Chapter 1
The First Attempts of Carbon Melting and Obtaining Diamond Phase of Carbon (1911–1939)

Abstract Astrophysical and terrestrial aspects of carbon investigations are discussed. Carbon and diamond structures are shown in comparison. A practical role of carbon in industry is underlined. The clue steady state experimental studies (starting with 1911 year), was discussed up to 1963 year. Particularly the estimation data of Leipunskiy (Russia) are shown to obtain diamond at high pressure (more than 40 kbar) for carbon with dissolved iron and at elevated temperature (higher 1500 K).

1.1 Astrophysical and Terrestrial Aspects of the Carbon Study

Carbon is a unique element of the periodic table, it is formed a huge amount of carbon compounds on the basis of carbon. Organic chemistry as a science emerged due to the existence of carbon. Not coincidentally, it belongs to the boundary matter between living and nonliving matter. One form of carbon—graphite is among the most refractory substances, which explains its widespread use in the industry. Construction of a complete phase diagram of carbon at high temperatures has always been the aim of the experimenters, because it allowed them to predict the properties required for practical applications. Modern energy industry, including pulse technique, required knowledge of the physical properties of carbon at high temperatures, normally comprised its liquid state. To solve this problem has not been enough steady state research methods, as for crucible there is no more refractory matter than the graphite itself. Transient research methods (rapid heating by laser or electric pulse current); have been intensively developed for several decades, first to study metals, and then graphite. The main problem under this study remains the measuring a true temperature of the specimen. There is evidence that for polycrystalline metals fast heating (up to fractions of a microsecond) may obtain, in general, the equilibrium thermal properties (enthalpy of the solid and liquid phase, heat capacity, heat of fusion) as well as temperature. Under graphite

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heating there are more significant features related to: its complex structure (anisotropy), sublimation of the solid phase, the density dependence of the manufacturing process, the initial heterogeneity of structure, etc. These features affect the measurement of temperature of graphite, especially near the melting point.

Motivation for scientists to study carbon has two major components: (1) astronomy and (2) the practical needs of space exploration and development of nuclear technology. We denote these two areas in more detail.

(1) The planets of our solar system (Mercury, Venus, Earth and Mars) are composed of silicates based on silicon. However, as was predicted by astronomers in 2005 [1] may exist planets consisting mainly of carbon. Theorists M. Kuchner, (Princeton University) and S. Seager (Carnegie Institution of Washington) presented a model in which some exoplanets (planets orbiting their stars) may consist mainly of carbon compounds. Carbon planets are more common in the center of the galaxy, because the carbon concentration is higher than near the solar system. Carbon planets contain carbon in various phase states. Kuchner and Seager believe that their idea is consistent with the discoveries of planets located close to their parent stars—much closer than Mercury is to the Sun. In such a planet, they argue, significantly more likely to survive at high temperatures near the star. Exoplanets revolve around stars (such as stars already discovered more than a hundred); most of them must contain a large amount of carbon, as resulted from the condensation of coal dust and gas rich in carbon. They may consist of solid carbon components, including silicon carbide SiC. On such planets cannot be excluded deposits of almost pure carbon. The upper layers of carbon deposits can be graphite, and the lower (due to pressure)—diamond.
Experimental confirmation of the existence of carbon planets appeared in 2010 [2]: an analysis of multi-wavelength photometry of the exoplanet WASP-12b showed a high concentration of carbon in the atmosphere. Recent images of Titan—Saturn obtained with the probe “Huygens” shows that the Methane Rivers and lakes are on its surface. Astrochemical Katharina Lodders from Washington University in St. Louis, Missouri, suggested that methane-rich atmosphere of Jupiter—proof that the planet was formed around of the carbon-based nucleus. The knowledge of the properties of carbon at high pressures and temperatures is one of the main problems in the physics of extreme conditions.

(2) Relevance of research on the properties of carbon depends on the fact that carbon and its compounds are increasingly used as structural materials for scientific and industrial high-temperature devices. For example, the development of space launch programs directly related to the search for new materials that can withstand significant thermal load (protective tiles on the “Buran-rocket”; nosecone missiles whose temperature reaches more than 3000 K at the entrance to the Earth’s atmosphere, and finally, the exhaust nozzle of the last missiles of the latest pattern. Nozzle of up-to date missiles performed on the basis of carbon compounds must to withstand a temperature

of about 4000–4500 K for 1–2 min. Such coatings are used to create micro-fuel spheres in nuclear technology. Matrixes for nuclear fuels consist mainly of compounds of refractory metals, carbides and carbon. Using carbon nuclear rocket engines and nuclear reactors requires accurate knowledge of the P-T phase diagram up to 1000 atmospheres. Investigation of high-temperature properties of these materials (high temperature carbides and graphite) and the task of research teams, as the calculation of practical problems of development (such as space, and new industrial technologies) requires knowledge of the properties of refractory materials, depending on the temperature. These properties should include substances primarily: density, resistivity, specific heat, heat capacity and thermal conductivity, for both solid and liquid states.

However, these studies have not only applied but also of great scientific importance. Development of science itself requires knowledge of the substance properties in a broad aspect, for example, the creation of phase diagrams of substances (depending on the pressure, density, composition, temperature)—allow to understand the behavior of materials in a wide temperature range and open the way for the creation of new and better materials. In particular, the study of the enthalpy and heat capacity is directly related to understand the cause of more intensive changes in heat capacity at high temperatures, the study of the role of structural processes as thermally activated formation of defects in the crystal lattice, un-harmonization of atomic vibrations, pre-melting. Finally, the establishment of a common theory of the liquid state is still awaiting its decision.

As an example, we recall that the phase diagram of carbon has not yet obtained the final form. To the melting point of graphite (4800 K), the experimental data are limited; moreover, still there is a debate in the scientific literature about the melting point of carbon. As for the properties of liquid carbon, the published data of direct experiment are rare. These properties can be obtained by applying to study the process of heating the carbon short pulse of electric current or laser pulse. Such heating during—nanoseconds or microseconds time interval very effectively as:

- loss of energy during the heating—low (fractions of a percent);
- specimen shape (cylindrical or rectangular) is preserved during heating;
- high-speed digital oscilloscope and pyrometer allow accurately record parameters (voltage, current, temperature) during heating.

Recall the difference in structures of diamond and graphite (Fig. 1.1), which are one and the same element—carbon. We use data from different reference books.

In diamond, each carbon atom has four tetrahedral located neighbors to form a cubic structure. Carbon atom has four valence electrons. Cubic structure corresponds to the maximum covalent bond, and all 4 electrons of each carbon atom forms a high-strong C–C bond, i.e. the conduction electrons are absent in the structure. Therefore, diamond has a high hardness and lack of conductivity, but (here's the paradox), good thermal conductivity. It is the hardest known substances. Breaking C–C bond (bond length 1.54 Å, hence the covalent radius of 1.54/2 = 0.77

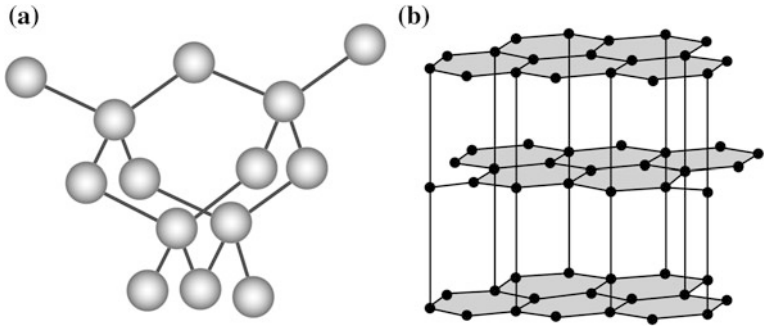


Fig. 1.1 (http://www.krugosvet.ru/enc/nauka_i_tehnika/himiya/UGLEROD.html) [3]. The structure of the diamond (**a**) and graphite (**b**). Parallel layers of graphite (**b**) are slightly displaced relative to each other. In rhombic lattice position of flat layers are not repeated over one layer in **a** hexagonal (as in this figure), but over two

Å) in tetrahedral coordination requires more energy, so the diamond, along with exceptional hardness, characterized by a high melting point.

Another allotropic form of carbon is graphite, very different from the properties of diamond. Graphite—a soft light layer of substance small crystals, characterized good electrical conductivity (if the initial density—high). Therefore, graphite is used where it is necessary to create high temperatures. High purity graphite is used in nuclear reactors as a neutron moderator. Graphite has a very high melting point (4800 K), but it is necessary to use high pressure for melting. Graphite is sublimated at ambient pressure and at a high temperature and cannot be transferred into the liquid state. Indeed, if the graphite specimen is heated for a long time at atmospheric pressure or in a vacuum, it sublimates only until the disappearance of the entire specimen.

The hexagonal structure of graphite is a condensed system of hexagonal rings with bond length of 1.42 Å (shorter than for diamond), but wherein each carbon atom has three (instead of four as in diamond) covalent bonds with three neighbors, and the fourth connection (3.4 Å) is too long for a covalent bond and weakly binds graphite layers stacked parallel to each other. It is the fourth electron of carbon determines thermal and electrical conductivity of graphite. This longer and less strong bond forms less compact graphite, which is reflected in its lower density compared to diamond (maximum density of 2.26 g/cm^3 for graphite, diamond—3.51 g/cm^3). For the same reason graphite slippery to the touch and flakes easily separates the substance that is used for the manufacture of lubricants and pencil rods. Many grades of graphite in the interests of industry are produced having a density is much lower (1.9–1.5) g/cm^3. This allows obtaining a solid structural material with good workability. Low-density graphite has a high porosity of such grades (it gives high electrical resistance). Therefore it is necessary to distinguish between bulk density of graphite (1.9–1.5) g/cm^3, which takes into account the presence of pores, and the X-ray density (2.26) g/cm^3, for which the presence of

pores is not considered. The quasi-monocrystalline graphite has a minimum number of pores, so it is approaching the bulk density of the X-ray.

Electrical conductivity of single crystals of graphite (density 2.26 g/cm^3) in a direction parallel to the basal plane is close to the metal, in the perpendicular—of hundreds or thousands of times smaller than that of metals.

Before proceeding to a brief review of earlier experimental studies and discussion of key studies on carbon, we should say that such a review was published in 1981 by Sheindlin [4] on the determination of the triple point parameters for graphite-liquid-gas sublimation curve and the boiling curve. Earlier (as the author [4] consider) these problems almost are not discussed in the domestic (Russian) literature.

Set out below is the point of view for the author of this book sometimes for publications already considered in [4] (1981), but this monograph focuses on pulse heating in recent years (the last 30 years since the publication of the survey [4], many new studies have appeared). Steady state research methods are thoroughly discussed in this monograph to show the problems of carbon investigation under slow heating of sublimated carbon. As for the beginning of experimental studies of graphite, let us mention the work [5] (1911 year) as one of the first and key. Ironically, still in 1911 it was clear for astute researchers that at atmospheric pressure there is no reason to expect melting graphite.

1.2 State of the Art with Graphite Melting in 1911 Year

The problem of graphite melting was considered in experimental study in 1911 [5]. In this work it has been criticized other work of the same year [6]. In the work [6] it was reported of sagging heated graphite rods, the presence of globular structures on the surface of the graphite pieces destroyed by electrical arc and gently rounded at the rods ends, as evidence of graphite melting at normal pressures. However, Watt and Mendenhall [5] prove in his experiments that the presence micro-globules and sagging graphite rods heated in the temperature range from 2150 °C up to temperatures of 3500–3800 °C cannot be related to the melting of graphite, but most likely indicates the condensation of steam and continuous growth plasticity graphite with increasing temperature.

Another observation in [5] is remarkable: there is an activity sublimation of the heated rods was watched at normal pressures. As with the surface and into the internal micro-cavities of the graphite rod, which leads to rod destruction to separate pieces to form an electrical arc between them. The melting rods are not observed in the report [5]. Curvature at the ends of the destroyed rod the authors explain the action of the electric arc that appears in the field gap of the rod. Temperature in [5] was measured with an optical pyrometer. The authors note that the measured surface temperature of 3250 °C, reassessed to the true 3500 °C (with extrapolation curve used suggested by the authors [5]). In a vacuum, only managed to fix the temperature up to 3100 °C in air at 1 atm—up to 3500 °C (reassessing

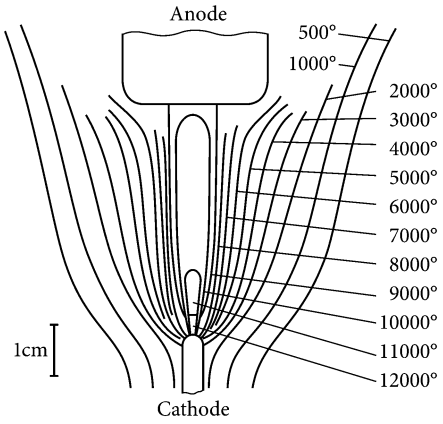


Fig. 1.2 The temperature distribution in different parts of the electric arc column (Illustration "The temperature in different parts of the cord of an electric arc"—from Great Soviet Encyclopedia)

gives a true temperature 3800 °C). The authors [5] considered that specimens are destroyed as soon as the inner temperature of the specimens (which is higher than the surface temperature) reaches the temperature of the arc. It is assumed that the measured pyrometer temperature of electric arc burning in the air, between the metal electrodes, is about 3800 °C. The reason for this conclusion is that the arc burning in air, was covered with a layer of metallic vapor (vapor of the electrodes) —it underestimates the measured temperature. In fact, the actual temperature of the electric arc is from 8000 to 12,000 K (Fig. 1.2).

It should be noted that Mendenhall is the author of the wedge blackbody model, which it was first proposed, designed and published in the same 1911 [7]. The question of measuring the melting temperature of carbon, including through the wedge blackbody model will be discussed in Sect. 7.2.

1.3 The First Substantial Experiments of Stationary Study of Graphite by Pirani 1925–1939

In 1923 Pirani and Alterthum [8] began to investigate the melting point of refractory metals under stationary heating by alternating electrical current, but the detailed investigation was set out in their study [9] in 1930. The control experiments were carried out on the metals.

Note experiment by Pirani in 1939 (under a small external pressure), which subsequent researchers has been interpreted differently, until the extreme view that Pirani melted carbon, which in fact was not. It often happens that the examination of original works of scientists allow us to formulate an adequate view of the results of their work, rather than their interpretation of other researchers. Consider the studies of Pirani [9] in more detail.

Metal rods of 7 mm in diameter were manufactured, and the small diameter holes were drilled perpendicular to the axis of the rods. Drilled holes played the role

of blackbody emitter at temperature measurements. The rods were heated by electrical alternating current in the atmosphere of neutral gas, and their temperature was measured by an optical pyrometer sighted inside the small hole. Moment of melting was detected in change luminosity holes and appearance of liquid metal from the hole. Further, in [9] states: if the rods are made of fused material with high reflectivity, such as nickel, the walls of drilled holes should be smoothed and the hole will therefore not look as blackbody radiation. Emissivity (the coefficient of radiation) should be only about 75 %. If the investigated material is made of pressed powder, then the surface of the drilled hole looks like a blackbody radiation because of a roughness [9].

For comparison, recall that for the wedge blackbody model mirror sidewalls gives a "black" radiation due to a larger number of reflections, see Chap. 4 of the temperature measurement, with the discussion on [5].

To test the efficiency of this method it was determined melting point of tungsten and molybdenum in [9]. Tungsten rods were pressed from pure metal powder (carbon content less than 0.01 %) and sintered at 1450 °C. Then, these rods were placed between two water-cooled clamps. Pyrometer was sited into the central drill. The rods were heated by AC (in a stream of hydrogen) to a temperature close to the melting point, and left them at that temperature for a while to complete sintering (a sign that—resistance becomes constant). Current fluctuations are aligned with regulation of the resistance by a transformer in the circuit. Then gradually increase a current, especially slowly near the melting temperature.

Since the location of the rod cross-section sighted its smallest, this is where there is a slight "overheating" of the material causes it to melt. The molten metal is sometimes stood out from the hole in the form of droplet. The external surface of the rod is lower because of radiation cooling and hydrogen jet, and it is approximately 80 °C lower than the temperature in the middle of the rod. Melting of the metal within the holes is always starting from the center to the exterior surface.

The temperature inside the hole was observed using a calibrated Kurlbaum-Holborn pyrometer. Under measurement the hole seemed bright circle on a dark surface of the wall, but at the time of melting at a very slow increase in temperature —a small dark spot suddenly appeared in the bright circle. With increasing in temperature all the hole suddenly becomes dark because the emissivity of the smooth molten surface significantly less than rough background. Thus the melting temperature was determined for molybdenum −2840 ± 40 K, and for tungsten 3660 ± 60 K.

The same method for determining the melting point was used by the author [9] to carbon. Figure 1.3 illustrates the experiences of coal melting under current 8000 A at 8 V, in a hydrogen atmosphere at a pressure of 800 mm Hg. Coal rod was made of pressed electro-graphite by Siemens Company (140 mm long and 37 mm in diameter). In the middle of the rod there was a transverse drilled hole diameter of 3 mm and a depth −18 mm (half of the diameter). This hole with allegedly spread and overflow carbon is shown in Fig. 1.3.

Figure 1.3 published in [9], it was shown exactly in this position (vertical specimen position). Consequently, bulging graphite did not constitute a fluid body;



Fig. 1.3 Graphite spread out of the drilled hole

it is probably hard and has a plastic state. Plasticity of carbon observed in the paper [5] (1911), which also discussed the problem of the graphite melting and its plasticity at high temperatures. During the publication of the works of M. Pirani 1923–1930 [8, 9] there was not perfect equipment for experimental studies of graphite at a high technical level and solid graphite sublimation were not considered. Pyrometer measuring of the graphite has not commented on by the author [9]. Result by the melting temperature of graphite (3500 °C)—is given in the hope that the methodology applied in [9] previously to metals at low ambient pressure will give a fair result for the carbon at low pressure (800 mm Hg). In fact, the author [9] observed graphite bulging out of the hole (3 mm in diameter). The graphite rod itself was heated slowly by alternating current. Pyrometer recorded the temperature of this bulged portion; the entire rod (diameter 37 mm) of course does not melt.

In [9] the author indicates the carbon melting point of the specimen as 3500 °C. Today, it is known that the melting point of carbon is 4800 K. Probably, the author

has watched the bulging of graphite from the hole and believed that graphite has melted. However, the appearance of the graphite from the hole may be explain due to the fact that at high temperatures, the graphite becomes highly plastic and with increasing in volume it is forced out of the hole. Thus, in [9], the carbon specimens were failed to melt and the graphite was observed only as bulging out of the hole.

1.4 Estimated Study for Obtaining Diamond by Leipunsky 1939

In 1939 Leipunsky [10] obtained an equilibrium phase diagram for carbon on the base of thermodynamic data for graphite and diamond (Fig. 1.4). Leipunsky have said: "*Only after the work of Nernst* [11], *who measured the heat capacity in 1911 for graphite and diamond, and the work of Rota* [12], *who obtained the heat of combustion for transition of graphite to diamond from the difference in the heat combustion of graphite and diamond* (*correct sign but wrong value*),—*it was possible to calculate the thermodynamic functions for graphite and diamond and determine the steady state conditions for both modifications*" [10, p. 1524].

Leipunsky performed thermodynamic calculations and extrapolated known data (at 1400 K) to a higher temperature and pressure. Volume change on graphite melting was not known. For most metals, it does not exceed 5 % of the volume. Taking this value into account Leipunsky expresses the dependence of the graphite melting temperature against pressure by the next equation:

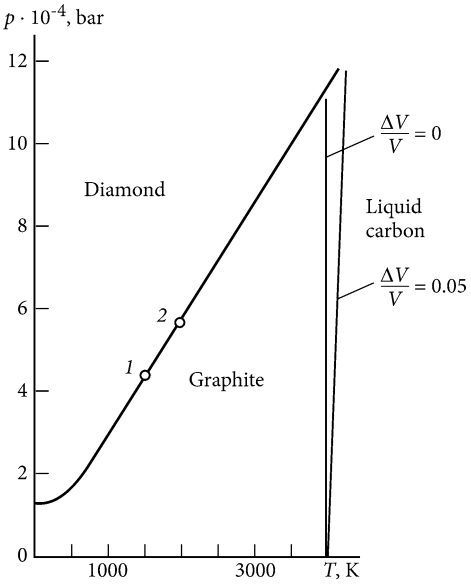


Fig. 1.4 Phase diagram of carbon proposed by Leipunsky in [10]: *1* minimum parameters (P = 42 kbar and T = 1500 K) for the crystallization of diamond from graphite and iron solution; *2* the same from the solid graphite (P = 60 kbar and T = 2000 K)

$$T = T_0 \times e^{\pm 0.05PV/Q,}$$

where T_0—initial known temperature; Q—heat of fusion for carbon.

In accordance with this formula: if for the pressure of 1 bar the melting temperature is 4000 K, then for 100 kbar pressure the melting temperature will rise by only 240 K and should be 4240 K (*Author of the monograph: It should be noted that the notion on the graphite as an ordinary metal unproductive because graphite increases its volume by 70 % at the melting point, see* Sect. 5.2).

Key recommendations of Leipunsky are as following. First, it is necessary to heat the graphite not less than 2000 K for carbon atoms can move from place to place. Secondly, it is necessary to compress graphite not less than 60,000 atmospheres. Leipunsky was the first who pointed out the possible way of diamond synthesis and predicted parameters at which a transition from graphite to diamond takes place in the presence of metal catalyst such as iron (on the grounds that the iron partially dissolves carbon).

Furthermore, Leipunsky considered the crystallization kinetics of the different forms of carbon, in particular transition graphite—diamond. Its main conclusions during the diamond crystallization contain: (1) the use of such pressures at which the diamond is more stable phase than graphite; (2) use of low transition rates, "*not to allow the advantages of graphite as a kinetically more likely environment*" [10, p. 1529]; (3) the use of such temperatures that reconstruction in the crystal lattice was possible, so that in case of graphite formation, the latter could go into a diamond. Leipunsky recommendations were extremely useful for further targeted experiments.

Using estimates of high-temperature kinetic reactions Leipunsky indicated lower limit of direct transition graphite-diamond (at least 40 kbar and 1250 K). Moreover, Leipunsky gives an example of diamond crystallization under cooling of the solution of carbon in iron. The latter technique is used by current technology of catalytic production of diamond in the presence of metals such as Fe, Ni, Co, etc. Leipunsky also supposed that the melting temperature of graphite is 4000 K, and it should slightly increase with increasing pressure.

Lower, we describe the work of Leipunsky according to the Journal [13]. Leipunsky tried to interest various departments to begin production of synthetic diamonds for industrial purposes, but never met understanding. For example, in the Ministry of Oil Industry at a special meeting at the department of drilling and hard materials, it was stated that they do not need diamonds. He also made a memorandum addressed to All-Union Economic Council on the organization of a special laboratory for the production of diamonds, but received no response. But later, when the United States sued the USSR for use diamonds in their patents with global circulation, Soviet officials have realized the problem, and created the following document.

Scientific discovery "Regularity of diamond formation (creation of artificial diamonds from graphite)".

Formula of the discovery "Theoretically established previously unknown conformity of crystallization (synthesis) of diamond from carbon—formation of diamond in the region of its stability in a liquid medium, dissolving carbon or come in unstable chemical compounds at a pressure and a temperature greater than 1400 K, *corresponding to the condition:*

$P > 5, 5 + 26, 42022\ 10^{-3}\ T$ K *(in thousand atmospheres)"*

Author: O.I. Leipunsky.

Number and date of priority: № 101, August ***1939***

Filing Date: January 5, ***1971***

Ovsey Ilyich Leipunsky—Doctor of Physical and Mathematical Sciences, disciple of the academicians Ya. Zel'dovich and N. Semenov, worked in the Atomic Project (for which he was awarded the Order of Lenin), participated in the first and all subsequent tests of atomic bombs near Semipalatinsk; in 1960s he became involved in the Institute of Chemical Physics (ICP) and deal with solid propellant.

Experimental study of P-T carbon phase diagram causes problems when performing normally incompatible requirements while maintaining a high temperature and high pressure for the specimen. With the development of technology of ultrahigh-pressure industry a possibility appeared first of synthesis of diamond, and then carefully examines the coexistence curve of the graphite- diamond, finding the minimum pressure and temperature at which the catalytic synthesis is still possible. Later, the American scientist Francis Bundy [14] succeeded in exploring the melting curve of graphite at very high pressures (up to 100 kbar), define the conditions of non-catalytic synthesis of diamond from graphite and obtain triple point parameters diamond-graphite-liquid ($P \sim 100$ kbar).

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