Ever since Antoine Lavoisier in 1792 and Smithson Tenet in 1797 demonstrated that diamond and graphite are allotropic forms of carbon, man has been interested in converting the relatively abundant graphite into much rarer diamond. Success in this endeavor, however, has only been achieved in recent years, and tiny crystals about 1/10 mm average diameter, valued at about $6000 per pound, are being quantity produced in direct competition with natural diamonds. These diamonds are used primarily in diamond grinding wheels.

Crystal Structure Information

The differences between graphite and diamond at the atomic level were not known until after X-ray diffraction techniques for the elucidation of crystal structures were developed during the 1910-20 decade. Diamond, one of the earliest crystals studied, was shown to consist of carbon atoms arranged in puckered, hexagonal rings lying approximately in the 111 crystallographic plane. (This is the natural cleavage plane of diamond.) These sheets of hexagonal, puckered rings are stacked one above the other in sequences such that atoms in every fourth plane duplicate the position of atoms in the first. By analogy to closest packings, this sequence is designated . . abcabc . . In this structure every carbon atom is surrounded by four other carbon atoms equidistant from the central carbon atom at angles of 109°28′ (the tetrahedral angle) from each other (see Fig. 1).

The arrangement of atoms in crystals of graphite is similar to that of diamond in that it consists of a parallel stacking of layers comprised of carbon atoms forming hexagonal rings. The hexagonal rings in graphite, however, are probably only very slightly puckered. The classical graphite structure indicates an . . abab . . stacking sequence for the layers (atoms in alternate layers occupy equivalent positions). According to some interpretations of the electron diffraction patterns given by graphite, the . . abcabc . . configuration (Fig. 2) is present to an appreciable extent in graphite. As with diamond, the cleavage plane is parallel to the stacked layers. However, graphite is cleaved with extreme ease compared to diamond.

In diamond, all distances between atoms are 1.54 Å. In graphite, the inter-atomic distances within a layer are all equal (1.42 Å). Individual planes in the graphite lattice, however, are spaced far apart (3.37 Å). This immediately
suggests that the bonding within the planes is different from the bonding between the atoms of neighboring planes. It is thought that the bonding between planes in the graphite crystal is of the van der Waals type.

Although the accepted ideas of the crystal structure for diamond have not changed since the earliest determination, there have been periodic questions concerning details of the crystal structure of graphite, and these question continue to the present day. There is no doubt, however, that the essential features of graphite are those of approximate hexagonal rings of carbon atoms arranged in layers separated a considerable distance apart relative to the distance between adjacent carbon atoms in the hexagonal rings.

To further characterize the differences on the atomic scale between graphite and diamond, it is necessary to look into the nature of the bonding between atoms. In diamond, the bonding is predominately covalent in nature and is due to the formation of \(sp^3\) hybrid bonds. All bonds within diamond are equivalent and are “aliphatic” in character. The bonds between carbon atoms in the hexagonal rings in graphite apparently have some double bond character. Therefore, the entire layer or sheet consists of a giant, two-dimensional resonating molecule—a molecule that is somewhat “aromatic” in character.\(^3,4\)

Because of the similarities in crystal structures, a cursory examination might lead to the conclusion that graphite could be converted to diamond by brute force; i.e., by applying sufficient pressure, the bonds between graphite layers would be shortened the proper amount and the hexagonal carbon rings would be forced to “pucker,” the whole process causing the atoms to conform to the diamond crystal lattice. The years have shown, however, that there are some complicating factors in this direct conversion of graphite to diamond.

**Thermodynamics and Kinetics of Conversion**

A modern day chemist knows that he must be concerned with two problems whenever he wants to bring about a chemical change. (A change from one polymorphic form to another may be regarded as a type of chemical change.) He must first consider the thermodynamic problem and second, the chemical kinetic or reaction rate problem. Chemical thermodynamics is concerned with the relative energies of the reactants and the products of a chemical reaction. Under conditions where the free energy of the reactant(s) \(F_r\) is greater than the free energy of the product(s) \(F_p\), the relative energy \(F_p - F_r = \Delta F\) is negative and the reaction has thermodynamic permission to proceed toward formation of the products. In the case at hand, the reactant is simply graphite and the product is diamond: \(C_{\text{graphite}} \rightleftharpoons C_{\text{diamond}}\). On the other hand, if \(\Delta F\) is positive, the reaction has thermodynamic permission to proceed in the opposite direction; i.e., the products (as the reaction is written) will proceed to transform into the reactants. Under conditions where \(\Delta F\) is zero, a stalemate (equilibrium) exists and there is
not net tendency for the reaction to proceed in either direction.

Thermodynamics does not give any information about the time required for a reaction to take place. The $\Delta F$ may, in many instances, have a large negative value, yet the reaction is found to proceed at an imperceptible rate. An oft quoted example of this situation is the bulb containing a mixture of hydrogen and oxygen gases. For the reaction, $\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}(g)$, the standard change in free energy is $-55,600$ cal. Nevertheless, the bulb may be kept for many years without detecting the formation of any water vapor.

It is the business of chemical kinetics to deal with the rates of chemical reactions. For this purpose theories and techniques for understanding the atomic and molecular processes (reaction mechanisms) taking place in chemical reactions have been developed. Application of the theory, couple with appropriate experiments, often points the way toward finding means of increasing or decreasing the rate of a given reaction.

Favorable Negative $\Delta F$ as Pressure Increases

For the reaction $\text{C}_{\text{graphite}} \rightarrow \text{C}_{\text{diamond}}$, $\Delta F^\circ = +692$ cal/g-atom at 25°C and 1 atmosphere pressure (5). This $\Delta F^\circ$ is not obtained by direct measurement but, as is the case with more thermochemical data, is calculated from measurements of heats of combustion, specific heats, compressibilities, thermal expansions, etc. The positive $\Delta F^\circ$ indicates that diamond is thermodynamically unstable with respect to graphite. However, diamonds have not been known to transform into graphite by any observable amount over periods of hundreds of years under ordinary conditions. The rate of reaction (conversion) must, therefore, be extremely slow. Increased temperature will accelerate most reactions and this is also true for the conversion of diamond to graphite. This transformation begins to proceed at an observable rate at a temperature in the neighborhood of 1200°C at 1 atm. At this pressure and temperature $\Delta F^\circ$ has increased to about $+2400$ cal indicating that higher temperatures decrease the thermodynamic stability of diamond. The $\Delta F^\circ$ for the graphite-diamond transition assumes its lowest value at the absolute zero of temperature

$$\Delta F^\circ_0 = +580 \text{ cal/g-atom at } 1 \text{ atmosphere}$$

In order to bring the graphite-diamond reaction into a region where $\Delta F^\circ$ is negative, it is necessary to apply pressure. The pressure required depends on the temperature—the higher the temperature, the greater must be the pressure.

Equilibrium is established when the free energy difference between the two allotropes is zero, i.e.,

$$\Delta F = \Delta H - T\Delta S = 0$$

The manner in which $\Delta F$ varies with pressure at a given temperature is given by

$$\left( \frac{\delta \Delta F}{\delta P} \right)_T = \Delta V$$

or by

$$\Delta F^\circ_T - \Delta F^\circ_0 = \int_P^0 \Delta V dP$$

where $\Delta V$ is a function of both $T$ and $P$. From these expressions the free energy difference at any pressure and temperature may be expressed as

$$\Delta F^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T + \int_0^P \Delta V dP$$

Data is available for evaluating $\Delta H^\circ_T$ and $\Delta S^\circ_T$ to 1200°K. Evaluation of the integral, however, involves some reasonable approximations. For additional details, the reader is referred to Berman and Simon (5).

A graph showing the approximate pressure-temperature relationship is shown in Figure 3. The line represents the pressure and corresponding temperature for which $\Delta F^\circ = 0$. Above the line $\Delta F^\circ$ is negative and diamond is the stable carbon allotrope. Conversely, graphite is stable in the positive $\Delta F^\circ$ region below the line.
Graphite, subjected to $P$-$T$ conditions above the line, should transform to diamond. Graphite has been subjected to conditions lying approximately below the solid line of Figure 4. Although part of this area overlaps the diamond stable region, diamond has not yet been observed to form directly from graphite under these conditions. Since the thermodynamic criteria for formation of diamond have been met, it must be concluded that kinetic considerations are controlling and are preventing the transformation from occurring in any practical length of time.

**Less Favorable Rate as Pressure Increases**

Increased temperature might ultimately increase the rate of transformation to a practical value, but increased temperature (to stay with the diamond stable region) calls for an increase in pressure beyond the range of the high pressure devices currently available.\(^2\) At this impasse an investigation of the rate process is enlightening. Although diamonds cannot yet be made by direct conversion from graphite, graphite can easily be made from diamond. Studies of this reverse transformation under high-pressure, high-temperature conditions can give information concerning the reaction mechanism.

Experiment shows that high pressure retards the rate of transformation of diamond to graphite. The theory of absolute reaction rates indicates for such a situation\(^6\) that

\[
\log \text{rate} = \text{constant} - \frac{\Delta V^\pm P}{RT}
\]

where $\Delta V^\pm$ is the molar difference in volume between diamond and the activated complex (the intermediate state or transition state), $P$ is the applied pressure, $T$ is the temperature, and $R$ is the molar gas constant. Although available experimental data are somewhat erratic, a plot of log rate versus $P$ leads to the inescapable conclusion that $\Delta V^\pm$ is at least 10 cc. Note that the molar volume of diamond is 3.42 cc, the molar volume of graphite 5.34 cc, and their difference in molar volume $\Delta V$ is only 1.92 cc. Obviously the transition state, with a molar volume $V^\pm$ of at least $(10 + 3.42)$ cc is a very open or expanded structure. It is reasonable to assume that the transition state for graphite-diamond conversion if the same as for the formation of graphite to diamond. This being the case, there arises the very frustrating but extremely interesting situation that higher pressure leads to more favorable thermodynamics (a more negative $\Delta F$) for the conversion of graphite to diamond, but at the same time, leads to less favorable reaction kinetics since it suppresses the formation of the expanded activated complex. At the pressures and temperatures to which graphite has been subjected, to the present time, reaction kinetics apparently have the upper hand and prevent the synthesis of diamond directly from graphite in any practical period of time. Additional information concerning thermodynamics and reaction rates, as applied to high pressure reactions, is set forth in reference 7.\(^7\)

**Success: Graphite $\rightarrow$ Diamond**

From the above analysis it would seem desirable to take the graphite lattice apart atom by atom and build the atoms one at a time into the diamond lattice. This might be accomplished by means of a solvent. Conceivably the proper solvent would take carbon atoms from graphite into solution as individual entities which, under the influence of proper thermal and concentration gradients would migrate through the solvent and precipitate as diamond. Nature gives some clues as to possible solvents.

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\(^2\) Note added in proof: DeCarli, P. S., and Jamieson, J. C., *Science*, 133, 1821 (1961), have just reported the synthesis of eight-micron-diameter diamond directly from rhombohedral graphite by means of an explosive shock. Transient pressure was estimated to reach 300,000 atm. An estimate of the temperature achieved was not given.
Diamonds are found imbedded in ferromagnesium silicates, from which they apparently crystallized, in the famous pipe mines of South Africa. A few diamonds have been found embedded in iron-nickel and in troilite (FeS) constituents of meteorites.

My first synthesis of diamond was based on the idea that diamonds might be crystallized from troilite. On December 16, 1954, at the General Electric Research Laboratories in Schenectady, New York, I performed an experiment in the “Belt” high pressure, high temperature apparatus with a cell arrangement as shown in Figure 5.

A brief diversion is necessary at this point to make a few comments concerning the apparatus. The “Belt” apparatus makes use of two opposing, conical pistons thrust into opposite ends of a symmetrical, tapered chamber (Figures 6, 7). Relative motion of the pistons with respect to the chamber is afforded by a compressible gasket. The solid pressure transmitting material used in the device serves also as electrical and thermal insulation. The design allows pressures greater than 100,000 atm to be continuously maintained simultaneously with temperatures above 2500°C (Temperatures estimated to be as high as 7000K have been maintained for a few seconds.) Development of this device opened a large, hitherto inaccessible thermodynamic region to scientific exploration. The relative simplicity of the design has made it an extremely useful and practical tool. (The theory of its operation and details concerning use, design, and development are to be found in references 9, 10, 11, and 12).

A second device (actually the first to be publicly disclosed) with the same pressure, temperature, and diamond synthesizing capabilities as the “Belt” was developed at Brigham Young University during 1956-1957. It is called the “Tetrahedral Anvil Press” and is currently finding considerable use as a research tool.

In the December 16 diamond synthesis run, the tapered pistons of the “Belt” apparatus were forced into the loaded chamber by a 223,000-pound thrust delivered by a hydraulic press. After one minute the load was reduced to 186,000 pounds. An electric current (60-cycle, alternating) was then passed through the assembly via the tapered pistons. Current was gradually increased over a period of 6 minutes to a maximum value of 346 amps. The voltage drop across the pistons was 1.84 v corresponding to a power dissipation of 636 w. The temperature inside the graphite tube at this power level was approximately 1650°C. The pressure, at the time, was thought to have been in the
neighborhood of 95,000 atmospheres. There has been some controversy over the calibration of high pressure apparatus recently, however, that would place the actual pressure as much as 20% below this figure. Even assuming the lower pressure value, however, the system was in a region of thermodynamic stability for diamond. Maximum temperature was maintained for about 3 minutes, after which it was lowered to room temperature in approximately five minutes. After the temperature had been lowered, 18 minutes were taken to reduce the pressure to 1 atm.

When the cell was broken open, dozens of tiny transparent crystals were found near the tantalum disc at the top end of the cell. Subsequent chemical, physical, and X-ray examinations conducted during the course of the next few days conclusively proved that the material was diamond. Pictures of these diamonds are shown in Figure 8. A powder X-ray diffraction pattern is shown in Figure 9 where arrows point to the diamond lines. The extraneous diffraction lines were caused by the presence of graphite and tantalum carbide. The “seed” diamond employed in this run was unchanged at the completion of the experiment. No new diamonds were found in its vicinity and subsequent runs without a diamond seed were successful.

During the period December 16 through December 31, 1954, I performed 27 high pressure experiments similar to the successful December 16 experiment with some changes in the various experimental parameters. Diamonds were made in 12 of these runs. Since FeS was known to be a non-stoichiometric type compound, usually with excess iron (Fe$_x$S where $x > 1.00$), pure iron was substituted for the FeS and diamonds were successfully grown in that solvent. Substitution of pure sulfur for FeS did not produce diamonds. Microscopic examination of the cell contents following a run with FeS or Fe disclosed that a black coating (removable by acid) covered the diamonds. Carbon atoms, derived from graphite or metallic carbides formed in the reaction mixture, apparently migrate through this film and precipitate as diamond. The film is probably iron. The tantalum (or more particularly tantalum carbide) which formed in the presence of carbon, seemed to aid diamond growth.

Of practical importance in locating the correct temperature for diamond formation was my observation that onset of diamond growth was signaled by a drop in heating current through the sample and a corresponding rise in voltage across the sample. As heating power was controlled by a variable auto transformer, it was only necessary to increase the power output of the transformer until this phenomenon took place. The power setting was then left unchanged for 2 or 3 minutes until diamond growth was about complete.

On December 31, 1954, Dr. H. Hugh Woodbury of the General Electric Laboratory duplicated my December 16 run and thus, to our knowledge, became the first man to duplicate the diamond synthesis claim of another.\(^3\)

\[^3\] At this point it was evident that a landmark in science had been reached. In reaching that landmark, I could take particular satisfaction in the following key contributions:

The design of the “Belt” apparatus that made experiments in the 100,000-atm, 2500°C-temperature range possible.

The discovery of a suitable combination of pressure, temperature, chemical ingredients, timing sequence, and cell arrangement for the synthesis of diamonds. It was extremely important that (a) the synthesis could be reproduced by myself and others; (b) diamond growth was very rapid; (c) diamond yields were significant—outstripping a million fold the concentration, relative to the growing matrix, of
Simple substitution of other transition metals for iron subsequently showed that many of these elements were suitable solvents for the synthesis of diamond.

By February 15, 1955, diamonds had been produced in about 100 separate runs in the General Electric Research Laboratory. On this date a press conference was held and the fact that diamonds had finally been made by man was announced to the world. However, details concerning the synthesis were not released. On October 22, 1957, the company announced that diamond production had successfully been carried through the pilot plant stage—more than 100,000 carats (a carat = 0.200 gram) having been produced up to that time. Thus, less than three years following the successful conclusion of a 100-plus years' search for a method to convert ordinary black carbon into diamond, man-made diamonds became a commercial product. Details of apparatus and methods of synthesis were finally released in the fall of 1959.

Following the February 15, 1955, synthesis announcement by the General Electric Co., several claims to prior synthesis were voiced. Only one of these claims has appeared in a technical journal. It appeared as an article entitled “Artificial Diamonds” by H. Liander in the ASEA (Allmänna Svenska Elektriska Aktiebolaget, Västerås, Sweden) Journal for May-June of 1955. The method of synthesis was not given but the statement was made that “ASEA produced its first diamonds on 15th February, 1953.” The experimental procedures were disclosed in 1960 and were similar to those used at General Electric.  

Literature Cited


11 “Proceedings of the Third Conference on Carbon” (held at University of Buffalo, Buffalo, N. Y., June, **1957**), Pergamon Press, London, pp. 75-84 by H. T. Hall.