there were 87 instances of dream recall. Table 1 presents the results according to the number of awakenings made on individual subjects. The table was set up in this manner in order to take into account the unequal number of awakenings per subject.

Of the 87 dreams recalled, color was present in 61, or 70.1 percent. Vaguely colored dreams were reported in an additional 11, or 12.6 percent, and no color responses were given in the remaining 15, or 17.3 percent.

Of the dreams in which color was reported, the color was given spontaneously in 22 dreams and only after some questioning in the other 39. In addition, at least one colored dream was reported by 31 of the 38 subjects (81.6 percent). At least one vaguely colored dream was reported by three more of the subjects. No color was present in the dreams of two of the subjects. Two additional subjects could not recall any dreams at these awakenings. Of the last four subjects, three were awakened only once and one was awakened twice. No attempt was made to determine the percentage of color in the content of single dreams.

A further check was made to see how frequently subjects reported color spontaneously after awakening when there was no investigator interest in the incidence of color. The same technique of awakening after rapid eye movements was used. Two hundred and eight transcribed dream narratives, collected from 16 subjects in two previous studies (*12, 14*) were available for examination and comparison. In these studies there was no interrogation about color. It was found that color was mentioned spontaneously in only 33 of the 208 dreams (15.9 percent). This figure is not significantly different from the percentage of spontaneous color responses in the present series of awakenings (25.3 percent or in 22 of the 87 recalled dreams). Our somewhat higher figure, although not significant, may be explained by the possibility that at some point after the first awakening the subjects were able to guess at the purpose of the study and consequently were more motivated to attend to and describe color. Despite this slight discrepancy in the two series, both substantiate the fact that the incidence of color in dreams cannot be assessed validly by working with spontaneous narratives of dreams even when the narratives immediately follow the dream experience.

In order to arrive at a more valid assessment of the percentage of color in dreams, some probing is necessary. Color is not a salient characteristic in dream reporting, and, indeed, may not be a frequently mentioned characteristic of descriptions of everyday events of waking life. The fact that color was present in 70 percent of the dreams, or in 83 percent when the Vaguely Colored category is included, suggests that dreaming should be considered a colored rather than a black-and-white phenomenon. It would appear that it is the lack of color rather than its presence in dream recall which requires explanation (*15*).

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References and Notes

1. C. S. Hall, *Scientific Am.* **184**, No. 5, 60 (1951).
2. W. S. Monroe, *Am. J. Psychol.* **9**, 413 (1897).
3. P. H. Knapp, *Psychoanal. Quart.* **25**, 325 (1956).
4. R. Husband, *J. Abnorm. Soc. Psychol.* **30**, 513 (1935).
5. W. C. Middleton, *J. Gen. Psychol.* **27**, 221 (1942).
6. M. F. DeMartino, *J. Clin. Psychol.* **9**, 199 (1953).
7. J. W. Lovett Doust, *J. Mental Sci.* **97**, 801 (1951).
8. F. Tapia, J. Werboff, G. Winokur, *J. Nervous Mental Disease* **127**, 119 (1958).
9. M. Bentley, *Am. J. Psychol.* **26**, 196 (1915).
10. E. S. Tauber and M. R. Green, *Am. J. Psychotherapy* **16**, 221 (1962).
11. E. Aserinsky and N. Kleitman, *Science* **118**, 273 (1953).
12. W. Dement and N. Kleitman, *J. Exptl. Psychol.* **53**, 339 (1957).
13. ———, *Electroencephalog. Clin. Neurophysiol.* **9**, 673 (1957).
14. W. Dement and E. Wolpert, *J. Exptl. Psychol.* **55**, 543 (1958).
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19 June 1962

Melting Point of Graphite at High Pressure: Heat of Fusion

In 1902, Ludwig reported that carbon rods, when heated electrically in a high-pressure atmosphere of hydrogen, exhibited abrupt, large rises in resistance at very high temperatures (*1*). He thought this form of carbon was liquid, or diamond-like, and tried to preserve it by rapid quenching. The material recovered was always graphite. In 1939 Basset published the results of extensive experiments in which carbon rods were electrically heated in an atmosphere of high-pressure argon (*2*). He found that the graphite-liquid-vapor triple point is at about 110 atmospheres and 4000°K, and that the melting point of graphite rises slowly with increase of pressure. In 1959, Noda reported (*3*) work, and results, similar to those of Basset. Theoretical studies of Pitzer and Clementi, published in 1959, suggested that the molecules of liquid carbon should be very long graphitic chains, and that the heat of fusion should be about 10 kcal/mole at 4000°K (*4*).

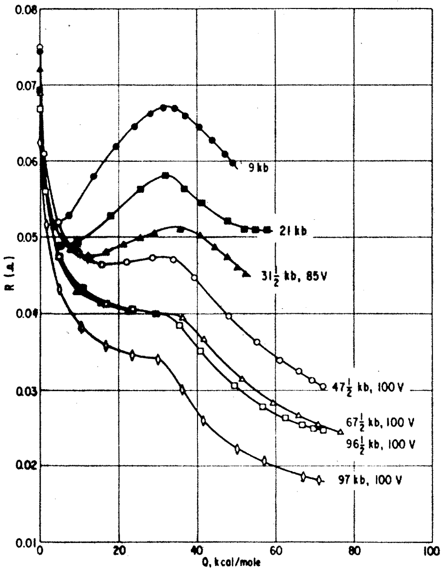

Fig. 1. Resistance versus energy insertion for samples of spectroscopic rod graphite flash-heated at various pressures.

The simultaneous development of improved high-pressure apparatus, processes, and techniques in recent years has made it possible to study graphite at very high pressures and temperatures. This paper briefly reports the main results of an experimental program aimed at determining the melting temperature of graphite as a function of pressure, the heat of fusion, and the pressure and temperature of the graphite-diamond-liquid triple point.

Modified "belt-type" high pressure apparatus was used (*5*). In the high-pressure cell the slender graphite test rod was surrounded by a sleeve of boron nitride, pyrophyllite, magnesia, or diamond powder. The graphite rod was transiently heated by passage of a pulse of electric current from a charged electrolytic capacitor. Transient heating was necessary because at the very high temperatures required for melting

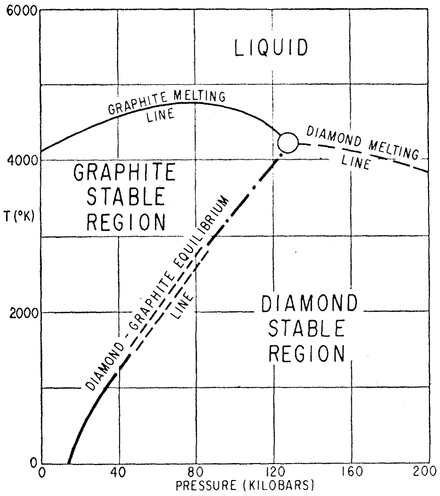

Fig. 2. Melting line of graphite as a function of pressure. Also the diamond-graphite equilibrium line, and the estimated diamond melting line.

graphite the walls would react, melt, or both, if held at the high temperatures. The period of energy insertion, about 5 milliseconds, was so small compared to the half cool-off time, about 30 milliseconds, that the process was approximately adiabatic. During a heating pulse, the voltage and current in the graphite rod were displayed on a two-channel oscillograph and photographed. From the voltage and current records, curves of heating power and of resistance plotted against time were derived. The power curve was integrated so that it gave a curve of inserted energy as a function of time. Then the resistance could be plotted as a function of the inserted energy. Later the temperature was derived from the inserted energy by integration of the curve of specific heat of graphite versus temperature.

The resistance versus temperature behavior of pure spectroscopic graphite rod at various pressures is shown in Fig. 1, where resistance is plotted against energy insertion. The initial temperature rise caused the resistance to drop rapidly. Further temperature rise caused the resistance to level out, or increase. Finally, a temperature was reached at which the resistance made an abrupt break downward. It was soon established beyond doubt that this downward break of resistance was associated with the onset of melting. Samples heated past this point showed grain structure characteristic of chilled castings, as well as a characteristically low final room-temperature resistance. Furthermore it was found that the resistance of the liquid state was the same for all the kinds of graphite tested regardless of their wide range of resistivity in the solid state.

The curves in Fig. 1 show that the resistance of solid graphite at the melting point at 9 kilobars was over twice that at 97 kilobars. The corresponding resistance ratio for the liquid state at these pressures is seen to be even greater. It is also evident that the melting point was higher in the mid-pressure range than it was at the lower and higher pressures.

A large number of experiments, in which different wall materials were used, showed that all wall materials became electrically conducting in varying degrees at very high temperatures. This caused a small fraction of the electrical energy to be shunted from the graphite rod. These losses, and the small losses due to thermal conduction during the heat-up period, were determined as well as possible and were subtracted from the gross electrical energy inputs in order to find the true energy to melting, and later, the true temperature of melting.

Table 1. Heat of fusion from heat-up data. Spectroscopic rod graphite, 48 kilobars.

Voltage of shot	Heat (kcal/mole) Inserted during fusion	Wall losses and liquid superheat	Applied to fusion	Fraction of sample fused	Heat of fusion (kcal/mole)
80	12	2.5	9.5	0.37	25
85	20	7.5	12.5	.52	24
90	29	12	17	.65	26
95	37	18	19	.77	24

Table 2. Heat of fusion from cool-off data. Spectroscopic rod graphite, 48 kilobars.

Voltage of shot	Freeze interval (msec)	Av. cooling rate* (kcal/mole per msec)	Heat (kcal/mole) Liquid superheat	Derived from solidification	Fraction melted	Heat of fusion (kcal/mole)
100	30	0.8	8	16	0.85	19
75	8	1.2	0	9.5	.30	32
80	11	1.05	0	11.5	.40	29
85	15	0.95	2.5	11.5	.55	21
90	20	.9	4	14	.65	22
95	29	.85	6	18	.75	24

*Determined from the parts of the cool-off curves after solidification.

Table 3. Fusion data for C, Si and Ge.

Element	T_m(°K)	ΔH_m (kcal/mole)	ΔS_m (cal/mole deg)
C	4600 (48kb)	25	5.4
Si	1683	11	6.5
Ge	1233	8.3	6.7

The final results on melting temperature are shown in Fig. 2. The melting line started at about 4100°K, rose to a flat maximum of 4600° to 4700°K at about 60 to 70 kilobars, then decreased to about 4100° to 4200°K at the triple point at about 120 to 130 kilobars. On the same chart the diamond-graphite equilibrium line (*6*) and the diamond melting line (not fully proved experimentally) are shown.

The location of the graphite-diamond-liquid triple point has been established by the graphite melting experiments described above, together with another set of experiments in which it was found that at pressures above about 120 to 130 kilobars and temperatures above about 3000°K graphite spontaneously transforms to diamond (*7*).

When the relationship between the inflections of the resistance curves and events in the graphite sample were established, and the electrical and thermal losses were known, it became possible to derive the heat absorbed by fusion during the melting period of the energy insertion, and the heat release upon freezing during the cool-off period. The values of the heat of fusion obtained by the two methods show satisfactory agreement. The derivations are summarized in Tables 1 and 2. The average of the values of the heat of fusion given in the tables is 24.6 kcal/mole. This work indicates, therefore, that the heat of fusion of graphite is about 25 kcal/mole at 48 kilobars' pressure. No measurements were made at any other pressures.

This value of the heat of fusion is 2.5 times that suggested by Pitzer and Clementi (*4*) for 4000°K. Perhaps the difference can be accounted for by the higher temperature of melting (about

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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References

1. A. Ludwig, *Z. Elektrochem.* **8**, 273 (1902).
2. M. J. Basset, *J. Phys. Radium* **10**, 217 (1939).
3. T. Noda, reported by H. Mu, *Proc. Intern. Symposium on High Temperature Technol.*, Asilomar Conference Grounds, Calif., 6–9 Oct. 1959 (Stanford Research Institute, Menlo Park, Calif.; McGraw-Hill, New York, 1960).
4. K. S. Pitzer and E. Clementi, *Science* **129**, 1287 (1959).
5. H. T. Hall, *Rev. Sci. Instr.* **31**, 125 (1960).
6. F. P. Bundy, H. P. Bovenkerk, H. M. Strong, R. H. Wentorf, Jr., *J. Chem. Phys.* **35**, 383 (1961).
7. F. P. Bundy, *Science* **137**, 1057 (1962).
8. B. J. Alder and R. H. Christian, *Phys. Rev. Letters*, **7**, 367 (1961).

12 September 1962

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 attemps 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 its 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).

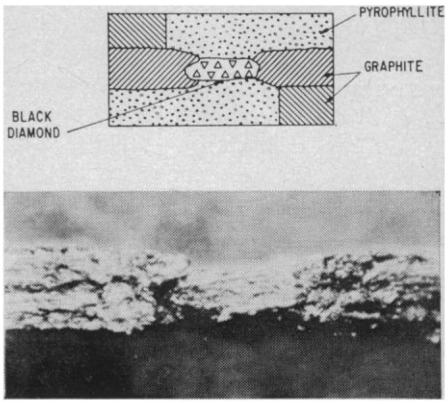

Fig. 1, (Top) Cross section of a high pressure sample after compression to 130 kilobars and flash heating to a temperature over about 3500°K. The center part of the graphite specimen bar, where the temperature was highest, converted to polycrystalline diamond. (Bottom) Photograph of the specimen after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

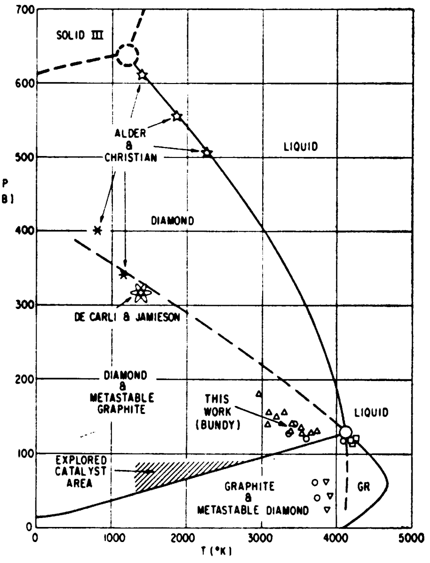

Fig. 2. Proposed phase diagram of carbon. The data points of the present investigation are shown as upright triangles, open circles, and squares. These indicate reaction to diamond, no reaction, and graphite melting, respectively.