

REVOLUTION IN DIAMOND SYNTHESIS: A unified mechanism of diamond crystallogenesis in nature and in laboratory synthesis. The law of diamond crystallogenesis.

Volodymyr Kaplunenko

"Nanomaterials and Nanotechnologies Ltd",

Ukraine

e-mail: kaplunenkov@gmail.com

Mykola Kosinov

"Nanomaterials and Nanotechnologies Ltd",

Ukraine

e-mail: nkosinov@ukr.net

Abstract. *A recently discovered revolutionary method of diamond synthesis [9], which does not require extreme pressure and temperature, challenges the generally accepted concept of diamond formation and forces it to be revised. A new mechanism of rapid diamond crystal growth is proposed, which can explain this phenomenon. In the new mechanism of diamond synthesis, the main active factor is electrons. We called it the "electronic mechanism of diamond crystallogenesis". The electronic mechanism of diamond synthesis shows that high pressure and temperature are not direct acting factors, they are a trigger that starts the real (electronic) mechanism of diamond synthesis. The electronic mechanism of diamond formation is masked by pressure and temperature and is not manifested explicitly. This has created the illusion that pressure and temperature are the acting factors of diamond formation. The electronic mechanism of diamond crystallogenesis is based on a catalytic process in which catalysis is realized by electrons. Electrons change the oxidation state of carbon, which "switches on" the Coulomb interaction and leads to the launch of the diamond synthesis reaction. A new formulation of diamond formation has been given: "Diamonds are formed from atomic carbon in the low oxidation state $C^{(-4)}$ ". Based on the mechanism of diamond crystallogenesis, the law of diamond crystallogenesis was derived. The basis for new technologies of ultra-fast diamond synthesis are discoveries in the field of catalysis, which fall under the concept of "catalyst-free catalysis". These are Electric-Field Catalysis, the concept of "electron as a catalyst" and overcoming the Sabatier prohibition. These three discoveries in the field of catalysis lead to new technologies of diamond synthesis, capable of greatly accelerating the process of diamond crystal growth. The processes of diamond formation and crystal growth, which in nature last for millions of years, can be implemented in laboratory conditions in a few hours.*

Keywords: *diamond synthesis, law of diamond crystallogenesis, catalyst-free catalysis, "electron as a catalyst" concept, oxidation degree concept, new paradigm of catalysis.*

1. Introduction

It takes nature a very long time to synthesize diamonds. This process takes millions (billions) of years. Natural diamonds are formed in the molten rock of the Earth's mantle, at a depth of 150 - 200 kilometers, where high pressure and temperature allow carbon to crystallize into diamond form. Kimberlite pipes serve as channels that bring diamonds to the surface. Diamonds are formed by the interaction of carbon-containing fluids or melts with surrounding mantle rocks.

In geology, a fluid is any liquid or gaseous medium that fills the pores and cracks in rocks. In the case of diamonds, fluids can include water, molten rock, gases, and dissolved components, including carbon.

Laboratory synthesis of diamonds is usually based on recreating the natural conditions of diamond formation in nature, that is, on creating high pressure and temperature. This is how the modern concept of diamond formation explains the genesis of diamonds.

2. What is wrong with the modern concept of diamond formation.

The modern concept of diamond formation is that high pressure and temperature are the direct factors in diamond crystallogensis. This concept faces many contradictions. Diamonds are also found in non-kimberlite rock types. Their formation cannot be explained by crystallization under high temperature and pressure conditions. Some geological data indicate the possibility of diamond crystallization outside the P-T stability region of diamonds [1]. There are still many dark spots in the origin of terrestrial diamonds. A great mystery was the discovery of diamonds in rocks that do not contain high-pressure minerals [2 - 4].

No less mysterious is the formation of natural diamonds as a result of hydrothermal processes. In nature, diamonds are often found in the presence of an aqueous phase. In some methods of laboratory diamond synthesis, water is the active medium. The important role of water in diamond synthesis has been noted in many studies [5 - 8].

Laboratory diamond synthesis has further challenged the correctness of the modern concept of diamond formation. Initially, laboratory diamonds were produced using the high-pressure high-temperature (HPHT) process, which was inspired by the method by which diamonds form on Earth. Now they are produced using chemical vapor deposition (CVD), which has never been observed in nature. The actual mechanism of diamond crystallogensis remains unsolved and a mysterious phenomenon.

Thus, geological and experimental data indicate that diamonds are formed in various physical and chemical conditions and in various geotectonic settings. The generally accepted mechanism of diamond formation, in which high pressure and temperature are considered as direct acting factors, does not explain such a variety of conditions of diamond origin. It is obvious that, together with pressure and temperature, there is an as yet undisclosed mechanism of diamond formation, which is successfully masked by pressure and temperature and is not manifested in an obvious form. This unknown mechanism of diamond formation needs to be deciphered.

3. Revolution in diamond synthesis.

Laboratory methods of diamond synthesis increasingly reveal the inconsistency of the modern concept of diamond formation. A revolutionary ultrafast method for synthesizing diamonds at atmospheric pressure and relatively low temperatures has been developed [9]. The method is based on a liquid metal mixture of gallium with impurities of iron, nickel and silicon. Methane and hydrogen serve as a source of carbon for diamond growth.

Unlike traditional methods, this technology operates at standard atmospheric pressure. The required temperature is significantly lower than the extreme conditions of the HPHT method. It is assumed that silicon in the alloy is necessary for the formation of the diamond lattice structure. It is believed that it promotes the binding of carbon atoms into a specific pyramidal structure characteristic of diamond.

Using this method, diamonds can be grown in 15 minutes, and the complete formation of the diamond film will take several hours. This new method does not require "seed crystals" traditionally used in the HPHT and CVD methods.

What is striking about this revolutionary method of diamond synthesis is that it is a catalytic method. The catalysts are iron, nickel and silicon. Perhaps this is why extreme pressure and temperature gave way to another active factor in the formation of diamonds. The nature of this mysterious factor has yet to be revealed.

This innovative approach could revolutionize diamond production by making it more affordable and efficient. This revolution in technology heralds a revolutionary change in the age-old concept of diamond formation. The record speed of diamond formation and the absence of extreme synthesis conditions call into question the generally accepted concept of diamond formation. A new ultra-fast method for synthesizing diamonds points to the inconsistency of the current concept of diamond formation and the need to revise it.

In the new concept of diamond formation, it is necessary to rethink the role of pressure and temperature. Their role is clearly exaggerated. Instead of pressure and temperature, it is necessary to identify the real active factor of diamond formation.

4. Electrical phenomena accompanying diamond synthesis

Natural diamond synthesis and laboratory methods of diamond synthesis are very different and, at first glance, have no common features. However, they have a common active factor. We believe that the role of the real active factor of diamond formation can be claimed by a factor of electrical nature. The electrical concept of diamond formation is capable of explaining the observed diversity of diamond origin conditions. To identify the general operating factor of electrical nature, we will analyze the conditions under which natural and laboratory diamond synthesis occurs. Below we will show that the electrical factor is invisibly present both in natural synthesis and in all known methods of artificial diamond synthesis. This electrical factor does not manifest itself clearly. It is masked by factors of non-electrical nature. For this reason, it remained unnoticed for a long time.

4.1. Baroelectric effect in diamond synthesis.

In the modern concept of diamond formation, it is generally accepted that pressure plays a decisive role in diamond synthesis. At the same time, the physical effects accompanying extreme pressure are not taken into account. In particular, the pressure gradient leads to the electrification of the substance. This phenomenon is known as the baroelectric effect [10].

The baroelectric effect [10] describes a phenomenon in which an electric field arises in a material due to mechanical stress, in particular, pressure gradients. This effect is caused by the redistribution of charge carriers (electrons) within the material as they move from areas with higher energy to areas with lower energy.

The baroelectric effect occurs in HPHT diamond synthesis. Pressure generates an additional active factor of an electrical nature. This active factor is from the class of fundamental interactions. It is represented by electrons. A transformation of the form "pressure - electrons" occurs. This transformation occurs due to the implementation of the Baro-electric effect.

Thus, both in natural synthesis and in laboratory HPHT synthesis, there is an additional factor - electrons generated under the action of pressure. Electrons claim the role of a direct active factor, instead of pressure. At the same time, pressure as a factor in diamond synthesis is not a direct active factor in diamond crystallogenesis. Pressure acts as a trigger to create an electron-rich environment.

4.2. Thermoelectric effects in diamond synthesis.

In the modern concept of diamond formation, it is generally accepted that temperature plays a decisive role in diamond synthesis. At the same time, the physical effects accompanying extreme temperatures are not taken into account. In particular, the temperature gradient leads to the electrification of matter. These phenomena are known as thermoelectric effects.

Thermoelectric effects (the Edison effect and the Seebeck effect) are an integral part of the diamond synthesis mechanism. This is especially evident in the presence of a catalyst [11–14]. On the surface, on the active centers of the catalyst, when dissimilar substances come into contact, high temperature gradients create conditions for electron transfer. Electrons change the charge state of the reagents, which increases their reactivity. Electrons generated as a result of the Edison and Seebeck effects act as catalysts for diamond synthesis.

Thus, temperature generates an additional active factor of an electrical nature. This active factor is from the class of fundamental interactions. These are fundamental particles - electrons. Electrons are more likely to be a direct active factor than temperature.

Both in natural synthesis and in laboratory HPHT synthesis, there are always additional participants - electrons generated under the influence of temperature. At the same time, temperature is not a direct active factor in diamond crystallogenesis. A transformation of the form “thermal energy – electrons” occurs. This transformation occurs due to the implementation of physical effects – the Edison effect and the Seebeck effect [11–14]. Temperature acts as a trigger to create an electron-rich environment.

4.3. Electrical Phenomena in CVD Diamond Synthesis.

CVD diamond synthesis, or Chemical Vapor Deposition, is a method for growing diamonds in laboratory conditions. The method is based on the layer-by-layer deposition of carbon atoms from the gas phase onto a diamond substrate. Unlike the HPHT method, CVD synthesis does not require extreme pressure. The carbon-containing gas mixture is ionized using microwave radiation, an electric arc, or a laser, forming a plasma. Plasma electrons are able to attach to carbon atoms, affecting their electrical behavior. The attachment of electrons to carbon atoms reduces their oxidation state. This creates conditions for diamond synthesis.

The CVD method is radically different from the HPHT method. If the HPHT method copies natural synthesis, then the CVD method has never been observed in nature. If there is a single undisclosed mechanism of diamond formation, then it should be common to HPHT and CVD. A common feature of HPHT and CVD are the electrical phenomena that accompany these methods of diamond synthesis.

Thus, in CVD synthesis, as in HPHT synthesis, there is also an additional factor of electrical nature - plasma electrons. Microwave radiation, an electric arc, or a laser act as a trigger for creating an electron-rich environment.

4.4. Electrical Phenomena in Detonation Diamond Synthesis

Detonation diamond synthesis is a method for producing diamonds using explosive decomposition of carbon-containing materials. [15, 16]. An explosive mixture containing a carbon source (e.g. graphite or soot) is detonated in a controlled environment. The detonation wave creates extreme pressure and temperature conditions. The detonation wave also creates an electrical double layer characterized by a potential difference. Within the detonation wave are electrons generated by the explosion. This physical phenomenon is called the "detonation electrical effect" [15]. This effect involves internal electrification at the detonation wave front in explosives.

As the detonation wave expands, electron adhesion is observed. Electrons are able to attach to the explosion products, contributing to the electrical behavior. The attachment of electrons to carbon atoms lowers their oxidation state. This triggers the diamond synthesis reaction. In detonation synthesis of diamond, electrons are more likely to play the role of a direct acting factor than pressure and temperature.

Thus, in the detonation synthesis of diamond there is an additional factor of electrical nature. These are electrons generated under the action of the detonation wave. Electrons claim to be a direct

acting factor. At the same time, pressure and temperature in the detonation wave are not direct acting factors of diamond crystallogenesi. The detonation wave generates electrons as a real acting factor of electrical nature. The pressure and temperature in the detonation wave act as a trigger to create an electron-rich environment.

4.5. Electrical phenomena in diamond synthesis using catalysts.

Direct HPHT synthesis of diamond from carbon materials occurs at very high pressures and temperatures. Using catalysts makes it possible to reduce the pressure and temperature parameters. Catalysts are usually used in a liquid state.

A revolutionary method of diamond synthesis [9] uses a liquid metal mixture of gallium with iron, nickel and silicon impurities. This made it possible to synthesize diamond at atmospheric pressure. Such an impressive result makes us look for the real "culprit" who provided the revolutionary breakthrough in diamond synthesis.

Recent discoveries in the field of catalysis [17 - 27] have shown that the real active factor in catalysis is electrons. Catalysts are effective carriers of electrons between reactants, but do not directly participate in the chemical reaction. Electrons change the oxidation states of the reactants, and thus create conditions for a chemical reaction that was impossible with the initial oxidation state of the reactants. Discoveries in the field of catalysis have led to a new paradigm of catalysis based on the concept of "*electron as a catalyst*" [23 - 27].

Thus, discoveries in the field of catalysis show that in the catalytic synthesis of diamond there is also an additional factor of an electrical nature. This additional factor is electrons. In the catalytic synthesis of diamond, electrons also act as a direct acting factor. However, catalysts are not direct acting factors in diamond crystallogenesi. Catalysts act as effective electron carriers.

4.6. Electrons as Catalysts for Diamond Synthesis

All laboratory diamond synthesis technologies show that the diamond synthesis mechanism is electrical in nature and is implemented with the participation of electrons. Electrons act as catalysts for diamond synthesis.

The study of the role of electrons as catalysts for chemical reactions has a long history. Ostwald was the first to draw attention to this [28]. Similar ideas were expressed by L. V. Piszhevsky [29-31]. The mechanism of catalysis, in which an important role is given to the transfer of electrons, was pointed out by S. Z. Roginsky [32]. Later, the idea of the electronic mechanism of catalysis was developed by Hauffe [33], Dowden [34], and Volkenshtein [35].

Currently, many examples of catalytic reactions have accumulated in which electrons act as catalysts [36-42]. A real breakthrough in understanding the role of electrons as catalysts for chemical reactions was the concept of "electron as catalyst" [17 - 21, 43]. Judging by the large number of publications, the development of the concept of "*electron as a catalyst*" is becoming a very promising area of research.

There is every reason to consider electrons as the main active factor in the mechanism of diamond synthesis. In the mechanism of diamond synthesis, pressure and temperature are accompanying factors. Everything indicates that the mechanism of diamond synthesis is based on a fundamental interaction that is realized with the participation of electrons.

5. Electronic Mechanism of Diamond Crystallogenesi

The contradictory modern concept of diamond formation forces us to look for another mechanism to explain the regularities of diamond crystallogenesi. It is necessary to find a single mechanism for diamond crystallogenesi that is realized both in nature and in laboratory synthesis.

It is shown above that the pressure and temperature gradients observed during diamond synthesis cause electrical phenomena. Electrical phenomena are observed not only during HPHT synthesis. They are also present during CVD synthesis, detonation synthesis, and synthesis using catalysts. Electrical phenomena are a common feature of all known methods of laboratory and natural diamond synthesis. The commonality of the electrical nature indicates the existence of a single mechanism for diamond crystallogenesis, realized both in nature and in laboratory synthesis.

We have proposed a new mechanism of diamond synthesis, which has an electrical nature. The new mechanism of diamond synthesis is suitable for explaining both laboratory and natural synthesis. It is realized both in extreme and normal conditions. The main actors in this mechanism of diamond synthesis are electrons. We called it the "*electronic mechanism of diamond crystallogenesis*". Under extreme conditions, the electronic mechanism of diamond formation is masked by pressure and temperature and does not manifest itself explicitly. This created the illusion that pressure and temperature are the active factors of diamond formation. Pressure and temperature masked the real mechanism of diamond synthesis, based on the fundamental interaction, which is realized with the participation of electrons. The basis of the electronic mechanism of diamond crystallogenesis is the catalytic process of diamond formation and crystal growth, in which catalysis is realized by electrons. Electrons act as catalysts for diamond synthesis both in addition to and instead of traditional catalysts. Electrons change the oxidation state of carbon, which leads to the launch of the diamond synthesis reaction.

Natural diamonds grow by this mechanism. Artificial diamonds grow by this mechanism. This is a single unified mechanism of diamond crystallogenesis, existing in nature and in laboratory synthesis. Below we describe the stages of the electronic mechanism of diamond crystallogenesis and show that fundamental electromagnetic interaction is realized in this mechanism of diamond synthesis.

5.1. Stages and participants of the electronic mechanism of diamond crystallogenesis.

Diamond formation is a multi-stage process. In the electronic mechanism of diamond crystallogenesis, the following main stages can be distinguished and their main participants can be designated:

1. The stage of formation of atomic carbon from a diamond precursor.
2. The stage of creating a medium containing electrons. At this stage, a medium containing free electrons is formed from carbon-containing and additional substances under the influence of external influences (pressure, temperature, microwave radiation, electric arc, laser, shock wave, restorers, catalysts, etc.).
3. The stage of changing the oxidation state of carbon. At this stage, under the influence of free electrons of the ionized environment, carbon lowers its oxidation state to C^{-4} . This is facilitated by catalysts, which are additional substances used in the synthesis. This is facilitated by fluids during the synthesis of diamonds in Nature. This is facilitated by reducing substances.
4. The stage of donor-acceptor interaction. At this stage, carbon in the oxidation state of -4 (C^{-4}) participates in donor-acceptor interaction with the surface of the diamond. Under the influence of the Coulomb force, the carbon atom is incorporated into the diamond structure. The Coulomb force is many orders of magnitude greater than any force actually achievable due to pressure.
5. The stage of formation of covalent bonds. At this stage, 4 covalent bonds are formed by the donor-acceptor mechanism. When carbon (C^{-4}) interacts with the diamond surface, the donor-acceptor interaction grows into a covalent bond. As a result, the carbon atom (C^{-4}) is naturally incorporated into the diamond structure.

The main participants in the electronic mechanism of diamond crystallogenesis are electrons and carbon atoms. Pressure, temperature, microwave radiation, electric arc, laser radiation, shock wave, reducing agents, etc. act as triggers for the creation of an environment saturated with electrons. If the electron-rich environment can be created in another way, then extreme pressure and temperature are not needed.

5.2. Lowering the oxidation state of carbon to C⁻⁴

Diamond has an atomic crystal lattice in which carbon atoms are located at the vertices and center of a tetrahedron. Each carbon atom in diamond forms four covalent sigma bonds with neighboring atoms. To realize all four bonds in diamond, four electrons are needed for each additional carbon atom. In this case, carbon will naturally become incorporated into the diamond's crystal structure. For this, carbon must have an oxidation state of -4:



Fig. 1. Change in the oxidation state of carbon (using graphite as an example) under the influence of electrons. C is a carbon atom; C⁻⁴ is a carbon atom in the lowest oxidation state; e is an electron.

Carbon in carbon-containing substances has oxidation states from -4 to +4, depending on the compound. In simple substances such as graphite and diamond, the oxidation state of carbon is 0. In compounds where carbon forms bonds with hydrogen, oxygen and other elements, the oxidation state can be both negative and positive. For example, in methane (CH₄), the oxidation state of carbon is -4, and in carbon dioxide (CO₂), it is +4.

The key stage in the mechanism of diamond formation is the decrease in the oxidation state of carbon to C⁻⁴ under the influence of electrons. Electron addition is a fundamental process that underlies many chemical transformations.

An important condition for the growth of a diamond crystal is the presence of conditions on the diamond surface for donor-acceptor interaction between carbon atoms and the crystal. This creates the conditions for the capture of carbon atoms in a low oxidation state (C⁻⁴) by the acceptor-type diamond surface. Donor-acceptor interaction refers to electromagnetic interaction. It is known that donor-acceptor interaction can develop into a covalent bond formed by the donor-acceptor mechanism.

The number of electrons required to reduce the oxidation state of carbon to C⁻⁴ for various carbon-containing substances depends on the oxidation state of carbon in them (Fig. 2).

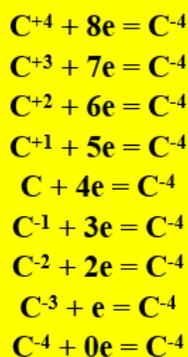


Fig. 2. Change in the oxidation state of carbon under the influence of electrons. C⁺⁴, ..., C⁻⁴ - carbon in carbon-containing substances; C⁻⁴ - carbon atom in the lowest oxidation state; e - electron.

5.3. Step-by-step crystal growth

Diamond in its normal state is an insulator and does not conduct electric current. This is due to the fact that all the electrons in its crystal lattice participate in strong covalent bonds and cannot move freely to transfer an electric charge. In the body of the diamond, all four bonds are involved. On the surface, this condition is not met. On the surface of grown diamonds, a hole accumulation layer is formed [44]. Due to this, acceptor-type surface states are formed [44].

When a carbon atom is attached to a crystal, the surface area becomes a diamond body and a new surface is formed. On the new surface, a hole accumulation layer is formed. Surface states of the acceptor type are formed again. This process is repeated cyclically. Fig. 3 shows a diagram of the step-by-step growth of a crystal and the formation of a diamond with an acceptor-type surface.

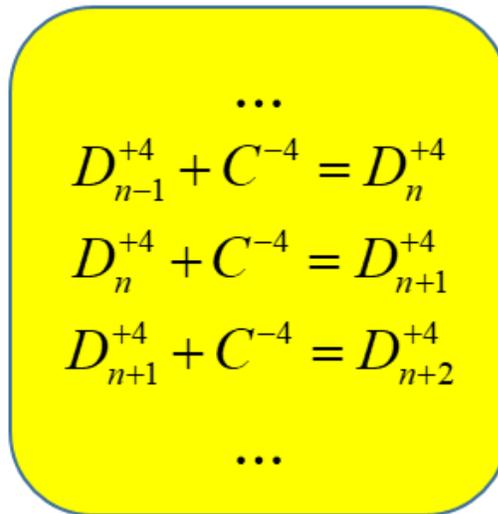


Fig. 3. Step-by-step crystal growth and formation of diamond with an acceptor-type surface. C^{-4} is a carbon atom in a low oxidation state; D_{n-1}^{+4} , D_n^{+4} , D_{n+1}^{+4} , D_{n+2}^{+4} are diamond with an acceptor-type surface at (n-1), n, (n+1), (n+2) steps of crystal growth.

5.4. Scheme of the electron mechanism of diamond crystallogenesis.

The interaction that occurs during the growth of a diamond crystal can be represented by the following chain diagram:

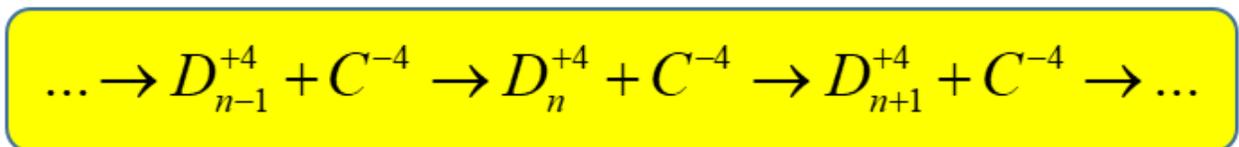


Fig. 4. Scheme of the electronic mechanism of diamond crystallogenesis. C^{-4} is a carbon atom in a low oxidation state; D_{n-1}^{+4} , D_n^{+4} , D_{n+1}^{+4} are diamonds with an acceptor-type surface at (n-1), n, (n+1) crystal growth steps.

Carbon in a low oxidation state (-4), which is an electron donor, and the acceptor-type diamond surface form ideal conditions for the growth of a diamond crystal. In the electronic mechanism of diamond crystallogenesis, donor-acceptor interaction of carbon atoms with the diamond crystal is realized.

The general scheme of the electronic mechanism of diamond crystallogenesis from various carbon-containing substances is shown in Fig. 5.

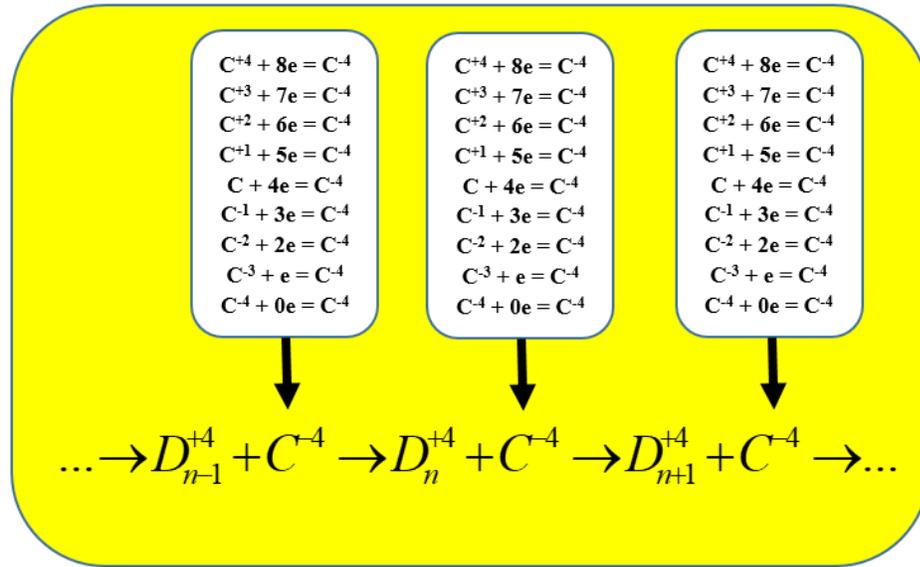


Fig. 5. General diagram of the electron mechanism of diamond crystallogenesis from various carbon-containing substances. C^{+4} -- C^{-4} - oxidation states of carbon; e - electron; D_{n-1}^{+4} , D_n^{+4} , D_{n+1}^{+4} - diamond with an acceptor-type surface at (n-1), n, (n+1) steps of crystal growth.

Thus, the real mechanism of diamond synthesis is electrical in nature. The mechanism of diamond synthesis implements a fundamental interaction that is realized with the participation of electrons. Electrons are the main acting factor in the mechanism of diamond synthesis. The mechanism of diamond crystallogenesis is based on fundamental electromagnetic interaction involving fundamental particles.

Donor-acceptor interaction refers to electromagnetic interaction. It is known that donor-acceptor interaction can develop into a covalent bond formed by the donor-acceptor mechanism.

Thus, in the process of diamond crystal growth, it is not mechanical forces that act, but electrostatic Coulomb forces. The carbon atom C^{-4} interacts electrostatically with the diamond surface. Under the influence of the Coulomb force, the C^{-4} carbon atom is naturally incorporated into the diamond structure. When introducing the carbon atom C^{-4} into the diamond structure, no pressure can compare with the Coulomb force, which is 42 orders of magnitude (!) greater than mechanical forces.

5.5. The Main Secret of Diamond Formation.

The reason why the secret of diamond formation was not revealed for a long time was that electrons were not considered as the main active factor in the crystallogenesis mechanism. For this reason, a very important stage of interaction of electrons with atomic carbon, as the only building material of diamond, was omitted from consideration.

The main secret of diamond formation is in one detail that was little paid attention to: the oxidation state of the carbon atoms that participated in the synthesis of diamond. In diamond precursors, carbon has an oxidation state from -4 to +4, depending on the compound. For unimpeded incorporation into the diamond structure, carbon must be in a low oxidation state of C^{-4} . Carbon can lower its oxidation state to -4 only by adding electrons. Four electrons at a carbon atom in a low oxidation state of C^{-4} provide the formation of 4 covalent bonds when the carbon atom is incorporated into the diamond structure. Covalent bonds are formed by the donor-acceptor mechanism.

Thus, in the mechanism of diamond crystallogenesis there is an important stage of interaction of electrons with atomic carbon. At this stage, the oxidation state of carbon decreases. This occurs under the influence of electrons.

In Fig. 6, using such diamond precursors as CO_2 , CH_4 , $\text{C}_2\text{H}_5\text{OH}$, graphite as an example, the main stages of diamond formation are shown. At the stage of interaction of electrons with atomic carbon, the oxidation state of carbon decreases to C^{-4} . Carbon dioxide requires 8 electrons per carbon atom. Alcohol requires 1 electron per carbon atom. Graphite requires 4 electrons per carbon atom.

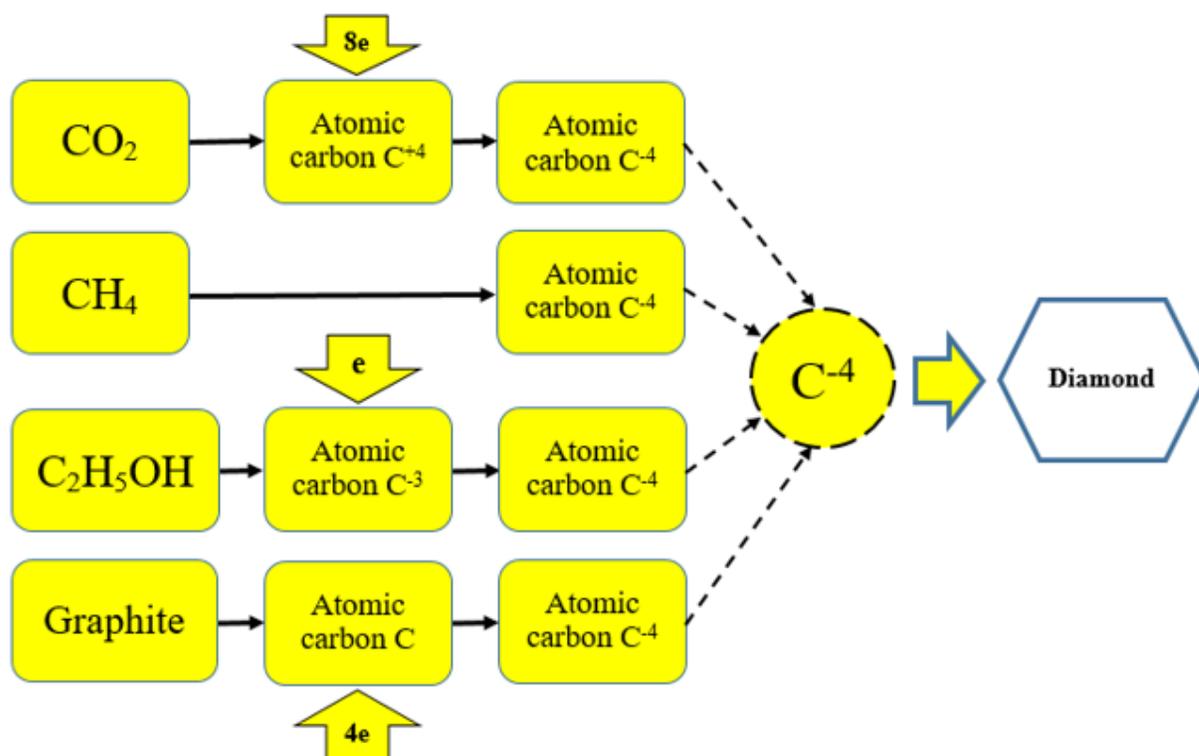


Fig. 6. The path from a carbon-containing substance to a diamond lies through atomic carbon in the oxidation state -4. C^{-4} is atomic carbon in the oxidation state -4; e is an electron

The electronic mechanism of diamond crystallogenesis shows that the path from a carbon-containing substance to diamond always goes through atomic carbon in the oxidation state of -4 (Fig. 6). The building material of diamond is carbon in the low oxidation state of C^{-4} . The low oxidation state of carbon C^{-4} creates ideal conditions for the incorporation of carbon atoms into the diamond structure.

Regardless of the diamond precursors, diamond formation follows the following path: precursor \rightarrow atomic carbon \rightarrow carbon C^{-4} \rightarrow diamond (Fig. 7).

Precursor \rightarrow Atomic carbon \rightarrow Carbon C^{-4} \rightarrow Diamond

Fig. 7. The path of diamond formation: from precursors to diamond.

The electronic mechanism of diamond crystallogenesis forces us to radically change the generally accepted concept of diamond formation. Both the conditions of diamond formation and the factors involved, as well as the main participants in the synthesis, are subject to revision. Instead of

the well-known formulation: “*Diamonds are formed from carbon*”, we give a new formulation (Fig. 8):

**"Diamonds are formed from atomic carbon
in the low oxidation state C⁻⁴"**

Fig. 8. New formulation of diamond formation.

The formulation "*Diamonds are formed from atomic carbon in the low oxidation state C⁻⁴*" reveals the main secret of diamond formation. The new formulation follows from the electronic mechanism of diamond crystallogenesis and brings to the forefront electrons and atomic carbon as the main participants in the diamond formation process.

6. Law of diamond crystallogenesis

For diamond crystallogenesis as a fundamental physical process, there is a physical law describing it. We present this law. The physical law of diamond crystallogenesis follows from the mechanism of diamond crystallogenesis based on the donor-acceptor interaction of carbon atoms C⁻⁴ with the diamond surface. The law of diamond crystallogenesis includes fundamental physical constants characterizing the participants in the process. The law of diamond crystallogenesis looks like this:

$$v_D = \frac{e \cdot M_e}{F \cdot t \cdot (q_C - q_{C_{\min}})}$$

Fig. 9. The law of diamond crystallogenesis. v_D is the rate of diamond formation (mol/s); e is the elementary charge; M_e is the number of free electrons participating in the synthesis; F is the Faraday constant; q_C is the oxidation state of carbon; $q_{C_{\min}}$ is the minimum oxidation state of carbon; t is the time of diamond synthesis.

6.1. Electron parameters in the diamond crystallogenesis law

The main actor in the mechanism of diamond formation is the electron. It is present in the formula of the law of diamond crystallogenesis in the form of a fundamental physical constant: the elementary charge e . From the law of diamond crystallogenesis it follows that the growth rate of diamond is proportional to the number of free electrons M_e . The law of diamond crystallogenesis includes the oxidation states of carbon q_C and $q_{C_{\min}}$. The key stage in the mechanism of diamond formation is the decrease in the oxidation state of carbon in a carbon-containing material to C⁻⁴ under the action of electrons.

6.2. Faraday constant in the law of diamond crystallogenesis

The law of diamond crystallogenesis (Fig. 9) includes the Faraday constant ($F = 9.64853321233100184 \times 10^4$ C/mol). This fundamental constant is a physicochemical constant. It is a connecting constant between physical and chemical quantities: the electron charge and the Avogadro number. It is known that the Faraday constant is included in the Nernst equation, the Goldman

equation, and Faraday's law of electrolysis. Now the Faraday constant has identified itself in the law of diamond crystallogenesis.

6.3. Carbon oxidation states in the diamond crystallogenesis law.

The law of diamond crystallogenesis indicates the key role of the oxidation state of carbon in the synthesis of diamond. It follows from the law of diamond crystallogenesis that the highest rate of diamond growth is achieved when using carbon-containing substances in which the degree of carbon oxidation is minimal. This is observed in practice when using methane (CH_4) as a diamond-forming gas.

An unusual feature of the diamond crystallogenesis law is the inclusion of the oxidation state of carbon in the formula of the law. Oxidation states are chemical characteristics of substances. Their presence in a physical law is an unusual phenomenon, since oxidation states are usually used in chemistry to describe the reactivity of substances. In our case, the oxidation state is included in the physical law as a parameter along with the fundamental physical constants.

In chemistry, the oxidation state is not a fundamental parameter. It is considered an auxiliary conventional quantity showing the conventional charge of an atom in a compound. The oxidation state is considered useful for understanding oxidation-reduction reactions. The oxidation state helps classify chemical substances and describe their properties. But nothing more.

The presence of oxidation states of carbon in the law of diamond crystallogenesis along with fundamental physical constants indicates the fundamental status of this parameter. The direct connection of the oxidation state with the reactivity of substances forces us to reconsider its status in chemistry. This is not just an auxiliary value, it is the most important characteristic of the reactivity of substances. The change in the oxidation state and its role in the fundamental electromagnetic interaction forces us to consider it as a fundamental parameter in physics. This is not just a conventional value, it is a parameter associated with the strength of electromagnetic interaction.

7. Diamond formation as a physicochemical process based on fundamental physical interaction.

The formulation: "Diamonds are formed from carbon" is too simplified. Diamond formation is a multi-stage physical and chemical process. In the mechanism of diamond crystallogenesis, both physical and chemical stages are intertwined. This is not a chemical reaction in the usual sense, since there is no change in the chemical composition of substances. There is a chemical stage in which the oxidation state of carbon changes to C^{-4} . It is preparatory. The stage of formation of the diamond crystal lattice by "prepared" carbon atoms C^{-4} is a physical process based on fundamental electromagnetic interaction.

Equally too simplified is the hypothesis of diamond formation by transforming the crystalline structure of graphite into the crystalline structure of diamond under high temperature and high pressure. This hypothesis does not take into account the most important chemical and physical stages of diamond formation based on fundamental electromagnetic interaction.

Using graphite as a precursor to diamond as an example, it is clear that the statement about the transformation of graphite into diamond by changing the structure of graphite and transforming the structure of graphite into the structure of diamond is erroneous. The electronic mechanism of diamond crystallogenesis shows that there is no direct transition from the graphite crystal structure to the diamond crystal structure. Instead of transforming the graphite crystal structure into the diamond crystal structure, a complete "disassembly" of the previous graphite structure to atomic carbon occurs. After this, the oxidation state of carbon changes to C^{-4} , and finally, the diamond structure is "assembled" from carbon atoms with a changed charge. There is no direct transformation of the graphite crystal lattice into the diamond crystal lattice.

A similar "disassembly" of the precursor to atomic carbon and subsequent "assembly" of diamond from carbon atoms is also characteristic of other diamond precursors. Regardless of the diamond precursors, diamond formation occurs along the following path: precursor \rightarrow atomic carbon \rightarrow carbon $C^{-4} \rightarrow$ diamond. Regardless of the diamond precursors, diamond formation occurs through the stages of precursor "disassembly" and the formation of the diamond crystal lattice from carbon C^{-4} atoms. At the stage of diamond crystal lattice formation, a physical process based on fundamental electromagnetic interaction is realized.

8. The role and place of catalysis in diamond synthesis

Since the electron mechanism of diamond crystallogenesis demonstrates all the signs of a catalytic process, modern achievements in the field of catalysis become useful for technologies of ultrafast diamond synthesis. These are new developments in the field of catalysis, which fall under the concept of "*catalyst-free catalysis*". This is Electric-Field Catalysis [45 - 59], the concept of "*electron as a catalyst*" [17 - 21] and overcoming the Sabatier ban [66]. These discoveries in the field of catalysis can become the basis for new technologies of ultrafast diamond synthesis. They confirm the key role of electrons in diamond synthesis. These three discoveries in the field of catalysis lead to new technologies of diamond synthesis, capable of greatly accelerating the process of diamond crystal growth.

8.1. Electric-Field Catalysis in Diamond Synthesis

The practice of catalysis shows that the diversity of catalysts is not limited to material catalysts. A catalyst can also be an immaterial object - a field. There have been studies in which the electric field is considered as a catalyst for chemical reactions [45 - 59]. The electric field is classified as a reagent and is called a "smart reagent" [60]. Recently, the number of works in which the role of electric fields in catalysis is studied has increased dramatically [61 - 65]. The electric field can be considered as a tool for controlling electrons in ultrafast diamond synthesis technologies.

8.2. Sabatier principle in diamond synthesis

There is a limit on the activity of the catalyst and the rate of catalysis, which sets the upper limit of the catalyst efficiency and the upper limit of the reaction rate. Catalysts that satisfy the Sabatier principle are effective [66]. Due to the catalyst, the reaction is accelerated, but it cannot proceed faster than allowed by the Sabatier principle.

For almost 100 years, the Sabatier principle was considered inviolable. Recently, the results of studies have been published [67, 68], in which the Sabatier maximum, which limits the rate of a chemical reaction, was exceeded for the first time by several orders of magnitude. This discovery became possible under conditions of a special external effect on the catalyst, in which the catalyst passes from a static state to a dynamic state. Activation of the catalyst, its transfer to a dynamic state, can be carried out by pulses of electric current, or pulsed lighting, or other pulsed energy effects [67, 68]. When the frequency of the external pulsed effect on the catalyst corresponds to the frequency of the chemical reaction, the reaction rate increases sharply due to catalytic resonance [67, 68].

Since diamond synthesis is a catalytic process involving electrons, the Sabatier principle applies to it. Using external influence, the Sabatier maximum can be overcome. Electrons are easily controlled by an external electric field. This opens up new possibilities for increasing the rate of diamond formation above the Sabatier maximum.

9. Conclusion

The current concept of diamond formation is clearly outdated and is becoming a brake on new diamond synthesis technologies. Both geological data and laboratory diamond synthesis indicate the possibility of diamond crystallization outside the P–T stability region of diamonds. Here we show that neither pressure nor temperature are direct acting factors in diamond formation.

We presented a new concept of diamond formation based on the fundamental electromagnetic interaction involving electrons. The law of diamond crystallogenesis is presented. A universal electronic mechanism of diamond crystallogenesis is revealed, suitable for explaining both laboratory and natural synthesis.

In the electronic mechanism of diamond crystallogenesis, a fundamental electromagnetic interaction is realized. Electrostatic Coulomb forces act during the growth of a diamond crystal. When a carbon atom is embedded in a diamond structure, no pressure can compare with the Coulomb force, which is 42 orders of magnitude (!) greater than mechanical forces.

The electronic mechanism of diamond crystallogenesis shows all the signs of a catalytic process in which electrons act as a catalyst. Electron catalysis of diamond formation opens the way to new ultra-fast diamond synthesis technologies that do not require extreme pressure and temperature. The processes of diamond formation and crystal growth, which in nature last for millions of years, can be implemented in laboratory conditions in a few hours.

The main secret of diamond formation is in one detail that has received little attention: the oxidation state of the carbon atoms that participated in the synthesis of diamond. In order for a diamond to form from carbon, carbon must be in a low oxidation state of C^{-4} . Then 4 electrons provide the formation of 4 covalent bonds when the carbon atom is incorporated into the diamond structure. Instead of the simplified formulation: “*Diamonds are formed from carbon,*” we give a complete formulation of diamond formation: “*Diamonds are formed from atomic carbon in the low oxidation state C^{-4} .*”

10. Conclusions

1. The generally accepted mechanism of diamond formation, in which high pressure and temperature are considered as direct factors in the formation of diamond from carbon, does not explain the diversity of conditions of diamond origin.

2. Pressure is not a direct factor in diamond crystallogenesis in either natural or laboratory synthesis. The pressure acts as a trigger that starts the electronic mechanism for diamond synthesis.

3. Temperature is not a direct factor in diamond crystallogenesis in either natural or laboratory synthesis. Temperature acts as a trigger that starts the electronic mechanism of diamond synthesis.

4. Catalysts are not direct factors in diamond crystallogenesis in laboratory synthesis. Catalysts provide efficient electron transfer in the electron mechanism of diamond crystallogenesis.

5. The real mechanism of diamond synthesis is of electrical nature. The mechanism of diamond synthesis implements a fundamental interaction that is realized with the participation of electrons. Electrons are the main active factor in the mechanism of diamond synthesis in all synthesis methods. Diamond formation is a physicochemical process based on a fundamental physical interaction.

6. The law of diamond crystallogenesis has been discovered. The law of diamond crystallogenesis includes fundamental physical and chemical constants.

7. The processes of diamond formation in nature and in artificial synthesis are of the same type. Both in nature and in artificial synthesis, a single electronic mechanism of diamond crystallogenesis is realized.

8. The universal electronic mechanism of diamond crystallogenesis includes the following stages: the stage of electron generation, the stage of changing the oxidation state of carbon, the stage of donor-acceptor interaction, the stage of formation of covalent bonds.

9. The key stages in the diamond formation mechanism are: the generation of electrons and the reduction of the oxidation state of carbon to C^{-4} under the action of electrons. This creates the conditions for the initiation of the diamond synthesis reaction.

10. The formulation that reveals the main secret of diamond formation is this: "*Diamonds are formed from atomic carbon in the low oxidation state C^{-4} .*"

11. Regardless of the diamond precursors, diamond formation occurs along the following path: precursor \rightarrow atomic carbon \rightarrow carbon C^{-4} \rightarrow diamond.

12. The electron mechanism of diamond crystallogenesis shows all the signs of a catalytic process in which the catalyst is electrons. Modern achievements in the field of catalysis are becoming useful for technologies of ultrafast diamond synthesis.

13. The processes of diamond formation and crystal growth, which in nature last for millions of years, can be implemented in laboratory conditions in a few hours.

References.

1. Kaminsky, F.V., Voropaev, S.A. Modern Concepts on Diamond Genesis. *Geochem. Int.* 59, 1038–1051 (2021). <https://doi.org/10.1134/S0016702921110033>
2. Farre-de-Pablo J., Proenza J.A., Gonzalez-Jimenez J.M. et al. A shallow origin for diamonds in ophiolitic chromitites // *Geology*. 2018. Vol. 47. № 1. P. 75-78. DOI: 10.1130/G45640.1
3. Pujol-Sola N., Garcia-Casco A., Proenza J.A. et al. Diamond forms during low pressure serpentinisation of oceanic lithosphere // *Geochemical Perspective Letters*. 2020. Vol. 15. P. 19-24. DOI: 10.7185/geochemlet.2029
4. Simakov S.K., Kouchi A., Mel'nik N.N. et al. Nanodiamond finding in the Hyblean shallow mantle xenoliths // *Scientific Reports*. 2015. Vol. 5. № 10765. DOI: 10.1038/srep10765
5. Israeli E.S., Harris J.W., Navon O. Brine inclusions in diamonds: a new upper mantle fluid // *Earth Plan. Sci. Lett.* 2001. V. 187. P.323–332.
6. Szymanski A., Abgarowicz E., Bakon A., Niedbalska A., Salacinski R., Sentek J. Diamond formed at low pressures and temperatures through liquid-phase hydrothermal synthesis // *Diam. Relat. Mater.* 1995. V. 4. P.234–235.
7. Wehley P.A., Tester J.W. Fundamental Kinetics of Methanol Oxidation in Supercritical Water // *Amer. Chem. Soc. Symp. Ser.* 1989. V. 406. P.259–275.
8. DeVries, R. Diamonds from warm water. *Nature* 385, 485 (1997). <https://doi.org/10.1038/385485a0>
9. Gong, Y., Luo, D., Choe, M. et al. Growth of diamond in liquid metal at 1 atm pressure. *Nature* 629, 348–354 (2024). <https://doi.org/10.1038/s41586-024-07339-7>
10. Baro-electric effect and celestial magnetism. Grigor'eva E.V., Grigoriev V.I., Pisanko Y.V., Rostovsky V.S. ISBN: 5-484-00212-5.
11. Achour A, Liu J, Peng P, Shaw C & Huang Z (2018) In-situ tuning of catalytic activity by thermoelectric effect for ethylene oxidation, *ACS Catalysis*, 8 (11) 10164-10172.
12. Achour A, Chen K, Reece MJ & Huang Z (2018) Enhanced thermoelectric performance of Cs doped BiCuSeO prepared through eco-friendly flux synthesis, *Journal of Alloys and Compounds*, 735 (February) 861-869.
13. Achour A, Chen K, Reece MJ & Huang Z (2018) Tuning of catalytic activity by thermoelectric materials for carbon dioxide hydrogenation, *Advanced Energy Materials*, 8 (5) Article No. 1701430.
14. Gallagher, J. Thermoelectric avenue. *Nat Energy* 2, 834 (2017). <https://doi.org/10.1038/s41560-017-0040-9>.
15. Bernard Hayes. The Detonation Electric Effect . *J. Appl. Phys.* 38, 507–511 (1967). <https://doi.org/10.1063/1.1709365>

16. Bernard Hayes, Electrical measurements in reaction zones of high explosives, Symposium (International) on Combustion, Volume 10, Issue 1, 1965, Pages 869-874, ISSN 0082-0784, [https://doi.org/10.1016/S0082-0784\(65\)80231-4](https://doi.org/10.1016/S0082-0784(65)80231-4).
(<https://www.sciencedirect.com/science/article/pii/S0082078465802314>)
17. Davis, D.; Vysotskiy, V.P.; Sajeev, Y.; Cederbaum, L.S. Electron Impact Catalytic Dissociation: Two-Bond Breaking by a Low-Energy Catalytic Electron. *Angew. Chem. Int. Ed.* 2011, 50, 4119–4122. <https://doi.org/10.1002/ange.20100512910>.
18. Studer, A., Curran, D. The electron is a catalyst. *Nature Chem* 6, 765–773 (2014)
19. Jiao, Y., Qiu, Y., Zhang, L. et al. Electron-catalysed molecular recognition. *Nature* 603, 265–270 (2022). <https://doi.org/10.1038/s41586-021-04377-3>
20. Julius Gemen, Rafal Klajn. Electron catalysis expands the supramolecular chemist's toolbox. May 2022. *Chem* 8(5):1183-1186. DOI: 10.1016/j.chempr.2022.04.022
21. Low energy electron catalyst: the electronic origin of catalytic strategies. [Daly Davis](#) and [Y. Sajeev](#). *Phys. Chem. Chem. Phys.*, 2016,18, 27715-27720. DOI <https://doi.org/10.1039/C6CP05480C>
22. Francke, R.; Little, R. D. "Electrons and Holes as Catalysts in Organic Electrosynthesis", *ChemElectroChem*, 2019, 6, 4373-4382 [<https://doi.org/10.1002/celec.201900432>]
23. Volodymyr Kaplunenko, Mykola Kosinov. Changing the paradigm of catalysis: breaking stereotypes. November 2022. DOI: [10.51582/interconf.19-20.11.2022.027](https://doi.org/10.51582/interconf.19-20.11.2022.027)
24. Volodymyr Kaplunenko, Mykola Kosinov. THE CONCEPT OF ELECTRON AS A CATALYST IS THE KEY TO UNLOCKING THE SECRETS OF CATALYSIS. January 2023. DOI: [10.13140/RG.2.2.22445.97760](https://doi.org/10.13140/RG.2.2.22445.97760)
25. Volodymyr Kaplunenko, Mykola Kosinov. FROM THE "ELECTRON AS A CATALYST" CONCEPT TO A NEW PARADIGM OF CATALYSIS. December 2022, DOI: [10.13140/RG.2.2.29232.64008](https://doi.org/10.13140/RG.2.2.29232.64008)
26. Volodymyr Kaplunenko, Mykola Kosinov. FROM THE "ELECTRON AS A CATALYST" CONCEPT TO THE LAWS OF CATALYSIS. DOI: [10.13140/RG.2.2.16467.86567](https://doi.org/10.13140/RG.2.2.16467.86567)
27. Volodymyr Kaplunenko, Mykola Kosinov. (2022). From the concept of "Electron as a catalyst" to a single mechanism of catalytic reactions. *Scientific Collection «InterConf+»*, 28(137), 339–357. <https://doi.org/10.51582/interconf.19-20.12.2022.036>
28. W. Ostwald, *Science of Colloids, Electrical Engineering, Heterogeneous Catalysis*, §9-10, 1932.
29. Pisarzhevsky L.V. Selected Works. Ed. Academy of Sciences of the Ukrainian SSR, 1936.
30. L. V. Pisarzhevsky, On the Theory of Heterogeneous Catalysis, *Bulletin of the Academy of Sciences of the USSR. VII series. Department of Mathematical and Natural Sciences*, 1933, Issue 4, 571–588
31. L.V. Pisarzhevsky and M.A. Rozenberg, *Inorganic Chemistry*, pp. 521-529, 1933.
32. Roginsky S.Z. Problems of kinetics and catalysis, VI, 10 (1949).
33. Hauff K. *Advances in Catalysis*.— 1957.— V. 9.— P. 187—203.
34. D. A. Dowden. *J. Chem. Soc.*, 1950, 242.
35. Volkenshtein, F. F. *The Electronic Theory of Catalysis on Semiconductors*. Pergamon Press, 1963.
36. Ryan Hawtof, Souvik Ghosh, Evan Guarr, Cheyan Xu, R. Mohan Sankaran, Julie Nicole Renner. Catalyst-free, highly selective synthesis of ammonia from nitrogen and water by a plasma electrolytic system // *Science Advances*. 2019. V. 5. eaat5778. DOI: 10.1126/sciadv.aat5778.
37. US Patent Application 20190292063. AMMONIA SYNTHESIS USING PLASMA-PRODUCED ELECTRONS. MIIK C01C 1/04; C25B 1/04; C25B 11/02; C25B 11/04. 09/26/2019.)

38. Rumbach, P., Bartels, D., Sankaran, R. et al. The solvation of electrons by an atmospheric-pressure plasma. *Nat Commun* 6, 7248 (2015). <https://doi.org/10.1038/ncomms8248>
39. Zhu, D., Zhang, L., Ruther, R. et al. Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction. *Nature Mater* 12, 836–841 (2013). <https://doi.org/10.1038/nmat3696>
40. Fast and Simple Evaluation of the Catalysis and Selectivity Induced by External Electric Fields. Pau Besalu-Sala, Miquel Sola, Josep M. Luis, and Miquel Torrent-Sucarrat. *ACS Catal.* 2021, 11, 14467–14479. <https://doi.org/10.1021/acscatal.1c04247>.
41. E. J. Hart und M. Anbar: *The Hydrated Electron*. Wiley-Inter-science, New York 1970. 267 Seiten. .)
42. Pau Besalu-Sala, Miquel Sola, Josep M. Luis, and Miquel Torrent-Sucarrat. Fast and Simple Evaluation of the Catalysis and Selectivity Induced by External Electric Fields. *ACS Catal.* 2021, 11, 14467–14479. <https://doi.org/10.1021/acscatal.1c04247>.
43. Lennart Ebersson, Catalysis by electron transfer in organic chemistry, *Journal of Molecular Catalysis*, Volume 20, Issue 1, 1983, Pages 27-52, ISSN 0304-5102 [https://doi.org/10.1016/0304-5102\(83\)83012-09](https://doi.org/10.1016/0304-5102(83)83012-09).
44. Junji Shirafuji, Takashi Sugino, Electrical properties of diamond surfaces, *Diamond and Related Materials*, Volume 5, Issues 6–8, 1996, Pages 706-713, ISSN 0925-9635, [https://doi.org/10.1016/0925-9635\(95\)00415-7](https://doi.org/10.1016/0925-9635(95)00415-7).
(<https://www.sciencedirect.com/science/article/pii/0925963595004157>)
45. Andrés, J. L.; Lledós, A.; Duran, M.; Bertrán, J. Electric Fields Acting as Catalysts in Chemical Reactions. An ab Initio Study of the Walden Inversion Reaction. *Chem. Phys. Lett.* 1988, 153, 82– 86. [https://doi.org/10.1016/0009-2614\(88\)80136-2](https://doi.org/10.1016/0009-2614(88)80136-2)
46. Carbonell, E.; Duran, M.; Lledós, A.; Bertrán, J. Catalysis of Friedel-Crafts Reactions by Electric Fields. *J. Phys. Chem. A* 1991, 95, 179–183. <https://doi.org/10.1021/j100154a036>
47. Giovanni Camera-Roda, Carlos A. Martin. Design of photocatalytic reactors made easy by considering the photons as immaterial reactants. *Solar Energy*. Volume 79, Issue 4, October 2005, Pages 343-352. <https://doi.org/10.1016/j.solener.2005.02.025>
48. Janhavi Dere Effect of an external electric field on the oxidation of CO to CO₂ on a nickel oxide catalyst December 1974 *Journal of Catalysis* 35(3):369-375 DOI: [10.1016/0021-9517\(74\)90219-X](https://doi.org/10.1016/0021-9517(74)90219-X)
49. Hidefumi Hiura, Atef Shalabney, Jino George. Vacuum-Field Catalysis: Accelerated Reactions by Vibrational Ultra Strong Coupling. 26.05.2021. DOI: [10.26434/chemrxiv.7234721.v4](https://doi.org/10.26434/chemrxiv.7234721.v4)
50. Hidefumi Hiura and Atef Shalabney. A Reaction Kinetic Model for Vacuum-Field Catalysis Based on Vibrational LightMatter Coupling. 07.08.2019. DOI: [10.26434/chemrxiv.9275777](https://doi.org/10.26434/chemrxiv.9275777)
51. Stoukides, M.; Vayenas, C. G. The Effect of Electrochemical Oxygen Pumping on the Rate and Selectivity of Ethylene Oxidation on Polycrystalline Silver. *J. Catal.* 1981, 70 (1), 137– 146, DOI: 10.1016/0021-9517(81)90323-7
52. Thejas S. Wesley, Yuriy Román-Leshkov and Yogesh Surendranath. Spontaneous Electric Fields Play a Key Role in Thermochemical Catalysis at Metal–Liquid Interfaces. *ACS Cent. Sci.* 2021, 7, 6, 1045–1055. Publication Date: June 2, 2021. <https://doi.org/10.1021/acscentsci.1c00293>)
53. Vayenas, C. G.; Bebelis, S.; Ladas, S. Dependence of Catalytic Rates on Catalyst Work Function. *Nature* 1990, 343, 625– 627, DOI: 10.1038/343625a0
54. Warburton, R. E.; Hutchison, P.; Jackson, M. N.; Pegis, M. L.; Surendranath, Y.; Hammes-Schiffer, S. Interfacial Field-Driven Proton-Coupled Electron Transfer at Graphite-Conjugated Organic Acids. *J. Am. Chem. Soc.* 2020, 142 (49), 20855– 20864, DOI: 10.1021/jacs.0c10632

55. Shaik, S.; Danovich, D.; Joy, J.; Wang, Z.; Stuyver, T. Electric-Field Mediated Chemistry: Uncovering and Exploiting the Potential of (Oriented) Electric Fields to Exert Chemical Catalysis and Reaction Control. *J. Am. Chem. Soc.* 2020, *142* (29), 12551– 12562, DOI: 10.1021/jacs.0c05128
56. Bockris, J. O.; Reddy, A.; Gamboa-Aldeco, M. *Modern Electrochemistry 2A: Fundamentals of Electrodics*, 2nd ed.; Springer: Boston, MA, 2000.
57. Nadia G. Léonard, Rakia Dhaoui, Teera Chantarojsiri, Jenny Y. Yang. Electric Fields in Catalysis: From Enzymes to Molecular Catalysts. *ACS Catal.* 2021, *11*, 17, 10923–10932. <https://doi.org/10.1021/acscatal.1c02084>.
58. Neophytides, S. G.; Tsiplakides, D.; Stonehart, P.; Jaksic, M. M.; Vayenas, C. G. Electrochemical Enhancement of a Catalytic Reaction in Aqueous Solution. *Nature* 1994, *370*, 45– 47, DOI: 10.1038/370045a0
59. Yuri N. Palyanov et al. Diamond formation in an electric field under deep Earth conditions. *Sci. Adv.* 2021, *7*, eabb4644(2021). DOI: 10.1126/sciadv.abb4644
60. Shaik, S.; Mandal, D.; Ramanan, R. Oriented Electric Fields as Future Smart Reagents in Chemistry. *Nat. Chem.* 2016, *8* (12), 1091– 1098, DOI: 10.1038/nchem.2651
61. Song Yu, Pascal Vermeeren, Trevor A Hamlin, F Matthias Bickelhaupt. How Oriented External Electric Fields Modulate Reactivity. *Chemistry*. 2021 Mar 26;27(18):5683-5693. doi: 10.1002/chem.202004906. Epub 2021 Jan 21.
62. H Hiura, A Shalabney and J George, ChemRxiv, 2018, DOI: 10.26434/chemrxiv.7234721.v4
63. A Thomas et al, *Science*, 2019, *363*, 615 (DOI: 10.1126/science.aau7742)
64. K Hirai et al, *Angew. Chem. Int. Ed.*, 2020, *59*, 5332 (DOI: 10.1002/anie.201915632)
65. Volodymyr Kaplunenko, Mykola Kosinov. Electric field - induced catalysis. Laws of field catalysis. DOI: [10.51582/interconf.19-20.10.2022.037](https://doi.org/10.51582/interconf.19-20.10.2022.037)
66. P. Sabatier, *La catalyse en chimie organique*, Librairie Polytechnique, Paris et Liège, 1920.
67. M. Alexander Ardagh, Omar A. Abdelrahman, and Paul J. Dauenhauer. Principles of Dynamic Heterogeneous Catalysis: Surface Resonance and Turnover Frequency Response. *ACS Catalysis*, 2019, *9* (8), 6929-6937. DOI: 10.1021/acscatal.9b01606
68. M. Alexander Ardagh, et. al. Catalytic resonance theory: superVolcanoes, catalytic molecular pumps, and oscillatory steady state. *Catalysis Science & Technology* 2019, *9* (18), 5058-5076. <https://doi.org/10.1039/C9CY01543D>