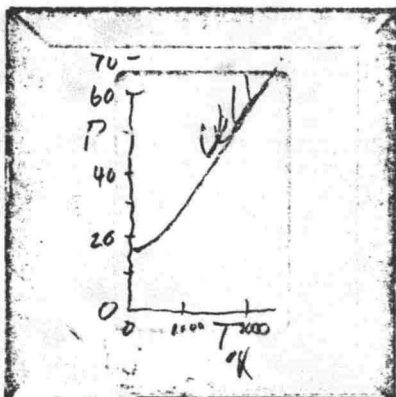
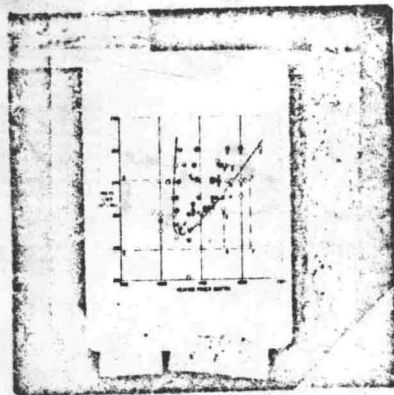
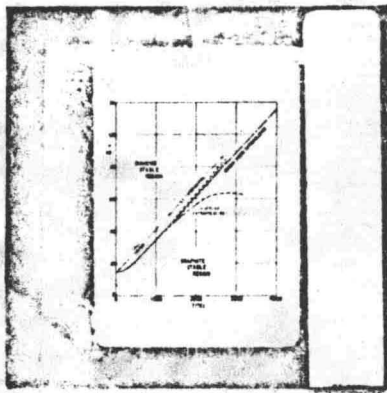
The thermodynamic and reaction characteristics of the BN system are very similar to those of the carbon system. This similarity is to be expected because the two cases are much alike in respect to their valence electron systems. Each pair of carbon atoms has eight valence electrons, and the same is true of a pair of boron and nitrogen atoms. Thus it is likely that the bonding in their crystal systems should be similar. (Slide 5). The BN system has been studied experimentally in considerable detail. In the fluxed process the cubic diamond form is always obtained. When the graphitic form is compressed statically, or by shock, at relatively low temperatures the wurtzitic (hexagonal) form is obtained. Once formed, the wurtzite form transforms to the zincblende (cubic) form quite sharply at 1800 - 2000°C, - as if there were a thermodynamic phase line there. However when reaction time vs temperature experiments are done it is found that the activation energy of the transformation is very high; - equivalent to vaporization. Furthermore, when a fluxing agent is added to the wurtzite form the conversion to the zincblende form goes at a lower temperature, whereas fluxing the zincblende form in P, T conditions in the "wurtzite area" does not cause any change.

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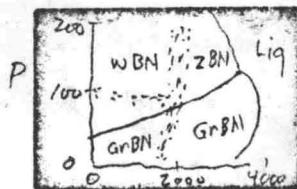
We conclude that in the carbon and BN systems the truly thermodynamically stable forms are graphitic, liquid, vapor, and diamond cubic. At pressures higher than those yet reached in laboratory experiments carbon and BN would be expected to go into β -tin-like metallic phases. According to the best related theory, pressures of well over a megabar would be required. That is for the future, - hopefully the near future.

Now I turn the presentation over to Tracy Hall who will discuss high-pressure, high-temperature apparatus capable of diamond and cubic boron nitride synthesis.

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