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## **THE CONCEPT OF "ELECTRON AS A CATALYST" IS THE KEY TO UNLOCKING THE SECRETS OF CATALYSIS**

***Abstract.** The discovery of electron and electric field catalysis led to the need to clarify and change the basic postulates of catalysis. The emergence of the "electron as a catalyst" concept revealed the contradictions of the current catalysis paradigm. The concept made it possible to formulate a new paradigm of catalysis. The article focuses on the most important aspects of the new paradigm of catalysis. The features of the general mechanism of catalytic reactions are considered. The origin of the laws of catalysis from the mechanisms of catalysis has been considered. In the model of the unified mechanism of catalysis, the stages of fundamental interaction and the stage of chemical interaction of the participants are distinguished. At the stage of fundamental interaction, the redox cycle of catalysis is realized. At this stage, there is an increase in the reactivity of the reagents. From the mechanisms of catalysis, the laws of catalysis as a function of the substance characteristics of the participants of the catalytic reaction are derived.*

***Key words:** redox cycle, the concept of "electron as a catalyst", the concept of two fundamental catalysts, the concept of the oxidation state, the relay donor-acceptor mechanism of catalysis, the laws of catalysis, the universal law of catalysis, the new paradigm of catalysis.*

### **1. Introduction**

The emergence of the concept of "electron as a catalyst" was a revolutionary event in catalysis. Against the background of unsuccessful attempts to create a general theory of catalysis, the concept of "electron as a catalyst" becomes the most fruitful. It has uncovered the contradictions of catalysis. It can lead to a radical revision of the existing paradigm of catalysis and provide answers to many unsolved problems of catalysis.

Ostwald and Pisarzhevsky were at the origin of this concept [1, 2]. The assumption that electrons take part in catalytic processes was made by Ostwald 90 years ago [1]. Ostwald drew attention to the fact that good catalysts are good conductors of electricity and easily give up electrons from their surface. Those catalysts that have the property of electron emission show high catalytic activity [1]. Similar ideas about the role of electrons in catalysis were expressed about 85 years ago by Pisarzhevsky [3, 4]. Pisarzhevsky stated: "the effect of the catalyst-platinum on oxygen molecules proves that the free electrons of the metal-catalyst take part in catalysis" [2]. The electrical mechanism of catalysis was pointed out by Berzellius long before the discovery of the electron [5, 6]: "the catalytic force must consist in some influence on the polarity of the atoms which it increases, decreases or changes so that in fact it is based on the excitation of electrical relations. These electrical relationships

have so far eluded our research". Roginsky pointed out the mechanism of catalysis, in which electron transfer plays an important role [7]. The idea of the electronic mechanism of catalysis was developed by Dowden [8], Hauff [9, 10], Volkenshtein [11]. The interest in studying the role of electrons in catalysis was so strong that attempts were even made to create an electronic theory of catalysis [8 - 12]. These attempts were unsuccessful. They did not lead to the emergence of a completed theory, nor did they reveal the general mechanism of catalysis, nor did they lead to the discovery of the laws of catalysis. Despite such great attention to the role of the electron in catalysis, in the works mentioned above, the electron was not considered to be a catalyst. It was given an auxiliary role in catalysis. This can explain the failure in the creation of the electron theory of catalysis.

A real breakthrough in the science of catalysis was the appearance of a series of articles in which the electron was defined as a catalyst [13-25]. Recently, electronic catalysis has become an independent field of research [14 - 25, 26 - 30]. Judging by the large number of publications, electron catalysis is becoming a rapidly developing area in catalysis. Recent advances in electron catalysis show the high potential and versatility of this strategy [14, 26 - 30].

In addition to electron catalysis, reactions in which the role of the catalyst is played by an electric field have been discovered [31-77]. For the first time in the history of catalysis, an immaterial object, the electric field, has claimed the role of a catalyst. More and more researchers conclude that "electric fields open up a new way to catalyze chemical reactions. [34 - 46]. The key role of the electric field in various types of catalysis has been revealed [70 - 72]. A new trend is forming in catalysis, which is based on the use of electric fields instead of material catalysts, and a new type of catalysis, electric field catalysis, has appeared in chemistry [44, 66, 67, 78, 79].

In addition to the external field, the influence of internal electric fields on catalytic activity and selectivity has been revealed [33, 41, 63]. Since spontaneous electric fields are present in all types of catalysis, [41] concluded that electrostatic phenomenology can be inherent in all types of catalysis.

The attribution of fields to catalysts forces a radical revision of the modern concept of catalysis and the search for new explanations of the mechanism of catalytic reactions. The generally accepted mechanism of catalysis, based on the formation of intermediate compounds of the catalyst with reagents, is not suitable for explaining the mechanism of field catalysis.

Because of the imperfection of the current paradigm of catalysis, some reactions involving electrons can be interpreted as "catalysis without a catalyst. It took more than 100 years after the discovery of the electron for this fundamental particle to be perceived as a participant in catalytic reactions in the role of a catalyst. It took about 150 years after the appearance of the electromagnetic field theory for the field, a fundamental immaterial object, to be viewed as a full participant in catalytic reactions and as a catalyst. In the current paradigm of catalysis there was no place for the two participants of catalysis that have a fundamental status in science. In this respect, the proton was "luckier". The important role of the proton in catalysis was immediately pointed out by Thomas Martin Lowry [80]. The proton in Lowry's theory appeared in the donor-acceptor mechanism of homogeneous catalysis several years after its discovery.

The emergence of fundamental catalysts in addition to the usual "non-fundamental" catalysts exposed the contradictions of catalysis. There was a need to get an answer to the main question: what should be considered a catalyst in catalytic reactions? In catalysis, it has become necessary to clarify the concepts and notions that have developed over two centuries.

## **2. What is considered a catalyst?**

An electron in catalyst status creates an unusual situation in catalysis. The electron cannot be ranked with other catalysts. The electron has a number of features that distinguish it from other catalysts. Electrons are ubiquitous; they are part of the substance of all known catalysts. The electron is not a chemical element. It is an elementary particle. This particle, unlike chemicals, has a fundamental status. The electron, when interacting, transfers the chemical to a new charge state. The interaction of the electron with the chemical substance is not a chemical reaction.

The question arises: what in a catalytic reaction is the true catalyst, the electrons or the traditional catalyst? Traditional catalysts necessarily include electrons. If the electron is given a place and a role as a catalyst, what role do substances that have traditionally been considered catalysts play? In this choice between an electron catalyst and a traditional catalyst, the electron has the definite advantage. The same applies to the proton.

An even deeper contradiction is related to the fundamental status of the electron and proton. The fundamental status of the electron and proton determine the nature of their interaction with other participants in the catalytic reaction. Neither the electron nor the proton are chemical elements. Their interaction with other participants belongs to the electromagnetic interaction. This is one of the four fundamental interactions known in nature.

Here we come to the key role of the fundamental interaction in catalytic reactions. The fundamental interaction involving fundamental objects leads to the breaking of intramolecular bonds in the reactants. Fundamental interactions can be a factor in changing the reactivity of chemicals. Traditional catalysts are not characterized by fundamental interaction. The role of fundamental interactions in catalysis has received little attention. Determining the place and role of fundamental interactions in catalytic reactions can open up new opportunities in catalysis research.

Historically, the term "catalyst" appeared together with the discovery of catalysis before the discovery of the electron (1897) and before the discovery of the proton (1919) and before the theory of the electromagnetic field (1864). The basic terms and definitions of catalysis have hardly changed for almost 200 years. New catalytic reactions involving electrons in the role of catalysts and reactions under the action of an electric field in the role of a catalyst require clarification of some of the postulates of catalysis. The participation of fundamental natural objects (the electron, the proton, and the electric field) in these reactions makes it necessary to consider the problems of catalysis from a different perspective.

## **3. From the concept of "electron as a catalyst" to the new paradigm of catalysis**

In catalysis, for the first time, the fundamental objects of nature began to be considered as catalysts. Fundamental catalysts have exposed the contradictions of catalysis. The main postulates of catalysis have been touched upon. The question of determining the type of interaction of new catalysts with reagents is acute. For fundamental objects, the interaction at the level of elementary particles is characteristic. This interaction is fundamentally different from chemical interaction. The emergence

of fundamental catalysts affects the central idea of catalysis about the formation of intermediate compounds and points to the need to develop a new paradigm of catalysis.

A new paradigm of catalysis has been proposed in [81 - 93]. The main goal of the creation of the new paradigm of catalysis is to reveal the general mechanism of catalytic reactions and to obtain the laws of catalysis. The new paradigm of catalysis is based on the idea that two fundamental catalysts exist in nature: the electron and the proton. The main function of the fundamental catalysts is to increase the reactivity of the reactants. In it, the concept of "electron as a catalyst" is extended to the concept of two fundamental catalysts (Fig. 1). In the new paradigm of catalysis, the number of reaction participants is expanded to four and the concept of oxidation state is introduced (Fig. 1). Such innovations resulted in the discovery of the general mechanism of catalytic reactions and the derivation of the laws of catalysis [86-91].

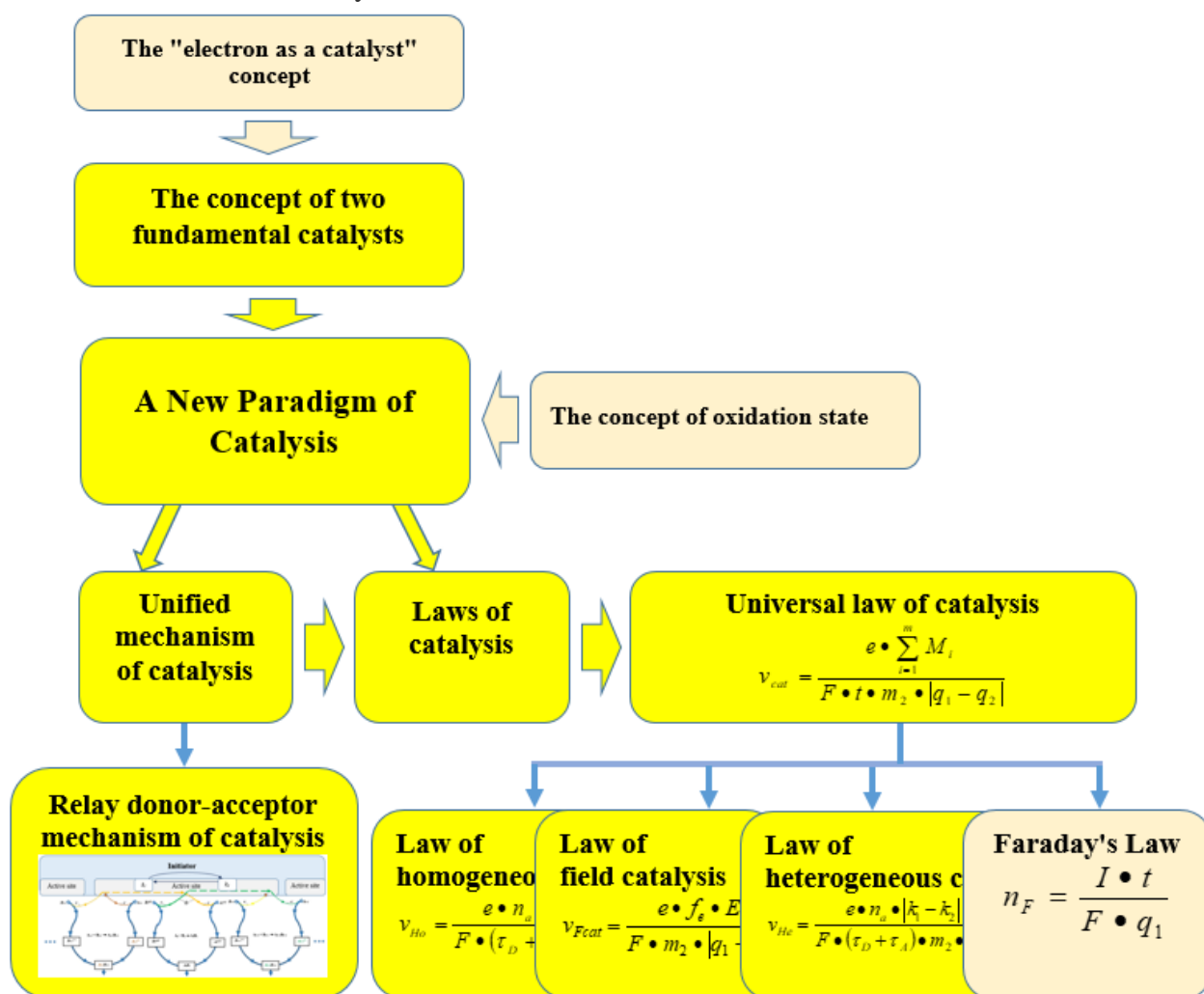


Fig. 1. From the concept of "electron as a catalyst" to the unified mechanism of catalysis and to the laws of catalysis.

#### 4. Changing the number of participants in the catalytic reaction in the new paradigm of catalysis

The "electron as a catalyst" concept has led to the need to revise the composition of the participants in catalytic reactions and to redistribute their role and place in catalytic processes [81, 82]. In the new paradigm of catalysis, the number of participants in the catalytic reaction is increased (Fig. 2).

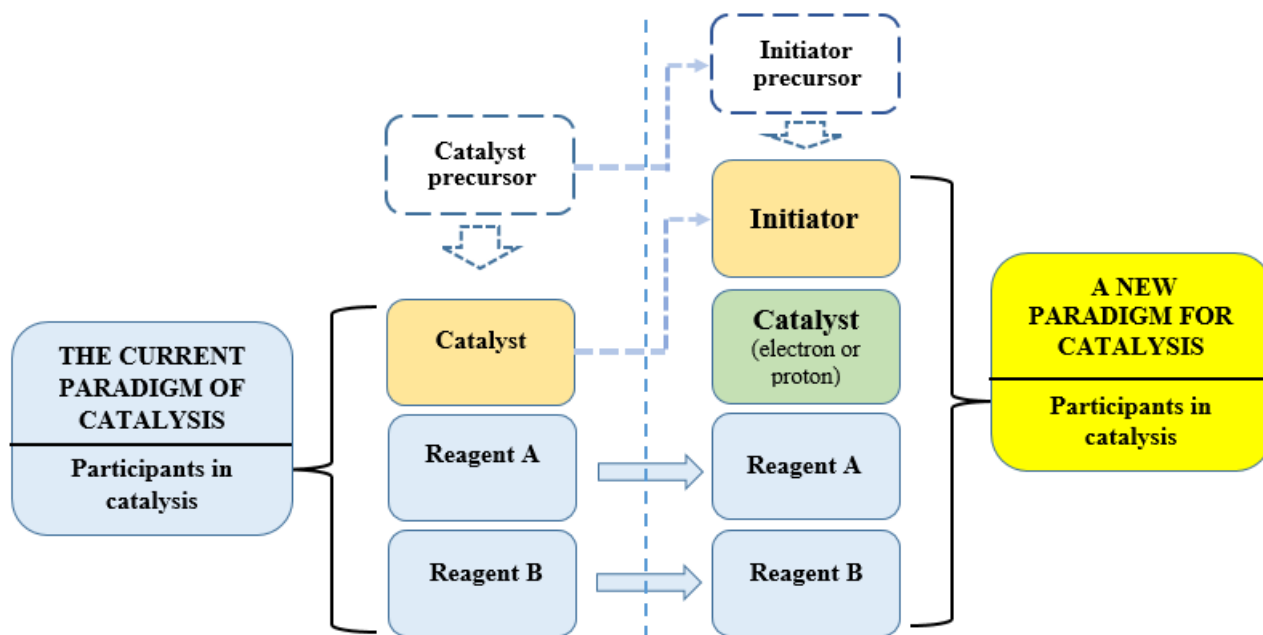


Fig. 2. Redistribution of roles and changes in the composition of the participants in the catalytic reaction in the new paradigm of catalysis.

The catalyst in a catalytic reaction is an elementary particle electron or proton. In the new paradigm of catalysis, traditional catalysts are assigned the role of initiators of the reaction. The initiator mediates the transfer of fundamental catalysts between reagents. Initiators in heterogeneous catalysis are substances that are electron donors and acceptors. Initiators in homogeneous catalysis are proton donors and acceptors. Initiators in organocatalysis are organic substances donors and acceptors of electrons. The initiator in field catalysis is the field as a generator of electrons in the substance of the reactants. The initiator in field catalysis is an electric field (electrostatic catalysis), electric current (electrocatalysis), light (photocatalysis, laser catalysis), ultrasound (cavitation catalysis), ionizing radiation (radiation catalysis), plasma (plasma catalysis), microwave radiation (microwave catalysis), etc.

The expansion of the composition of participants in catalytic reactions has posed new challenges and entailed additional requirements. The role and place for all participants in the mechanisms of catalysis and in catalytic cycles must be determined. The quantitative characteristics of the participants must be identified and their influence on the rate of catalysis must be determined.

## 5. The concept of two fundamental catalysts

The emergence of the concept of "electron as a catalyst" gave rise to the situation of "competing catalysts" in catalysis. The question of what should be considered a catalyst came to the forefront? In this competition, the electron has more chances to take the place of a catalyst and move the current catalysts to the background. For this, the electron has obvious advantages: the status of a fundamental object instead of an ordinary chemical substance; fundamental interaction with reagents instead of chemical interaction; and the presence of electrons in traditional catalysts. These are the features of the new catalyst that determine its universality. The ubiquity of electrons also works to the advantage of electrons being catalysts for chemical reactions. Until catalysis labeled the electron as a catalyst, its role was lost in the variety of types of catalysis. With the appearance of an electrically charged particle in the role of a catalyst, a common feature in the mechanisms of different types of catalysis emerged. The common feature was the transfer of electric charges in catalytic reactions. This unifying feature directly points to the common nature of all types of catalysis. An electrically charged elementary particle (electron) designated itself as the main acting factor in catalysis. All of the above applies equally to the proton.

Even more advantageous for the electron as a catalyst is its fundamental status. The electron is the second catalyst after the proton that has fundamental status in science. The fundamental status of the electron and proton makes them special and unique catalysts in comparison to ordinary chemical catalysts. Among the entire family of matter catalysts, only these two particles are fundamental catalysts. The role of a third fundamental catalyst could be claimed by a field within the framework of the concept "electric field as a catalyst". But in this case, it is necessary to take into account that the field is not a real object. In addition, the nature of the interaction of the electric field with matter is different. The field does not interact with reagents directly, but indirectly through electrically charged particles - electron and proton. Thus, the whole set of fundamental catalysts is reduced to two fundamental particles - the electron and the proton. Therefore, it is logical to switch from the concepts "electron as a catalyst" and "proton as a catalyst" to the idea of the existence of two universal catalysts in nature.

We proposed that a special status for the electron and proton in catalysis be accepted [81 - 83]. We proposed to consider these elementary particles not as additions to the family of known catalysts, but as the only fundamental and universal catalysts. In the new paradigm of catalysis, these two fundamental catalysts were introduced as reaction participants. They have sidelined the known catalysts and defined a new role for them. It is the role of initiators of catalytic reactions, electron and proton carriers and suppliers.

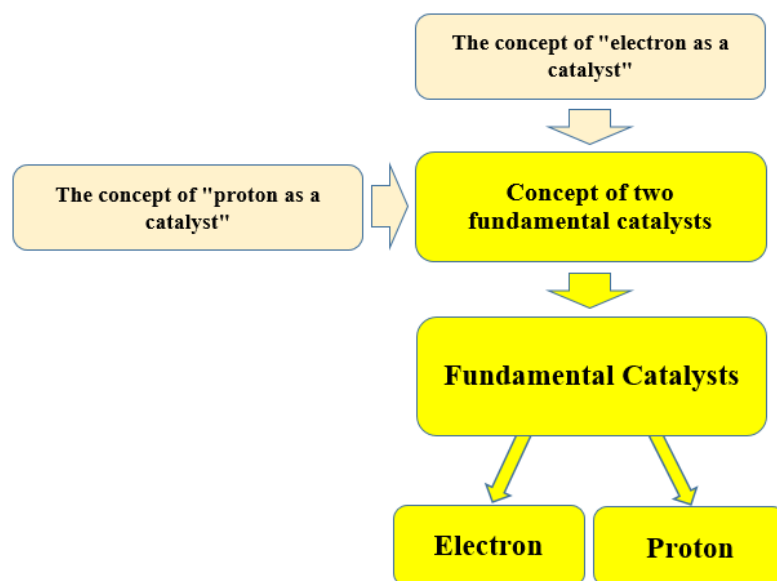


Fig. 3. From the concept of "electron as a catalyst" to the concept of two fundamental catalysts.

The radical revision of the role of electrons and protons in catalysis is justified by their fundamental status and by the ubiquity of electrons and protons in nature and in chemical reactions. The electric charges of the fundamental catalysts are the main acting factor in increasing the reactivity of the reactants. In the new paradigm of catalysis, the nature of the interaction between the catalyst and the reactants has been revised. The fundamental interaction stage has been singled out in the catalysis mechanism. The interaction of fundamental catalysts with reagents precedes the stage of chemical interaction of reagents.

## 6. The concept of the oxidation state in catalysis

The concept of "electron as a catalyst" forces attention to the role and place of the oxidation state in catalytic reactions. The concept of the oxidation state is a natural complement to the "electron as a catalyst" concept. These concepts are interrelated and close in meaning. Both concepts are based on the role of electrons in chemical reactions.

The history of the oxidation state concept goes back about 200 years [94 - 96]. Despite the fact that the oxidation state of substances is widely used in chemistry, it is considered to be an auxiliary conventional value that has no physical meaning [97 - 100]. There has long been much debate among scientists about the role of the oxidation state in chemistry [101 - 107]. There is a well-known opinion of Linus Pauling, who said: "If scientific progress continues, the next generation may have a theory of valence that is sufficiently precise and powerful to permit chemistry to be classed along with physics as an exact science." [105, 106].

The state of oxidation is used in chemistry for such purposes [102, 103, 104]:

1. As a descriptor.
2. As a parameter in chemical nomenclature.
3. As a variable for tabulation or plotting.
4. As a value related to d-electron configurations of transition-metal (TM) ions in compounds.
5. As a formalized basis for balancing redox equations.

Interest in the state of oxidation in catalysis emerged quite a long time ago [108 - 111]. Early studies on the role of the oxidation state in catalytic reactions concluded that the activity and selectivity of the catalytic process depend on the oxidation state [110, 111]. In [107, 108] it is noted that "valence chemistry is of fundamental importance in catalysis science," and "management of the oxidation state provides the key to future catalysis research. The shift of emphasis to the fundamental status of the oxidation state is not accidental. This is due to the fundamental status of the electron and its central role in the oxidation state concept.

The number of papers investigating the influence of the oxidation state of the catalyst on the efficiency of catalysis is constantly growing [112 - 116]. The emphasis in these works is on the fact that oxidation states can predict the reactivity of substances and their chemical activity. There are many examples of catalytic reactions in which the state of oxidation plays a key role. But there have been no in-depth studies of the role and place of the oxidation state in catalysis. The role of oxidation states in catalysis has been underestimated. Until now, the oxidation state remains an auxiliary conventional value in chemistry. In studies of the effect of the oxidation state on the efficiency of catalysis, the main focus has been on the oxidation state of the catalyst. The influence of the oxidation state of the reagents fell out of the researchers' field of vision. The universal nature of the oxidation state in catalytic reactions was out of the researchers' sight.

In [81-83], the concept of the oxidation state was used as part of the new paradigm of catalysis. The oxidation states are used as quantitative values in the laws and equations of catalysis [81 - 93]. Fig. 4 shows the place of oxidation states in the laws of catalysis and in the mechanisms of catalysis. Instead of auxiliary conventional values, the oxidation states in the new catalysis paradigm act as quantitative values.

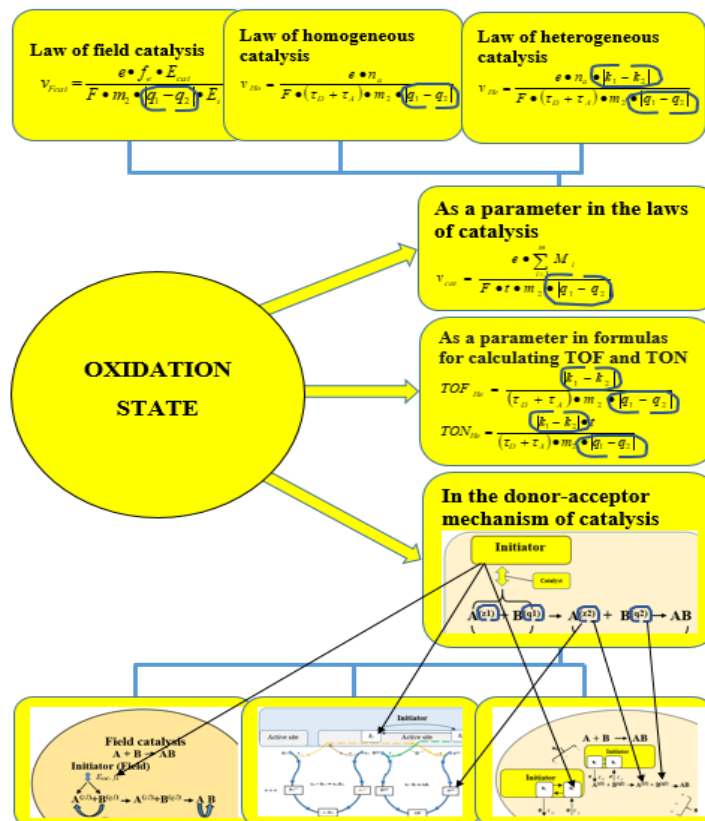


Fig. 4. Oxidation states in the laws of catalysis and in the mechanisms of catalysis.



The change in the oxidation state of the reactants is directly related to the donor (acceptor) function of the participants in the catalytic reaction. The change in the oxidation state of the participants sets the value of the electric charge transferred (received) in the donor (acceptor) half-cycle of catalysis. The presence of oxidation states in the laws and formulas of catalysis takes on a physical meaning. For example, for heterogeneous catalysis, the amount of change in the oxidation state is directly related to the number of electrons transferred (received) by the active center [88, 91].

In Fig. 5, the example of heterogeneous catalysis shows the changes in the oxidation state of the reaction participants on the model of the catalysis mechanism. In the reaction, there is a cyclic change in the oxidation state of the active centers of the initiator from state  $k_1$  to state  $k_2$  and back. Reagents A and B under the action of electrons have a unidirectional change in the oxidation state. Reagent A goes from the oxidation state  $A^{(z_1)}$  to the oxidation state  $A^{(z_2)}$ . Reagent B from the oxidation state  $B^{(q_1)}$  goes to the oxidation state  $B^{(q_2)}$ . The change in the oxidation state of the initiator and reagents is due to electron transfer. The reagents in the changed charge state  $A^{(z_2)}$  and  $B^{(q_2)}$  (modified reagents) enter into chemical interaction. As a result, a charge-neutral molecule AB of the reaction product is formed.

Thus, the mechanism of action of the fundamental catalysts consists in a change in the charge state of the reactants. A consequence of the change in the charge state of the reactants is an increase in their reactivity. The charge-conjugated reactants  $A^{(z_2)}$  and  $B^{(q_2)}$  easily react.

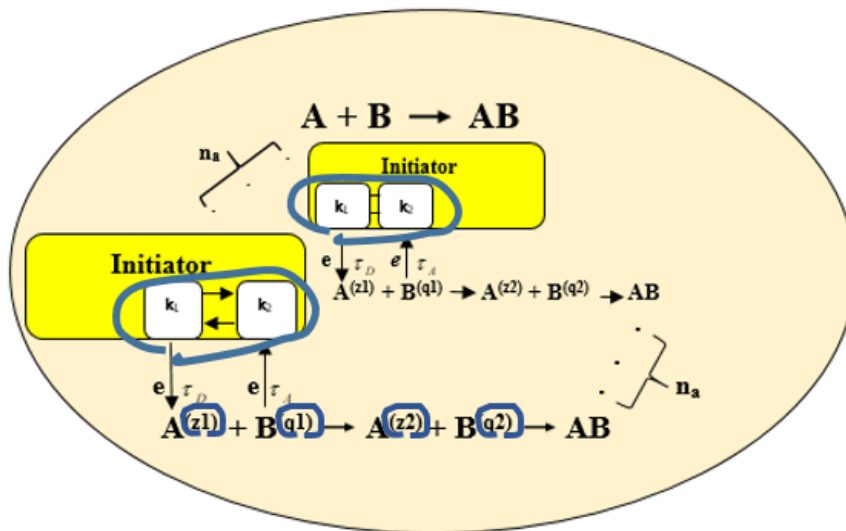
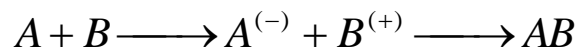


Fig. 5. Changes in the oxidation state of the reaction participants in the mechanism of heterogeneous catalysis.  $A$ ,  $B$  - reagents;  $AB$  - reaction product;  $A^{(z_1)}$  - reagent A in initial charge state;  $B^{(q_1)}$  - reagent B in initial charge state;  $A^{(z_2)}$  - reagent A in final charge state;  $B^{(q_2)}$  - reagent B in final charge state;  $k_1$  - initial oxidation state of initiator;  $k_2$  - final oxidation state of the initiator;  $e^-$  - electrons;  $n_a$  - number of active sites;  $\tau_D$  - donor half-cycle time;  $\tau_A$  - acceptor half-cycle time;  $q_1$ ,  $z_1$  - oxidation states of reactants in the initial product;  $q_2$ ,  $z_2$  - oxidation states of reactants in the final product.

## 7. The fundamental interaction stage in the catalysis mechanism

In the framework of the new paradigm of catalysis, the common feature that is characteristic of different catalytic reactions and different types of catalysis has been revealed. This feature is a

change in the charge state (oxidation state) of the reaction participants. The charge state changes under the action of fundamental catalysts (electrons, protons) [81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93]. A simplified scheme of the catalytic reaction can be represented as (Fig. 6):



A general scheme of the catalytic reaction can be represented as (Fig. 6):

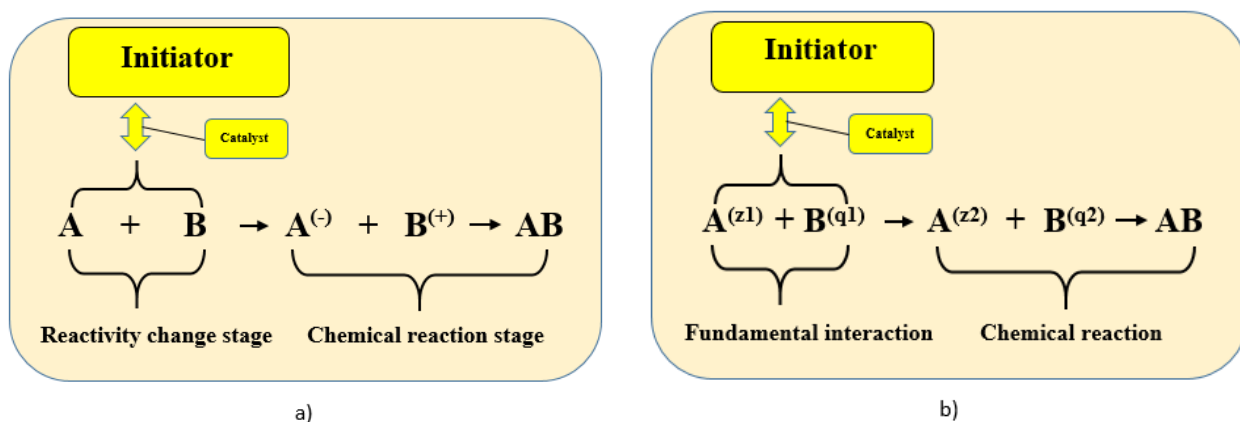
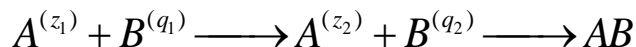


Fig. 6. Scheme of the catalysis mechanism. a) - simplified scheme; c) - general scheme;  $A$ ,  $B$  - reagents;  $A^{(-)}$  - reagent  $A$  in the changed charge state;  $B^{(+)}$  - reagent  $B$  in the changed charge state;  $A^{(z_1)}$  - reagent  $A$  in the initial charge state;  $B^{(q_1)}$  - reagent  $B$  in initial charge state;  $A^{(z_2)}$  - reagent  $A$  in final charge state;  $B^{(q_2)}$  - reagent  $B$  in final charge state;  $AB$  - reaction product.

Two enlarged stages are distinguished in the mechanism of catalysis. The first stage is the stage of change of reactivity of reagents under the action of electrons and protons. The main feature of this stage is the fundamental nature of the interaction between the participants in the catalytic reaction. The second stage is the direct chemical reaction of the modified reactants. The stage of changing the reactivity (the stage of fundamental interaction) of reactants is the main stage. It precedes the chemical reaction. At this stage, changes in the charge state of the reactants and the initiator under the action of electrons and protons occur. The remarkable catalytic properties of the free electron and proton stem from the fundamental nature of the interaction. This electromagnetic interaction is one of the four fundamental interactions of Nature. The stage of changing the reactivity of reagents is completed by the appearance of modified reagents. Modified reagents are reagents in a modified charge state.

The main scenario of catalysis is played out at the stage of fundamental interaction of the reaction participants. At this stage, adsorption and desorption processes take place, electric charge transfer takes place, and the oxidation state of the initiator and reagents is changed. This is the most complex stage of catalysis. Disclosure of the processes that take place at this stage gives answers to many of the mysteries of catalysis. At this stage, the fundamental interaction of initiator with reagents and catalyst with reagents is realized in the mechanism of catalysis. At this stage, the charge state of the reactants changes. The consequence of this is an increase in their reactivity. The catalytic reaction

is completed at the second stage by chemical interaction of the modified reactants. A charge-neutral molecule of the reaction product is formed.

### 8. The unified mechanism of catalytic reactions. The relay donor-acceptor mechanism of catalysis.

The relay donor-acceptor mechanism of catalysis was proposed in [81, 82, 83]. It is a universal catalysis mechanism for both electron and proton catalysis. As an example, a scheme of the relay donor-acceptor mechanism of heterogeneous catalysis is shown in Fig. 7. In the mechanism of heterogeneous catalysis, electrons are transferred from one reactant to another through an intermediary. The intermediary is the active site of the initiator. At this stage there is a change in the charge state of the reactants. The chemical reaction takes place between the charge-conjugated (modified) reactants in a changed state of oxidation ( $A_i^{(z_2)}$ ,  $B_i^{(q_2)}$ ) with the formation of a neutral molecule  $A_iB_i$ . The electrostatic interaction of the reactants in the modified charge state reduces the energy barrier of the reaction. This increases the reaction rate.

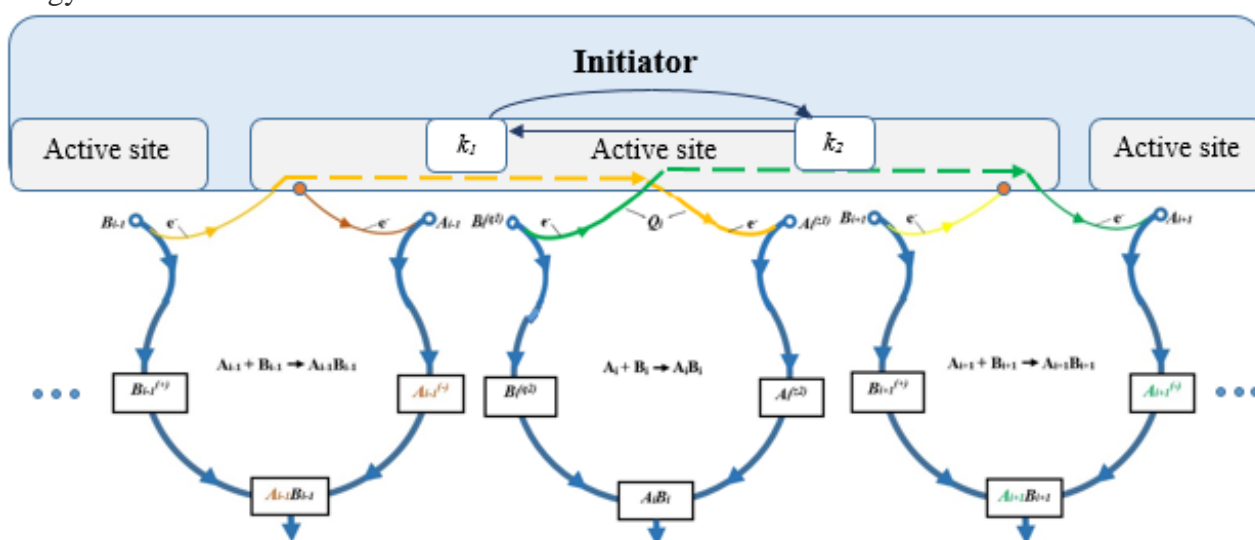


Fig. 7. Diagram of the relay donor-acceptor mechanism of heterogeneous catalysis.  $A_i$ ,  $B_i$  - reagents participating in the  $i$ -th elementary reaction;  $A_{i-1}$ ,  $B_{i-1}$  - reagents participating in the  $(i-1)$ -th elementary reaction;  $A_{i+1}$ ,  $B_{i+1}$  - reagents participating in the  $(i+1)$ -th elementary reaction;  $A_iB_i$  - product of the  $i$ -th elementary reaction;  $A_{i-1}B_{i-1}$  - product of  $(i-1)$ -th elementary reaction;  $A_{i+1}B_{i+1}$  - product of  $(i+1)$ -th elementary reaction;  $A_i^{(z_1)}$  - reagent  $A_i$  in the initial charge state;  $B_i^{(q_1)}$  - reagent  $B_i$  in the initial charge state;  $A_i^{(z_2)}$  - reagent  $A_i$  in the final charge state;  $B_i^{(q_2)}$  - reagent  $B_i$  in the final charge state;  $k_1$  - initial oxidation state of the initiator;  $k_2$  - final oxidation state of the initiator;  $q_1$ ,  $z_1$  - oxidation states of reagents in the initial product;  $q_2$ ,  $z_2$  - states of oxidation of reactants in the final product;  $e^-$  - electrons;  $Q$  - electric charge;  $(A_i + B_i \rightarrow A_iB_i)$   $i$ - elementary reaction;  $(A_{i-1} + B_{i-1} \rightarrow A_{i-1}B_{i-1})$   $(i-1)$ -elementary reaction;  $(A_{i+1} + B_{i+1} \rightarrow A_{i+1}B_{i+1})$   $(i+1)$ -elementary reaction.

The scheme of the relay donor-acceptor mechanism of field catalysis is shown in Fig. 8. In the mechanism of field catalysis, direct electron transfer from one reactant to another occurs at the fundamental interaction stage. This occurs under the influence of an external electric field. At this stage, there is a change in the charge state of the reactants. The next stage is a chemical reaction between the charge-conjugated (modified) reactants in a changed state of oxidation ( $A_i^{(z_2)}$ ,  $B_i^{(q_2)}$ ). A

neutral molecule,  $A_iB_i$ , is formed. The direction of charge transfer in the reaction depends on the polarity of the applied electric field. Depending on the polarity of the electric field (+E or -E), both acceleration and deceleration of the reaction are possible.

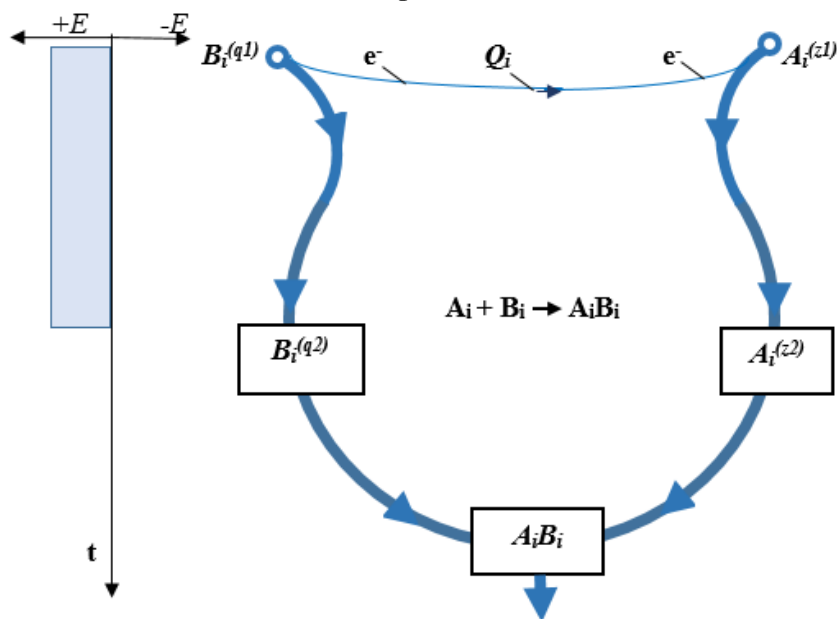
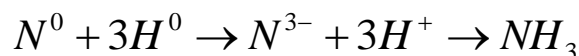


Fig. 8. Schematic of the relay donor-acceptor mechanism of field catalysis.

$A_i$ ,  $B_i$  - reagents participating in the  $i$ -th elementary reaction;  $A_iB_i$  - product of the  $i$ -th elementary reaction;  $A_i^{(z1)}$  - reagent  $A_i$  in the initial charge state;  $B_i^{(q1)}$  - reagent  $B_i$  in the initial charge state;  $A_i^{(z2)}$  - reagent  $A_i$  in the final charge state;  $B_i^{(q2)}$  - reagent  $B_i$  in the final charge state;  $q_1$ ,  $z_1$  - states of oxidation of reagents in the initial product;  $q_2$ ,  $z_2$  - states of oxidation of reagents in the final product;  $e^-$  - electrons;  $Q$  - electric charge;  $(A_i + B_i \rightarrow A_iB_i)$   $i$ - elementary reaction; +E, -E - electric field;  $t$  - time.

## 9. Scheme of the mechanism of heterogeneous catalysis by the example of ammonia synthesis reaction

Scheme of the mechanism of the elementary catalytic reaction of ammonia production from nitrogen and hydrogen is shown in Fig. 9. The elementary reaction is carried out at the atomic level according to the scheme:



The reaction is catalyzed by electrons. Hydrogen atoms transfer electrons to the active site and move to the charge state  $H^+$ . The active site goes from the charge state  $k_1$  to the charge state with the oxidation state  $k_2$ . The nitrogen atom receives electrons from the active site and goes to the charge state  $N^{3-}$ . The chemical reaction takes place between the charge-conjugated (modified) reactants in a modified oxidation state ( $H^+$ ,  $N^{3-}$ ). As a result, a neutral  $NH_3$  molecule is formed.

The catalytic cycle of the initiator is realized in the mechanism of catalysis. The active site of the initiator changes its charge state and passes from the  $k_1$  state to the  $k_2$  state and back. Quantitative characteristics of the initiator catalytic cycle are the charge state change  $gdubin$  ( $k_1 - k_2$ ); donor half-

cycle time ( $\tau_D$ ); and acceptor half-cycle time ( $\tau_A$ ). The reaction takes place at the atomic level. Adsorption processes make the largest contribution to the  $\tau_D$  and  $\tau_A$  values [117].

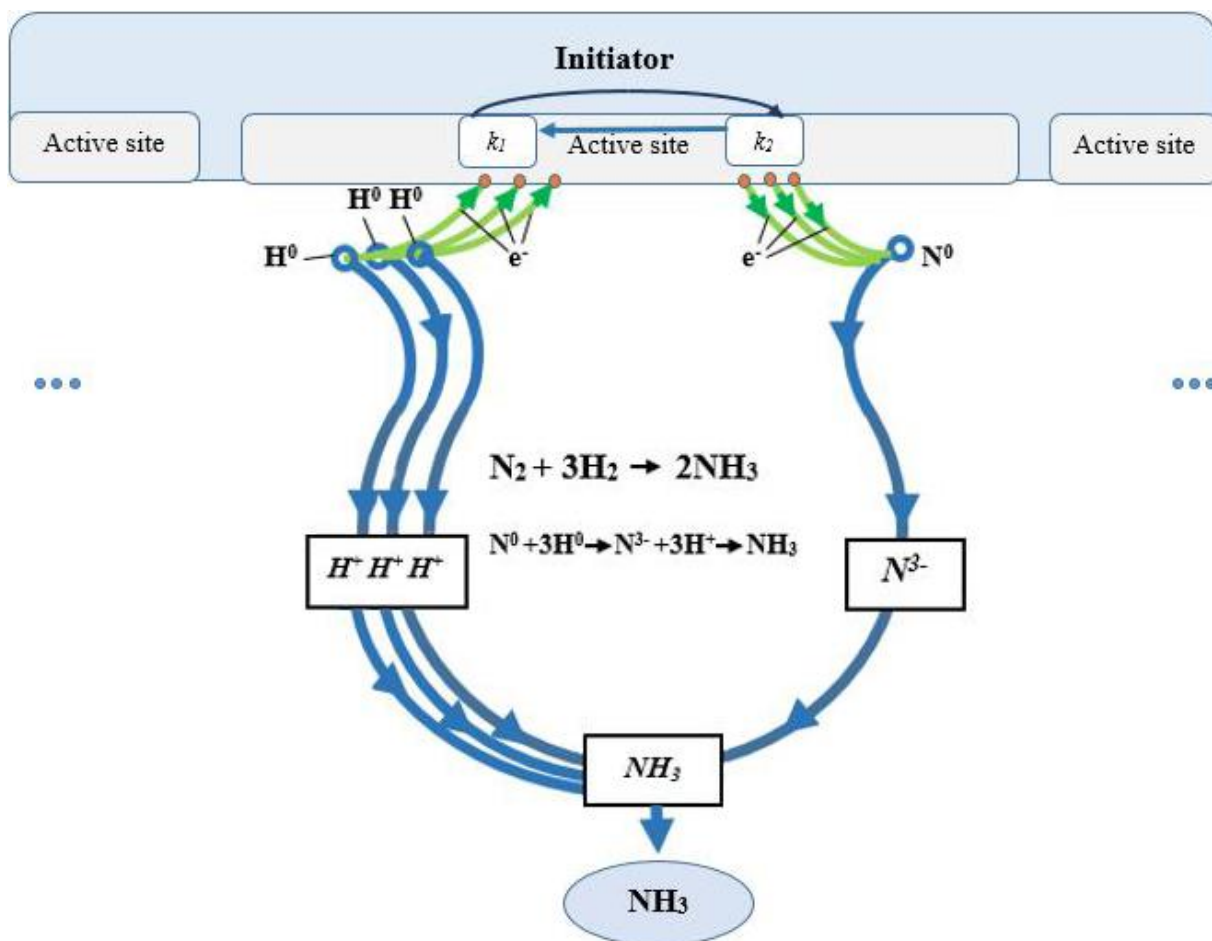


Fig. 9. Schematic diagram of the relay donor-acceptor mechanism of heterogeneous catalysis by the example of ammonia synthesis from nitrogen and hydrogen.

$H^0$  - hydrogen atom in the initial charge state;  $N^0$  - nitrogen atom in the initial charge state;  $H^+$  - hydrogen atom in the final charge state;  $N^{3-}$  - nitrogen atom in the final charge state;  $k_1$  - initial oxidation state of the active initiator site;  $k_2$  - final oxidation state of the active initiator site;  $e^-$  - electrons.

## 10. Peculiarities of the catalytic cycle in the donor-acceptor mechanism of catalysis

Let's consider peculiarities of catalytic cycle on the example of heterogeneous catalysis. The diagrams (Fig. 5, Fig. 7) show that in the donor-acceptor mechanism of heterogeneous catalysis a cycle of charge states of the active site of the initiator is realized. In the catalytic reaction, there is a cyclic change in the electric charge of the initiator's active sites without a change in its chemical composition. The active site of the initiator changes its charge state and passes from the  $k_1$  state to the  $k_2$  state and back. As we see, instead of the catalytic cycle with participation of intermediate chemical compounds in the donor-acceptor mechanism of catalysis, a catalytic cycle of charge states is realized. The cycle of states instead of the chemical cycle is realized. This is the redox cycle of catalysis. This

cycle occurs at the stage of fundamental interaction of the reaction participants. It precedes the chemical reaction of modified reactants. The intermediate states of reactants A and B are their states in the modified oxidation degree  $A^{(z_2)}$  and  $B^{(q_2)}$ . The intermediate state of the initiator is the charge state of the active centers in the modified oxidation degree  $k_2$ .

## 11. Characteristics of the redox cycle of catalysis

The most important quantities that relate to the redox cycle of catalysis are the time intervals and (Fig. 5). The total value  $(\tau_D + \tau_A)$  sets the duration of the catalytic cycle of the initiator. The main time-setting factor in the mechanism of heterogeneous catalysis is the adsorption processes of the reactants. For this reason, catalytic reactions are very sensitive to reaction conditions: temperature, pressure, concentration, and mixing. In [86, 88] it was proposed to use Redox frequency (ROF) and Redox number (RON) as characteristics of the catalytic cycle:

$$ROF = \frac{1}{\tau_D + \tau_A}; RON = \frac{t}{\tau_D + \tau_A}.$$

RON is the number of catalytic cycles of the initiator per reaction time. ROF is the turnover frequency of the initiator catalytic cycle. This is the main reference frequency of the catalytic process. This frequency synchronizes the catalytic process and sets the rate of catalysis. The discovery of catalytic resonance [118] indicates that synchronizing an external electrical action with the ROF frequency can be a powerful strategy to obtain reaction rates beyond the limiting Sabatier volcano.

ROF is related by a certain ratio to TOF. The ratio of the ROF to TOF frequency of the initiator catalytic cycle gives the reduction number [81] of the catalysis  $\sigma$ :

$$\sigma = \frac{ROF}{TOF} = \frac{RON}{TON} = \frac{m_2 \cdot |q_1 - q_2|}{|k_1 - k_2|}$$

The reduction number of catalysis indicates how many times the cycle of changing the oxidation state of the initiator must be repeated before one molecule of the final product is formed. As we can see, ROF and RON values are related to TOF and TON via Horiuti numbers [81, 87, 119].

The question arises: who starts and spins this "wheel" of the catalytic reaction? From the mechanism of catalysis, we see that this function is performed by the reagents. Reagents realize this function in the donor-acceptor mechanism of catalysis by transferring electrons to the active site and receiving electrons from the active site (Fig. 5, Fig. 7, Fig. 9). The duration of the redox cycle of catalysis is most significantly affected by the processes of adsorption and desorption of reagents.

## 12. From the characteristics of the reaction participants to the laws and equations of catalysis

It was shown in [81 - 93] that the substance characteristics of the reaction participants are directly included in the law of catalysis rate, in the TOF and TON formulas, and in other equations of catalysis (Fig. 10). The characteristics of the fundamental catalysts are the fundamental constants (e, F). The characteristics of the initiator are its oxidation states ( $k_1, k_2$ ), the number of active sites ( $n_a$ ), and the time intervals ( $t_D, t_A$ ). The field characteristics are energy and frequency ( $E_{cat}, f_e$ ). Reagent

characteristics are their charge states ( $z_1, z_2, q_1, q_2$ ), ionization energy ( $E_i$ ) and the number of reagent atoms ( $m_1, m_2$ ) in the reaction product molecule.

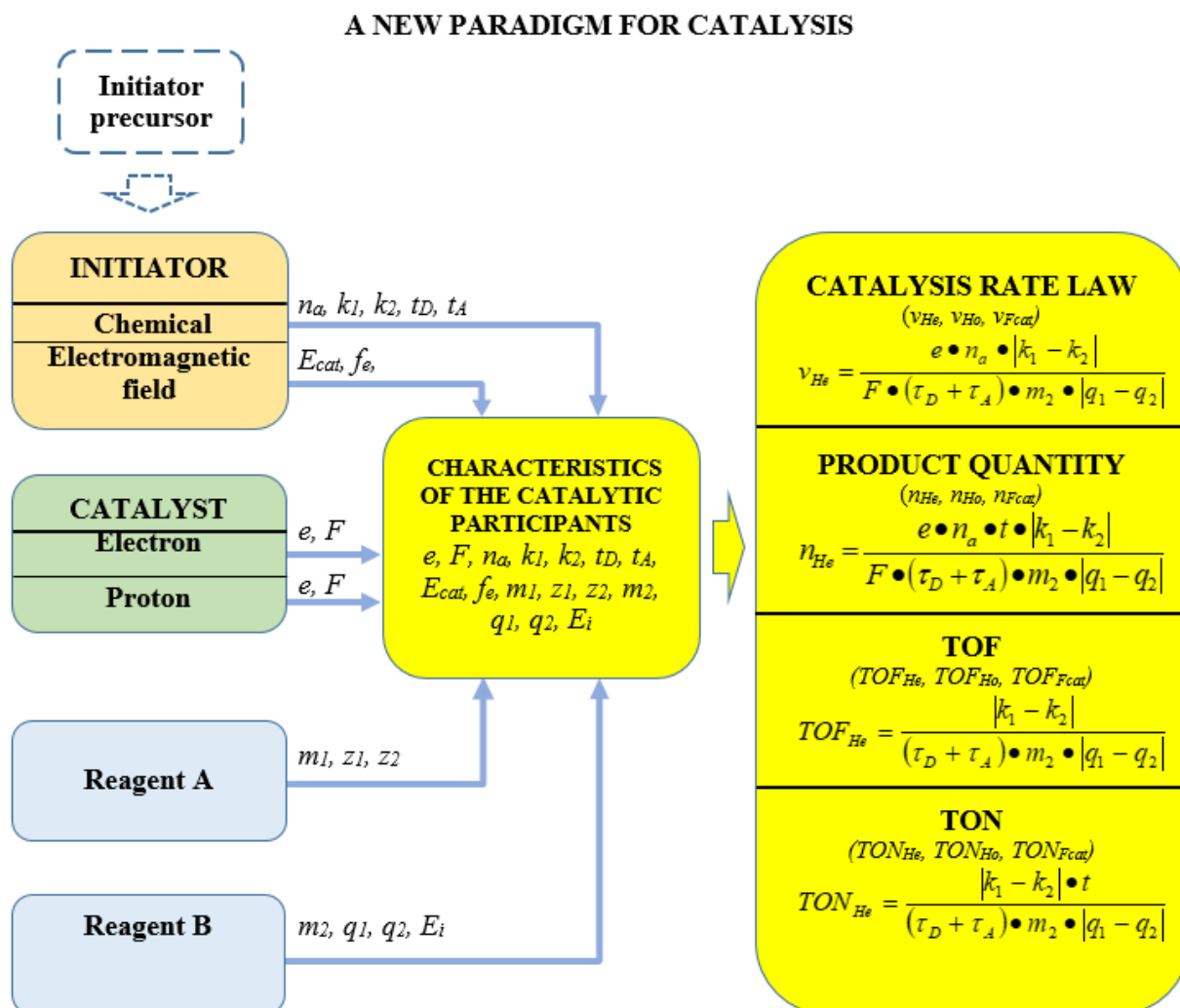


Fig. 10: Characteristics of the reaction participants set the values of the catalytic characteristics

In the new paradigm of catalysis, the law of catalytic rate is defined as the amount of catalytic reaction product per unit time (mol/s). The laws of catalysis are derived as applied to the elementary catalytic reaction. They follow directly from the mechanism of catalysis. The laws of catalysis are presented as functions of the substance characteristics of all participants in the reaction. Particular laws of catalysis follow directly from the mechanism model of the corresponding type of catalysis. In essence, each law of catalysis is the mathematical equivalent of the mechanism of the corresponding type of catalysis. The characteristics of the reaction participants are included in the laws and equations of catalysis as parameters.

### 13. The laws of catalysis as mathematical equivalents of the mechanism of catalysis.

Fig. 11 shows the origin of the laws of catalysis from the relay donor-acceptor mechanism of catalysis on the example of heterogeneous catalysis. The laws of catalysis are presented as mathematical equivalents of the catalysis mechanism model.

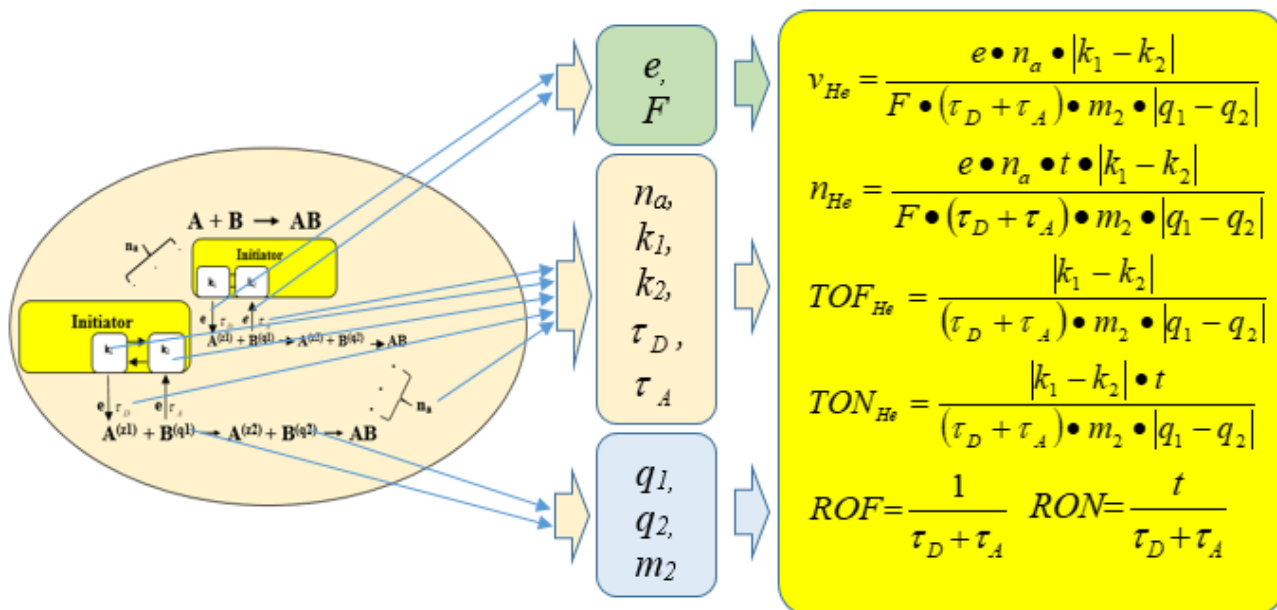


Fig. 11: The laws of catalysis derive from the relay donor-acceptor mechanism of catalysis.

#### 14. Characteristics of the participants of the catalytic reaction in the laws of catalysis.

Fig. 12 shows the characteristics of the participants of the catalytic reaction in the law of catalysis rate on the example of heterogeneous catalysis.

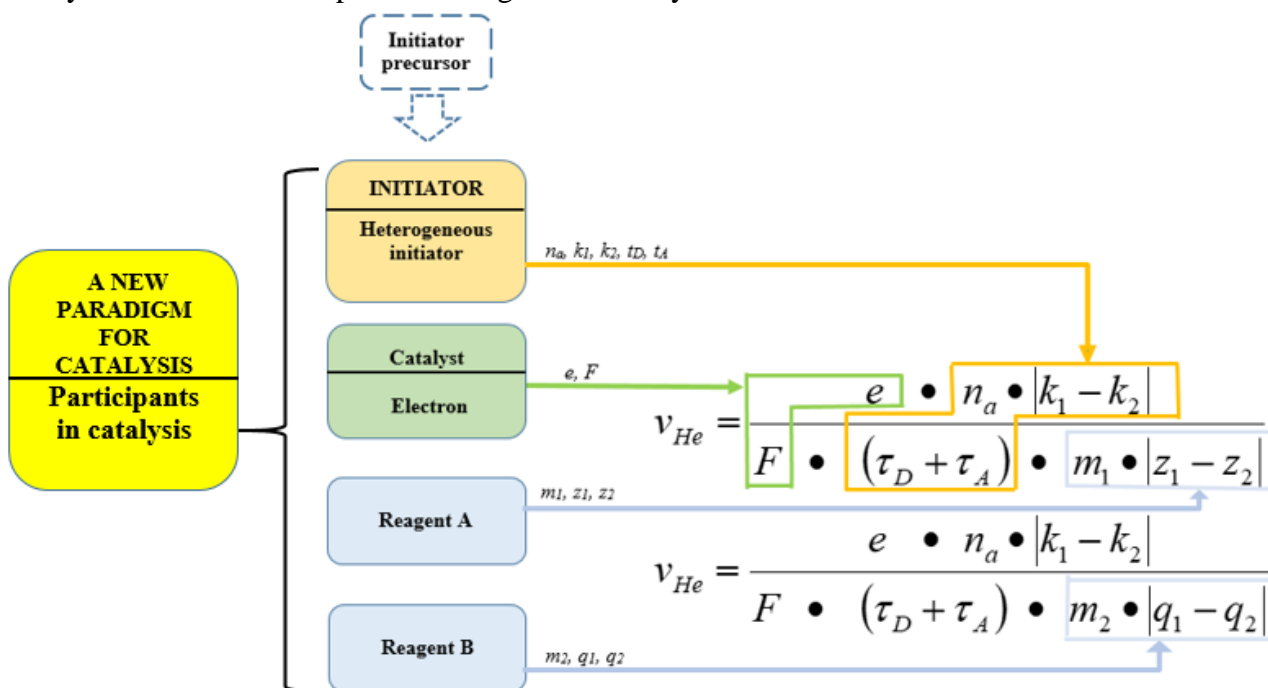


Fig. 12: Characteristics of the participants in the catalytic reaction in the rate law of heterogeneous catalysis.

The catalyst (electron), as a fundamental object, is represented in the law of catalysis by the fundamental constants  $e, F$  [120]. The initiator is represented by the oxidation states ( $k_1, k_2$ ), the



number of active sites ( $n_a$ ), and the time intervals ( $t_D$ ,  $t_A$ ). Reagents are represented by their charge states ( $z_1$ ,  $z_2$ ,  $q_1$ ,  $q_2$ ) and the number of reagent atoms ( $m_1$ ,  $m_2$ ) in the reagent product molecule.

### **15. The unified nature of all types of catalysis.**

The confirmation of the unified nature of catalysis is the following:

1. In all types of catalysis the same mechanism of catalysis is realized.
2. The common feature in various catalytic reactions is the transfer of electric charges by electrons and protons.
3. Electron and proton, as electrically charged elementary particles, are catalysts in all types of catalysis.
4. The universal law of catalysis has been obtained. From the universal law, the laws of heterogeneous, homogeneous, combined, field catalysis and the law of Faraday's electrolysis follow as particular results [81, 82, 91].

### **16. Catalysis - a fundamental chemical-physical phenomenon**

Catalysis is increasingly being categorized as a class of fundamental phenomena [121 - 124]. As evidence of the fundamental status of catalysis, the following attributes can be cited:

1. The fundamental particles electron and proton are the catalysts.
2. In catalytic reactions, at the initial stage, the fundamental electromagnetic interaction between the reaction participants is realized.
3. Donor-acceptor interaction is a particular case of fundamental interaction of electric charges.
4. The fundamental constant (Faraday's constant) is the interaction constant in the laws of catalysis.
5. The equations of the laws of catalysis include fundamental constants: Faraday's constant, electron charge, Avogadro's number.
6. The laws of catalysis have similarities and common features with the fundamental physical laws [84]. The laws of catalysis complement the family of fundamental laws (Fig. 13).
7. In catalytic reactions, the fundamental law of nature, the law of conservation of electric charge, is fulfilled.

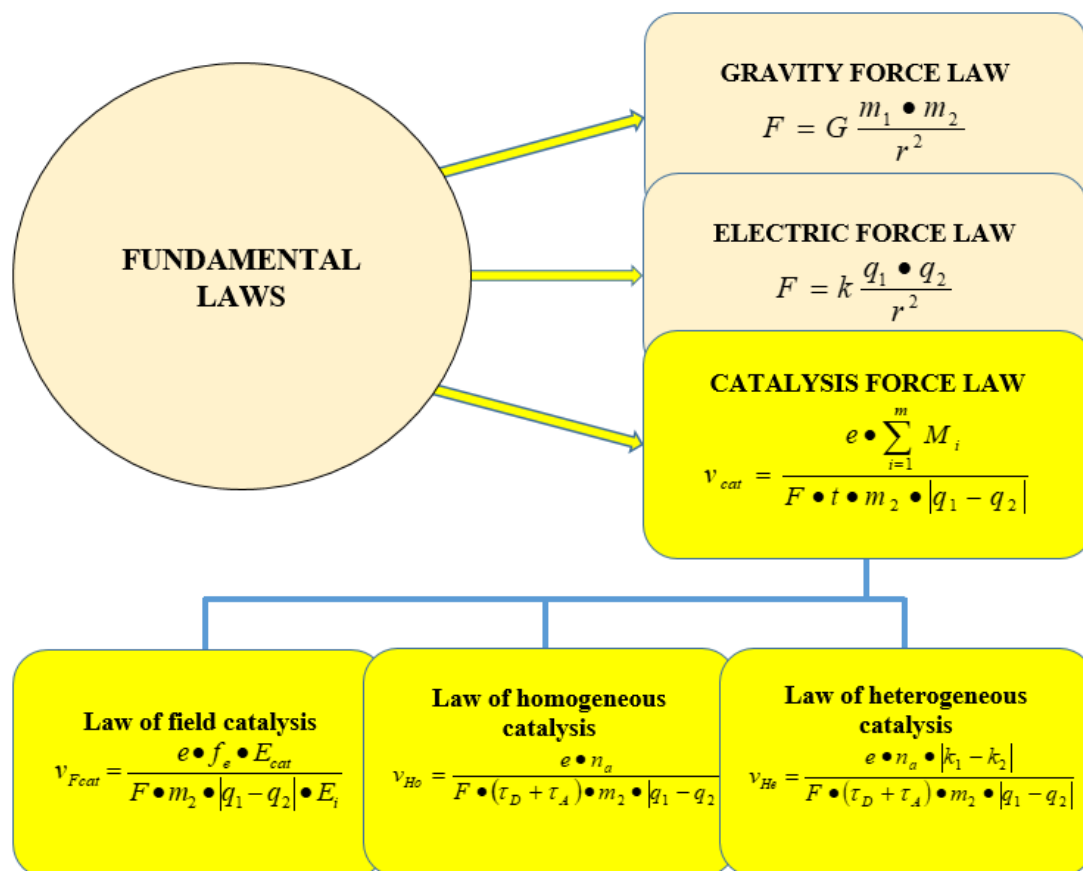


Fig. 13. Laws of catalysis as a supplement to the fundamental laws of nature.

## 17. Conclusion

The concept of "electron as a catalyst" becomes the most fruitful in the science of catalysis. With the emergence of the concept of "electron as a catalyst" and the concept of "electric field as a catalyst", fundamental catalysts in catalysis have designated themselves. These two concepts allow us to eliminate the contradictions that have accumulated in catalysis during its almost 200-year history.

The result of the development of the "electron as a catalyst" concept was a new paradigm of catalysis. Within the new paradigm, the unified donor-acceptor mechanism of catalytic reactions was revealed. From the mechanism of catalysis, a universal law of the rate of catalysis was derived. The laws and equations of heterogeneous, homogeneous, field, combined catalysis, and Faraday's law of electrolysis follow from this law as particular results. The parameters in the laws of catalysis are the chemical and physical characteristics of the reaction participants. The concept of "electron as a catalyst," the concept of two fundamental catalysts, and the concept of oxidation state were the main missing links in the science of catalysis.

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