



TODAY SERIES

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*May 1967*

*179 pages*

**HIGH PRESSURES**  
**(To 100,000 Atmospheres at 1,500°C)**

by

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## 5. The Synthesis of Diamond

### Biblical References to Diamond

In discussing the synthesis of diamond, some historical aspects concerning diamond will be of interest. In recorded history, diamond is first mentioned in the Old Testament. In the 28th chapter of Exodus, there is some discussion concerning the priestly garments to be made for Aaron, the brother of Moses. These garments were to be made "for glory and for beauty". One of the garments was to be a breast plate and was described, beginning with the 16th verse, as follows:

"16 Foursquare it shall be being doubled; a span shall be the length thereof, and a span shall be the breadth thereof.

17 And thou shalt set in it settings of stones, even four rows of stones. The first row shall be a sardius, a topaz, and a carbuncle: this shall be the first row.

18 And the second row shall be an emerald, a sapphire, and a diamond.

19 And the third row a ligure, an agate, and an amethyst.

20 And the fourth row a beryl, and an onyx, and a jasper: they shall be set in gold in their inclosings.

21 And the stones shall be with the names of the children of Israel, twelve, according to their names, like the engravings of a signet; every one with his name shall they be according to the twelve tribes. "

Obviously, diamond was recognized as a precious and

object even at this early date.

A second biblical reference to diamond appears in Ezekial chapter 28 verse 13 and also indicates that diamond was considered precious and beautiful and was used for adornment.

There is a third biblical reference to diamond. It occurs in the book of Jeremiah, chapter 17 verse 1. "The sin of Judah is written with a pen of iron and with the point of a diamond. It is graven upon the table of their heart and upon the horns of your alters. "This reference clearly indicates that diamond was known as a hard substance, and was used to write or scribe on other materials. The book of Jeremiah is thought to have been written about 700 B. C. No doubt, people even at this ancient date, recognized diamond was the hardest of all substances and used it as a graving tool. This "industrial" use of diamond has persisted to the present day. The two major uses of diamond, then, are the use as a gem, and the use as a hard material for scribing, cutting, and grinding.

### Early Diamond Fields

The earliest known diamonds are thought to have come from India; a diamond mining industry having originated there sometime around 700 B. C. Most of what is known concerning the Indian mines comes from the writings of a French traveler, Tavernier. He visited the Indian fields, which were located on the banks of the Kistna river in 1665. At one location he saw about 60,000 people working the aluvial diggings. The men would dig gravel from the banks of the

river, deposit the material in baskets, which the women and children would carry away and patiently sort to find the diamonds. Diamond concentration was probably of the order of one part in 60,000,000 by weight. Consequently, finding a diamond was a tedious process. Diamonds were discovered in Borneo about 600 A.D, and soon supplemented the Indian source.

The next diamond discovery occurred in the jungles of Brazil near the town of Tejuco in the province of Minas Geraes. Here, in the year 1726, miners were panning for gold in swift upland streams. At this time in history, Brazil was a Portuguese province. The port of Goa on the west coast of India was also under Portuguese control. This port was somewhat of a business center for the mining trade and also for diamond trading. A prospector by the name of Bernardo daFonseca Lobo, who was familiar with mining in general and diamonds in particular, had recently arrived from Goa to investigate gold mining in Brazil. The miners gathered around their camp fires and played cards every night. Fonseca Lobo quickly noticed that they used some bright pebbles for counters in their card games and that these bright pebbles were diamonds. The gold miners did not know that the pebbles which had been found in their pans along with the gold were diamonds. In the panning process, of course, lighter rocks and minerals are washed over the rim of the pan while heavy minerals and rocks sink to the bottom. Diamond has a density of 3.5, not nearly so high as that of gold (density 19.3), yet higher than that of the average silicate rock found in the river gravels.

The news of Fonseca's discovery of diamonds in the gold fields soon spread to Lisbon and to other parts of Europe. The town of Tejuco was renamed Diamantina and the Portuguese Government stepped in, ordered out the entire gold-mining population and gave mining rights to a few favored planters. There ensued a considerable amount of interesting trouble as a result. This will not be discussed here. Suffice it to say that the Brazilian fields soon became an important source of diamonds. The South African Diamond Fields

The world's most important source of diamonds was discovered in South Africa in 1866. Accounts of the discovery vary, but the following account is probably as accurate as any. Near the junction of the Vaal and Orange Rivers, land was being homesteaded by Dutch farmers. There were many pretty, colored silicate rocks in the banks of the Orange River which the children used for play things. It was a common sight to see such pebbles around the yards of the farm houses. In the year 1866, the children of a poor Boer farmer named Jacobs picked up a bright, transparent pebble on the banks of the river and dropped it on the farmhouse floor. The mother, Vrouw Jacobs, was attracted to the stone and happened to talk to a neighbor by the name of Schalk vanNiekerk about it. Niekerk asked if he might buy it. The story is told that Vrouw Jacobs laughingly gave the stone to him. Niekerk, in turn gave the stone to John O'Reilly, a trader, and asked him to find out if it had any value. The stone was eventually placed in the hands of a

geologist by the name of W.G. Atherstone of Grahamstown, who determined it to be a diamond weighing 21 carats and worth about \$2,500. This event, of course, created considerable excitement.

Farming was difficult, and was temporarily abandoned while people searched the rivers for diamonds. However, the search was unfruitful for awhile. It went on for 10 months before another diamond was found. Then 14 more months passed without any appreciable find until in March of 1869 a witch doctor by the name of Booi found an 83 1/2 carat stone on the banks of the Orange River. Schalk van Niekerk bought this stone for 500 sheep, 10 oxen, and a horse. He sold the stone for \$55,000 and it later became the famous "Star of South Africa" diamond. This, of course, again created great interest and diamond diggers of all ages and nationalities flocked to the region.

While the diggers were busy in the river gravels, a near-by farmer by the name of DuToit was building a new house out of a clay-like dirt obtained on his farmland. While troweling this material, he struck a hard object which, when plucked from the wall, was found to be a diamond. This apparently was the first recorded instance in which a diamond had been found in something other than a river gravel. The clay had been obtained from a "pan" (shallow depression) on DuToit's farm. On digging further in the pan, additional diamonds were discovered. Within the space of a year, several additional pans were found that contained diamonds. These were called "dry diggings," and here it was that the city of Kimberley was founded. The clay came

to be called "yellow ground." As the yellow was worked to greater depths it disappeared and was supplanted by a harder blue ground (kimberlite). It was discovered that the yellow ground was simply blue ground which had been weathered by its proximity to the surface. The blue ground still contained diamonds, and attracted diamond diggers as honey attracts flies.

As time went on the various digger's claims were consolidated until two opposing giants owned most of them. One was Cecil John Rhodes, the son of an Oxford clergyman. The other called himself "Barney Barnato," the grandson of a Jewish rabbi. Rhodes' company was called the DeBeers Consolidated, while Barnato's was the Kimberley Central. These men slugged it out, so to speak, for control of the fields for some time. However, in 1889 DeBeers Consolidated bought out the Kimberley Central with a single check written on the Cape of Good Hope Bank Limited, Kimberley Branch, in the amount of 5,338,650 pounds (approximately 25,000,000 dollars at that date). Thus, Cecil Rhodes became king of the diamond fields. He quickly improved diamond mining techniques and ventured into other mining interests. The empire he formed, which was backed financially by the great house of Rothchild, rapidly expanded and through the years has become the world's greatest cartel and interlocking corporation. Rhodes was later knighted, becoming Sir Cecil Rhodes. The Rhodes scholarships in Great Britain are named for him.

Geological Origin of Diamonds

Geologists, later studying the dry diggings, found that the blue ground was volcanic in origin, at least it seemed to have been molten at one time and had been extruded through pipes and fissures in the earth. It was assumed that the diamonds were formed deep within the earth at high pressures and temperatures and then had been brought to the surface by the volcanic action. There are a number of theories concerning the formation of the diamonds found in the pipes. None of them are satisfactory. The pipes, however, are regarded as the primary source of most natural diamonds. The aluvial diamonds (that is, the diamonds found in the river gravels) are assumed to have originated in the pipes and were then washed into the rivers by the forces of nature over long periods of geological history. That this is true is evident in South Africa. However, in other regions such as the diamond fields of Brazil, India, and Borneo, the pipes have never been discovered.

The blue ground or Kimberlite is also found in other countries. It occurs in Pike County, Arkansas, and contains diamonds. Diamonds were mined commercially here about the time of World War I. The diamond concentration, however, is so low that it is not commercially feasible to mine at the present time. However, the area is commercially exploited as a tourist attraction. For \$1.50 per day one can enter a fenced-in area and search for diamonds with hand tools. In recent



years diamonds have been discovered in Russia in an area that is similar geologically up to the region in which diamonds are found in South Africa.

### Diamond Cutting

Approximately 80% of the diamonds mined annually are of industrial quality. Generally these are the diamonds containing flaws, fissures, inclusions, and other features that make them unsuitable for gem use. Only 20% of the diamonds mined (on a weight basis) are of such quality that they may be cut and polished to produce a faceted gem. On a dollar basis, the 20% of gems have a greater total value than the total value of the 80% industrials.

Diamonds tend to crystallize in an octahedral crystal shape. However, octahedra formed with a high degree of perfection are rare. No doubt the early diamonds, prized for their beauty, were the very rare, perfectly crystallized specimens. For the most part, only royal monarchs were in possession of such diadems. Generally, lesser persons were forbidden to wear such jewels by royal decree. In the Fifteenth Century, however, diamonds became very fashionable in the French Court and the demand for them no doubt would have soon depleted the supply of naturally beautiful crystals. But fortunately, a Belgian by the name of Ludwig van Berquem in about

1475 introduced the idea of using diamond powder mixed with a little olive oil on a spinning wheel to cut facets on rough diamonds and thus bring out their inner beauty. This skill was soon developed to a high degree. In the middle of the Seventeenth Century, the brilliant cut still seen in today's engagement rings was invented. There are 58 facets on a brilliant-cut diamond, and this number of facets has been cut on diamonds smaller than a pin head.

Diamond, although it is the hardest and strongest of all substance when subjected to a steady push, is brittle and can rapidly be reduced to dust by repeated blows of a hammer. This is the manner in which most diamond dust or powder is prepared.

#### Industrial Diamond

The use of diamond powder to produce facets on gem diamonds constituted the primary "industrial" use for diamonds for a considerable period of time. However, other industrial uses began *to come* into being about the time of World War I. With the invention of cemented tungsten carbide in the late 1920's the use of diamond grit in grinding wheels expanded rapidly because diamond is the only material that is effective in cutting and grinding this very dense and hard substance. Since World War II the use of diamond grit, powder and larger stones has grown at a phenomenal rate.

In the year 1961 world industrial diamond sales totaled 20,000,000 carats, of which 12,000,000 carats was fine grit for use in diamond wheels. One carat equals 200 milligrams. The current price of diamond grit is around \$2.65 per carat, which amounts to about \$6,000 per pound. Larger diamonds used in drilling bits and single point tools are worth much more than this.

There is a general principle of tool construction that, while obvious, is often overlooked by the layman. This principle states that the tool, to be effective, must be harder than the material being worked. Consider the work of a cabinet maker. His task is to cut, form, and shape wood to build a cabinet. One of the tools he will use is a saw which is usually constructed of steel. Steel is used because it is much harder than the wood and thus is effective in cutting it. One would not ordinarily think of using a wooden saw to cut lumber. The metal saw also had a builder, and tools were required for its fabrication. Rollers, cutters, and drills were used in its manufacture and these tools were, no doubt, harder than the relatively soft steel used in wood cutting saws. Then there must have been a harder tool that made the tool that made the saw that made the cabinet, and so it goes-sort of reminiscent of a nursery rhyme.

There are some landmark materials in the scale of hardness of which tools are constructed. One of these has already been mentioned. It is cemented tungsten carbide, the same material used in many high pressure devices. This substance is not ordinarily found in consumer products such as automobiles, vacuum cleaners, refrigerators, bicycles, and so forth. However, if one should visit a factory where these products are manufactured, tungsten carbide tools, jigs, fixtures, and dies would be found in abundance. It has already been mentioned that diamond is the only substance of sufficient hardness to be effective in shaping tungsten carbide tools and most of the diamond consumed each year around the world is used for this purpose. Now, diamond itself is shaped into various forms to make diamond-pointed tools. Since nothing exists, at least at the present time, that is harder than diamond, diamond must be used to cut, shape, and form itself. This is a slow, laborious process and is akin to the problem that a carpenter would have in cutting his lumber with a wooden saw.

The foregoing introduction to the subject of diamonds contains but a tiny fraction of what might be said, but will, perhaps provide useful background for a discussion of the synthesis of diamonds which will now begin.

## Chemical Nature of Diamond

The great French chemist Antoine La Voisier discovered in 1772 that, chemically, diamond was nothing but carbon. This same revealing discovery was made by Smithson Tenet in 1797. Carbon had been known previously in the form of graphite and as various soots and as lamp black. The coke used in steel making is also principally carbon. Graphite is the substance erroneously called "lead" in the ordinary lead pencil (the graphite in a lead pencil contains clay as an additive to increase its hardness). Graphite has a bulk density of about 2.0, is soft, unctious, conducts electricity, is black in color, and opaque to visible light. It is sufficiently common that it can be purchased for about 35 cents per pound. Diamond, on the other hand, which is also composed of carbon, is the hardest known substance, is transparent, does not conduct electricity, and in its least expensive form is worth \$6,000 per pound. Diamonds of gem quality are worth millions of dollars per pound.

### Diamond Synthesis Claims

As soon as it was known that diamond and graphite were allotropes (chemically the same), scientists became interested in transforming the inexpensive graphite into the valuable diamond.

From the time of La Voiser there have been many claims to the synthesis of diamond. However, prior to the General Electric Company announcement on February 15, 1955, there had been no certain examples of diamond production in the laboratory. References covering the period from about 1830 to 1920 concerning attempts to synthesize diamond, have been given by J.W. Mellor.

Another important reference work concerning diamond is that of Fersmann and Goldschmidt.<sup>5.2</sup> This book contains 376 references concerning diamond and includes about 50 references concerning, or important to, the synthesis of diamond.

#### Moissan and Hannay

Of all diamond synthesis claims, those of Henri Moissan and J.B. Hannay have attracted the most attention. Henri Moissan claimed to have made diamonds by dissolving sugar charcoal in molten iron and other metals and quenching the solution in cold water or molten lead. He assumed that diamond crystallized under the great pressure supposedly developed by the contraction of the cool mass of metal. When the metal was dissolved in acids, a residue remained that contained tiny amounts of hard material that Moissan assumed to be diamond. Modern-day attempts to duplicate Moissan's experiments, however, have been unsuccessful.

In the year 1880 Hannay reported that he had made diamonds by heating bone oil and lithium metal to a red heat in sealed wrought-iron tubes . Seventy-seven of the eighty tubes in which he conducted experiments exploded. Diamonds were supposedly found in the non-exploding tubes. Diamonds of gem quality, reputed to be Hannay's, are on display in the British Museum. Attempts to duplicate Hannay's experiments have not produced diamond. Consequently, scientists of today generally assume that Hannay did not make diamonds. X-ray florescence examination of Hannay's "diamonds" have shown that these stones contain the usual impurities of natural diamonds. Many of Hannay's contemporaries, including Lord Rayleigh, regarded Hannay's claimed synthesis to be fraudulent, and it is likely that they were correct. There was no attempt to deceive on the part of Moissan. He just lacked the modern tools that would have made analysis positive. It is unfortunate that his small residues are not still available, for they could be readily subjected an x-ray and other non-destructive analysis to determine their constitution. It has been suggested that Moissan's microscopic size crystals could have been carbides or spinels.

### General Electric

The history of attempts to make diamond at the General

Electric Company goes back to 1941. Zay Jeffereys of G.E.'s Carboly Department was the prime mover behind a project, at that time, in which the Carborundum Company, Norton Company, and General Electric, entered into a five-year agreement with P.W. Bridgman to fund the construction of apparatus and to conduct some diamond-making experiments. Because of the war, this work was carried on for less than two years. The most significant results of this work were obtained from experiments in which graphite was heated to 3,000°C for a few seconds at pressures up to 30,000 atmospheres by a thermite-type reactions. These experiments demonstrated, for the first time, a pressure effect on the transition in which diamond is converted to graphite.

Administrative officials of the General Electric Research Laboratory became interested in the diamond problem about 1950. It was decided that the research would be carried out in the mechanical investigation section of the Chemistry Department. Mr. A.J. Nerad was manager of the mechanical investigation section, and Dr. A.L. Marshall was manager of the Chemistry Department. Beginning at a little later date attempts to synthesize diamond were also carried out in the Laboratory's metallurgical department. A non-equilibrium approach was used there and high pressure was not involved.



The first men to be assigned to the problem in the Mechanical Investigation Section were Drs. F.P. Bundy and H.M. Strong, two physicists. Shortly, it was decided that two physical chemists should also work on the project. Consequently, a meeting of the laboratory's physical chemists was called wherein this information was made known. There was little interest. Most chemists were aware of the unsuccessful 125 year effort of scientists to make diamonds, and that those previously concerned with the problem had included such men as La Voisier, Boyle, Moissan, Crooke, Davey, Friedel, Berthelot, Parsons, Tamman, Despretz, Ludwig, Bridgman, Leibish, and Vohler. I was the only member of the G.E. group of physical chemists interested in spending time on such a long-shot, little-chance-of-success, project. Consequently, I received the assignment, and assumed an active role in the work late in 1951.

In 1952, a second physical chemist, Dr. R.H. Wentorf, Jr., a recent graduate of the University of Wisconsin, came to General Electric and became associated with this project. Each of the four of us was free to go his own way within the limitations of the financial support given him.

### Chemistry and Apparatus

The work naturally divided itself into two areas; chemistry and apparatus design. Apparatus for obtaining the high pressures and temperatures that theoretical evidence indicated would be necessary for producing diamonds was unknown at this time. As concerns the transformation of graphite into diamond, there was no a priori reason that graphite should behave in this manner. Even though it might, there was the possibility that pressures and temperatures required for direct transformation might be much higher than that required for an indirect synthesis from other forms of carbon or from carbon-containing substances. Catalysts also might be necessary. Drs. Bundy and Strong were busily concerned with apparatus design when I entered the project. Therefore, my attention was directed to the chemical problems, particularly chemical systems that might yield carbon under various conditions. Research, in this connection, was conducted at room pressure.

In 1952, Bundy devised his "saucer" apparatus, already discussed in chapter 3. As can be imagined, one of the first experiments performed in this apparatus was the subjection of graphite to the maximum pressure-temperature conditions it produced. Disappointingly, the graphite did not transform to diamond. Bundy and Strong experimented with various chemical systems in this device, also without success. The conclusion from this work was that

higher pressures and temperatures would probably be necessary to affect a synthesis. At this point I had the opportunity to use the Bundy's saucer to try some ideas obtained in my one atmosphere experimentation. These, too, were unsuccessful.

### Development of the Belt Apparatus

By December of 1952 it appeared that it would be a long time before apparatus for use at higher pressures would be available. Consequently, I became interested in the problem of apparatus design, and on December 31 conceived the design for a high pressure device that came to be known as the "half-belt." The half-belt was a single ended, that is, there was only one tapered piston and the tapered chamber had a closed end or bottom. One month later I conceived the idea of a double-ended device, the "belt", which has already been described in chapter 3. It was in this apparatus that diamonds were first made and are continuing to be manufactured today.

The "half-belt" was constructed immediately and tested early in February, 1953. In the opinion of my associates, the half-belt did not work very well, so when I proposed to build the "belt" no financial support for its construction was received. After several months of frustration, I became impatient, took the plans to the shop and asked them to work on the device during slack periods.

The first belt was completed in July of 1953, and its vital components, the tapered pistons and the tapered cylinder were constructed of hardened tool steel. A photograph of the first apparatus is shown in Fig. 5.1.

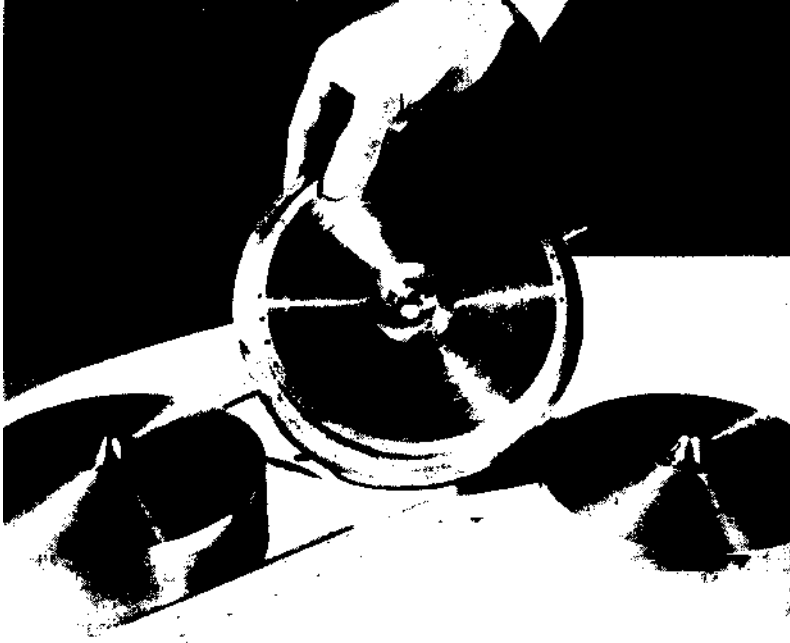


Fig. 5.1

Photograph of first belt apparatus.

This apparatus was shown to be capable of pressures near 55, 000 atmospheres on a relatively large volume of material, and could be heated to high temperature. The fact that the belt was a significant piece of equipment slowly became evident to my associates and the management so that permission was finally obtained to have the

vital components constructed of cemented tungsten carbide. These parts were delivered in December of 1953 and it was soon discovered that the belt was capable of simultaneously obtaining pressures of the order of 100,000 atmospheres at temperatures beyond 2,000 °C.

### The First Synthesis

Calculations based on known thermodynamic information, including compressibilities of diamond and graphite, had indicated that diamonds could be made at a pressure of 40,000 atmospheres directly from graphite. Consequently, it was disappointing, indeed, when I was completely unsuccessful in transforming graphite to diamond in the belt apparatus.

This caused me to turn to experiments involving carbon release from various compounds and the use of catalysts that might make the released carbon appear as diamond or that might aid graphite to transform to diamond. Such experiments were unsuccessful until December 16, 1954. Up to that time I had puzzled considerably over the problem of how diamonds might have been formed in the depths of the earth in the blue ground of the South African pipes.

Now, it was known in 1954 that there was another "primary" though very rare, source of natural diamond. Microscopic diamonds

had been found in fragments of the Canyon Diablo Meteorite from Meteor Crater Arizona, and also in a few other nickel-iron meteorites. The sulfide mineral, troillite, seemed to be associated with these tiny diamonds, and in fact, often surrounded them. These diamonds, then, were found in an entirely different matrix than the diamonds of South Africa. The kimberlite (blue ground) in which diamonds are found is a very complex conglomeration of basic silicate rocks. It may be, I thought, that diamonds can be produced in more than one type of environment and that the iron-sulfide mineral, troillite, may have played a key role in transforming graphite to diamond. Consequently, I placed some iron sulfide in a graphite tube that was closed at its ends with graphite disks. The graphite tube was to serve as an electrical resistance heater-container for the iron sulfide-and in addition, was to supply the carbon that would hopefully transform to diamond. Tantalum disks were used to carry the heating current from the current rings to the graphite tube. The tapered pistons (punches) of the apparatus were forced into the chamber by a 223,000 pound thrust from a hydraulic press. After one minute, the load was reduced to 186,000 pounds. Heating current was then applied and gradually increased over a period of 6 minutes to a maximum value of 346 amps, at which point the voltage drop across the punches was 1.8 volt, corresponding to a power dissipation of about

636 watts. At this wattage, the temperature inside the sample was around 1650 °C. Pressure, on the scale used at that time, was 95,000 atmospheres. Subsequent improvement of the pressure scale indicates, however, that the actual pressure was probably around 70,000 atmospheres. Maximum temperature was held for about 3 minutes and was then decreased over a period of about 5 minutes to room temperature. Then 18 minutes were taken to reduce the pressure to one atmosphere.

On opening the chamber, it broke near the junction of the tantalum end disk and the graphite tube, and I immediately observed the sparkle of tiny triangular faces. Having previously examined a number of natural diamonds, I immediately recognized that this material possessed the external surface features of tiny diamonds. My emotions were overwhelming. They were characterized by great excitement, rapid heartbeat, trembling, and weakness. It took several minutes to regain my composure, and then I examined the crystals under a microscope. They consisted of a polycrystalline mass of tiny, incomplete octahedra with characteristic growth triangles and etch pits on the crystal faces. I was certain that this material was diamond. Conclusive evidence that this was so was obtained in a few days on an x-ray diffraction film which clearly showed the proper diffraction lines.

While waiting for the x-ray pattern to be obtained, I had burned some of the crystals in oxygen and obtained carbon-dioxide; had performed index of refraction, density and hardness tests, all of which confirmed the existence of diamond. During the next 15 days, I made 27 runs all based on the original experiment or variations thereof. My intent was to learn what had taken place. Diamonds were made in 12 of these runs. Thus the original experiment could readily be duplicated.

On December 31, 1954, Dr. H. Hugh Woodbury, a G.E. Physicist, duplicated my original experiment and also made diamonds. On January 17 and 18 of 1955, Dr. Richard Oriani of the Metallurgical Department duplicated my original run three times, and Dr. H. Hugh Woodbury also repeated my December 16 run three times. These experiments were performed under careful scrutiny of the management and diamonds were made in all six runs. This, then, was the first confirmed laboratory synthesis of diamond. Highly important was the fact that diamonds were grown in only one to three minutes time, they had been grown in relatively high concentration, and the yield was sufficient to immediately establish the possibility of commercial production.

Technical Aspects of Diamond Synthesis



Having briefly related the story of the first diamond synthesis, it would be worthwhile to turn to some of the technical aspects. The differences between graphite and diamond on an atomic scale were not known until the 1910-20 decade after x-ray diffraction techniques for determining crystal structure had been developed. Diamond was one of the earliest crystals studied and was shown to consist of carbon atoms arranged in puckered hexagonal rings which were located in the 111 crystallographic plane. Orthographic projections of the diamond space lattice are shown in Fig. 5.2.

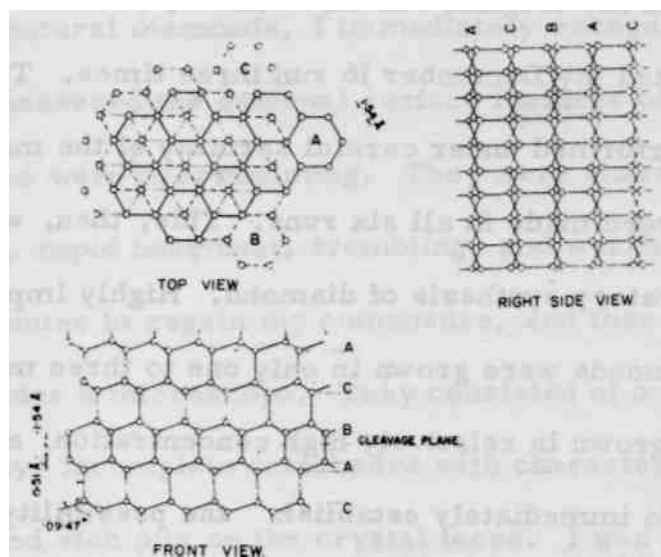


Fig. 5.2

Orthographic projections of diamond space lattice. For aid in visualization, the hexagonal rings of layer A are outlined with solid lines in the top view. Layer B hexagons are outlined by dashes, and layer C hexagons with dots.

It is to be noted that the 111 crystal plane is the natural cleavage plane of diamond, since bonds located perpendicular to this plane are the longest and weakest. The sheets of hexagonal puckered planes are arranged one above another in sequences such that atoms in every fourth layer duplicate the positions in the first layer. In hexagonal closest packing terminology, this sequence would be designated...abcabc.... In the diamond structure, each carbon atom is surrounded by four other carbon atoms located at equal distances from the central atoms with the bonds to these atoms making angles of  $109^{\circ} 28'$  with each other. This, of course, is the tetrahedral angle.

The arrangement of atoms in crystals of graphite is similar to that in diamond, since it also consists of layers of hexagonal carbon rings. In graphite, however, the hexagonal rings are flat or only very slightly puckered. The classical graphite structure has an . . .abab. . .stacking arrangement of the layers. In this arrangement, atoms in alternate layers occupy equivalent positions. Electron diffraction studies have indicated that the . . .abcabc. . . stacking sequence (rhombohedral graphite) is also present in graphite. <sup>5.4, 5.5</sup> Orthographic projections of the latter sequence are shown in Fig. 5.3. The cleavage plane in graphite is the same as that in diamond; i.e.

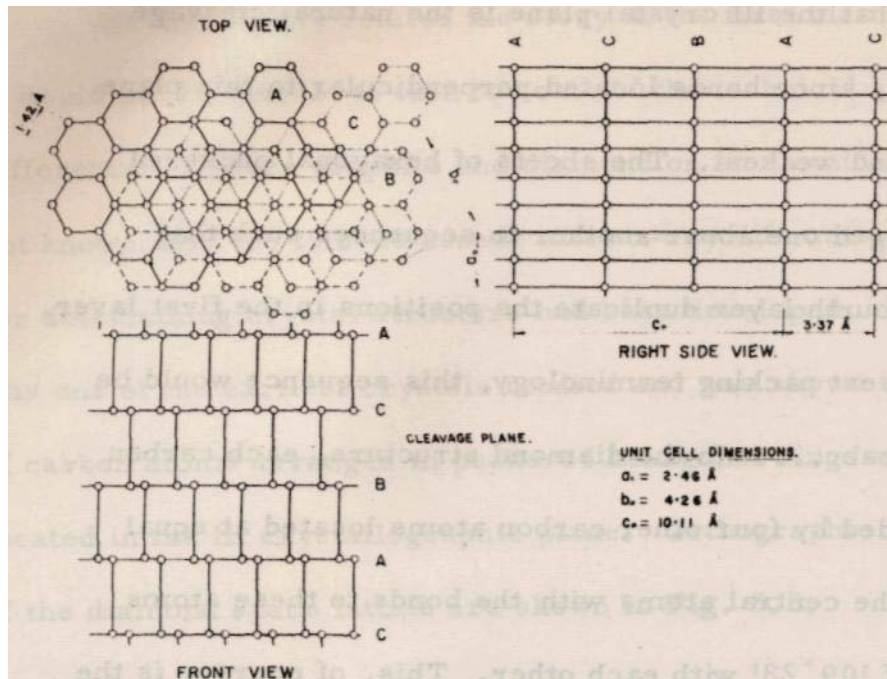


Fig. 5.3

it is parallel to the stacked layers. The bonding between layers in graphite, however, is much weaker and the bonds are much longer. Consequently, graphite is cleaved with extreme ease. All the inter-atomic distances between atoms in diamond are 1.54 Å.

Within the individual layers in graphite the inter-atomic distances are 1.42 Å and are all equal. The individual planes in the graphite lattice, however, are 3.37 Å apart.

Bonding between planes in the graphite crystal is of the Vanderwalls type. In the diamond crystal, chemical bonding is predominately covalent in nature and is due to the formation of  $sp^3$  Hybrid

bonds. All of these bonds are equivalent and are "aliphatic" in nature. The bonds between carbon atoms in the hexagonal rings of graphite have double bond character, and the entire layer or sheet consists of a giant, two-dimensional, resonating molecule which is "aromatic" in character. <sup>5.6, 5.7</sup>

#### Direct Graphite-Diamond Conversion

Since the crystal structures of graphite and diamond possess these similarities, it would seem that a moderate pressure would shorten the bonds between the graphite layers the proper amount, causing the hexagonal carbon rings to "pucker" with the end result that the atoms conform to the diamond crystal lattice. However, formation of diamond by this kind of a process takes considerably more pressure than was anticipated.

The first direct synthesis of diamond from graphite, without the aid of a catalyst, was reported by DeCarli and Jamieson in 1961. <sup>5.8</sup> They synthesized eight micron diameter diamonds directly from rhombohedral graphite by means of explosive shock in which pressure was estimated to reach 300,000 atmospheres. The temperature achieved in the shock wave was not given. Incidentally, their explosive process is now commercial and such diamond can be purchased from the Allied Chemical Division of General Chemical for

about \$4.00 per carat. This diamond powder is so fine that few, if any, commercial uses are known for it at the present time.

Subsequent to DeCarli and Jamieson's report, F.P. Bundy of the General Electric Laboratory reported the direct conversion of graphite to diamond without the aid of catalyst using pressures above 125, 000 atmospheres and transient temperatures in the 3,000 ° C range. He found, under these conditions, that the graphite spontaneously collapsed to polycrystalline diamond.

In this synthesis, he used a very small belt apparatus in which the anvil tips were only 0.060 inches apart and the sample cell was only 0.080 inches in diameter. The graphite served as its own heater; a capacitor discharge supplying the current.<sup>5,9</sup> At the present time, commercial production of diamond by direct conversion in static apparatus is not practical.

#### "Catalytic" Conversion of Graphite to Diamond

To return to the problem of diamond synthesis by means of a catalyst, a chemist knows that two problems must be considered when it is desired to bring about a chemical change (a change from one polymorphic form to another may be regarded as a simple type of chemical change). The first problem involves the thermodynamics of the reaction; the second concerns chemical kinetics or reaction

rates. Thermodynamics dictates that, when the free energy of the reactants is greater than the free energy of the products, the difference in free energy  $\Delta F$  is negative and the reaction has thermodynamic permission to proceed toward formation of the products. In the case under consideration, the reactant is simply graphite and the product is diamond. In situations where  $\Delta F$  is positive reaction has thermodynamic permission to proceed in the opposite direction.

Thermodynamics, of course, does not give any information concerning the time required for a reaction to take place. There are many instances in which the  $\Delta F$  may have a large negative value, yet the reaction proceeds at an imperceptible rate.

Reaction rate theory is not nearly as well developed as the field of thermodynamics. However, theories and techniques for understanding the atomic and molecular processes taking place in chemical reactions have developed to the point where a little theory, coupled with appropriate experiments, can often point the way toward finding the means for increasing or decreasing the rate of a given reaction.

For the reaction C graphite— C diamond,  $\Delta F = + 692$  Cal/g-atom at 25°C and one atmosphere pressure.<sup>5,10</sup> Berman and Simon calculated this value of  $\Delta F$  from measured heats of

combustion, specific heats, compressibilities, and thermal expansions. The  $+\Delta F$ , of course, indicates that diamond is thermo-dynamically unstable with respect to graphite. However, diamonds have not been observed to transform into graphite by any visible amount over periods of hundreds of years under ordinary ambient conditions. The reaction rate for this conversion, therefore, is extremely slow. At elevated temperatures, however, the transformations of graphite to diamond begins to proceed at an observable rate in the neighborhood of  $1200^{\circ}\text{C}$ . at one atmosphere. At this pressure and temperature,  $\Delta F$  has increased to about  $+2400$  calories, indicating a decrease in the thermodynamic stability of diamond with increasing temperatures. At absolute zero where  $\Delta F^{\circ}$  for the graphite-diamond transition assumes its lowest value,  $\Delta F_0^{\circ} = 580$  cal/g-atom at one atmosphere.

#### Graphite-Diamond Equilibrium

Pressure is necessary in order to bring the graphite diamond reaction into a region where  $\Delta F$  is negative. The pressure required depends on the temperature; the higher the temperature, the greater 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  $(\partial\Delta F/\partial P)_T = \Delta V$

or by

$$\Delta F_T^P - \Delta F_T^\circ = \int_0^P \Delta V dP$$

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:

$$\Delta F_T^P = \Delta H_T^\circ - T\Delta S_T^\circ + \int_0^P \Delta V dP$$

Data is available for evaluating  $\Delta H_T^\circ$  and  $\Delta S_T^\circ$  to 1,200° K. Evaluation of the integral, however, involves some reasonable approximations. For additional details the reader is referred to the paper of Berman and Simon.<sup>5,11</sup>

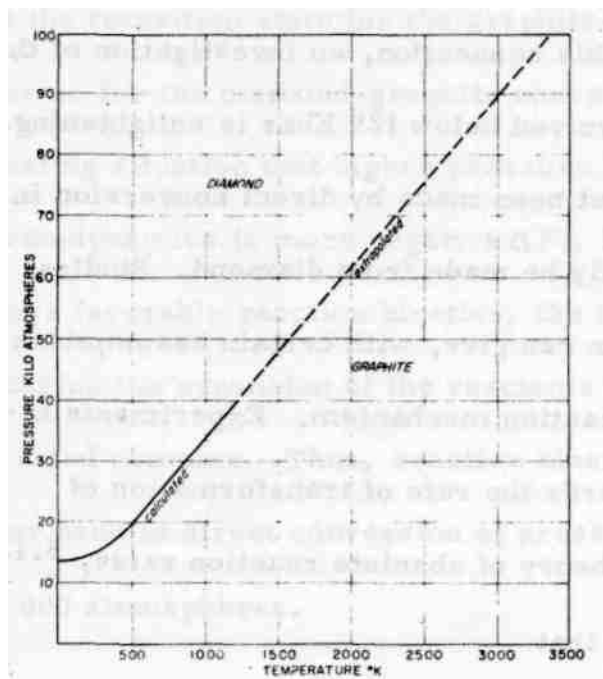


Fig. 5.4 .  
The graphite-diamond  
equilibrium curve (after  
Berman and Simon).



A graphite-diamond equilibrium curve (after Berman and Simon) is shown in Fig. 5.4. The line indicates the pressure and temperature for which  $\Delta F^\circ = 0$ . Above the line,  $\Delta F^\circ$  is negative, and diamond is the stable carbon allotrope. Graphite is stable in the positive  $\Delta F$  region below the line. From a thermodynamic view point, graphite subjected to P-T conditions above the line should transform to diamond. At pressures below about 125, 000 atmospheres, graphite has not been observed to transform directly to diamond and, since the thermodynamic criteria for formation of diamond can be met in experimental apparatus below this pressure, it must be concluded that kinetic considerations are controlling in this region and prevent the transformation from taking place in any practical period of time. In this connection, an investigation of the rate process that might be involved below 125 Kbar is enlightening. Although diamonds have not yet been made by direct conversion in this region, graphite can easily be made from diamond. Studies of this reverse transformation can give, with certain assumptions, information concerning the reaction mechanism. Experiments have shown that high pressure retards the rate of transformation of graphite to diamond and the theory of absolute reaction rates,<sup>5,12</sup> indicates for such a situation that

$$\log \text{ rate} = \text{constant} - (\Delta V^{\ddagger}P/RT)$$

where  $\Delta V^{\ddagger}$  is the molar difference in volume between diamond and the activated complex (the intermediate state or transition state), P is the applied the pressure, T is the temperature, and R is the molar gas constant. Although available experimental data are somewhat limited and erratic a plot of log rate vs. P leads to the conclusion that  $\Delta V$  is at least 10cc.

The molar volume of diamond is 3.42cc. The molar volume of graphite is 5.34cc, and their difference,  $\Delta V$ , is only 1.92 cc. The transition state, with a molar volume V of at least (10 + 3.42cc), must be a very open, expanded structure. Making the assumption that the transition state for the graphite-diamond conversion is the same as for the diamond-graphite conversion, there arises the interesting situation that higher pressure leads to more favorable thermodynamics (a more negative  $\Delta F$ ), but at the same time, leads to less favorable reaction kinetics, the increased pressure further hindering the expansion of the reactants into the large volume of the activated complex. Thus, reaction kinetics apparently have the upper hand in direct conversion at pressures up to the vicinity of 125,000 atmospheres.

### Solvent-Catalysts

The above analysis indicates the desirability of somehow taking the graphite lattice apart, and replacing the atoms, one at a time, into a diamond lattice. This might conceivably be accomplished by means of a solvent. A solvent might take carbon atoms from graphite into solution as individual entities which, under the influence of proper thermal and concentration gradients, could migrate through the solvent and precipitate in cooler regions as diamond. This has been assumed to be the process taking place in the pipes, or at least in regions below the pipes in the South African kimberlite. Experiments have been performed that show that carbon is somewhat soluble in kimberlite. However, in the laboratory at pressures as high as 100,000 atmospheres, simultaneously with temperatures in the diamond stable region, graphite has been dissolved in kimberlite, other silicates and also in such substances as lead and silver and has been precipitated but not as diamond. It has always come out of solution as graphite. This would seem to indicate that (at least in the pressure-temperature regions investigated) mere solvency is not enough. Other forces or agencies must be required that are probably catalytic in nature.

I have already related some details of the first successful diamond synthesis in which diamonds formed in the vicinity of a

tantalum disk when graphite and the mineral troilite were present. Since FeS (troilite) was known to be a non-stoichiometric compound, usually with excess iron, I substituted pure iron for the FeS and diamonds were grown. I also substituted pure sulfur for the FeS but this didn't produce diamond. Microscopic examination of the cell contents following a run with FeS or Fe disclosed that a blackish coating (removable by acid) covered the diamonds. This coating was probably iron. Carbon atoms, derived from graphite or metallic carbides formed in the reaction mixture, apparently migrate through this film and precipitate as diamond. Simple substitution of other transition metals for the iron subsequently showed many of these elements to be efficacious in producing diamond. This was particularly true with nickel. These elements are all solvents for carbon, but in addition, must possess some catalytic power for properly orienting carbon atoms so that tetrahedral bonds and, subsequently diamond is formed. The tantalum, or perhaps tantalum carbide which formed in the presence of the carbon, in my early experiments seemed to aid diamond growth and has a role that is not understood. In the years that have gone by since diamond was first made there have been innumerable experiments performed using alloys of various metals to find the best catalyst-solvent for the synthesis of diamond.

## Alloy Catalysts

One goal of these experiments is to find an alloy that will reduce the pressure and temperature required for synthesis. As a practical matter, this will reduce apparatus breakage. Tungsten carbide components such as anvils and pistons and cylinders are very expensive, and any reduction achieved in the failure of these components is very worthwhile.

Different alloys and impurity additions also affect the crystal growth. Size and shape of crystal, as well as degree of perfection is important. Different types of alloys may also affect the amount and type of inclusions of foreign material within the diamond crystals. In this connection, diamond grit for use in plastic-bonded wheels works best when it has a certain degree of friability. As the grinding wheels spin at high speed, grinding a substance such as tungsten carbide, the sharp points of the tiny grits act as miniature cutting tools, removing minute chips of the substance being ground. In the process, these tiny points become worn and are rounded. The dulled cutting edges are no longer effective in performing their job. Frictional forces tending to pull the grit from the plastic bond are less on the sharp point than they are on the dulled point. Consequently, if the grit has the proper friability it will break when the frictional force

on the rounded edge becomes sufficient. When this occurs, additional jagged points and edges are produced which again are effective in performing their grinding task. By a stroke of luck, the first synthetic diamonds had a proper amount of built-in friability (due to inclusions, fissures, poor growth, etc.) and performed more satisfactorily in plastic bonded wheels (sometimes called resin bonded wheels) when grinding tungsten carbide than did diamond grinding wheels which utilized natural diamond grit. As a matter of fact, in some grinding operations, General Electric's man-made diamonds performed 100 times as well as natural diamonds. (performance was based on the weight of tungsten carbide ground away compared to the loss in weight of diamonds in the grinding wheel).

#### Natural-Synthetic Competition

Most of the grinding wheels being built today are resin bonded. This situation, therefore, started a minor revolution in the diamond grit industry. The producers of natural diamonds had to devise means for selecting various types of grits to meet this challenge. While the General Electric grit performed phenomenally in resin-bonded wheels, its performance in metal-bonded wheels was poor. In metal bonded wheels a metallic matrix binds and holds the grits to the rim of the wheel. In a metallic bond, a very strong, blocky grit seems to be

desirable. Manufacturers have now learned how to make this kind of grit and have met the natural competition in this area. Competition from manufactured diamond has also resulted in other grading procedures that select specific types of grit for certain types of grinding operations. This is one more proof that competition is a great thing for improving technology and ultimately consumer products.

General Electric probably has something like fifty per cent of the diamond grit business in the United States. Their product is also marketed abroad. There are no other synthetic diamond grit producers in the United States at the present time. However, the producers abroad are rapidly increasing. The deBeers syndicate (the producers of the natural material) now manufacture diamonds in South Africa and also in Ireland. Diamond grit is being manufactured in Sweden, Austria, Germany, Japan, China, and Russia, and probably also in other countries. All the producers seem to be using the belt apparatus or, to a limited extent, multi-anvil type presses. They also seem to be using transition metal catalysts or alloys thereof. Since the General Electric Company holds world-wide patents on the metallic catalysts and the belt apparatus, it is inevitable that some litigation concerning patent matters has occurred.

### Manufactured Diamond Sizes and Prices

The largest size synthetic diamond currently marketed is about 40 mesh. Smaller grit ranging all the way down to sub-micron sizes is, of course, also available. Material large enough for drilling bits such as are used in oil fields and mining operations have not yet appeared on the market. The manufacturers, however, are pursuing the problem of producing larger diamonds with vigor. General Electric has produced larger crystals on an experimental basis. Some crystals, about 1/4" across, each weighing about 2 carats, were displayed at the Seattle World's Fair in 1962. These rough octahedra were grown in a multi-step process by adding a layer of material at a time. The crystals are very imperfect and are not strong because of imperfections between the layers and internal strains within the crystal. Anything that could be called a gem quality diamond has not yet been produced.

The price of natural and synthetic diamond grit is comparable, being in the neighborhood of \$2.65 a carat. In view of the current demand for diamond grit, the price would certainly be much higher if the synthetic material had not entered the market. Diamond grit, manufactured by man, can be produced in sufficient quantities to meet any foreseeable market. There need be no dependency whatever on



the natural material. The capacity to produce could quickly exceed current demand; new uses for diamond grit are needed.

### Hexagonal Diamond

In 1963, Aust and Drickamer reported a large and sharp increase in electrical resistance in single crystal graphite beginning at a pressure near 150 kb.<sup>5.13</sup> On decreasing pressure, the high resistance persisted to lower pressures. Material from the tiny cell (supported Bridgman anvils) was submitted to x-ray diffraction analysis. From the analysis, Aust and Drickamer concluded that a "permanent," new, cubic form of graphite had been recovered. It was later discovered that the "new" x-ray diffraction pattern was due to AgCl, one of the constituents of the cell. Actually, the graphite had reverted to normal graphite on returning to room pressure. The resistance change, however, had accurately indicated the formation of a new carbon phase while the graphite was under pressure. Heating the high resistance phase under pressure causes the electrical resistance to increase further, thus indicating the new phase to be a semiconductor.

Hanneman, Strong, and Bundy<sup>5.14</sup> have succeeded in "setting" this high pressure phase by heating well annealed pyrolytic graphite or single crystal graphite to temperatures above 1,000° C while the starting

material is subjected to a compression greater than 130 kb along its c axis. This "hexagonal diamond" is recoverable upon lowering the temperature before reducing pressure to room conditions. The material is hard and apparently abrasive, but the largest crystals are only about 200° A across.

Hexagonal diamond, mingled with cubic (ordinary) diamond, has also been made by the du Pont Company by means of an explosive process. The du Pont Company has supplied samples of their material to a number of companies for evaluation. Grains of this material, large enough for possible commercial use, have been made by "shock" sintering of the 50-100 A size particles produced in the direct graphite-diamond transition. The hexagonal-diamond content in the mixture is usually less than 10% but may be as high as 40%. No publications concerning the du Pont research have yet appeared.

However, patent application concerning the process has been filed in the Netherlands.<sup>5.15</sup> In this connection, it is interesting to note that patent applications filed in the United States (and many other countries) are not open to public inspection. Information concerning the invention and application is only made available after the patent has issued. In the Netherlands and some other countries, all the details of the invention contained in the application become available

at the time of filing even though a patent will not be granted until a later date. Consequently, companies striving to keep abreast of the latest in patentable developments keep an eye on applications in countries such as the Netherlands.

The DuPont patent application indicates that graphite particles of theoretical density are dispersed in a metal matrix which serves as the shock plate (to be driven by the explosive). The metal matrix also serves to rapidly quench (cool) the newly formed diamond after passage of the shock front and thus prevents reversion to graphite when the pressure falls after passage of the front. The pressure generated by the explosive wave traveling through the plate is calculated to be in the range of 700-1400 kb. This pressure transient lasts for a few microseconds.

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