

4600°K) at 48 kilobars. The experimental value of 25 kcal/mole for the heat of fusion gives an entropy of fusion which is comparable to those of the neighboring group IV elements, Si and Ge, as shown in Table 3.

From the variation of the melting temperature with pressure shown in Fig. 2, it follows that at "low" pressures the specific volume of liquid carbon is greater than that of graphite, while at higher pressures the reverse is true.

The melting line of diamond is also believed to have a negative slope, as in the cases of silicon and germanium. The main experimental basis for this belief is the abrupt 15 percent decrease in specific volume of carbon observed by Alder and Christian at about 600 kilobars and 1300°K in shock compression tests of graphites (8). This phenomenon is interpreted to be melting of diamond. Thus the diamond melting line must extend between the triple point shown in Fig. 2 and about 1300°K at roughly 600 kilobars.

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Direct Conversion of Graphite to Diamond in Static Pressure Apparatus

In the past there have been many serious attempts to form diamond by a direct transformation from graphite (1-4). Most of these attempts have been unsuccessful. In 1961 DeCarli and Jamieson announced the retrieval of very small diamond particles from low-density graphic samples which had been shock compressed to about 300 kilobars' pressure at about 1300°K (2). Also, in late 1961 Alder and Christian reported quantitative pressure-specific volume data taken from experiments on the shock compression of graphite (3).

While they did not retrieve any diamond material, their specific volume and compressibility data indicated that their samples compressed to diamond density at pressures in the range of 300 to 400 kilobars. Apparently at 300 kilobars, full density graphites do not shock compress to diamond density and do not yield retrievable diamond (2-4).

Recently at this laboratory a pressure apparatus has been developed in which "three-dimensional" samples can be compressed to nearly 200 kilobars and can be transiently heated to temperatures above 4000°K. The apparatus is a modification of a "belt" design (5). The transient heating is generated by the discharge of a large electrolytic capacitor through the specimen while it is contained in the pressure chamber.

One type of sample was pill-shaped, 0.080 inch in diameter, 0.060 inch thick. It was made in three layers of equal thickness. The graphite specimen was a rectangular bar which rested along the diameter of the center layer. The remainder of the center layer consisted of "quarter-moon" pieces of pyrophyllite stone. The top and bottom layers of the sample structure consisted of "quarter-moon" graphite electrode pieces, and "three-quarter-moon" pyrophyllite stone pieces oriented so that one end of the graphite bar specimen was connected to the top piston of the apparatus and the other end to the bottom piston. The arrangement is shown in section in Fig. 1 (top), where the center part of the graphite specimen bar is shown after it had been converted to diamond.

When the specimen was compressed to a pressure of about 130 kilobars, which is the iron transition pressure (6), and the temperature was raised by flash heating to more than about 3300°K, the center section of the graphite bar collapsed abruptly to a cemented mass of very fine diamond crystallites, as shown in Fig. 1. When the threshold temperature was reached, the diamond reaction proceeded very rapidly; and it was essentially complete within 2 or 3 milliseconds. Simultaneously with the transformation of graphite to diamond, the electrical resistance of the cell increased abruptly to a nonconducting condition. X-ray diffraction analysis, scratch tests on sapphire and boron carbide, and density tests proved clearly that the converted material was diamond. In fact the required change of density is shown clearly in Fig. 1 (bottom).

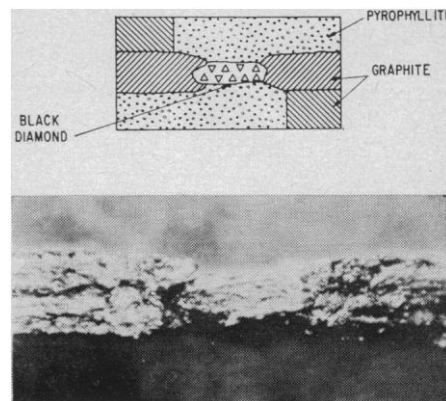


Fig. 1, (Top) Cross section of a high pressure sample after compression to 130 kilobars and flash heating to a temperature over about 3500°K. The center part of the graphite specimen bar, where the temperature was highest, converted to polycrystalline diamond. (Bottom) Photograph of the specimen after the reaction. The increase in density of the carbon is evident by the change of thickness.

The experiment was repeated many times with variation of cell geometries, wall materials, and types of graphite. While there were minor differences related to the electrical and mechanical characteristics of the graphites and the wall materials, the reaction appeared to have fairly well defined thresholds of pressure and temperature.

Tests were also made on mixtures of graphite and diamond powder, graphite and hexagonal boron nitride, graphite and nickel powder, and pencil "lead." In the first case the particles of

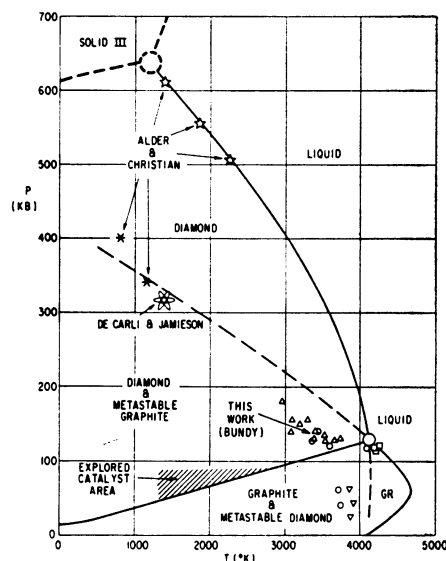


Fig. 2. Proposed phase diagram of carbon. The data points of the present investigation are shown as upright triangles, open circles, and squares. These indicate reaction to diamond, no reaction, and graphite melting, respectively.

diamond were unaffected while the graphite transformed to diamond. The mixture of graphite and hexagonal boron nitride transformed to a composite of diamond and cubic boron nitride. The mixture of graphite and nickel powder was converted to a composite of diamond in which the nickel particles were entrapped. The pencil "lead," which is a mechanical mixture of graphite and clay, became converted to diamond, stishovite (7), and small amounts of other unidentified materials.

The quantitative results of the experiments are shown in Fig. 2. The upright triangles indicate the pressures and temperatures at which the graphite-to-diamond reaction started. The open circles show the maximum temperatures reached at a given pressure in those experiments in which there was no reaction. Squares indicate the onset of melting of graphite. The inverted triangles show the conditions at which rapid complete graphitization of diamond took place. The cluster of upright triangles establishes quite clearly a threshold line or band at which graphite transformed very rapidly to diamond.

On the same diagram are shown points of pressure and temperature taken directly or indirectly from the data in the publications of DeCarli and Jamieson and of Alder and Christian (3). All of these data points, together with my own work on the melting line of graphite (8) and the published work on the diamond-graphite equilibrium line (9), rather well establish the phase diagram for carbon. By analogy with the behavior of indium antimonide (10), silicon, and germanium (11-13) at high pressure it is proposed here that around 600 to 700 kilobars the diamond melting line terminates in a triple point which joins liquid, diamond, and a third solid phase of carbon which is 15 to 20 percent more dense than diamond, and is metallic. Because the density of this proposed "carbon III" would be slightly greater than the liquid, its melting temperature showed increase with pressure, in the manner shown.

The pressure-temperature line which marks the threshold of the spontaneous transformation of graphite to diamond is of interest in at least two respects. First, it appears to be closely related to the extension of the graphite melting line, or what may be considered to be the melting line of metastable graphite. This line, together with the data of Alder and Christian, plotted on a pres-

sure-volume diagram, predicts that graphite should, at room temperature, transform spontaneously to diamond at a pressure of about 400 to 450 kilobars. The fact that such a room-temperature transition has not yet been reported indicates that pressures of this magnitude have not yet been attained in static pressure apparatus.

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Circadian Rhythm in the in vitro Response of Mouse Adrenal to Adrenocorticotrophic Hormone

Abstract. Adrenal corticosterone production resulting from adrenocorticotrophic hormone (ACTH) stimulation in vitro depends upon the time of gland removal. This rhythm in adrenal reactivity to ACTH is out of phase with the corticosterone rhythm in serum of the mice used as donors of adrenals. The responsiveness of the gland to exogenous ACTH is highest when serum corticosterone levels are lowest.

In the mouse, the circadian (*circa*, about; *dies*, day) rhythm in corticosterone of serum (1) and adrenal (2) can be studied in vivo under conditions standardized with respect to the physical environment and the history of the animals, including their genetic background. On a regimen providing for light from 0600 to 1800, alternating with darkness, corticosterone levels in mouse serum and adrenal are highest at about 1600 and lowest at about 0400. The occurrence of peak levels in adrenal and blood corticoste-

roid in this nocturnally active rodent differs from that recorded for blood and urinary steroid levels in diurnally active men, but in mice, as well as men, spontaneous adrenal activation occurs prior to the onset of daily activity (1).

The adrenal cycle is not a mere direct and immediate reaction to extrinsic stimuli acting upon the gland via ACTH stimulation. In the face of fluctuating pituitary or central nervous system stimulation which influences the state of the adrenal at any one time, periodic changes in the metabolism of the mouse adrenal itself may contribute critically to the gland's intrinsic circadian cycle. Our in vitro studies, initiated to define any inherently periodic contribution of the adrenal itself to its reactive behavior and to correlate these effects with spontaneous changes in adrenal activity observed in vivo, document quite clearly the need for defining the state of an organ or organism studied in terms of its circadian rhythms (3).

Inbred male C (Bagg albino) mice, 3 months of age, were housed singly for 1 week prior to the study in three experimental rooms kept at $24^{\circ} \pm 0.5^{\circ}\text{C}$, with light from 0600 to 1800, alternating with darkness. Purina Fox Chow and tap water were available to the mice from weaning until sacrifice. Additional conditions for circadian periodicity analysis have been described elsewhere (4). Seven groups, each composed of 60 mice, were sacrificed every 4 hours, starting at 0800 on the day of study and ending at 0800 the next day. At each time point, 12 pools of blood, each from five mice, were obtained for determination of serum corticosterone.

Immediately after decapitation the adrenal glands were removed, defatted, quartered (5), and placed in 25-ml erlenmeyer flasks. Each flask contained 10 adrenals in 2.0 ml of a Krebs-Ringer bicarbonate buffer, pH 7.4 containing glucose (2 g/liter). Ovine ACTH (Parke, Davis and Co.) in doses of 0.04, 0.4, and 4.0 International Units, was added at the start of incubation. At each of the seven time points, additional adrenals were incubated without ACTH or frozen for direct extraction of steroid. An additional series of flasks containing progesterone-4- C^{14} in the incubation fluid served to explore the extent of conversion of this material to other adrenal steroids (6). All flasks were run in duplicate. The incubations were carried