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The chemical synthesis of diamond. Aspects of the general theory

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Abstract. The theory of the synthesis of diamond by the polycondensation of light carbon-containing molecules is examined, and the optimum stoichiometric, thermodynamic, and kinetic conditions for diamond and graphite polycondensation and the reverse conversion of diamond and graphite by water vapour and carbon dioxide are described. The formation of critical nuclei of diamond shows no specific restrictions, and can take place under static conditions. The growth of these nuclei and their transformation into macrocrystals require specific macrokinetic conditions, which can be produced only in non-equilibrium open catalytic systems. The conclusions from the theory are confirmed by analysis of the conditions of experiments on the growth of diamond crystals and the synthesis of diamond films on various supports, and of the formation and growth of diamond meta-crystals in nature. The bibliography contains 74 references.

I. Introduction

It is now becoming increasingly evident that diamond can be formed not only at high pressures and temperatures by the polymorphic transformation of graphite but also at medium and low pressures by the transformation of simple carbon-containing molecules. The extension of ideas about possible conditions of diamond formation applies not only to artificial synthesis but also to natural deposits. Until recently the formation of diamonds under natural conditions was assumed to be explained by the pallial (mantle) hypothesis [super-high pressure (SHP) conditions]. An important contribution to the establishment of the polygenetic hypothesis of diamond formation was made by work on the epitaxial growth of single crystals and the synthesis of diamond films from the gas phase at low pressures,[1-7] and also by facts revealed by the study of kimberlite[55-57] and non-kimberlite[66-70] diamond deposits. From the viewpoint of the polygenetic approach to diamond formation, which takes account of not only physical factors but also, and primarily, chemical factors, both the polycondensation of light carbon-containing species without SHP, and the polymorphic transformation of graphite into diamond by the action of SHP, but not without the involvement of certain chemical factors, are possible.

The possible high-pressure formation of diamond is confirmed by the present industrial production of diamonds by static synthesis at 1300 – 1400 K and 45 – 50 kbar, and also by the production of diamonds by explosion (detonation) at pressures up to 150 kbar, containing as the principal phase the hexagonal polytype of diamond — lonsdaleite. This is consistent with the discovery of lonsdaleite-containing polycrystalline diamonds in meteoric impact products with distinct traces of the action of SHP, and with the discovery of minerals formed at high pressures as inclusions in kimberlite diamonds. SHP was not critical, however, for the formation of kimberlite and more particularly non-kimberlite diamond deposits, similar to the Kokchetav deposit. The conservatism of various workers who consider that the high-pressure route is the only path to diamond formation is related to the neglect of chemical factors in diamond synthesis. Thus the solution to the problem of the genesis of natural diamonds lies not in the search for new evidence of their pallial (mantle) origin but in the accurate discrimination of the conditions for possible routes to the formation of diamond.

The present review provides a theoretical justification of the conditions of the chemical synthesis of diamond from small carbon-containing molecules without the use of high pressure. This synthesis is being successfully reproduced in laboratories, and is undoubtedly a source of diamonds in various types of natural deposit.

II. The chemical synthesis of diamond from light carbon-containing molecules

The general concept of the chemical synthesis of diamond from the gas phase at atmospheric pressure has been discussed.[8] The analysis of experimental data on the synthesis of diamond films by different authors has established the optimum conditions for the formation of diamond in relation to the atomic composition (H, C, O) of the original gas phase, its temperature, and the temperature of the support on which the diamond film is deposited.

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The optimum range of diamond formation corresponds to a definite atomic ratio H : C : O. With increase in the temperature of the gas mixture there is a significant increase in the rate of diamond formation and a decrease in the influence of the nature of the original molecules. The deposition of diamond on the support, which may be practically any solid material, takes place at 700–1600 K; increasing the temperature of the support or going beyond the stoichiometric boundary of the diamond range (at H : C : O ratios characteristic of reducing conditions) gives 'non-diamond carbon'. All points of the H–C–O diagram corresponding to the syntheses carried out lie in a narrow diamond range close to the CO–H line, with rare exceptions, observed in experiments with mixtures enriched in oxygen or hydrogen and in experiments in which the influence of the nature of the original molecules and the support is appreciable.

In most of the studies analysed in the work cited,[8] increase in the temperature of the source of carbon (gas mixture or plasma) was the chief factor giving a high rate of formation of diamond films. Thus in addition to thermal heating, use was made of various methods of preparing the gas mixtures (high-frequency heating at low pressure, oxygen–acetylene flames, a high-voltage glow discharge, microwave or laser heating of plasma), which made possible a 10^2-10^3-fold increase in the rate of diamond formation, compared with thermal heating.

Naturally, increase in the temperature of the gas mixture from 400–800 K to 7000 K, leading to degradation of the molecules and levelling of the composition of the gas–plasma mixture, fully explains the fact that the position of the diamond range on the H–C–O diagram at high temperatures of preparation of the gas mixture is determined mainly by the H : C : O ratio in it, and not by the nature of the component molecules. This can be regarded as corresponding to a decrease in the role of chemical factors and an increase in the importance of physical factors in the formation of diamond films. This view is far from the truth, however, for the decisive role of chemical factors, even in experiments with a hot plasma, is related to the fact that the diamond range corresponds to a definite stoichiometric H : C : O ratio, and the formation of each new C–C bond in the diamond lattice is a chemical polycondensation process, taking place on the support at a comparatively low temperature and independent of the temperature of the plasma and the nature of the light carbon-containing species involved in the process.

Of course, with change in temperature the composition of the gas–plasma mixture changes, from that corresponding to the original mixture of components to some equilibrium composition, which is the same for all isostoichiometric mixtures. The specific mechanisms of formation of the new C–C bonds will differ in their elementary stages, but in all cases the process remains a chemical process. It is influenced strongly not only by stoichiometric but also by thermodynamic and kinetic conditions, and also by effects related to the non-equilibrium nature of open catalytic systems.

In the work cited,[8] most attention was paid to the stochiometric conditions of the synthesis of diamond from the gas phase, and no consideration was given to the other conditions of this chemical process, which are of no less importance for ensuring its stability. In the present review we have tried to fill this gap and to show the influence of various factors on the chemistry of the transformations of light carbon-containing molecules leading to the formation of diamond and non-diamond carbon and their conversion into gaseous products in the processes of chemical synthesis at low and medium pressures. Most attention is paid not to the formation of diamond films from the components of a high-temperature plasma[8] but to the heterogeneous-catalytic processes taking place under isothermal conditions with identical temperatures of the gas phase and the support or the nucleus of the diamond crystal. The last case reveals most fully and clearly the essential chemical nature of the diamond synthesis, which differs from the synthesis from a high-temperature plasma only in the details of the mechanism.

At low temperatures of the gas phase, the diamond material is formed by the polycondensation of the original molecules by a molecular mechanism. In a high-temperature plasma, the polycondensation involves both the undissociated original molecules and small molecules formed by the decomposition of the original molecules, and also ions and radical species. Thus the mechanism of the process may be to a large extent ionic and radical. In both cases, however, all the stages of the process take place at the temperature of the support, and diamond formation involves the polycondensation of light species with the necessary participation of the support and the diamond film growing on it. In other words, this is a heterogeneous-catalytic process. The catalysts may be the support, the diamond material formed on it, and various non-stoichiometric components of the gas phase.

The examination of the chemical aspect of the general theory of the synthesis of diamond from light carbon-containing molecules cannot be restricted to the question of diamond synthesis, without considering the polycondensation synthesis of graphite, graphite-like materials, and other condensation products (CP), often called 'non-diamond carbon'. The processes of diamond and graphite polycondensation are related chemical processes having the same stoichiometry and similar thermodynamics and differing only in the kinetic conditions and mechanisms. Thus the determination of the optimum kinetic conditions of diamond polycondensation compared with the conditions of graphite polycondensation is acquiring decisive importance in the development of the general theory of the chemical synthesis of diamond.

A basis for the discussion of the specific features of the kinetic conditions of diamond synthesis is provided by the results of systematic studies over many years in the following directions.

1. Work on the chemical synthesis of diamond at atmospheric pressure; the study of the chemistry of the surface of diamond crystals and the catalytic transformation of diamond in its reactions with gaseous and liquid media; the study of the mechanism of the oxidation of diamond material in its reaction with CO_2, H_2O, and other oxidants, and the conditions of the selective oxidation of graphite and other forms of non-diamond carbon in the presence of diamond; and the determination of the influence of various factors on the prevention of the oxidation of graphite under oxidising conditions.[9–14]

2. Work on the study of the nature and mechanism of formation of the polycondensation products of organic substances on heterogeneous catalysts, accompanying almost any organic catalytic reaction; the determination of the role of condensation products in stationary and non-stationary open catalytic systems; and the study of the influence of various factors on the polycondensation process, the degree of molecular condensation, the extent of aromatic condensation, the ratio of volatile and non-volatile condensation products, and the discrimination between the conditions for diamond and aromatic polycondensation.[15–18]

3. Work on the investigation of the conditions of diamond formation, the characteristics of the distribution of diamonds in deposits, and their mineral and geochemical associations with the surrounding medium; the establishment of correlations between the diamond-bearing character of various kimberlite pipes of Yakutia, the catalytic properties of the rock (in the oxidation of diamond by water vapour and carbon dioxide), and the oxidation potential and concentration of non-diamond carbon and bitumens[19–23] to develop a physicochemical criterion of diamond-bearing character; and the study of the properties of diamonds and the conditions of diamond formation in deposits of other types—metasomatic (Kokchetav), impact (Popigay), etc.

4. Work on the creation of models of the growth of diamond crystals and the abiogenic synthesis of hydrocarbons, bitumens, and graphite-like substances in the polycondensation of CO with H_2 and other light molecules in open catalytic systems,[19,24] and the development of the theory of non-equilibrium open catalytic systems[25,26] and evolution chemistry.[27]

III. The stoichiometric and thermodynamic conditions of diamond and graphite polycondensation

Published data[15-22,24,25] show that at the same temperatures at atmospheric or low pressures with the participation of heterogeneous catalysts (K), polycondensation of carbon-containing molecules A can take place with the formation of various solid products and the removal of various light molecules L:

$$nA \overset{K}{\rightleftharpoons} A_nK \rightarrow \{A_n - mL\}K + mL ,$$

$$A + \{A_n - mL\}K \rightleftharpoons \{A_{n+1} - mL\}K \rightarrow$$

$$\rightarrow \{A_{n+1} - (m+1)L\}K + L , \quad (i)$$

where $\{A_n - mL\}$, $\{A_{n+1} - (m+1)L\}$ represent the solid polyconden-sation products and other forms of non-diamond carbon or diamond.

Graphite (aromatic) and diamond polycondensation processes take place under their own specific kinetic conditions, but have the same or similar stoichiometric and thermodynamic parameters. Thus to distinguish the diamond range it is not sufficient to take as a basis the stoichiometric atomic ratio H : C : O, as was done in the work cited,[8] since in the same range the diamond and graphite polycondensation processes are equally probable.

In the work cited,[8] it was possible to distinguish the diamond range only because the diamond film syntheses examined were characterised by specific kinetic conditions which ensured that the experimental points lay in this range. Other factors were not examined. A definite role in the neglect of the kinetic conditions of the processes was also played by the observed[8] levelling of the influence of the nature of the molecules in equiatomic mixtures with increase in the temperature of the plasma. Although this is not inconsistent with the chemical nature of diamond synthesis, it reduces the stoichiometric conditions to the same equilibrium composition of the dissociation products of any isostoichiometric mixture, which is the case only for the highest-temperature plasma. If, however, the gas–plasma mixture contains undissociated molecules, or if an undissociated gas mixture heated to the temperature of the support is used, then it is obvious that the conditions of the polycondensation (1) for a definite atomic ratio H : C : O will differ not only in the kinetic factors but also in the stoichiometry and thermodynamics of the transformations of each of the equiatomic mixtures taken, according to each possible transformation direction.

This can be seen by examining the stoichiometry and thermodynamics of the reactions on which the polycondensation process (1) is based. We can take the series of simplest reactions giving graphite and diamond[15,19,24,25]

$$2CO \rightleftarrows C(\text{diamond}) + CO_2 , \quad (2)$$

$$2CO \rightleftarrows C(\text{graphite}) + CO_2 , \quad (2')$$

$$CO + H_2 \rightleftarrows C(\text{diamond}) + H_2O , \quad (3)$$

$$CO + H_2 \rightleftarrows C(\text{graphite}) + H_2O , \quad (3')$$

$$CH_4 + CO_2 \rightleftarrows 2C(\text{diamond}) + 2H_2O , \quad (4)$$

$$CH_4 + CO_2 \rightleftarrows 2C(\text{graphite}) + 2H_2O . \quad (4')$$

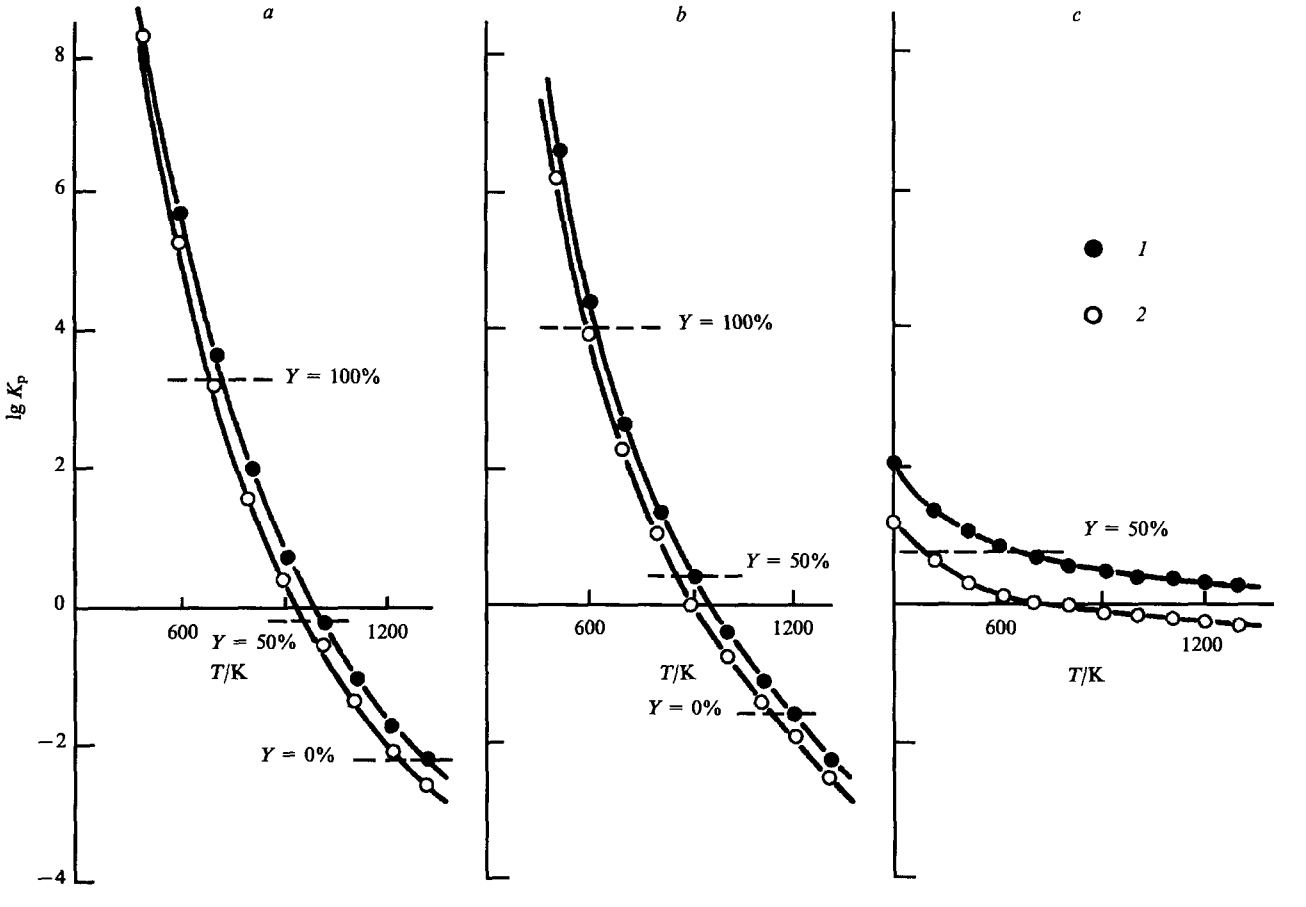


Figure 1. Thermodynamic conditions of the synthesis of graphite (*1*) and diamond (*2*) at P = 1 atm (Y is the degree of transformation); synthesis by the reactions: *a*, (2), (2′); *b*, (3), (3′); *c*, (4), (4′).

There are many analogous processes, for example

$$CH_3OH \rightleftarrows C(\text{diamond}) + H_2O + H_2 , \quad (5)$$

$$CH_3OH \rightleftarrows C(\text{graphite}) + H_2O + H_2 , \quad (5')$$

and also reactions involving solid components

$$CO + 2FeO \rightleftarrows C(\text{diamond}) + Fe_2O_3 , \quad (6)$$

$$CO_2 + 4FeO \rightleftarrows C(\text{diamond}) + 2Fe_2O_3 . \quad (7)$$

All these processes are thermodynamically possible, and the thermodynamic conditions for the diamond or graphite polycondensation processes to take place, although not the same, are nevertheless fairly similar (Fig. 1).

The thermodynamic conditions of different versions of the polycondensation (1) within a given type also differ from one another. For example, for the diamond polycondensation of methanol, in addition to version (5), it is possible to suggest at least another three:

$$2CH_3OH = C(\text{diamond}) + CO_2 + 4H_2 , \quad (8)$$

$$2CH_3OH = C(\text{diamond}) + CO + H_2O + 3H_2 , \quad (9)$$

$$2CH_3OH = C(\text{diamond}) + CH_2O + H_2O + 2H_2, \quad (10)$$

having different stoichiometries and thermodynamics (Fig. 2).

For diamond polycondensation from mixtures of different substances equiatomic with methanol we again have different thermodynamics for all four versions with different stoichiometries (Table 1).

There will be similar differences in the thermodynamic conditions for the processes of aromatic (graphite) polycondensation from the same original substances and mixtures. The calculations given were carried out for the formation of diamond and graphite, which are the products of the limiting stages of the polycondensation (1). The genealogical series of products of the diamond and graphite polycondensation processes (Tables 2 and 3 and Fig. 3), however, may also include the products of an intermediate stage of the polycondensation.

$$\left.\begin{array}{l} CH_3OH \\ C_2H_5OH + H_2O \\ C_2H_4 + 2H_2O \\ CH_2O + H_2 \end{array}\right\} \rightarrow \left\{\begin{array}{l} C(\text{diamond}) + H_2O + H_2 \\ C(\text{diamond}) + CO_2 + 4H_2 \\ C(\text{diamond}) + CO + H_2O + 3H_2 \\ C(\text{diamond}) + CH_2O + H_2O + 2H_2 \end{array}\right. \quad (11)$$

The extent of the polycondensation in these series is characterised by the ratio of the number of functional groups or hydrogen atoms on the peripheral parts of the polycyclic molecules of the condensation product to the total number of carbon atoms in the rings.[15,16] For example, for the hydrocarbon monomers A in the genealogical series of condensation products of the graphite series the atomic ratio H : C decreases from 1 to 0 on going from the simplest products (A = C_2H_2) to polycyclic aromatic hydrocarbons (PAH) and graphite, with a simultaneous increase in the specific (per monomer unit) decrease in the thermodynamic potential of process (1) (Fig. 4). In large crystals of diamond or graphite, or in carbon fibres, in which the polycyclic network of the PAH is coiled to form a tube, the H : C ratio approaches zero, but does not reach it. In the fullerenes[28] (C_{60} and others), however, the polycyclic carbon network is coiled into a closed sphere, leading to the limiting degree of aromatic polycondensation and a ratio H : C = 0.

The degree of aromatic polycondensation is related to the equilibrium degrees of transformation of A into different condensation products, which have their maximum values for the formation of the end member of this series, namely graphite. The degree of the transformation of A into diamond in all the parallel

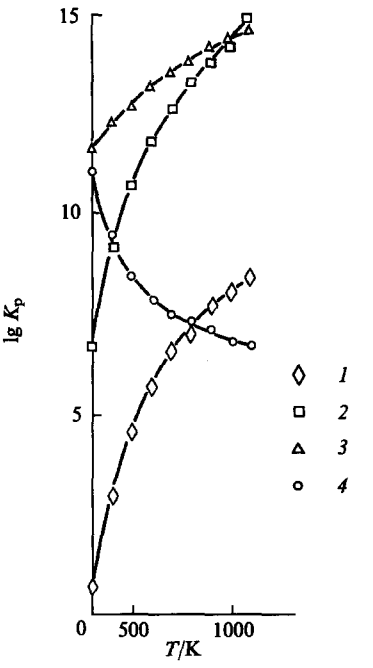


Figure 2. Thermodynamic conditions of the diamond polycondensation of methanol; synthesis by the reactions: *1*, (5); *2*, (8); *3* (9); *4*, (10).

reactions (2) and (2'), (3) and (3'), etc. is lower than the degree of transformation into graphite, and much higher than the equilibrium degree of transformation of CO + H_2 into PAH (see Fig. 4).

None of these differences, however, is significant for the polycondensation (1) taking place to give diamond or graphite, since the calculated thermodynamically equilibrium degrees of transformation characterise only the possibility that the reactions will take place spontaneously, and the question of whether they actually take place is determined by the kinetic conditions, which are different for each reaction.

The kinetic conditions include not only the actual characteristics of the interaction of the molecules and the mechanism of the reaction but also the effects of catalysts, other

Table 1. Values of lg K_p for the diamond polycondensation of CH_3OH, $C_2H_5OH + H_2O$, $C_2H_4 + 2H_2O$, and $CH_2O + H_2$ to give the products of reaction (11) for different degrees of transformation *Y*.

Reaction		*Y* (%)		
		100	50	0
CH_3OH		+1.69	−0.48	−4.00
$C_2H_5OH + H_2O$		+1.64	−0.60	−5.41
$C_2H_4 + 2H_2O$	$\rightleftarrows C(\text{diamond}) + H_2O + H_2$	+2.29	+0.13	−3.40
$CH_2O + H_2$		+2.00	0.00	−2.00
CH_3OH		+3.70	−0.73	−9.11
$C_2H_5OH + H_2O$		+4.30	−0.13	−8.51
$C_2H_4 + 2H_2O$	$\rightleftarrows C(\text{diamond}) + CO_2 + 4H_2$	+6.39	0.00	−9.14
$CH_2O + H_2$		+3.15	+0.35	−1.76
CH_3OH		+2.72	−1.71	−10.09
$C_2H_5OH + H_2O$		+1.62	−0.67	−7.60
$C_2H_4 + 2H_2O$	$\rightleftarrows C(\text{diamond}) + CO +$	+4.21	−0.13	−7.17
$CH_2O + H_2$	$H_2O + 3H_2$	+3.15	+0.35	−1.76
CH_3OH		+2.80	−0.80	−8.60
$C_2H_5OH + H_2O$		+1.64	−0.60	−5.41
$C_2H_4 + 2H_2O$	$\rightleftarrows C(\text{diamond}) + CH_2O +$	+4.11	−0.10	−5.69
$CH_2O + H_2$	$H_2O + 2H_2$	+2.00	0.00	−2.00

Table 2. Genealogical series of products of diamond polycondensation with allowance for the changes in the composition and size of the macromolecules.

Size of molecule (crystal)/mm	Diamond-hydrocarbons (C_nH_x)	Diamond-alcohols ($C_nO_xH_x$)	Diamond-ketones (C_nO_x)	Atomic ratio $C:C_{surf}$
		Molecular species		
3.5×10^{-7}	Adamantane	Tetrahydroxyadamantane-hexanone $C_{10}(OH)_4O_6$		1
$10^{-7}-10^{-6}$	Polycyclic	Polycyclic diamond-alcohols	Polycyclic diamond-ketones	1.3–13
$10^{-6}-10^{-4}$	Colloidal	Colloidal diamond-alcohols	Colloidal diamond-ketones	1.3–130
		Crystals		
$10^{-4}-10^{-1}$	Microcrystals of diamond with a hydrogen cover	Microcrystals of diamond with a hydroxyl cover	Microcrystals of diamond with a carbonyl cover	130–130×10^3
> 0.1	Macrocrystals of diamond with a hydrogen cover	Macrocrystals of diamond with a hydroxyl cover	Macrocrystals of diamond with a carbonyl cover	$> 130 \times 10^3$

non-stoichiometric components, and factors determining material exchange, the level of non-equilibrium character in the open system, etc. When favourable kinetic conditions are created, some of the thermodynamically possible reactions will take place, while others may be completely eliminated or largely suppressed, and in some cases this leads to diamond polycondensation under thermodynamic conditions favourable for graphite polycondensation.

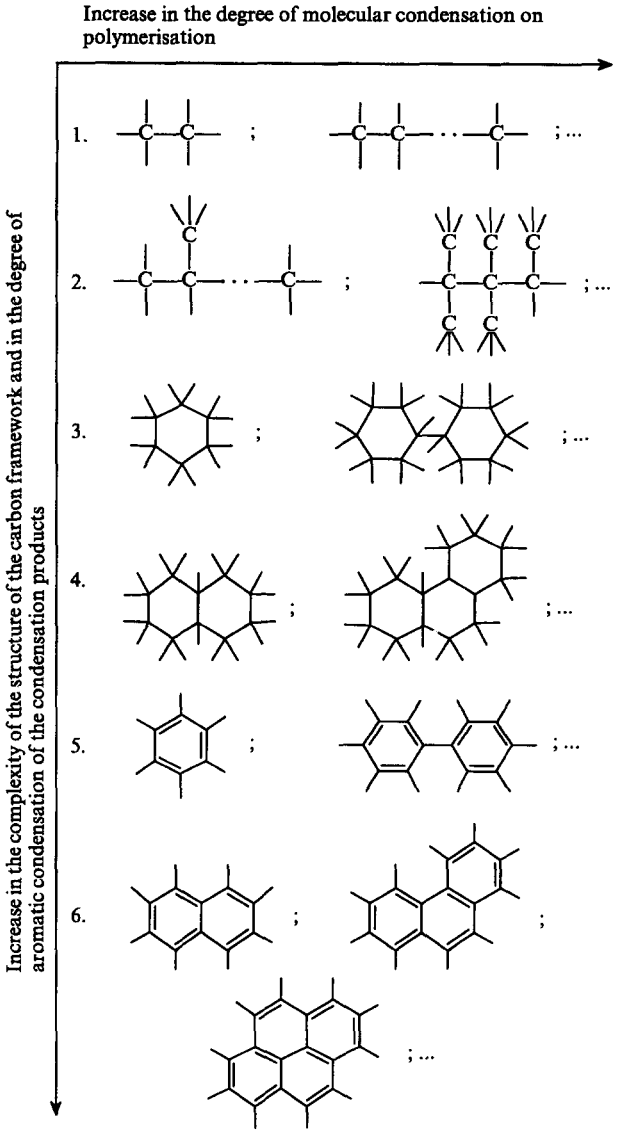
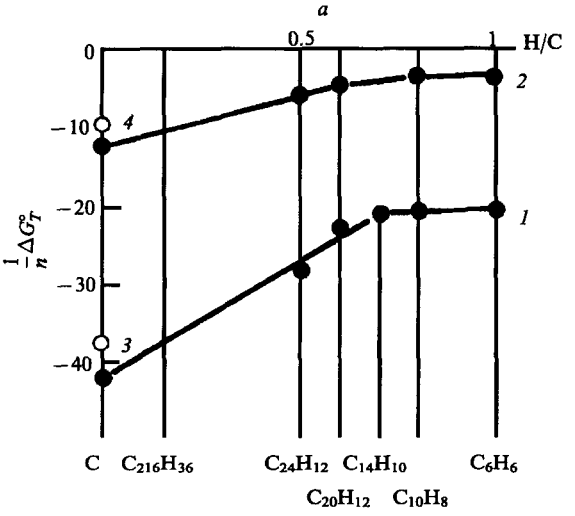


Figure 3. Natural genealogical classification of the condensation products of the graphite series.



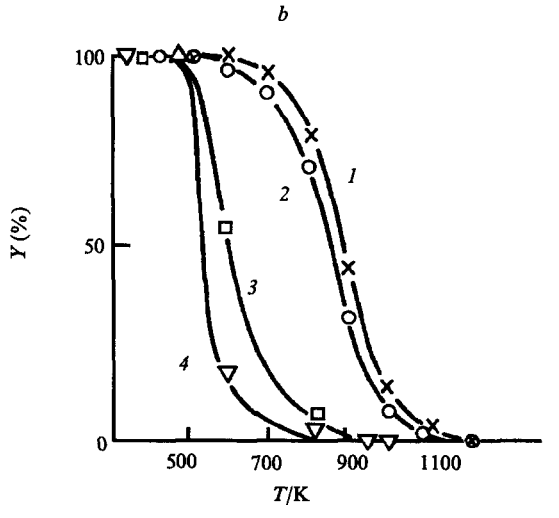
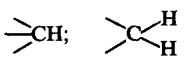
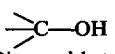
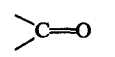


Figure 4. Relationship between the degree of polycondensation and the thermodynamic potential (*a*) and the equilibrium degree of transformation (*b*); *a*, dependence of the specific decrease in the Gibbs potential per monomeric unit on the atomic ratio H/C in the condensation products (CP) for their formation by the reactions $nC_2H_2 \rightleftharpoons \{(C_2H_2)_n\} \rightarrow \{(C_2H_2)_n\} - mH_2$ at 1000 K (*1*, *3*) and $CO + H_2 \rightarrow CP + H_2O$ at 700 K (*2*, *4*); *1*, *2*, CP of the graphite series; *3*, *4*, diamond; *b*, equilibrium degrees of transformation of a $CO + H_2$ mixture with the formation of graphite (*1*), diamond (*2*), coronene (*3*), and naphthalene (*4*).

Table 3. The crystal characteristics and functional groups in genealogical series of diamond polycondensation.

Series	Crystal habit	Face	a^*
Diamond-hydrocarbons 	Octahedron, cubi-octahedron, rhombododecahedron	{111} {100}, {111} {100}	1.3
Diamond-alcohols 	Octahedron, rhombododecahedron	{111}, {100}	1.8
Diamond-ketones 	Cube	{110}	2.6

* $C/C_{surf} = 10^n a$.

IV. The kinetic conditions of diamond and graphite polycondensation

The most important factor creating favourable kinetic conditions for diamond polycondensation and the preservation and accumulation of diamond material with unfavourable conditions for the formation and preservation of graphite condensation products (non-diamond carbon) is the selection of catalysts and conditions for which the rate of formation of diamond (v_{di}) by reactions (2)–(5) is greater than the rate of formation of graphite (v_{gr}) by reactions (2′)–(5′) and, which is most important, the rate of oxidation of graphite $v_{o(gr)}$ is much greater than the rate of oxidation of diamond $v_{o(di)}$:

$$C(\text{diamond})[C(\text{graphite})] + H_2O(CO_2, O_2) \xrightarrow{v_o} CO + H_2. \quad (12)$$

The conditions

$$v_{di} > v_{gr}\,;\; v_{o(di)} \ll v_{o(gr)} \quad (13)$$

can obviously be produced in systems with a sufficiently high initial oxidation potential, in which reactions which are the reverse of reactions (2)–(5) or (2′)–(5′) and other polycondensation processes leading to the formation of diamond or graphite are possible. Thus the hatched diamond range established[8] on the H–C–O atomic diagram (Fig. 5) lies between a range with a high reduction potential (the range corresponding to hydrocarbons, whose polycondensation gives mainly graphite and other forms of non-diamond carbon) and a range with a high oxidation potential [the range corresponding to H_2O, CO_2, O_2, in which neither diamond nor graphite can be formed and preserved, since they undergo complete conversion according to Eqn. (12)].

This range should also be restricted in the direction corresponding to mixtures very rich in hydrogen, where hydrogenolysis of diamond and graphite with the rupture of C–C bonds is possible

$$C(\text{diamond})[C(\text{graphite})] + 2H_2 \rightarrow CH_4\,. \quad (14)$$

This process can take place, however, only when specific hydrogenolysis catalysts are present. The fact that diamond films have been synthesised in mixtures with a large excess of molecular hydrogen[8] is apparently due to the absence of these catalysts and the greater ease of hydrogenolysis of graphite compared with diamond.

The range very rich in carbon on the atomic diagram can be represented essentially by different types of solid polycondensation products. These products cannot be transferred to the vapour phase without degradation, and the possible synthesis of diamond from them reduces to the polymorphic transformation of graphite, for which the thermodynamic conditions are unfavourable without super-high pressure even with allowance for intermediate gasification

$$C(\text{graphite}) + CO_2 \rightarrow [2CO] \rightarrow C(\text{diamond}) + CO_2\,. \quad (15)$$

A number of experimental studies[9–12,15,16,19,20,24] have proved the existence of ranges with different oxidation potentials, in which it is possible to have polycondensation of hydrocarbons and other organic substances with the formation of condensation products of the graphite series and polycondensation of CO, H_2, CO_2, CH_4, H_2O mixtures with the predominant formation of diamond, and also complete conversion of diamond, graphite, and other condensation products by the action of water vapour, carbon dioxide, and certain other oxidants.

The hydrogenolysis of C–C bonds has been studied in the work[30,31] on the gasification of coals and on the hydrogenation of diamond in the presence of metallic catalysts.

It was established that: it is easy to find kinetic conditions favourable for graphite polycondensation, and much more difficult to find kinetic conditions favourable for diamond polycondensation;[15,16,19] there exist kinetic conditions under which graphite is oxidised, and diamond is not oxidised[11,12] or is oxidised much more slowly;[32] the nature of the catalysts has a strong influence on the rate of oxidation of diamond, and a mutual influence of different catalysts and substances in the vapour phase on the kinetics of the oxidation is observed, as far as its complete inhibition.[10,11] The formation of different functional groups on the diamond surface in its chemical reactions with the gas and liquid phases,[13,14] and the influence of the functional covering on the physical and chemical properties of diamond,[14] were established.

The data obtained brought us closer to an understanding of the mechanism of the oxidation of diamond by carbon dioxide and water vapour at 900–1300 K and of the reverse process, that is the synthesis of diamond by reactions (2)–(5). They made it possible to determine the necessary synthesis conditions and catalysts [since under conditions close to the equilibrium for

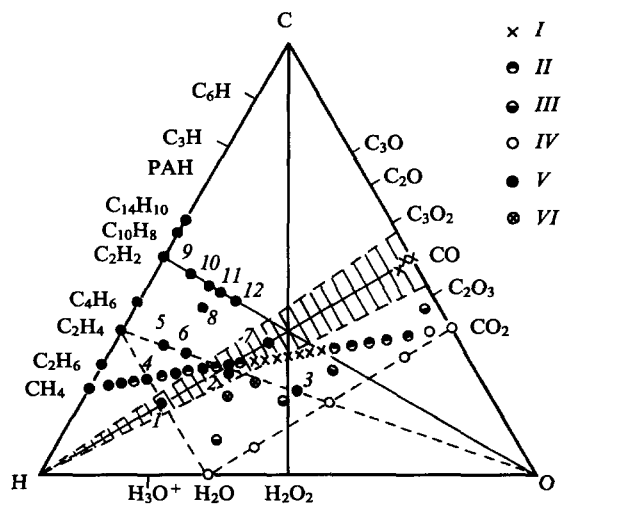


Figure 5. Diagram showing the stoichiometric conditions of the processes of diamond and graphite polycondensation and the conversion of diamond and graphite materials by oxidising agents, with points obtained in the experiments of the authors: *I*, the formation of diamond material on a diamond support by the growth of the diamond lattice; *II*, the graphitisation of a diamond support under the conditions of an experiment with $CH_4 + CO_2$ mixtures; *III*, the selective oxidation of graphite and the preservation of diamond in reaction (12); *IV*, the complete oxidation of graphite and diamond; *V*, the formation of condensation products of the graphite series from individual organic substances; *VI*, the formation of a diamond film outside the diamond range (from the data of Carrington and coworkers[35]); *1*, methanol; *2*, formaldehyde, acetic acid; *3*, formic acid; *4*, ethanol; *5*, acetone; *6*, acetaldehyde; *7*, pyruvic acid; *8*, acrolein; *9*, phenol; *10*, furan; *11*, dihydroxybenzenes; *12*, phloroglucinol.

reactions (2)–(5) the catalysts of the forward and reverse reactions are the same]. The catalysts chosen for these processes were the ions of the alkali, alkaline earth, lanthanide, and heavy elements present in kimberlites.[9–11] The most active were potassium among the alkali metals, strontium among the alkaline earth elements, lanthanum among the lanthanides, and chromium, nickel, cobalt, and iron among the heavy elements.

The above catalysts and conditions have been used repeatedly for the synthesis of diamond at 1073–1233 K and atmospheric pressure under isothermal conditions by growing diamond material on the faces of diamond crystals (seed crystals) and diamond powders by reactions (2)–(4). Since the conditions and results of these syntheses have not been described, they are given in the present review. Fig. 5 shows points corresponding to the stoichiometry of the original substances and mixtures in the diamond syntheses which we have carried out.

The results of some of the experiments on the synthesis of diamond can be considered.

Since the rate of growth of the diamond material under isothermal conditions at 1150 K was found to be very low (~ 1 μm d^{-1}) along the normal to the {111} face, the experiments were carried out not only on single crystals (in this case it is possible to monitor both the change in mass and the surface) but also on natural diamond powders with a particle size of 3–5 μm (in this case it is possible to monitor only the change in mass). The following gases and gas mixtures were used as the sources of carbon: CO, $CO + H_2$, $CO + H_2O$, $CO_2 + CH_4$. In the last case the influence of change in the composition of the mixture (from pure CO_2 to pure CH_4) on the course of the reaction was studied. The experiments with single crystals were carried out using KOH melts and solutions of manganese oxide in molten KOH, and also molten boron glasses containing the ions of chromium, copper, manganese, etc. The studies were carried out in platinum reactors at 700–1200 K. Typical results of the experiments are given in Fig. 6 for the single crystals, and in Fig. 7 for the diamond powders.

Fig. 6*a* shows that the growth of the diamond material on a diamond crystal takes place only in a narrow range of compositions of the $CH_4 + CO_2$ mixture, with a maximum rate at 30 vol.% CH_4 and 1180 K (with increase in temperature to 1230 K the height of the maximum decreases, and its position is displaced to 42 vol.% CH_4). In the ranges richer in CO_2 or CH_4, the diamond support shows a mass loss, taking place as a result of the graphitisation of diamond, accelerated by CO_2, and as a result of the direct oxidation of diamond by carbon dioxide. The mass characteristics of the diamond product, given in Fig. 6*a*, correspond to pure diamond, since after the experiments all the graphite obtained by the graphitisation, and the other non-diamond carbon deposited on the surface of the diamond crystals by the polycondensation of methane in the range of high CH_4 concentrations, were completely removed using Moissan mixture and perchloric acid.

The fact that the synthesis of diamond material takes place not only in the narrow zone where the weight increases but also in the graphitisation zones adjoining it is confirmed by the appearance on the {111} diamond faces of specific growth formations — reversed-parallel triangular and hexagonal indentations. In the oxidative solution of diamond by the action of CO_2, H_2O, and other oxidants, only directly-oriented triangular indentations are formed.[33] These facts indicate not only growth in the zone indicated but also recrystallisation of the diamond material.

The characteristics of the thermodynamics of the transformation of $CH_4 + CO_2$ mixtures with different compositions at different temperatures are hardly reflected in any way in the kinetics of the processes of growth, recrystallisation, and graphitisation of the diamond material (see Fig. 6*b*). This proves again that favourable thermodynamic conditions are not sufficient for diamond polycondensation to take place, and that the kinetic conditions are of the greatest importance.

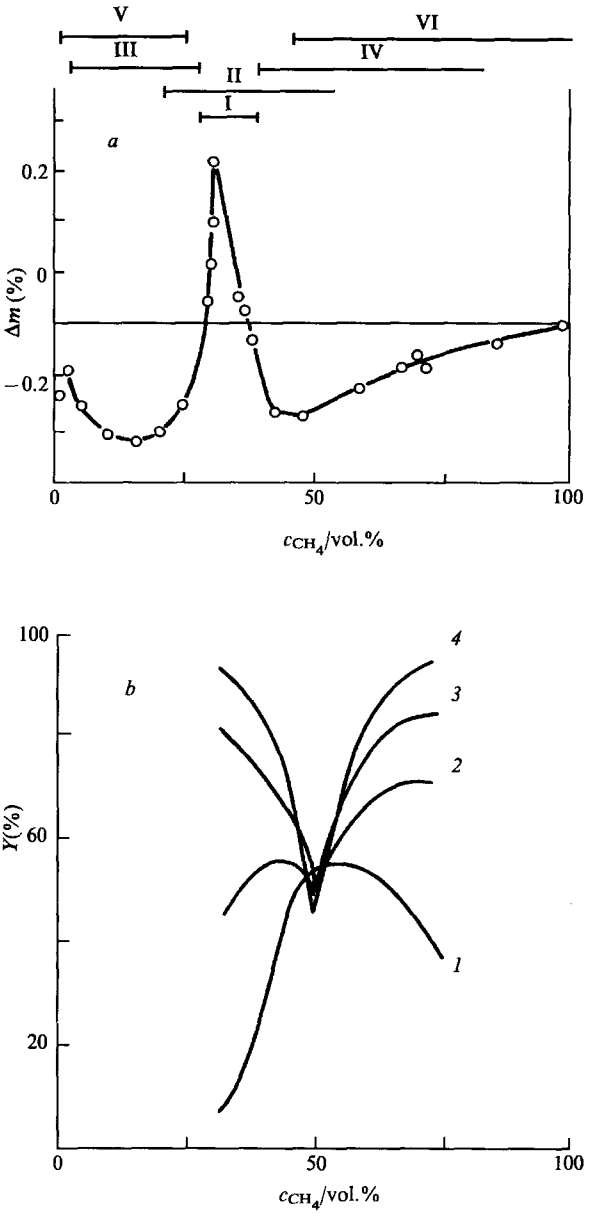


Figure 6. The results of experiments on the growth of diamond material on the {111} face of a diamond support by reaction (4) in a melt of the catalyst KOH (K_2CO_3); *a*, influence of the composition of the reaction mixture $CH_4 + CO_2$ on the change in the mass of the diamond support (T = 1180 K); ranges: *I*, growth of diamond; *II*, recrystallisation of diamond; *III*, *IV*, oxidation of diamond by CO_2; *V*, formation of condensation products of the graphite series from CH_4; *b*, equilibrium degree of transformation of $CH_4 + CO_2$ mixtures with different compositions into diamond at 673 (*1*), 873 (*2*), 1073 (*3*), and 1273 K (*4*).

The rate of growth of the diamond material on the powder in the polycondensation of CO depends markedly on the composition of the gas mixture, and is increased by small quantities of hydrogen (Fig. 7).

The data obtained indicate that at 1200 K the rate of growth of the diamond material corresponds to 0.8–1.5 carbon monolayers per hour; with decrease in temperature to 700 K it decreases to 0.06 monolayer per hour. This observation is consistent with published data,[34] according to which the rate of growth of diamond powders from CO at 1273 K has the values 0.0025 mass% per hour and 0.1 mass% per hour on powders with particle sizes of 53 μm and 1 μm respectively.

Fig. 5 shows that not all the points corresponding to diamond syntheses lie within the stoichiometric boundaries of the "diamond range" established by Bachmann and coworkers,[8] and that some are displaced considerably into the selective-oxidation zone. It is true that they do not lie in the complete-oxidation zone (the H_2O-CO_2-O triangle), but they lie below the lower boundary of Bachmann's diamond zone. The points corresponding to the formation of diamond films, established by Carrington and coworkers[35] and noted as exceptions by Bachmann,[8] also lie below this boundary. All these deviations are evidently not accidental, and are related to the fact that in the zone below the boundary indicated by Bachmann[8] as far as the upper boundary of the zone corresponding to the complete oxidation of diamond by water vapour and carbon dioxide (the line H_2O-CO_2), the formation of diamond is possible under certain kinetic conditions, while under other conditions it will be oxidised. These conditions are characteristic of non-equilibrium states of open catalytic systems, and they are extremely favourable for the recrystallisation and growth of crystals of the highest quality.

Thus in addition to Bachmann's diamond range, in which diamond and graphite may be formed under constant-growth conditions, it is also necessary to distinguish the recrystallisation diamond range $H-C_2O_3-CO_2-H_2O-H$ (Fig. 5), in which diamond may be formed mainly under growth–solution conditions. In this range and on its boundary with the Bachmann range, conditions are created for the formation of the purest diamond material without non-diamond carbon impurities. For example, to obtain a polycrystalline diamond film completely free from non-diamond carbon impurity (synthesis from microwave plasma) it is sufficient to add only 2.2 vol.% O_2 to the $CO+H_2$ mixture.[36]

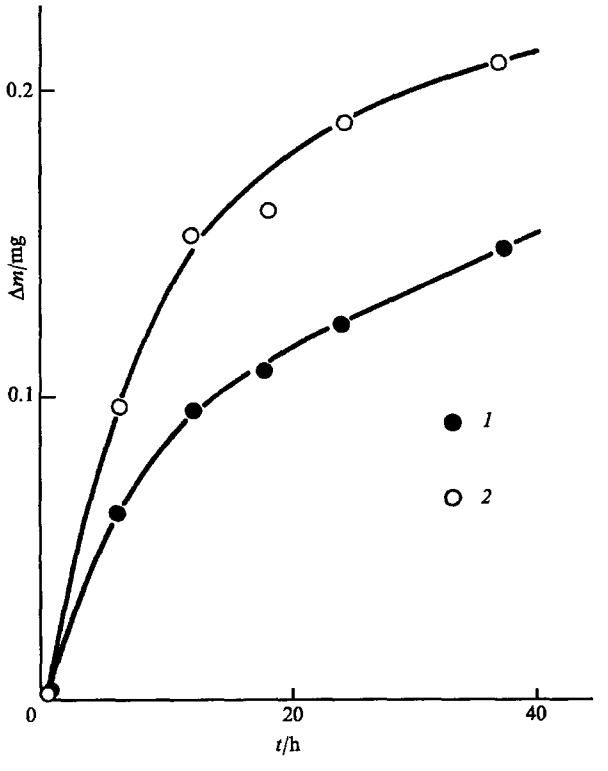


Figure 7. The growth of diamond material in the polycondensation of CO by reactions (2) and (3) on AP 3/5 natural diamond powder (T = 1123 K): *1*, input CO saturated with water vapour (32 mmHg); *2*, input CO saturated with water vapour (32 mmHg) after the establishment of the equilibrium $CO+H_2O \rightleftharpoons CO_2+H_2$; weight of powder in each series of experiments 6 mg; rate of supply of CO 0.5 litre h^{-1}; an increase in mass of 0.1 mg corresponds to the growth of 25 carbon monolayers.

The zones corresponding to the graphitisation of the diamond support by the action of CO_2 in experiments with CH_4+CO_2 mixtures extend both into the recrystallisation zone at high concentrations of CO_2 in the mixture and into the Bachmann diamond range and beyond it into the zone corresponding to the formation of non-diamond carbon with a high reduction potential, where graphitisation is accompanied by the additional formation of condensation products from the excess of methane (Figs. 5 and 6*a*). However, judging from studies of the nature and mechanism of formation of condensation products from individual organic substances,[15,16] the formation of condensation products of the graphite series by the polycondensation of various monomers A takes place readily throughout the entire $CH_4-C_2H_2-CO-C_2O_3-H_3O^+-CH_4$ zone (Fig. 5), including the Bachmann diamond range. This proves again that carrying out the polycondensation (1) under the stoichiometric conditions of the diamond range does not necessarily lead to the formation of diamond, which requires the creation of favourable kinetic conditions (13) for diamond polycondensation.

V. The polycondensation mechanism of the formation of diamond and non-diamond carbon

1. Polycondensation mechanism and genealogical series of condensation products

Without dwelling on the familiar facts that diamond and graphite are allotropic forms of carbon, crystallising in two different forms, we shall concentrate attention on the chemical and genetic aspects of the polymorphism and allotropy of carbon in diamond and graphite directly related to the chemical and genetic problems of their formation.

Formally, crystals of diamond and graphite are macromolecules; a single crystal of diamond is a three-dimensional macromolecule, and a single crystal of graphite is a stack of planar macromolecules. This approach leads to the recognition of the existence of a carbon ring and peripheral functional groups localising the free valences of the carbon atoms on the surfaces of the diamond crystal and the edges of the polycyclic graphite macromolecule emerging on to the faces of the graphite crystal prism.

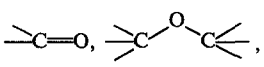
The introduction of each new carbon atom into the diamond or graphite lattice and the formation of the corresponding chemical bonds result from the processes of the polycondensation (1) of the original light carbon-containing molecules A with the reactive groups of the condensation product $\{A_n-mL\}$, which may be elements of the diamond or graphite lattice on the surface of the crystals. There are differences, however, in the details of the mechanism of the polycondensation giving the diamond or graphite material. There are also differences in the composition and structure of the condensation products which are the genealogical precursors of diamond and graphite, and the two directions of the polycondensation (1) have their own genealogical series (Tables 2 and 3 and Fig. 3). It is only in the lower stages of the polycondensation, involving the formation of linear and branched carbon–carbon chains and non-aromatic rings, that the compositions and structures of the condensation products are identical in the diamond and aromatic polycondensation series, with sp^3-configuration of the carbon atoms. The series differ completely, however, even at the stage corresponding to the formation of adamantane and its derivatives in the case of diamond polycondensation and to the formation of aromatic polycyclic compounds with sp^2-hybridisation of the carbon atoms in the case of graphite polycondensation.

The extent of the aromatic and diamond polycondensation in the genealogical series increases with decrease in the ratio of the number of surface functional groups to the number of carbon atoms in the ring of the macromolecule (Table 2).

Both the diamond and the graphite series may contain surface functional groups of different kinds, depending on the composition of the original monomers A, the conditions of the

polycondensation (1), and the subsequent chemical treatment of the condensation product. Thus for a monofunctional covering, the entire genealogical series of condensation products can be related to the corresponding class of organic substances, for example hydrocarbons, monohydric alcohols, etc. Thus the products of the diamond condensation of the original carbon-containing substances may contain series of diamond-hydrocarbons, diamond-alcohols, and diamond-ketones, differing chemically in their surface properties and even in their crystal habits (Tables 2 and 3).

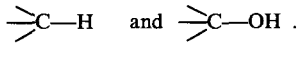
A particular functional covering can be produced on diamond not only by diamond polycondensation but also by special modifying chemical treatment of diamond crystals and powder. In particular, a hydrogen covering can be completely replaced by a hydroxyl covering, or vice versa, by treating diamond with water vapour or hydrogen respectively at 1073 K. This is reflected in the changes in the infrared spectra and the contact angles of wetting by water (in the range 0–90°). For different treatment conditions, the following groups have been detected on a diamond surface:[13,14,37,38]

–H, –OH, –Me, –COOH, –OMe, , –Cl, –Br.

Similar results have been obtained for graphites and coals. Thus the carbon material obtained by the polycondensation of benzene or ethylene contains the groups

,

and that obtained from acetone contains the alternating groups[15]

.

Many publications (for example by Rudenko and coworkers[15,16]) describe the mechanisms of the polycondensation (1) as series of simple repeatedly alternating reactions (addition of the monomer A, removal of different light molecules L, cyclisation, isomerisation, etc.) leading to the successive formation of all the more complex condensation products of the corresponding genealogical series. A particularly large number of studies have been devoted to the aromatic condensation of organic substances. The complexity of the mechanism of diamond polycondensation is indicated by the mechanism of the reverse processes of the oxidation of diamond by water vapour and carbon dioxide.[9,11]

2. Macrostructural forms of graphite and diamond polycondensation products

The formation of the diamond and graphite material is influenced considerably by the mechanism of formation of their macrostructural supermolecular forms. Additional macrokinetic conditions must be established, which when combined with the molecular mechanism of the polycondensation (1) lead to the production of a particular macrostructural form of the diamond or graphite material. For one combination this will be a polycrystalline diamond film, for another a three-dimensional polycrystalline aggregate, and for a third a single crystal of diamond, and the formation of a particular macrostructure will be determined not by the conditions of the polycondensation (1) but by the factors facilitating or preventing the formation of new crystallisation nuclei and determining the intensity and form of the reagent fluxes and the ratios of their rates to the rate of reaction (1), by factors related to the equilibrium in the open catalytic systems, etc.

It is well known that these macrokinetic factors influence the production of various macrostructural forms of graphite (carbonaceous) material,[15] which can be obtained as anisotropic films, polycrystalline or vitreous graphite, carbon spirals, dendrites, hollow carbon fibres, or spherical fullerene molecules.[28] For the production of particular macrostructures, specific additional conditions must be established. For example, the formation of graphite spirals and dendrites, which have an internal spiral structure, takes place during the polycondensation of n-hexanol only in the regions where screw dislocations emerge on the single crystals of nickel, and does not take place on defect-free regions of the face of cubic nickel.[39] Catalytic corrosion of the nickel crystal at the base of the carbon dendrite is observed, and nickel is transferred to the carbon material, in which the nickel is not present in the dispersed state but forms a spiral of crystalline hexagonal nickel, analogous to the graphite spiral (the concentration of nickel in the carbon dendrite reaches 6 mass%). These data indicate that the carbon spirals grow from the base.

Completely different conditions must be established in the formation of carbon fibres having the form of tubes with a constant diameter of ~500 Å and consisting of a polycyclic graphite macromolecule coiled coaxially with the axis of the fibre. The carbon fibres grow from the tip, and a necessary condition for their growth is the presence on the tip of the fibre of a catalyst crystal which is commensurate with the diameter of the fibre and which acts as the 'operator' for its growth.[40]

Fibres and spirals are also formed in the chemical synthesis of diamond. Filamentary acicular crystals of diamond with lengths up to 400 μm grow on diamond seed crystals in the presence of metallic catalysts (Fe, Ni, Mn, etc.) both at low pressures from the vapour phase[41,42] and under SHP conditions from solutions of carbon in the metals.[43,44] Diamond filaments and needles with a diameter : length ratio of 1 : 20 usually grow along the normal to the {110} face of the diamond seed crystal[42,43] at a rate of up to 200 μm h^{-1};[41] this is much greater than the rate of growth of diamond powders. These macrostructural forms are present at the tip of the metal catalyst crystal.[41,42]

Au does not bring about the formation of diamond filaments at low pressures,[42] but brings about the production of different skeletal forms of diamond and its dendrites under SHP conditions.[44] The production of diamond fibres in the form of spirals has been observed in the regions where screw dislocations emerge on a diamond seed crystal.[45] The growth of filamentary crystals of diamond has been observed[46] on the projections and edges of seed crystals on different supports (diamond, garnet, mica) by the action of the electron beam directly in an electron microscope in a high vacuum. The source of carbon was the residual vapour of the oil in a vacuum of 10^{-4}–10^{-6} mmHg. Thus the growth of diamond as single-crystal filaments is brought about by a number of specific factors, and pressure does not play a significant role.

Diamond spirals of filaments with a thickness of 0.6 μm with a step and diameter of 2.5 μm and a length of up to 75 μm were found by us in AP 5/3 diamond powder after experiments on its further growth by reaction (2) at 1220 K in the presence of a melt of MnO in B_2O_3. The diamond spirals were joined to the diamond seed crystal, and in one case the formation of two spirals joined by one seed particle and lying at an angle to one another was observed. In this case the growth of the diamond spirals apparently takes place on the diamond particles at regions corresponding to the emergence of screw dislocations, which have an increased ability to bring about diamond polycondensation. This is confirmed by the fact that the calculated rate of formation of diamond by the growth of the diamond spiral is greater by several powers of ten than the average rate of the layer growth of diamond material on the {111} face.

A unique theoretically possible macrostructural form of diamond material that can be distinguished corresponds to macrocrystals (molecular species) with dimensions of 100–1000 Å, having a high ratio of the number of surface carbon atoms, and hence number of functional groups, to the number of internal carbon atoms in the particle, and exhibiting colloidal

properties as a consequence of the polarity of the functional groups (Table 2). Colloidal diamonds should have unique physical and chemical properties, differing from those of diamond micro-powders and the organic substances formed by diamond polycondensation. In particular, colloidal diamonds should not have abrasive properties, and on the contrary may be good lubricants. Some parameters of detonation diamonds, produced by the explosion of chemical substances, are close to those corresponding to a colloidal form of diamond material.[47]

A unique position among the macrostructural forms of diamond material is occupied by epitaxial molecular films (several carbon atom layers) with a regular single-crystal structure. They may be formed by a chemical mechanism analogous to crystallisation, for example in any of the reactions (2)–(4), in the presence of non-equilibrium concentrations of the starting materials when the crystal faces of the support show a two-dimensional crystal-structural similarity (crystal-chemical correspondence) to the arrangement of the carbon atoms on one of the faces of diamond. The existence of this crystal-structural correspondence with a low value of the coefficient of surface tension with respect to diamond leads to the production of a strong field in the crystalline support, capable of initiating on it the growth of an isomorphous diamond lattice, which as it were extends the lattice of the support.

3. The formation of equilibrium epitaxial films of diamond and the non-equilibrium growth of macroscopic crystals of diamond

According to the model of the growth of diamond crystals in open catalytic systems,[19] two-dimensional diamond films may be the nuclei for the growth of diamond crystals. The growth of a microscopic diamond crystal requires a constant displacement of the equilibrium of reactions (2)–(4) to the right under the conditions of non-equilibrium of an open catalytic system, whereas the formation of macroscopic epitaxial film–nuclei can also take place in a closed system before its equilibrium is established.

When equilibrium is established in reactions (2)–(4) and the kinetic conditions of diamond polycondensation are established in the presence of a suitable matrix–crystal face, an equilibrium epitaxial diamond film of several carbon atom layers is necessarily formed, and will be stable under these conditions.

The possibility of the formation of two-dimensional equilibrium nuclei of a new phase on a support with the properties indicated is established by de Wolff's theory, and also by the principle of minimum Gibbs–Curie surface free energy and the crystal-growth theorems of Gibbs, Volmer, and others. Using these theories it is possible to calculate the work of formation of a two-dimensional critical (equilibrium) nucleus with allowance for its parameters, the specific inter-phase free energies at the nucleus–crystal–medium boundaries (ΔG), and also the critical size (l) and the rate of formation of a nucleus with super-critical perimeter (J)

$$\Delta G = -\frac{\varepsilon^2}{4\gamma h \Delta G_v}; \quad l = -\frac{\varepsilon}{2\gamma h \Delta G_v}; \quad J = la \exp\left(-\frac{\Delta G}{kT}\right),$$

where ε is the specific boundary free energy; γ a coefficient which makes it possible to calculate the area of the nucleus; γl^2 the area of the nucleus; h the height of the nucleus; ΔG_v the free energy of the medium,

$$\Delta G_v = \frac{kT}{\Omega} \ln \frac{p}{p_{equil}},$$

p the partial pressure of the gas; p_{equil} the equilibrium pressure of the gas; Ω the volume of one carbon atom in the crystal; and a a coefficient which depends on the frequency of the molecular collisions and on pressure.

Without knowing the values of a, γ, and ε it is impossible to calculate the specific parameters of the nuclei (for example the number of atomic layers in the epitaxial film). The above expressions have been used successfully[1] to determine the ratio of the rates and work of formation of epitaxial nuclei of diamond and graphite on the {111} face of a diamond support. It was shown that the equilibrium gas pressures for the formation of the diamond nuclei are twice those for the formation of graphite, and that the ratio of the rates of formation of the nuclei has a maximum value at a definite ratio of the partial and equilibrium pressures. Thus the most favourable range for the epitaxial growth of diamond will correspond to p/p_{equil}(graphite) = $2^{2.7}$.

From our viewpoint, however, this calculation, which is based on thermodynamic data, is of no significance for determining the most favourable range for the epitaxial synthesis of diamond, since this is determined entirely by the differences between the kinetic conditions for the synthesis of diamond and graphite.

At the same time it would be useful to know the specific parameters of the diamond critical nuclei obtained as equilibrium epitaxial films on the faces of minerals with the properties required for epitaxy.

It can readily be shown that there is a relationship between the thickness of the epitaxial diamond film, expressed as the number of carbon atomic layers (δ), and its two-dimensional size ($d = 2r$) and the equilibrium degree of transformation (Y) into diamond by reactions (2)–(4) at a definite temperature and pressure. A corresponding relationship should naturally exist for epitaxial films of graphite. The differences between the ratios of these parameters for diamond and graphite should not be of particular interest to us, since the formation of a particular epitaxial film is determined entirely by the kinetic conditions, and we are considering cases with kinetic conditions favourable for the synthesis of diamond.

For a microscopic volume with local equilibrium of the reactions, the quantities indicated are related to one another as follows:

$$\delta = \frac{c_{loc}}{c_1} Y\beta,$$

where c_{loc} is the number of carbon atoms in the volume of the local equilibrium, in a hemisphere with a volume of $(\frac{2}{3})\pi r^3$; c_1 the number of carbon atoms in one monolayer with an area of πr^2; and β the relative volume concentration of the substance A in the volume of the local equilibrium (if the volume is occupied by a gas, $\beta = 1$; if it is occupied by a solution of A in a melt or by a solid, $\beta \neq 1$). A model of the region of local equilibrium on the surface of the support is shown in Fig. 8.

Having determined the values of c_{loc} and c_1 with allowance for the fact that only half of the starting materials A in reactions (2) and (3) corresponds to the number of carbon atoms taken in the calculation,

$$c_{loc} = \frac{1}{3}\pi r^3 \frac{N_A}{V_0},$$

(V_0 is the volume of a mole of gas under normal conditions, and N_A is Avogadro's number) and

$$c_1 = \frac{\pi r^2}{\gamma},$$

(γ is the area occupied by one carbon atom on the {111} face of diamond, equal to 5.5 Å^2), we obtain

$$\delta = \frac{1}{3}\frac{\beta\gamma r Y N_A P_0}{273R}. \qquad (16)$$

The results of the calculation of δ for different values of r and different temperatures of the equilibrium of reactions (2) and (3) for $\beta = 1$ and $P_0 = 1$ atm are given in Table 4. The value of δ is

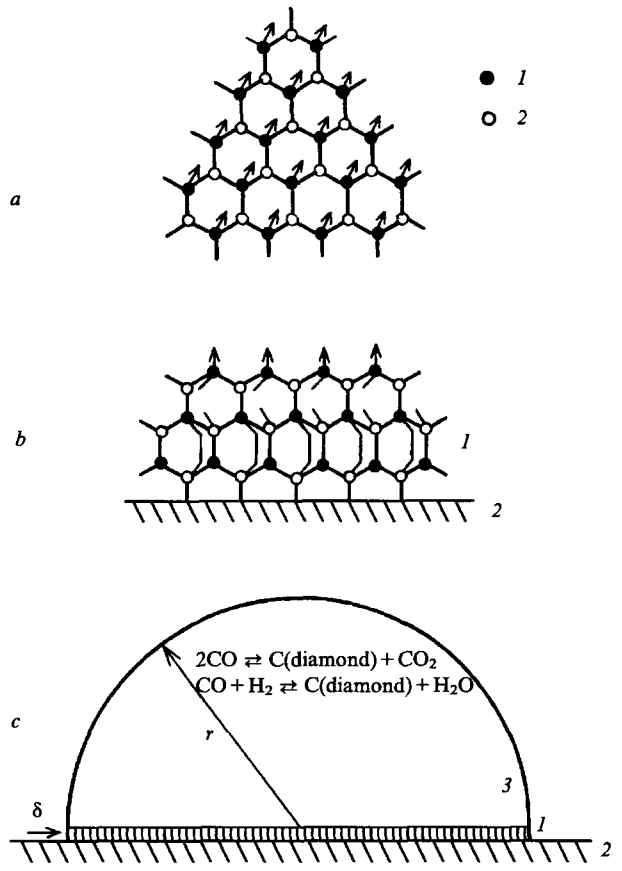


Figure 8. The formation of an equilibrium epitaxial film of diamond on supports showing a crystal-structural correspondence with the arrangement of the carbon atoms on the {111} face of diamond; *a*, view of a critical nucleus from above; the arrows indicate the free valences of carbon, lying at an angle of 90° to the {111} surface and localised by the functional groups; *1*, *2*, carbon atoms of the upper and lower sheets respectively; *b*, view of a critical nucleus from the side; *1*, three-layer epitaxial film of diamond; *2*, face of the mineral support; *c*, model of the region of local equilibrium on the surface of the support, bringing about the epitaxial growth of the diamond film; *1*, epitaxial film (nucleus) with thickness δ and diameter $d = 2r$; *2*, support; *3*, hemisphere bounding the range of local equilibrium of reactions (2) and (3).

proportional to the pressure (P) as it increases from the normal value (P_0) to the critical value (P_{cr}), and is independent of pressure for $P_0 > P_{cr}$.

Table 4 shows that the thickness of the epitaxial film in the critical nuclei of diamond may be greater, the greater the size of the nucleus and the volume of the local equilibrium in which the film is formed, and the lower the temperature of the synthesis. The increase in δ and δ/d with decrease in temperature reaches a limiting value at 400–600 K. The ratio of the thickness of the film to the diameter δ/d in the limit is independent of the diameter of the nucleus and is equal to 3300.

Thus the formation and preservation of the equilibrium epitaxial diamond films which are the critical nuclei for the crystallisation of diamond do not require exotic conditions, and can take place in a static closed system. The only factors making possible the formation of these films are the presence of the starting materials A for the diamond polycondensation in the local volume and the establishment of favourable kinetic conditions, including the presence of suitable matrix–minerals for the epitaxial growth of the diamond material.

In some cases the factor of epitaxial growth of critical diamond nuclei may be particularly favourable. This is indicated by the accelerating action of fullerenes on the synthesis of

Table 4. Number of atomic layers of carbon (δ) in the equilibrium epitaxial film of diamond for different nucleus diameters and reaction temperatures, calculated with the use of Eqn. (16).

T/K	Y (%)	d/μm		
		1	10	100
	$2CO \rightleftarrows C(diamond) + CO_2$			
400	100	1.4	13.6	135.5
500	100	1.4	13.6	135.5
600	99.90	1.4	13.5	135.4
700	98.85	1.3	13.4	134.0
800	92.75	1.3	12.6	125.7
900	71.06	1.0	9.6	96.3
1000	31.51	0.4	4.3	42.7
1100	8.21	0.1	1.1	11.1
	$CO + H_2 \rightleftarrows C(diamond) + H_2O$			
400	100	1.4	13.6	135.5
500	99.93	1.3	13.4	134.3
600	98.95	1.3	13.4	134.1
700	92.93	1.3	12.6	126.0
800	71.99	1.0	9.8	97.5
900	32.43	0.4	4.4	43.9
1000	8.60	0.1	1.2	11.7
1100	2.20	0.03	0.3	3.0

diamond films on a silicon support.[47] The deposition of C_{60} on silicon increases the rate of growth of the film by a factor of 10^4, and the deposition of C_{70} increases it by a factor of 10^{10}. Thus the presence on silicon of spherical fullerene molecules, whose surface consists of a 'parquet' of six-membered and five-membered carbon rings, increases the rate of diamond formation by a factor of at least 10^4, and the presence of the pyrene structural elements in the C_{70} molecule leads to a further increase in the rate of growth of the diamond film by a factor of 10^6. This case evidently shows not only the more favourable crystal-structural correspondence between the structural elements of the fullerenes and diamond, compared with the silicon lattice, but also the accelerating action of the spherical deformations of the pyrene and triphenylene structural elements of the fullerenes.

Pressure is not a decisive factor, since epitaxial films may be formed at low, high, and super-high pressures. Thus since minerals capable of bringing about the epitaxial growth of diamond are widely distributed, it may be concluded that the appearance of nuclei for the crystallisation of diamond has never been the limiting stage of the formation of diamond deposits in nature. In nature, an excess of diamond nuclei should evidently exist. At the same time, when all other favourable conditions for diamond polycondensation are established, the formation of natural deposits containing diamond macro-crystals might have been limited by a range of additional macroscopic conditions required to bring about the growth of crystals under the non-equilibrium conditions of an open catalytic system functioning for a prolonged period.

The macrokinetic conditions for the formation of diamond nuclei and for their growth to give macro-crystals differ considerably, despite the same optimum conditions of competition between the processes of formation and conversion of diamond and graphite materials (13). It is possible to have combinations of conditions leading to competition between the processes of the formation of nuclei (n) and the growth of crystals (c), between the processes of the formation and the oxidative solution of the diamond material of nuclei and crystals (o), and also between the processes of the formation of small and large crystals. The ratio of the degrees of transformation (Y_n, Y_c, Y_o) of the substance in these processes with the formation and oxidation of the diamond material, and the conditions for movement into

the recrystallisation zone shown in Fig. 5, are given by the diagram in Fig. 9. The vertices of the diagram correspond to 100% transformation in the formation of the diamond material as nuclei, the growth of crystals, and the oxidation of diamond material. The diagram contains zones corresponding to the complete oxidation of the diamond material (Y_oAOC), the preferential formation of the diamond material as nuclei (Y_nAOB), and the growth of diamond crystals (Y_cBOC).

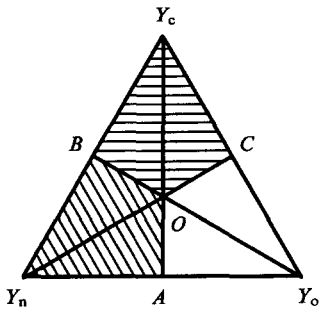


Figure 9. Diagram showing the degrees of transformation of the material in the competing processes of diamond formation and the oxidation of the diamond material (the vertices correspond to 100% degrees of transformation); Y_nAOB is the zone of nucleus formation; Y_cBOC the zone of crystal growth; Y_oAOC the zone of complete oxidative solution of the diamond material; the AOC the recrystallisation line.

Under the conditions of diamond polycondensation corresponding to the vertex Y_n, only the formation of nuclei takes place, and under the conditions corresponding to the apex Y_c, all the diamond material formed grows into crystals; on going from Y_n to Y_c, the number of nuclei (crystals) formed decreases sharply from infinitely large to 1. Under growth conditions without competition between the processes of nucleus formation and crystal growth and the processes of oxidation of the diamond material, however, the quality of the diamond crystals will be poor, because of various inclusions, dislocations, and polycrystalline aggregates.

Under conditions bringing about the dynamic process of growth and oxidation of diamond in the recrystallisation zone, corresponding to the line AOC in Fig. 9,

$$Y_{di} = Y_l = Y_o = 50\%;\ V_c = V_o;\ Y_{di} = Y_n + Y_c;\ Y_n \to 0,$$

the formation of large defect-free crystals of the highest quality is possible. The formation of new nuclei is almost completely suppressed

$$V_c \geqslant V_o;\quad V_n = 0.$$

These conditions were created in an experiment on the further growth of single crystals of diamond from $CH_4 + CO_2$ mixtures in alkaline melts. Fig. 6*a* shows that the recrystallisation zone includes the range of observed increase in the weight of the diamond material, and is appreciably broader than this range, that is recrystallisation changes in the diamond crystal are observed, corresponding both to an increase in its mass as a result of the formation of new diamond material and to a mass loss as a result of oxidation. Other examples of recrystallisation changes in single crystals of diamond and powders are known.[10,23,49]

For example, excellent photographs have been obtained[49] of successive recrystallisation changes on the surface of single crystals of diamond under the catalytic action of molten NaOH containing Ni^{2+} ions at 1100 K in a gaseous medium containing air.

Moving from the vertex Y_c to the point C in Fig. 9 corresponds to the change from reducing conditions of diamond polycondensation to oxidising conditions. According to the results of studies[10,23] of the change in the habit of diamond crystals during partial oxidative solution and data[36,50] on the relationship between the habit of diamond crystals and the oxidation potential of the growth medium, this is reflected in a change in the morphology of the diamond crystals formed. Thus under reducing conditions a $CO + H_2$ mixture gives cubic crystals; when traces of O_2 are added to the mixture, cubo-octahedral crystals are formed; and at an O_2 concentration of 2.2%, only octahedral diamond crystals are formed.[36] Increase in the oxidation potential of a kimberlite deposit, characterised by the change in the ratio Fe^{III}/Fe^{II}, leads to a change from octahedral diamond crystals with smooth faces to rhombododecahedral and rounded forms as a result of oxidative solution.[50] With further increase in the oxidation potential, however, when $v_o > v_c$, combustion of the finer diamond crystals with preservation of the large crystals will take place, and the size of distribution of the diamond crystals will change, as confirmed by the displacement of the maximum of this distribution towards large diamonds and the absence of fine diamonds in a number of kimberlite pipes of Yakutia.[51]

VI. A model of the non-equilibrium growth of diamond crystals in a macroscopic open catalytic system

When the polycondensation process (1) takes place in a macroscopic open catalytic system (a flow reactor) with the constant supply of the original light carbon-containing molecules A or their mixtures with the product A + L at a rate w_f and the removal of the light reaction products L, non-stationary conditions may be established

$$A \to \left\{ \frac{nA_n \to \{A - mL\} + mL}{\sum\{A_n - mL\}_i K} \right\} \to L, \qquad (17)$$

when the condensation product $\{A_n - mL\}$ formed by the reactions (2)–(4), (2′)–(4′), etc. remains in the constitution sphere of the system on the catalyst K and gradually accumulates as the diamond or graphite material $\sum\{A_n - mL\}_i$. The removal of the products L = CO_2, H_2O, etc. capable of oxidising the condensation product, and the displacement of the equilibrium in the system, lead to the establishment of a stationary (stable) non-equilibrium, and continuous growth of the diamond or graphite material takes place. When the products of reactions (2)–(4) and (2′)–(4′) enter the system (17) together with the starting materials, however, the rate of exchange of the materials and the effect of non-equilibrium growth of the condensation products decrease. We have used this model to describe the growth of diamond crystals in kimberlite deposits[19] and the abiogenic synthesis of hydrocarbons,[24] and also to describe non-stationary polymolecular processes involving the condensation products.[17]

As noted above, the direction of process (1) towards the formation of diamond material requires favourable kinetic conditions. If these conditions are observed, then a definite decrease in the intensity of material exchange and in the non-equilibrium character of the system (17) as a result of the retarding action of the products is favourable for the formation of large diamond crystals of good quality, since it moves the process into the dynamic conditions of growth and oxidation characteristic of the recrystallisation zone. This corresponds to the zone situated between the lower boundary of Bachmann's diamond range and the line $H_2O - CO_2$ in Fig. 5 or the lines AO and OC in Fig. 9.

At the same time, the continuous growth of diamond crystals on top of the initially formed equilibrium epitaxial films is possible only under non-equilibrium conditions. The apparent contradiction arises because the growth of the crystals, as well as the formation of epitaxial films, can take place at different degrees of non-equilibrium, but when equilibrium is reached, only the epitaxial film can be formed and exist.

The macroscopic open catalytic system (17), in which favourable kinetic conditions are created for diamond polycondensation by reactions (2)–(4), can exist for wide variations in the specific kinetic and macrokinetic conditions: from limiting non-equilibrium to close to equilibrium; from reactions taking place in the kinetic range to reactions taking place in the diffusion range; from conditions leading to the formation of only epitaxial films (nuclei) to conditions leading to the growth of single crystals; and from conditions leading to an increase in the number of nuclei to conditions preventing the formation of new nuclei and bringing about the growth of large crystals. A diagram of such a macroscopic open catalytic system with allowance for varied local conditions of diamond synthesis is given in Fig. 10. These conditions are characterised by different combinations of the rate of flow of the materials

$$w_f = w_{lf} + w_{diff},$$

(where w_{lf} is the rate of linear flow along the gas-transport channels, pores, and cracks, and w_{diff} the rate of diffusion through the pores) and the rate of formation and accumulation of the diamond material in the crystallisation centres

$$v_c = \frac{d[\{A_n - mL\}]}{dt},$$

which is a function of temperature, the rate of flow of the materials, and the composition of the mixture A + L, that is

$$v_c = \varphi[T, w_f, (A + L)].$$

In Fig. 10, *A* is the gas-transport channel through which the reacting mixture A + L moves under the influence of a pressure gradient at a rate w_{lf}; *B* the porous environment of the gas-transport channel, in which the reacting mixture diffuses under the influence of a pressure gradient at a rate w_{diff}; the total rate of flow through the non-equilibrium zone is $w_f = w_{ef} + w_{diff}$; *C* is the boundary of the non-equilibrium zone, at which $v_c = 0$ at $(A + L)_{equil}$; within the zone $v_c > 0$; $v_c < w_f$; *I* is the kinetic range in which diamond polycondensation takes place, including the extrakinetic range (*I'*) on the walls of the gas-transport channel ($v_c > v_{diff}$; $v_c < w_{lf}$; $w_{diff} < w_{lf}$) and the intrakinetic range (*I''*) in the porous wall ($v_c < w_{diff}$); and *II* the diffusion range in which diamond polycondensation takes place ($v_c > w_{diff}$).

With allowance for possible gradients in the pressure and in the concentrations of the starting materials A at the inlet and outlet of the system (Fig. 10), the model can be used to describe diamond polycondensation in the preparation of polycrystalline diamond films on supports by the reaction of the latter with a gas–plasma flux of original carbon-containing substances, for processes in ordinary catalytic flow reactors, and in the natural open catalytic systems produced in the fractures, cracks, and other gas-transport channels in the degassing paths in the earth's minerals.

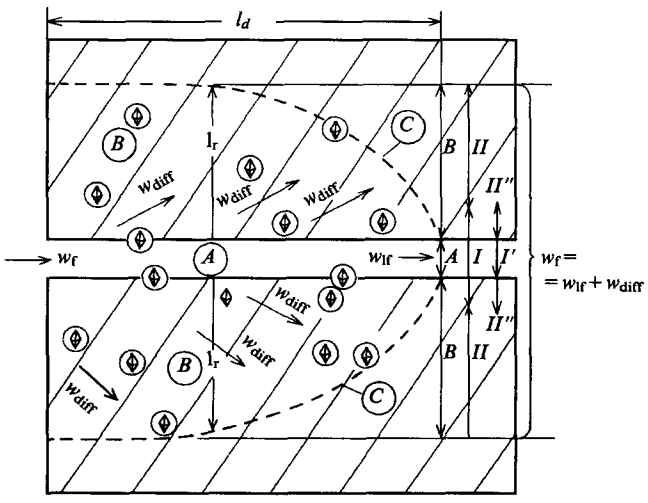


Figure 10. Model of the non-equilibrium zone in the macroscopic open system (17), bounded by the longitudinal and transverse ranges corresponding to the conditions for the growth of diamond crystals.

In the last cases the model makes it possible to describe not only the processes of diamond synthesis taking place at

$$v_c < w_f,$$

in the kinetic range but also syntheses in the diffusion paths, when

$$v_c > w_{diff}.$$

These conditions are ensured by the porosity of the catalysts in experimental flow reactors or by the porosity and diffusion gas-permeability of the rocks surrounding the fluid-transport channels in natural diamond deposits.

For constant values of *T*, w_f, and w_{diff}, the rate of growth of the diamond crystal will depend only on the composition of the mixture of carbon-containing starting materials and products passing into the system and into each local zone in which individual crystals grow

$$v_c = \varphi(A + L),$$

and for the equilibrium composition of the mixture, $v_c = 0$ ($v_c > 0$ only for a non-equilibrium composition).

Thus the growth of diamond crystals in the polycondensation reactions (2)–(4) etc. will be determined entirely by the macroscopic conditions maintaining non-equilibrium in the system (17).

According to the theory of open catalytic systems,[25,26] the extent to which a macroscopic open system deviates from equilibrium (ρ) is directly related to the potential degree of transformation $\tilde{Y}$ of the original mixture A + L in the system. The relationship between these parameters and the composition of the gas mixture entering the system (17) is shown in Fig. 11*a*. The figure shows that the maximum degree of non-equilibrium character $\rho = 1$ and the maximum value of the potential degree of transformation for the forward reactions (2)–(4), determined from the equation

$$\tilde{Y} = \frac{M_A(c) - M_A(equil.)}{M_A(c)}.$$

[$M_A(c)$ and $M_A(equil.)$ are the mole fractions of the substance A in mixtures with the current and equilibrium compositions respectively], are reached when the pure starting material A is supplied, and that these quantities are equal to zero when the equilibrium mixture is supplied. The same applies to the back reactions (2)–(4) when super-equilibrium quantities of oxidising products (CO_2, H_2O) are supplied to the system (17), if $\tilde{Y}$ is determined in terms of the mole fractions of L in the mixtures A + L.

By taking account of the fact that the composition A + L will change, approaching the equilibrium composition $(A + L)_{equil}$, along the direction of flow of the reaction mixture in the system as a result of reaction (1), it is possible to determine the longitudinal distance to which the polycondensation process will extend, l_d. This distance will be greater, the greater the difference between the composition of the entering mixture $(A + L)_{current}$ and the equilibrium composition (Fig. 11*b*). In the same way it is possible to estimate the transverse distance l_r to which non-equilibrium conditions of diamond polycondensation will extend in a macroscopic reactor (Fig. 10). In both cases the boundary of the non-equilibrium range in which the growth of diamond crystals is possible is determined by the approach of the composition of the mixture to the equilibrium composition, that is the actual range is finite.

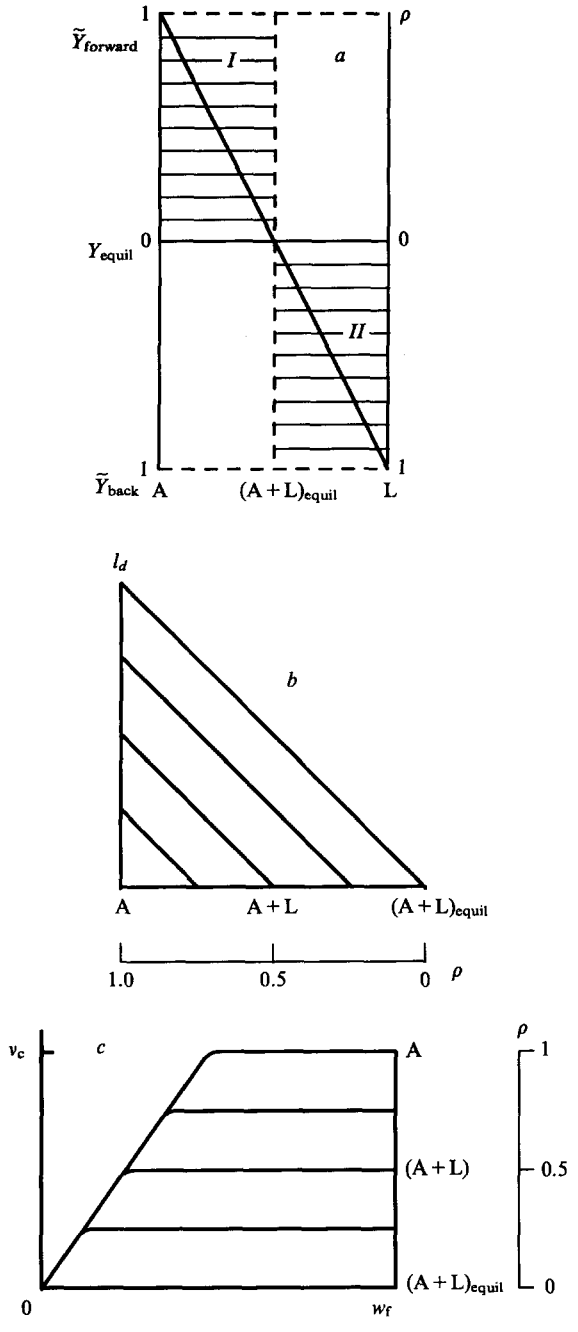


Figure 11. Relationship between the potential degree of transformation (*a*), the longitudinal distance to which the non-equilibrium conditions extend (*b*), and the rate of growth of diamond crystals (*c*) on the one hand and the rate of flow and the extent to which the composition of the reaction mixture entering the open catalytic system deviates from the equilibrium composition on the other; *a*: *I*, diamond polycondensation by reaction (1); *II*, conversion by reaction (12).

The non-equilibrium of system (17) as a whole and in each local zone in it, however, will be determined not only by the composition of the reaction mixture entering the system and the changes which it undergoes in reaction (1) but also by the ratio of the rate of polycondensation v_c and the rate of flow w_f and by the actual value of w_f (Fig. 11*c*). Non-equilibrium conditions in the open system are established with the condition that, essentially, reaction (1) is of zeroth order with respect to A, and there is a decrease in the value of v_c as the composition of the entering mixture approaches the equilibrium composition $(A+L)_{equil}$ and in the value of w_f at which the change to the non-equilibrium range takes place.

The last feature acquires great importance in the establishment of recrystallisation conditions (Fig. 9) at the boundary between the growth and the oxidative solution of diamond. These conditions are favourable for the prevention of the formation of new nuclei, for the oxidative solution of excess nuclei and fine crystals, and for the growth of the largest crystals of highest quality.

VII. An analysis of the conditions of formation of diamond in experiments and in various natural deposits

1 Experiments on the growth of polycrystalline diamond films from plasma on different supports and the epitaxial growth of single crystals

All known facts in the chemical synthesis of diamond at low pressures, both as polycrystalline films on different supports and in the growth of the diamond lattice in epitaxial films and single crystals, are consistent with the proposed model of the polycondensation growth of diamond material under the non-equilibrium conditions of open catalytic systems. In all observed cases of the formation and accumulation of diamond material in macroquantities, kinetic conditions have always been observed for the diamond condensation of the original light molecules [by reactions (2)–(4) etc.] in the non-equilibrium zones of the open catalytic systems, including primarily the macrokinetic conditions ensuring stationary non-equilibrium in the diamond crystal growth zones.

The slight differences between the kinetic and macrokinetic parameters in observed cases of diamond synthesis at low pressures do not go beyond the range of optimum conditions. Thus in the growth of polycrystalline diamond films on supports in a gas–plasma stream, the observed ratio of the rate of formation of the diamond material to the rate of flow is

$$v_c \ll w_f,$$

ensuring stable zeroth order of reaction (1) with respect to the original carbon-forming material and the maximum degree of non-equilibrium character. The process of diamond material formation takes place in the kinetic range (range *I* in Fig. 10), or more precisely in the extra-kinetic range (*I'*) on the wall of the gas-transport channel A.

In the case of the growth of a single-crystal lattice on a diamond seed crystal (in a solution of metal oxides in a molten alkali metal hydroxide), studied by us (Fig. 6), however, reaction (1) took place in the diffusion zone (zone *B* in Fig. 10), in which the transport of the reacting material to the growing diamond crystal took place from the gas-transport range A by diffusion through the melt, and

$$w_{diff} \ll w_f.$$

Reaction (1) in the diffusion zone was dependent on the thickness of the catalyst layer and took place either in the intra-kinetic range (range *II'* in Fig. 10), when

$$v_c < w_{diff},$$

or in the intra-diffusion range (range *II* in Fig. 10), when

$$v_c > w_{diff}.$$

The two sets of conditions are equally favourable for the growth of the diamond crystal, since they lie within the range of non-equilibrium of the open catalytic system. The boundaries of the non-equilibrium zone for constant values of w_f and w_{diff}, however, are determined only by the depletion of the reaction mixture in the direction of the fluxes of w_f and w_{diff} and by the approach of its composition to the equilibrium composition (range *C* in Fig. 10).

2. Facts indicating the growth of diamond metacrystals in the solid phase of kimberlite deposits

The optimum conditions for the growth of diamond crystals according to the model(17) can readily be established in kimberlite pipes, which are the funnels of characteristic volcanoes with an explosive action, filled with breccia, that is a porous rock with a large number of gas-transport channels, through which the degassing of the minerals of the earth took place (and in some cases is still taking place) from deep fractures, to which the pipes are confined. The gases liberated contain all the starting materials and products of reactions (2)–(4), and the kimberlites contain all known active catalysts of the formation of epitaxial nuclei and the synthesis of diamonds, from heavy metal ions to alkali metal ions.

In different parts of the pipe there may arise local regions with the properties of the non-equilibrium open catalytic system (17), having favourable micro- and macro-kinetic conditions for diamond polycondensation (1), corresponding to the model given in Fig. 10. The growth of diamond crystals will take place with ideal exchange of the materials in the system (17), when $v_c \ll w_f$ and the gas mixture A + L has a non-equilibrium composition. These conditions are established in the gas-transport channels.

The growth of diamond crystals will also take place in the diffusion zones (range *B* in Fig. 10), where $w_{diff} \ll w_f$: in the intra-kinetic range for $v_c < w_{diff}$ or in the intra-diffusion range for $v_c > w_{diff}$. In the diffusion zones of the porous solid filling the pipe, the rate of growth v_c will decrease in the radial direction relative to the transport channel as the composition of the mixture approaches the equilibrium composition $(A+L)_{equil}$; at the boundary of the non-equilibrium zone (range *C* in Fig. 10), reaction (1) necessarily moves into the intra-kinetic range as a result of the decrease in v_c to $v_c < w_{diff}$, and at the boundary of the non-equilibrium zone the reaction stops ($v_c = 0$). The growth of the diamond crystals also stops with decrease in the flow rate ($w_{diff} \to 0$).

In any case—when the composition A + L approaches the equilibrium composition or when the open system becomes static—the growth of the diamond crystals stops. The absence of direct removal of CO_2 and H_2O from the growing crystal under the specific conditions of a kimberlite deposit may be replaced by another mechanism of displacement of the equilibrium in reactions (2)–(4), leading to further growth.

This mechanism may be the accumulation of CO_2 and H_2O by the surrounding solid material, accompanied by allochemical changes in it

$$2CO \rightleftarrows C(\text{diamond}) + CO_2;\ CO_2 + M = MCO_3\ , \qquad (18)$$

$$CO + H_2 \rightleftarrows C(\text{diamond}) + H_2O\ ;$$

$$4H_2O + 3Mg_2SiO_4 = Mg_6[Si_4O_{10}](OH)_8\ . \qquad (19)$$

Carbonate and serpentine coatings, which do not oxidise diamond, should be formed round the diamond crystals. Special experiments have shown that at 1073–1273 K an oxidising action is shown only by free CO_2, and not by molten carbonates,[8,9] and that diamond does not dissolve in silicate melts.[9]

The carbonate and serpentine coatings detected round kimberlite diamonds and various characteristics of their composition and structure confirm that reactions (18) and (19) take place.[19,22,53] In kimberlite pipes of Yakutia, the primary contacts of diamonds with kimberlites and eclogites in fact indicate allochemical changes in the surrounding rock, revealed not only by the formation of layer mineral coatings but also by aureoles of chemical changes in the surrounding rock.[19,22] Cataclastic changes in the surrounding rock have also been revealed[19] by the formation of oriented micro-cracks and micro-displacements as a result of the increase in the volume of the diamond meta-crystal growing in the solid medium; this should be observed if reactions (18) and (19) take place with a constant supply of the starting materials of reactions (2) and (3) to the growing crystal.

The secondary contacts of diamond crystals with kimberlite breccia, taken by Rudenko and coworkers[53] as a typical case, are not accompanied by allochemical or cataclastic changes in the surrounding rock, and in this case the diamonds are xenocrysts. In the primary contacts, the growth of diamond as a meta-crystal in the solid medium is confirmed by the observed fractionation of carbon isotopes in reaction (18). For example, according to published data,[54] the carbonate carbon of the coating is lighter ($\delta^{13}C$ from −6.7‰ to −7.6‰) than the carbon of the carbonates in the surrounding kimberlite ($\delta^{13}C$ from −6.9‰ to −8.2‰) situated outside the zone of chemical changes.

These facts not only confirm the model of the growth of diamond crystals in the catalytic system (17) as a whole but also make it possible to deduce its details with allowance for the chemical and metasomatic processes (18) and (19), which maintain the disequilibrium in the system and ensure favourable conditions for diamond polycondensation.

The favourable kinetic conditions for diamond polycondensation, created in the formation of kimberlite deposits, are extended by the possible inclusion in the synthesis of reactions (6) and (7), which also take place under conditions corresponding to the constant displacement of the equilibrium as a result of the binding of the products with oxidising properties by surrounding solid minerals. Minerals containing divalent iron are converted into minerals containing trivalent iron, and the thermodynamic equilibrium of reactions (6) and (7) is displaced completely to the right ($\lg K_p$ at 1000 K has the values 35.6 and 71.1 respectively).

The duration of the preservation of the stationary non-equilibrium in reactions (6), (7), (18), and (19) ensuring the growth of the diamond crystal in the solid phase will naturally be determined by the concentration of the appropriate minerals in the local volume accessible for allochemical changes. For reactions (6) and (7) these are minerals containing Fe^{II}, for reaction (18) they are alkaline earth metal oxides and silicates, and for reaction (19) they are olivine and other silicates. Reactions (6), (7), (18), and (19), which extend the favourable conditions for diamond polycondensation, have undoubtedly been of considerable importance in the formation of kimberlite deposits.

The model of the growth of diamond crystals in non-equilibrium open catalytic systems is consistent with many other facts established during the exploration and exploitation of kimberlite deposits:[55,56] the existence of diamond-bearing and non-diamond-bearing kimberlite pipes with similar chemical compositions and locations,and a decrease in diamond-bearing character with depth;[55,57,61] the non-equilibrium nature of the distribution of diamonds along horizons and the correlation of the distribution with the characteristics of the morphology of the crystals;[54,56,57,60,62] and the correlation of the diamond-bearing character of individual sections of the pipes with the catalytic activity of the kimberlites in the reactions which are the reverse of reactions (2) and (3), and with the concentration of juvenile bitumens and the oxidation potential. This is also confirmed by the presence in the pipes of xenoliths of diamond-bearing and non-diamond-bearing eclogites with identical compositions,[63,64] the rare occurrence of diamond-bearing eclogites and the very high concentration of diamonds in them, the uniformity of the morphological characteristics and dimensions of eclogite diamonds, and the non-uniformity of the distribution of diamond crystals in the xenolith of eclogite, which are confined to the surface of the xenolith or to cracks intersecting the xenolith.[64–66] For example, in a xenolith of a diamond-bearing eclogite intersected by a serpentine vein, found in the Mir pipe in Yakutia, all the diamonds were confined to this vein.[66]

All these facts can be explained using the model of the chemical synthesis and growth of diamond crystals in open catalytic systems under non-equilibrium conditions. This model may be established under crustal conditions in the formation of kimberlite pipes or veins in degassing paths in the interior of the earth, and are not associated with super-high pressures.

The same facts cannot be explained, however, by assuming that diamonds are formed in the mantle at super-high pressures and removed from it.

The pallial (mantle) hypothesis is not consistent with the kinetic conditions of the formation and preservation of diamonds examined above. In the equilibrium magma of the mantle, only equilibrium epitaxial films of diamond on the faces of various minerals can be formed independently of the pressure by reactions (2)–(4) and exist for an unlimited time. Diamond crystals formed in the mantle at super-high pressure as a result of the polymorphic transformation of graphite under reducing conditions can exist for a long time only in the absence of CO_2 and H_2O, which is unlikely. Under non-equilibrium conditions in the mantle when open catalytic systems are produced, diamond crystals can be formed by reactions (2)–(4), etc., as in the crust, without super-high pressures. They will exist, however, so long as the non-equilibrium of system (17) is preserved and the exchange of materials continues, but will undergo combustion by the reverse reactions (2) and (3), or graphitisation, when these conditions break down {for example if there is a change in the composition of the mixture of light molecules A + L passing through the system (17) and super-equilibrium concentrations $[CO_2]$ and $[H_2O]$ appear in it as a result of the removal of the magma into the crust or on to the surface and as a result of a decrease in pressure}.

3. Facts relating to the growth of diamond crystals under the metasomatic conditions of the earth's crust without super-high pressure

Certain specific conditions of the formation of kimberlite pipes and paragenetic associations of diamond with high-pressure minerals have led a number of workers to assume that a leading role is played by the mantle production of kimberlite diamonds, that is by high pressures and temperatures. The recently established existence of non-kimberlite diamonds,[67–71] which eliminates completely high-pressure conditions for their formation, however, not only makes it necessary to doubt again the universal mantle hypothesis but also provides convincing confirmation of the model of the growth of diamond crystals in non-equilibrium open systems.

Metasomatic diamonds of the Kokchetav deposit. In the eighties, the Kokchetav (Kumdykul'skoe) deposit of fine diamonds with a cubic habit was discovered in Kazakhstan, occurring together with flaky graphite formations as a vein, localised in an old fracture, and formed as a result of metasomatic changes in the surrounding rocks by the reaction of the latter with products of the earth's degassing, passing along the fracture.[67–69] Diamonds with dimensions of 0.02–0.07 mm are present in very high concentrations in garnet–mica gneiss, garnet pyroxenites, marbles, and skarns. These minerals were formed as a result of metasomatic changes by the reaction of all types of rock intersected by the diamond-containing vein with gaseous fluids at 1000–1300 K and pressures not exceeding 6–9 kbar. At the same time, diamonds have not been found at a distance from the vein in corresponding surrounding rocks which have not undergone metasomatic changes. In the diamond-containing rocks the diamonds are found as inclusions in crystals of practically all the minerals (almandite, pyroxene, mica, quartz, etc.), and are often localised in micro-cracks and in the contacts between granules of other minerals.† In the axial zone of the deposit, richest in diamonds, there are very fine crystals (0.02–0.07 mm), and the less rich peripheral zones contain the largest crystals (up to 0.1–0.5 mm), and also contain pseudomorphs of graphite after diamond, not found in the other zones. In addition to diamonds, the diamond-containing rocks contain flaky graphite, formed at the same time as the diamond. The concentration of this graphite is 10^2 times the diamond concentration.

All this indicates the polycondensation of juvenile carbon-containing gases in the non-equilibrium open catalytic system (17), taking place in the diamond and graphite directions simultaneously and accompanied by the metasomatic transformation of the rocks surrounding the fluid-transport channels. The polycondensation has taken place under strongly reducing conditions with the predominant formation of graphite material, as shown not only by the higher yields of graphite material compared with diamond but also by the predominance of the cubic habit of the diamond crystals.[67] In this case the diamond material has been obtained under conditions leading to the preferential growth of nuclei (zone Y_nAOB in Fig. 9), as confirmed by the very high concentration of fine crystals in the rock and by the abundance of negative skeletal forms.

The model (17) is also consistent with the observed[69] distribution of diamonds relative to the axis of the diamond-containing ore vein. In the peripheral regions of the vein with a high oxidation potential and diffusion flow conditions, situated at the boundary of the non-equilibrium zone under conditions with $v_c < w_{diff}$, close to the conditions of the recrystallisation zone (COA in Fig. 9), the formation of nuclei has been retarded, and the diamond material has been deposited as larger crystals. This model is also consistent with the formation of paramorphs of graphite after diamond in the peripheral regions of the vein at the boundary of the non-equilibrium zone (range C in Fig. 10). The graphitisation of diamond

$$C(\text{diamond}) \rightarrow C(\text{graphite}),$$

accelerated by CO_2, will have favourable conditions as the composition of the diffusing gases (CO, H_2, CO_2) approaches the equilibrium composition and with the corresponding increase in the CO_2 concentration after the completion of the metasomatic changes, and also after the weakening or complete cessation of degassing, which gives non-equilibrium concentrations of the starting materials of reactions (2), (3), etc. The non-equilibrium character of the open catalytic system (17), which ensures favourable conditions for the synthesis of diamond and prevents graphitisation, disappears.

Pseudomorphs of graphite after diamond in the Beni Bouchera deposit (Morocco). Equally convincing confirmation of the model being considered is provided by the discovery of pseudomorphs of graphite after octahedral crystals of diamond[70, 71] in the laminated pluton of the ultrabasic rocks of the Beni Bouchera deposit, formed at temperatures of 770–1070 K and pressures not exceeding 5 kbar. In this deposit, between layers of flaky graphite, there is a lens of clinopyroxenites, in which all the graphite is present as pseudomorphs after graphite crystals with dimensions of 0.2–8 mm. The paramorphs constitute up to 15% of the volume of the rock. The concentration and size of the pseudomorphs are greatest at the centre of the lens.

In contrast to the metasomatic diamonds of the Kokchetav deposit, all the primary diamonds of the diamond-containing layer of the Beni Bouchera deposit have been completely converted into graphite pseudomorphs. The formation of the primary diamonds in this case has been associated with metamorphic changes in the cupola section of the pluton during its degassing and the movement of the carbon-containing fluids, and diffusion processes have predominated in the flux of fluids directed along the pressure gradient, that is

$$w_{diff} > w_f.$$

As a result of this last feature, the metamorphised part of the pluton has been formed as rhythmic layers. The production of this rhythmic diffusion stratification of the pluton indicates the prolonged action of the fluxes of the directed exchange of materials in this macroscopic open system and the development of self-organisation processes characteristic of these non-equilibrium systems.[72]

† The concentration of diamond granules is so high that it has been possible to study the distribution of their inclusions in the crystals of other minerals, in microcracks, and in the space between the granules from micrographs.[67–69]

The existence of the macroscopic open system (17) in the pluton degassing flux, which has given a mixture

$$\text{C(diamond)} + \overset{\downarrow}{\overline{\text{CO}_2 \rightarrow [2\text{CO}] \rightarrow \text{C(graphite)} + \text{CO}_2}} ,$$

of carbon-containing light molecules and other substances which bring about metasomatic changes in part of the pluton and the enclosing sedimentary rocks, has led to the development of all forms of the polycondensation process (1) and to the appearance of a zone most favourable for diamond polycondensation, together with zones in which ordinary flaky graphite has been formed. The conversion of diamond into graphite, irreversible at low pressures, has taken place, however, after the completion of the production of the pluton and the formation of the diamond and graphite deposits.

As in the case of the Kokchetav deposits, the start of graphitisation has been due mainly to a decrease in the non-equilibrium character of system (17) of diamond polycondensation as a result of a change in the composition of the entering gases, since only diamond polycondensation can oppose graphitisation under the same temperature conditions. The more favourable nature of the kinetic conditions for diamond polycondensation compared with graphite polycondensation reduces to the appropriate ratio of the rates (13). The graphitisation of diamond will become possible if a change in the composition of the gas-forming components or the cessation of the material exchange flux through the system (17) bring the conditions for reactions (2) and (2′) close to the equilibrium conditions and the reverse reactions (2) and (2′) take place to an insignificant extent in the presence of prepared crystals of diamond and graphite at a CO_2 concentration slightly greater than its equilibrium value.

The mechanism of this topochemical process may be the intermediate local conversion of diamond with the participation of CO_2 as catalyst, and the driving force may be the decrease in the thermodynamic potential in the polymorphic transformation of the diamond lattice into the graphite lattice. At super-high pressures, the reverse reaction (15) may take place with the same catalyst.

VIII. Summary

A large number of experimental facts and observations of natural phenomena confirm the model of the polycondensation synthesis of diamond from light-carbon-containing molecules by reactions of the type

$$2\text{CO} \rightleftarrows \text{C(diamond)} + \text{CO}_2 ,$$

$$\text{CO} + \text{H}_2 \rightleftarrows \text{C(diamond)} + \text{H}_2\text{O} ,$$

$$\text{CH}_4 + \text{CO}_2 \rightleftarrows 2\text{C(diamond)} + 2\text{H}_2\text{O} ,$$

at low pressures (not corresponding to the super-high pressures of the graphite $\rightleftharpoons$ diamond phase transformation). The chemical synthesis of diamond crystals has been observed in various open non-equilibrium catalytic systems differing in the scale of the observations.

The theory of this synthesis takes account of the stoichiometric, thermodynamic, and kinetic conditions of diamond polycondensation and the growth of diamond films and crystals. It defines the boundary and optimum conditions for the establishment of this complex process against a background of the aromatic polycondensation of the same original carbon-containing molecules leading to the production of graphite and other forms of non-diamond carbon. The general level of the oxidation potential and the difference between the kinetic conditions of diamond and graphite polycondensation is of considerable importance for determining the optimum conditions.

In addition to the conditions of the formation of new C–C bonds in the growth of the diamond lattice, the proposed theory examines the kinetic and macrokinetic conditions of formation of equilibrium epitaxial diamond films on crystal faces showing a crystal-structural correspondence with the arrangement of the carbon atoms on the faces of diamond, and also the conditions of the growth of macroscopic diamond crystals. It has been shown that equilibrium epitaxial films on appropriate supports (diamond critical nuclei) should be formed easily under static conditions. Their thickness, expressed as the number of carbon atomic layers, depends on the temperature and the size of the region of local equilibrium containing the original molecules of the polycondensation, but the ratio of the thickness of the film to the diameter is always constant and equal to 3×10^{-4}. At the same time the growth of the critical nuclei to give diamond macro-crystals requires special and rare (compared with those for the formation of the nuclei themselves) macrokinetic conditions. The growth of diamond macro-crystals by successive chemical synthesis is possible only in an open catalytic system operating in stationary fashion and ensuring a constant supply of the original carbon-containing molecules and the removal of product (CO_2 and H_2O) capable of displacing the equilibrium in the reverse direction.

The theory of the chemical synthesis of diamond essentially substantiates the possibility of the so-called metastable crystallisation of diamonds from the fluid or gas phase without super-high pressure, postulated by various authors in the formation of natural[73] and synthetic[2,74] diamonds. From the viewpoint of this theory, however, the actual term "metastable crystallisation of diamond" does not correspond to reality, since in it, metastability is defined with respect to the range of thermodynamic stability of diamond in the graphite $\rightleftharpoons$ diamond process, previously assumed to be the only possible route for the formation of diamond. We are dealing, however, with other processes of diamond synthesis with different thermodynamics, having its own ranges of stability of the diamond material under both equilibrium and non-equilibrium conditions.

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