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FROM THE "ELECTRON AS A CATALYST" CONCEPT TO THE LAWS OF CATALYSIS

Abstract. *The model of the unified mechanism of catalytic reactions within the framework of a new paradigm of catalysis was proposed as the development of the conception "electron as a catalyst". The model of the unified mechanism of catalysis made it possible to obtain the universal law of the catalytic rate. From the universal law of catalysis, the laws of heterogeneous, homogeneous, field catalysis, and Faraday's law of electrolysis follow as particular results. The laws and equations of catalysis are the mathematical equivalents of the mechanism of catalysis. The laws of catalysis are represented by equations in which the characteristics of the substance of the catalyst and other reaction participants are parameters.*

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

1. Introduction

The current period in the history of catalysis is characterized by the accumulation of a huge number of experimental results. Some results do not fit into the principles and postulates of the current paradigm of catalysis. This makes it necessary to consider the problem of the catalytic phenomenon from fundamentally new positions. Recently, many new catalytic reactions have been discovered. These include catalysis by electrons, catalysis by electric field, plasma, microwaves, ultrasound, ionic liquids, catalysis under supercritical conditions, etc. These catalytic reactions are becoming a challenge to the modern paradigm of catalysis and the modern understanding of the nature of catalysis [1, 2, 3]. The discovery of dynamic catalysis, catalytic resonance, and overcoming the Sabatier maximum [4 - 7] make it necessary to look for a connection between these phenomena and the nature of the catalysts. Following the discovery of new reactions, new concepts and theories emerged, such as "electron as a catalyst" [8 - 20], "electric field as a catalyst" [21 - 44], the theory of catalytic resonance [5, 6].

The emergence of the electron and the electric field as catalysts in catalysis has raised many questions about the nature of catalysis and the mechanics of catalytic reactions. The peculiarity of these catalysts is that they are fundamental objects of nature. They, along with the proton, do not belong to the chemical elements. The field is not a substance. They literally burst into catalysis and immediately showed themselves in an unusual way. The appearance of the electron in the status of a catalyst labeled itself as catalysis different from traditional catalysis [8 - 18, 45 - 50]. The field manifested itself as a non-

material catalyst, and as a "smart reagent" [51, 52]. The proton has shown itself to be both a catalyst and a reagent [53, 54]. More and more reports are appearing about catalysis without a catalyst [55 - 59]. Therefore, the answer to the question of what should be considered a catalyst in catalytic reactions becomes especially relevant. In catalysis, a major revision of the concepts and ideas that have developed over two centuries is brewing.

The reason why some reactions are perceived as catalysis without a catalyst is the imperfection and contradictions of the current catalysis paradigm. The practice of catalysis is ahead of the theory of catalysis. Catalysis without a catalyst is the most serious challenge to the current catalysis paradigm. Speaking of catalytic reactions without a catalyst, it should be understood that there are catalysts in the reactions themselves. Only these are unusual catalysts. They do not belong to chemical elements or to chemical substances. They have the status of fundamental objects of nature. Fundamental objects have a different nature of interaction with reagents. The current paradigm of catalysis does not know such catalysts. The current catalysis paradigm has overlooked fundamental catalysts.

Electron catalysis is becoming an independent field of research [9 - 20, 60 - 64]. In [9 - 13] the role of the electron as a catalyst in chemical reactions was thoroughly investigated. The development of this concept can lead to a revision of the current concept of the catalytic phenomenon. The concept of "*electron as a catalyst*" gives hope for the disclosure of the mystery of catalysts and the mystery of the single mechanism of catalytic reactions. Judging by the large number of publications, electronic catalysis is becoming a rapidly developing area in catalysis. Recent advances in electronic catalysis show the high potential and versatility of this strategy [12, 60 - 64].

The diversity of catalytic reactions and the multitude of types of catalysis creates the illusion of their uniqueness and dissimilarity. A false notion is created that special and different mechanisms of catalysis are implemented in catalytic reactions. In this diversity, it is difficult to see the common features and unified nature of catalysis. In catalysis, the time has come to generalize the accumulated experimental results. The time has come to identify common features in catalytic reactions and, on this basis, to reveal the unified nature of all types of catalysis. To solve these problems, we will identify and examine the common features inherent in catalytic reactions. Reactions that are catalyzed by electrons and new ideas about the role of electrons in catalysis are a good basis for revealing the mechanisms of catalytic reactions and discovering the laws of catalysis.

Using the concept of "*electron as catalyst*," we set out to solve the following problems:

1. To reveal the unified mechanism of catalytic reactions.
2. To obtain an analytical description of the interaction of participants in a catalytic reaction.
3. Obtain the laws of catalysis from the mechanisms of catalysis.

2. The New Paradigm of Catalysis

The emergence of fundamental objects (electron, proton, and electric field) in catalysis science has exposed and deepened the contradictions of the current catalysis paradigm [65]. A cosmetic approach and a simple refinement of the current catalysis paradigm are not enough to eliminate the contradictions. A radical revision of the current catalysis paradigm is necessary [65].

In [65], the concept of "*electron as a catalyst*" was supplemented with the concept of two fundamental catalysts and the concept of oxidation state. Based on the combined concepts, a new paradigm of catalysis has been proposed. The new paradigm of catalysis is built on the idea of the

existence in nature of two fundamental catalysts: the electron and the proton. The main function of the fundamental catalysts is to increase the reactivity of reagents. In the new paradigm of catalysis, the number of participants in the catalytic reaction is increased. In the old paradigm of catalysis, the participants in the process include the catalyst and the reactants. In the new paradigm of catalysis the participants include initiator, catalyst and reagents (Fig. 1).

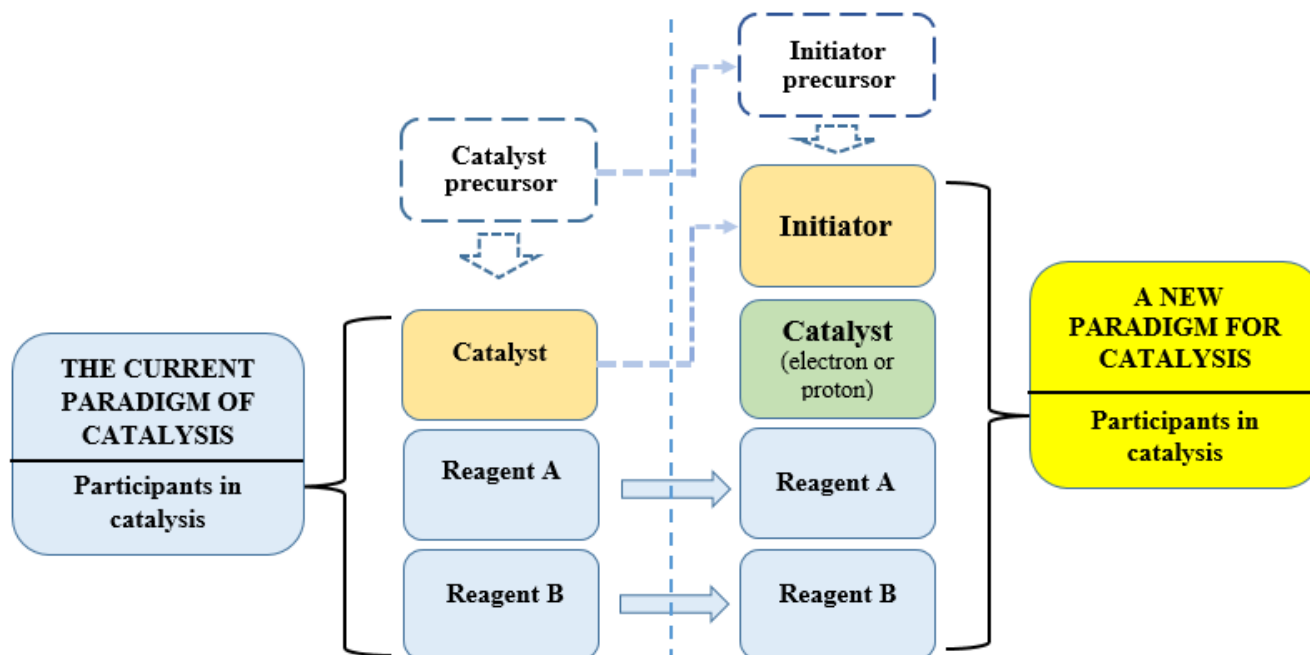


Fig. 1. Expanded composition of catalytic reaction participants in the new catalysis paradigm.

Within the new paradigm of catalysis with the appearance of fundamental catalysts, the need to clarify the terms and definitions has arisen. First of all, this applies to those substances that were traditionally considered to be catalysts. In [65] it was proposed to use the term "catalyst precursor" for them until a more suitable definition appeared. Perhaps a more appropriate term for them would be the name "Initiators".

3. The concept of two fundamental catalysts

The appearance of the electron as a catalyst in catalysis is not an ordinary event. The ubiquity of electrons and their presence in all catalytic reactions without exception together and next to known catalysts creates an unusual situation in catalysis. The question arises: what now counts as a catalyst? With the emergence of the concept of "*electron as a catalyst*" in catalysis, a situation of "*competing catalysts*" arose. In this competition, the electron has a better chance to move the current catalysts into the background. To this end, 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. This determines the universality of the new catalyst. In addition, the ubiquity of electrons finally reveals a common feature that is present in the mechanisms of all catalytic reactions. Until there was a fundamental catalyst (electron) in catalysis, this common feature was lost in the variety of types of catalysis and did not manifest itself. This common feature in the mechanisms of catalysis is the transfer of electric charges by electrons. All of the above applies equally to the proton. Catalysis is a kinetic

phenomenon. The kinetics of catalysis consists in the transfer of electric charges by electrons and protons. A study of the kinetics of electric charge transfer gives unambiguous indications of the mechanism of catalysis. The kinetics of catalytic reactions is fully determined by the rate of electric charge transfer by electrons and protons.

The electron is the second catalyst after the proton, which has a fundamental status in science. In accepting the concepts of "*electron as a catalyst*" and "*proton as a catalyst*", the most important thing must be taken into account: electron and proton are fundamental particles. Their fundamental status makes them special and unique compared to ordinary chemical catalysts. Among the entire family of real 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 "*electric field as a catalyst*" concept. 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. The emergence of fundamental catalysts in catalysis allows us to take the next step and move on to the idea of the existence of only two universal catalysts in nature, while for traditional catalysts it is necessary to reveal their true role and place in catalysis.

In the new paradigm of catalysis, the electron and proton have a special status. These elementary particles are viewed not as additions to the family of known catalysts, but as the only fundamental and universal catalysts. The electric charges of the fundamental catalysts are the main active factor in increasing the reactivity of chemicals. In the new paradigm of catalysis, the nature of the interaction between the catalyst and the reactants is reconsidered. The interaction of fundamental objects does not refer to chemical interaction. This radical revision of the role of electrons and protons in catalysis is justified by their fundamental status and the ubiquity of electrons and protons in nature and in chemical reactions. The fundamental status of electrons and protons in catalysis makes it possible to obtain an analytical description of the mechanism of interaction between the participants in a catalytic reaction and, on this basis, to obtain the laws and equations of catalysis.

4. The problem of the law of catalysis rate

The rate of chemical reactions is determined by an empirical equation as a function of the concentration of reactants and the rate constant. Much effort has been made in chemistry to find out what the reaction rate depends on. Rate equations have been obtained as a function of reactant concentration (law of acting masses, Michaelis–Menten kinetics), temperature (Arrhenius equation, Eyring–Polanyi equation), activation energy (Arrhenius equation), pressure (Clapeyron-Mendeleev equation), solvent polarity (Leidler-Eyring equation, Dimroth-Reinhardt equation) and acid or base strength (Brønsted catalysis equation).

A peculiarity of the equations is that they reflect the dependence of the reaction rate on the reaction conditions. Much attention has been paid to the influence of the reaction conditions on the reaction rate. But the influence of the characteristics of the catalyst on the reaction rate has not been studied. For catalytic reactions, there is a critical need for a different reaction rate equation. What is needed is an equation that displays the effect of the catalyst on the rate. In catalysis, there is still no equation that establishes the dependence of the reaction rate on the characteristics of the catalyst

substance. Moreover, in the two-century history of catalysis, it has not been possible to find out which key factor of the catalyst determines the catalytic activity. It is not known what characteristics of the catalyst substance determine the speed of the catalytic reaction. For these reasons in catalysis, we have to be satisfied with empirical equations. Both the law of acting masses, the Michaelis-Menten equation, and the Arrhenius equation are empirical equations. These equations have nothing to do with any particular mechanism of catalysis. In catalysis, there is a need for equations derived from a particular mechanism of catalysis. The direct transfer of empirical rate laws from an ordinary chemical reaction to a catalytic reaction does not allow us to find out the influence of the characteristics of the catalyst substance on the reaction rate.

There are many indications that catalysis is a fundamental phenomenon, but the science of catalysis does not have the laws of catalysis in its arsenal. The catalyst, which by definition accelerates a reaction, is not represented in the rate equations by its characteristics. This fact is a great paradox in catalysis. This is the problem with the law of catalysis rate in the current catalysis paradigm. Perhaps this is one of the reasons why in catalysis it has not been possible to create a general theory explaining the mechanism of action of catalysts, in spite of the fact that the reactions have been experimentally studied quite well.

The desire to obtain not an empirical, but an analytical description of the mechanism of interaction between the participants in a catalytic reaction encounters great difficulties. The interaction of reagent "A" with reagent "B" in the presence of a catalyst does not have a strict analytical solution in catalysis. In a catalytic reaction, the number of reactants interacting with each other is greater than in an ordinary reaction. A third participant, the catalyst, is added to the reactants. The problem of obtaining a general analytical description of the interaction of the participants in a catalytic reaction is similar to the problem of obtaining a general solution to the three-body problem in physics. In physics, it has been shown that the three-body problem does not have a strict analytical solution. In the new paradigm of catalysis, this problem becomes even more complicated because the number of reaction participants is increased to four (Fig. 1).

Obtaining an analytical law of the catalytic rate as a function of the characteristics of the catalyst substance to replace the empirical law is an urgent need in the science of catalysis. Solving this problem will make it possible to develop targeted strategies for selecting catalysts for specific reactions. Here we show that the transition from empirical equations to analytical equations is possible and is not an unsolvable problem in catalysis. We propose the following roadmap for solving this problem.

1. Conversion of the general problem of the interaction of many participants in a catalytic reaction to the problems of pairwise interaction of the participants in catalysis at different stages of catalysis.
2. Identification of common features in the mechanisms of catalytic reactions and obtaining a model of the universal mechanism of catalysis.
3. Determination of the characteristics of the catalyst substance on which the rate of catalysis depends.
4. Using the characteristics of the reaction participants as parameters in the laws of catalysis.
5. Obtaining the rate law as the mathematical equivalent of the corresponding model of the catalytic reaction mechanism.
6. Obtaining a universal law of catalysis as the mathematical equivalent of a universal mechanism of catalysis.

5. Conversion of the general problem of the interaction of the participants in catalysis to the private problems of pairwise interaction.

Our goal is to obtain a strict analytical description of the catalytic reaction and to obtain the laws of catalysis that follow from the mechanism of catalysis. At first glance, solving this problem seems completely unrealistic, considering that in the new paradigm of catalysis, the number of participants in the catalytic reaction has increased. Below we will show that the model of the interaction of many reaction participants allows for a reduction. It can be reduced to the model of a stage-by-stage interaction of the participants in catalysis. By analogy with the physics problem, we can say that the many-body problem is reduced to a two-body problem. Decomposition of a complex system into noninteracting subsystems is the key to solving the problem of the analytical law of the rate of catalysis. This approach is in full accordance with one of the main provisions of chemical kinetics - the principle of independence of the rates of elementary reactions. Fig. 2 shows the non-interacting subsystems of the general mechanism of catalysis, in which the stage-by-stage interaction of the catalysis participants is realized.

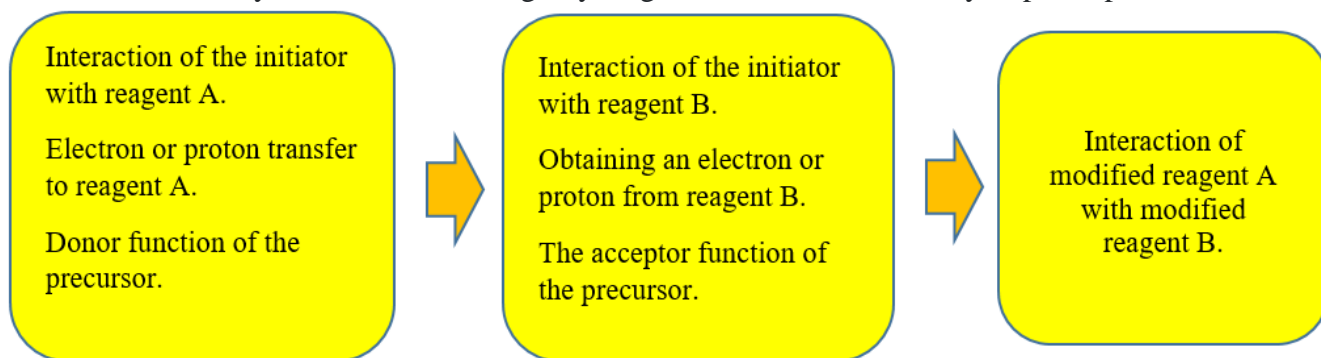


Fig. 2. Staged pairwise interaction of the participants of the catalytic reaction.

6. The problem of determining the mechanism of catalysis

The discovery of another catalytic reaction immediately poses the problem of figuring out the mechanism of the new reaction. The mechanisms of catalysis are so complex that no general theory explaining the mechanism of action of catalysts has been created so far. Therefore, a special explanation of the reaction mechanisms has to be found for almost every specific case [66, 67]. The mechanisms of catalytic reactions are not fully understood and are still widely discussed [68, 69]. Sometimes it is even difficult to determine whether the reaction proceeds as a homogeneous-catalytic process or follows the mechanism of heterogeneous catalysis [70].

Over the long history of catalysis, attempts have been made to reveal the general mechanism of catalytic reactions. The most common catalytic reaction mechanisms are the Langmuir-Hinshelwood mechanism, the Langmuir-Rideal (Rideal-Eley) mechanism, and the Mars-Van Krevelen mechanism. According to the Langmuir-Hinshelwood mechanism, product formation occurs as a result of elementary reactions between adsorbed particles [71]. The Langmuir-Rideal mechanism is a heterogeneous reaction mechanism involving interaction stages between an adsorbed particle and a particle in the homogeneous phase. The Mars-Van Krevelen mechanism is based on the fact that there is an active form of oxygen in the catalyst that is involved in the interaction with the oxidizable reagent. The Mars-Van Krevelen mechanism is used for a wide range of catalytic reactions [72 - 74]. Currently, powerful computational

and experimental methods have been developed to probe reaction mechanisms in catalysis [75 - 76]. In catalysis, the search for a universal mechanism of catalytic reactions continues unabated [77].

Throughout the history of catalysis, neither exclusive nor general models of catalytic mechanisms have led to the scientific classification of catalysts according to their mechanisms of action, nor to the discovery of the laws of catalysis. Some very important general factor of catalysis escaped the attention of researchers and was not considered in the models of catalysis mechanisms. The concept of "*electron as a catalyst*" provides a clue and allows us to identify this common factor in catalysis.

7. The concept of the oxidation state as the key to uncovering the unified mechanism of catalysis

The concept of "*electron as a catalyst*" draws 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 catalyst*" concept. These concepts are interrelated and close in meaning. In the concept of the oxidation state, the electron has a defining role. In the mechanism of catalysis involving electrons or protons, the transfer of electrons or protons to the reactants leads to a change in the oxidation state of the reactants and an increase in their reactivity [65, 78].

The oxidation states need to be considered as an important factor in the mechanism of catalysis. This factor has received insufficient attention in catalysis. The role of oxidation states in the catalysis mechanism has been underestimated. No in-depth studies of the role and place of the oxidation state as quantitative quantities in the catalysis mechanism have been conducted [78]. The increase in the reactivity of reactants directly depends on changes in their charge state. We have used the concept of oxidation states to reveal the mechanism of catalysis [78 - 89]. We used the oxidation states of the participants in the catalytic reaction as quantitative values in deriving the laws of catalysis [78 - 89]. The change in the oxidation state of the reactants is directly related to the electron or proton transfer in the reaction. The change in the state of oxidation of the reactant sets the value of the electric charge transferred to the reactant.

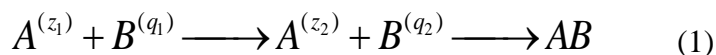
Common features in the mechanisms of various types of catalysis are changes in the charge state of the initiator and the reactants. This is an important common factor in the mechanism of catalysis that has long escaped the attention of researchers. The concept of oxidation states as quantitative values has been one of the missing links in the science of catalysis.

In this article, we show that in catalytic reactions, a general mechanism is realized based on the transfer of electrical charges between the initiator, catalyst, and reactants. A quantitative measure of this process is the change in the charge state of the reaction participants. The main function performed by this mechanism of catalysis is to change the reactivity of the reactants. We have called this mechanism the relay donor-acceptor mechanism of catalysis [65, 89]. It was developed by combining the oxidation state concept with the concept of two fundamental catalysts.

8. Two basic stages in the mechanisms of electron and proton catalysis.

The concept of the oxidation state allows us to identify the common features inherent to catalytic reactions. A hypothetical chemical reaction that takes place without a catalyst can be represented by the following scheme: $A + B \rightarrow AB$. The same reaction in the presence of a catalyst (electron or proton) will

follow the following simplified scheme: $A + B \rightarrow A^{(-)} + B^{(+)} \rightarrow AB$. In a generalized form, the reaction can be represented by the following scheme (Fig. 3):



This scheme takes into account a common feature in the mechanisms of catalytic reactions. This sign is a change in the charge state (oxidation state) of the participants in the reaction under the action of an electron or proton.

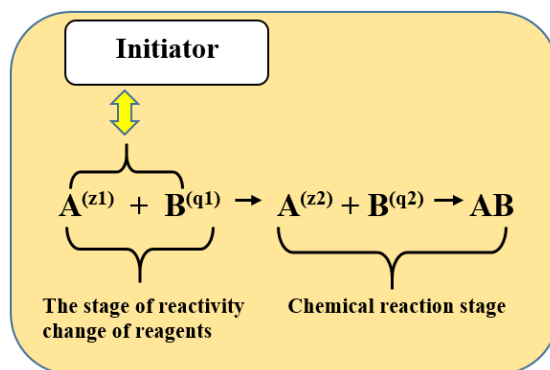


Fig. 3. General scheme of catalysis mechanism in the new paradigm. A , B - reactants; AB - reaction product; $A^{(z_1)}$ - reagent A in the initial charge state; $B^{(q_1)}$ - reagent B in the initial charge state; $A^{(z_2)}$ - reagent A in the final charge state; $B^{(q_2)}$ - reagent B in the final charge state.

Reduction of the model of interaction of many participants of catalysis to the model of stage-by-stage interaction of the participants allowed us to distinguish two enlarged stages in the mechanism of catalysis. The first stage is the change in the reactivity of reactants under the action of electrons and protons. The second stage is the direct chemical reaction of the modified reactants. The division into stages is made on the basis of the type of interaction between the participants in the process.

The stage of changing the reactivity 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 occur under the action of electrons and protons. The remarkable catalytic properties of the free electron and proton stem from the fundamental nature of the interaction in which elementary particles participate. This electromagnetic interaction is one of the four fundamental interactions of Nature. The stage of changing the reactivity of reactants is completed by the appearance of modified reactants, i.e., reactants in a changed charge state.

The main scenario of catalysis is played out at the stage of changing the reactivity of reagents. 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. The main feature of this stage is the fundamental nature of the interaction of participants in the catalytic reaction. This is the most complicated stage of catalysis. Disclosure of the processes occurring at this stage will provide answers to many of the mysteries of catalysis. At this stage in the mechanism of catalysis the pairwise fundamental interaction of initiator with reagents and catalyst with reagents is realized. As a result, there is a change in the charge state of the reactants, the consequence of which is an increase in their reactivity. The catalytic reaction is completed at the second stage by the chemical interaction of the modified reactants with the formation of a charge-neutral molecule of the reaction product.

9. Mechanism of changing the reactivity of reagents

In heterogeneous catalysis, the transfer of electric charges is carried out by electrons. The scheme of the mechanism of change in the reactivity of reagents in heterogeneous catalysis is shown in Fig. 4. The scheme of the catalysis mechanism shows the characteristics of the participants in the process.

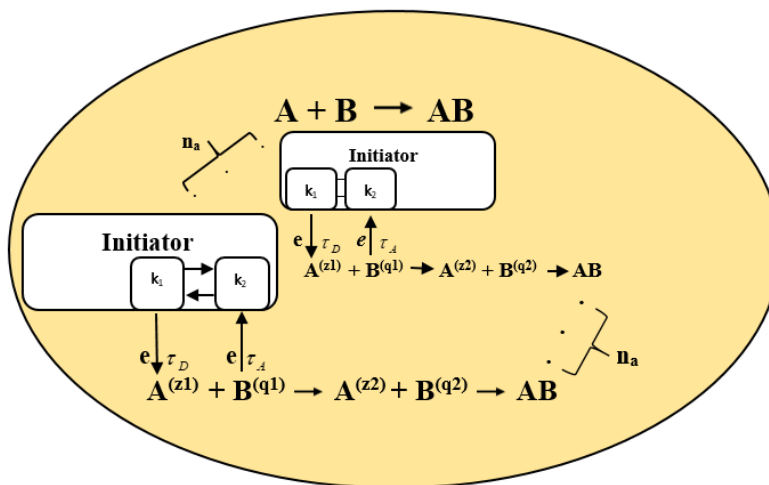


Fig. 4. Scheme of the mechanism of heterogeneous catalysis and characteristics of the catalysis participants. A, B - reagents; AB - reaction product; $A^{(z_1)}$ - reagent A in initial charge state; $B^{(q_1)}$ - reagent B in initial charge state; $A^{(z_2)}$ - reagent A in final charge state; $B^{(q_2)}$ - reagent B in final charge state; k_1 - initial state of initiator oxidation; k_2 - final oxidation state of the initiator; e^- - electrons; n_a - number of active sites; τ_D - donor half-cycle time; τ_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.

In homogeneous catalysis, the transfer of electric charges is carried out by protons. Scheme of the mechanism of change in the reactivity of reagents in homogeneous catalysis is shown in Fig. 5. The diagram of the catalysis mechanism shows the characteristics of the participants.

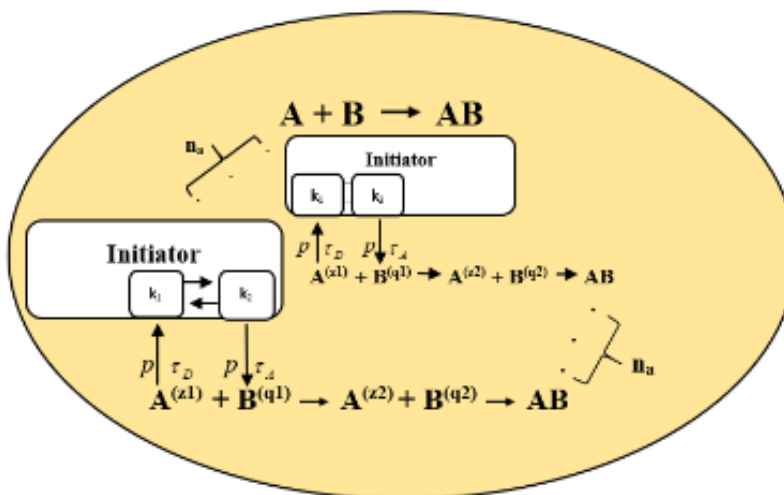


Fig. 5. Scheme of the mechanism of homogeneous catalysis and characteristics of the catalysis participants. A, B - reagents; AB - reaction product; $A^{(z_1)}$ - reagent A in initial charge state; $B^{(q_1)}$ - reagent B in initial charge state; $A^{(z_2)}$ - reagent A in final charge state; $B^{(q_2)}$ - reagent B in final charge state; k_1 - initial state of initiator oxidation; k_2 - final oxidation state of the initiator; n_a - number of active sites; τ_D - donor half-cycle time; τ_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; p - protons.

In field catalysis, the transfer of electric charges is carried out by electrons. Scheme of the mechanism of change in the reactivity of reagents in field catalysis is shown in Fig. 6. The diagram of the catalysis mechanism shows the characteristics of the participants.

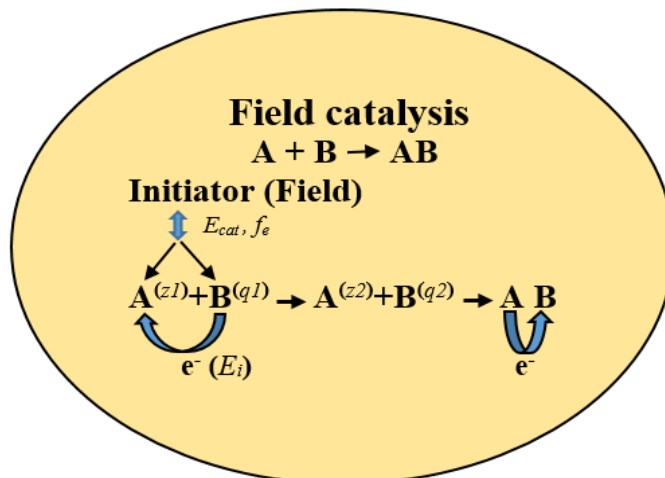


Fig. 6. Scheme of the field catalysis mechanism and characteristics of the catalysis participants. A, B - reagents; AB - reaction product; A^(z1) - reagent A in initial charge state; B^(q1) - reagent B in initial charge state; A^(z2) - reagent A in final charge state; B^(q2) - reagent B in final charge state; e⁻ - electrons; q₁, z₁ — states of oxidation of reactants in initial product; q₂, z₂ — states of oxidation of reactants in final product; E_{cat}- energy; E_i- ionization energy; f_e - frequency.

Scheme of the mechanism of combined catalysis is shown in Fig. 7. The scheme of the mechanism of catalysis shows the characteristics of the participants in the process.

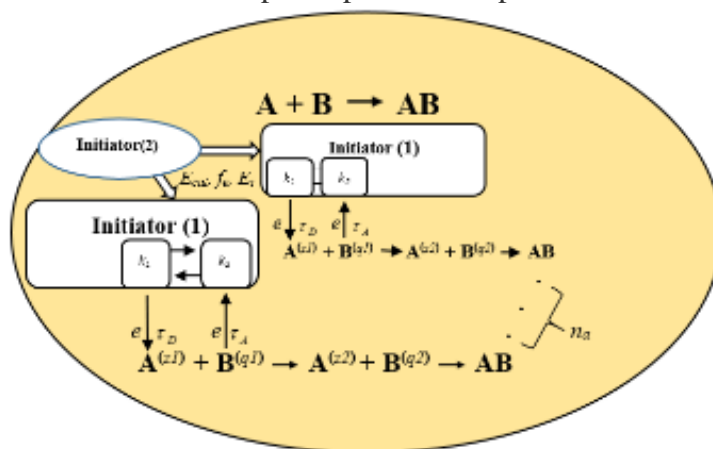


Fig. 7. Schematic of the mechanism of combined catalysis and characteristics of the participants of catalysis.

The models of the mechanisms of heterogeneous, homogeneous, field, and combined catalysis show commonalities and similarities. The dynamics of the charge states of the catalytic participants is a common feature in the mechanisms of different types of catalysis (Fig. 8). The initiator cyclically changes the oxidation state from k₁ to k₂ and back. The stage of changing the reactivity of reagents in different types of catalysis has its own characteristics, but uniformly ends with the formation of modified reagents. Modified reactants are reactants in a modified oxidation state A^(z2) and B^(q2). All catalytic reactions end in the second stage with the chemical interaction of the modified reagents.

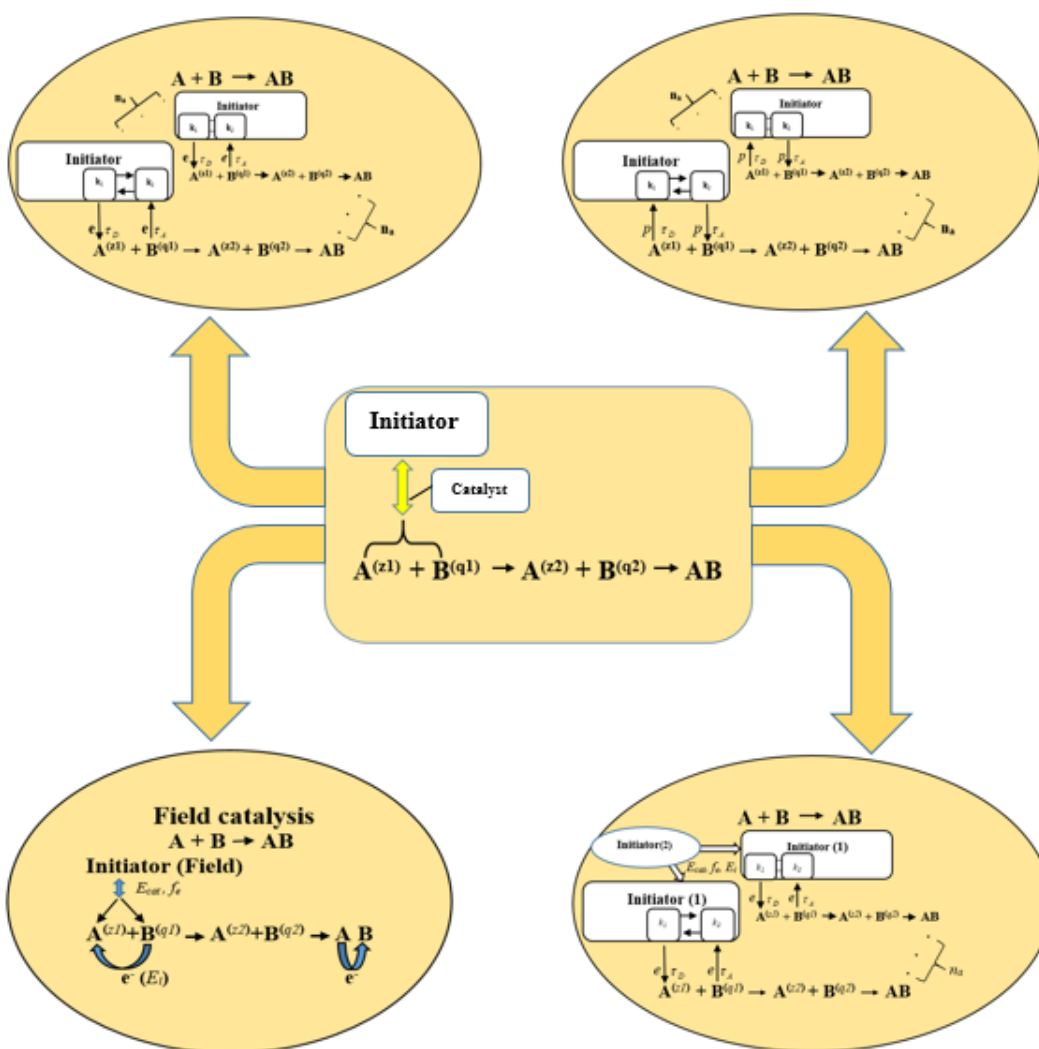


Fig. 8. Dynamics of the charge states of the participants as a common feature in the mechanisms of different types of catalysis.

The separation of two stages in the mechanisms of catalysis on the basis of the type of interaction between the participants in the process makes it possible to reveal the mechanism for increasing the reactivity of the reagents. The secret of increasing the reactivity of the reactants was one of the main secrets of catalysis. With the disclosure of this secret, the role of two fundamental catalysts in the mechanism of catalysis as the main participants in catalysis is revealed. With the disclosure of this secret, it becomes possible to discover the laws of catalysis. The schemes of catalysis mechanisms demonstrate the common nature of different types of catalysis.

10. Relay donor-acceptor mechanism as a universal mechanism of catalysis.

Using the example of heterogeneous catalysis, let us consider a model of the mechanism of catalysis with emphasis on elementary reactions of catalysis. The common features in the mechanisms of catalytic reactions are the transfer of electric charges by electrons and protons and the change in the oxidation state of the reactants with their participation. These processes are realized at the stage of changing the reactivity of the reactants. This is the relay donor-acceptor mechanism of catalysis. It is implemented according to a single-type scheme and is a universal mechanism of catalysis with the

participation of both electrons and protons. The scheme of the relay donor-acceptor mechanism of heterogeneous catalysis is shown in Fig. 9.

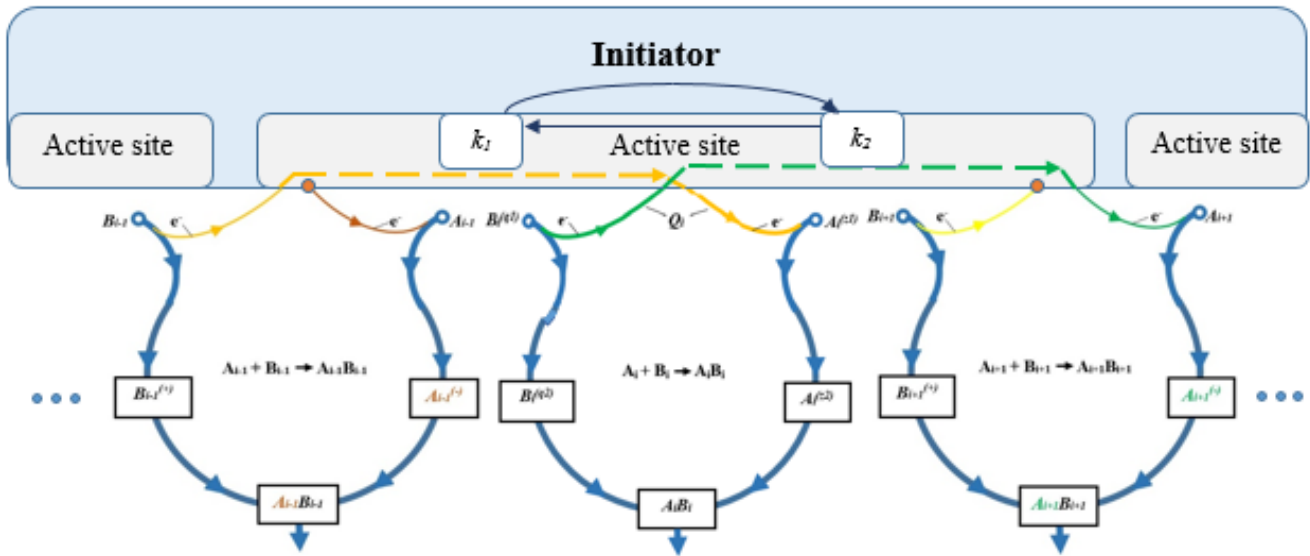


Fig. 9. Diagram of the relay donor-acceptor mechanism of heterogeneous catalysis. A_i, B_i - reagents participating in the i -th elementary reaction; A_{i-1}, B_{i-1} - reagents participating in the $(i-1)$ -th elementary reaction; A_{i+1}, B_{i+1} - reagents participating in the $(i+1)$ -th elementary reaction; $A_i B_i$ - 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; $(A_i + B_i \rightarrow A_i B_i)$ - 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 initiator, which is in the oxidation state k_1 , transfers electrons to reagent A_i , and goes to the charge state with the oxidation state k_2 . The initiator then restores its original charge state k_1 with the electrons received from reagent B_i . Reagent A_i changes its charge state from z_1 to z_2 . Reagent B_i changes its charge state from q_1 to q_2 . The electrons obtained by the initiator are relayed (relayed electrons) to the next reagent A_{i+1} and will be part of the product formed by the other reaction participants in the next $(i+1)$ -stage of catalysis.

The chemical reaction takes place between the charge-conjugated (modified) reagents in a modified oxidation state with the formation of a neutral molecule $A_i B_i$. Electron transfer from the reagent to the initiator causes both the reagent and the initiator to change their charge state. Both the reagent that received an electron and the reagent that gave up an electron change their charge state. According to the law of conservation of charge, the reagents can stay in the changed charge state for a long time, until there is a condition for the mutual compensation of electric charges and the formation of a neutral molecule. In this case, the electric forces come into play. Electrostatic effects are known to make the greatest contribution to catalysis [90]. The electrostatic interaction of the reactants in a changed charge state reduces the energy barrier of the reaction and allows the reaction to proceed at a higher rate.

The catalytic cycle of the initiator is realized in the mechanism of catalysis. The active site of the initiator changes its charge state and goes from the k_1 state to the k_2 state and back. The initiator catalytic cycle has the following quantitative characteristics: the charge state change g ($k_1 - k_2$); donor

halfcycle time (τ_D); and acceptor halfcycle time (τ_A). The quantitative characteristics of the participants of catalysis are used as parameters in the laws and equations of catalysis.

An important conclusion follows from the relay donor-acceptor mechanism of catalysis: a change in the reactivity of the reactants can lead to both acceleration and deceleration of the reaction. This depends on the direction of electron or proton transfer to the reactants, as well as on the depth of change in the oxidation degree (k_1 to k_2). The catalytic reaction rate can be controlled by changing the direction of electron or proton transfer to the reactants or by changing the depth of change in the oxidation degree ($k_1 - k_2$). This mechanism for controlling the reaction rate can be reacted in combined catalysis.

11. Characteristics of reaction participants affecting the rate of catalysis.

In order to derive a law of the rate of catalysis from the mechanism of catalysis, it is necessary to determine the characteristics of the substances of the catalytic participants that affect the rate of the catalytic reaction. From the mechanisms of catalysis it follows that such characteristics of the initiator are its states of oxidation (k_1, k_2), the number of active sites (n_a), time intervals (τ_D, τ_A). The characteristics of the field initiator are energy and frequency (E_{cat}, f_e). Characteristics of fundamental catalysts are fundamental constants (e, F). Characteristics of reactants are their charge states (z_1, z_2, q_1, q_2) and ionization energy (E_i). The characteristics of the reaction product are the number of reagent atoms (m_1, m_2) in the reaction product molecule.

FIG. 10 shows redistribution of roles of participants of catalysis and their characteristics ($e, F, n_a, k_1, k_2, \tau_D, \tau_A, E_{cat}, f_e, m_1, z_1, z_2, m_2, q_1, q_2, E_i$) that affect the reaction rate.

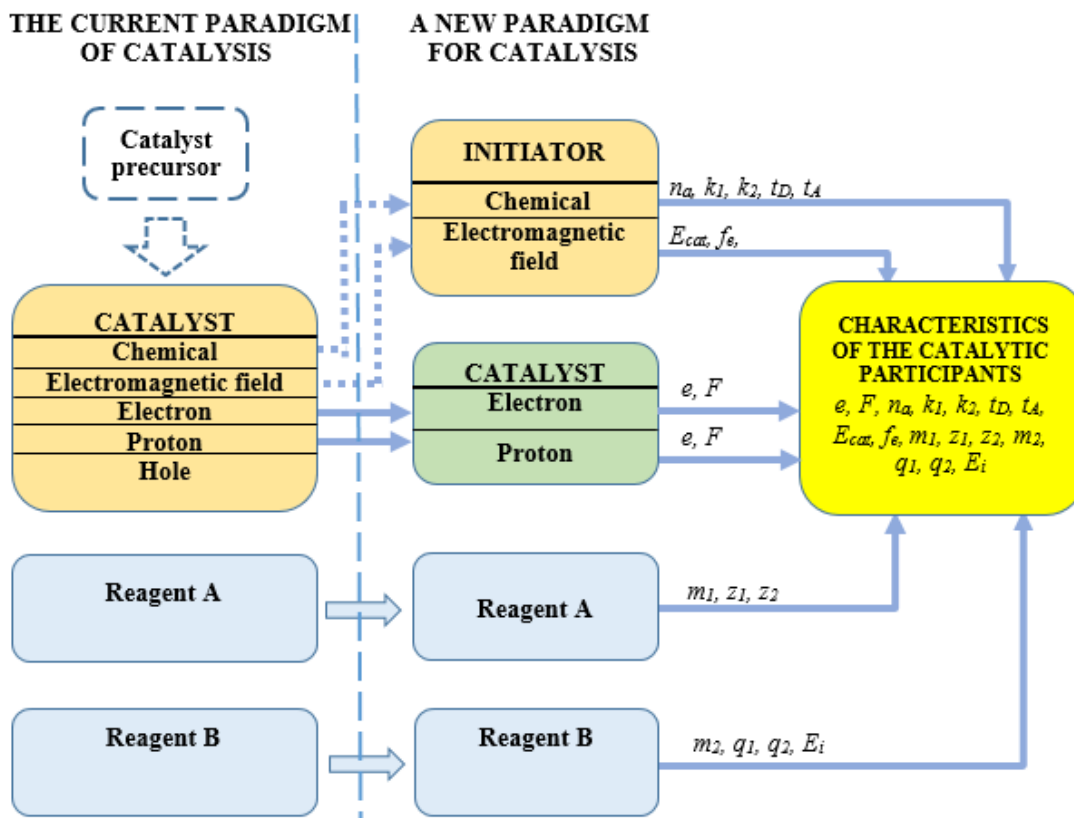


Fig. 10. Redistribution of the roles of the participants in the catalysis and their characteristics.

The conditions under which a catalytic reaction takes place must be considered as influencing the specific characteristics of the reaction participants. These conditions include temperature, pressure, concentration of reactants, mixing, etc. The conditions of the catalytic reaction affect the following characteristics of the participants: k_1 , k_2 , τ_D , τ_A . This influence can be accounted for in the equations of catalysis in the form of temperature coefficients, pressure dependence coefficients, etc., with respect to the listed characteristics.

12. Laws of catalysis

Within the new paradigm of catalysis, we set out to reveal the unified mechanism of catalysis and to obtain the laws of catalysis as a function of the characteristics of the participants in the catalytic reaction: catalyst initiator, and reagents. The laws of catalysis directly follow from the relay donor-acceptor mechanism of catalysis [85-89]. The laws and equations of heterogeneous, homogeneous, and field catalysis are shown in Fig. 11 [85, 87, 88, 89].

a)

b)

c)

Fig.11. Laws and equations of heterogeneous (a), homogeneous (b) and field (c) catalysis.

13. The universal law of catalysis rate

The universal law of catalysis rate is represented by the following equivalent formulas [88]:

$$v_{cat} = \frac{Q_{\Sigma}}{F \bullet t \bullet m_2 \bullet |q_1 - q_2|} \quad v_{cat} = \frac{\sum_{i=1}^m Q_i}{F \bullet t \bullet m_2 \bullet |q_1 - q_2|} \quad v_{cat} = \frac{e \bullet \sum_{i=1}^m M_i}{F \bullet t \bullet m_2 \bullet |q_1 - q_2|} \quad (2)$$

where: e is the electric charge of the electron (proton); M_i is the number of electrons (protons) transferred to the reactant in the elementary reaction of catalysis; M_e is the number of electrons (protons) transferred to the reactant during the reaction of catalysis; Q_{Σ} - is the total electric charge transferred to the reactant during the reaction of catalysis; Q_i - electric charge transferred to the reactant in the elementary reaction of catalysis; m - number of elementary reactions; F - Faraday's constant; q_1 - state of oxidation of the reactant in the initial product; q_2 - state of oxidation of the reactant in the final product; m_2 - number of reactant atoms in the final product molecule; t - catalytic reaction time.

The value in the numerator is the total electric charge received by the reactants during the reaction time. Figure 12 shows the equations that follow from the universal law of the rate of catalysis.

$$v_{cat} = \frac{Q_{\Sigma}}{F \cdot t \cdot m_2 \cdot |q_1 - q_2|}$$

$$n_{cat} = \frac{Q_{\Sigma}}{F \cdot m_2 \cdot |q_1 - q_2|}$$

$$TOF_{cat} = \frac{Q_{\Sigma}}{e \cdot n_a \cdot t \cdot m_2 \cdot |q_1 - q_2|}$$

$$TON_{cat} = \frac{Q_{\Sigma}}{e \cdot n_a \cdot m_2 \cdot |q_1 - q_2|}$$

Fig.12. Universal law of catalysis rate and catalysis equations.

The universal catalysis rate law is derived as a generalization of the laws of heterogeneous, homogeneous, and field catalysis. In the new paradigm of catalysis, the laws of catalytic rate are 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 and follow directly from the mechanism of catalysis. The laws of catalysis are presented as functions of the substance characteristics of all reaction participants. Particular laws of catalysis follow directly from the mechanism model of the corresponding type of catalysis. In essence, each law of catalysis is a mathematical equivalent of the mechanism of the corresponding type of catalysis. The characteristics of the reaction participants enter the laws and equations of catalysis as parameters.

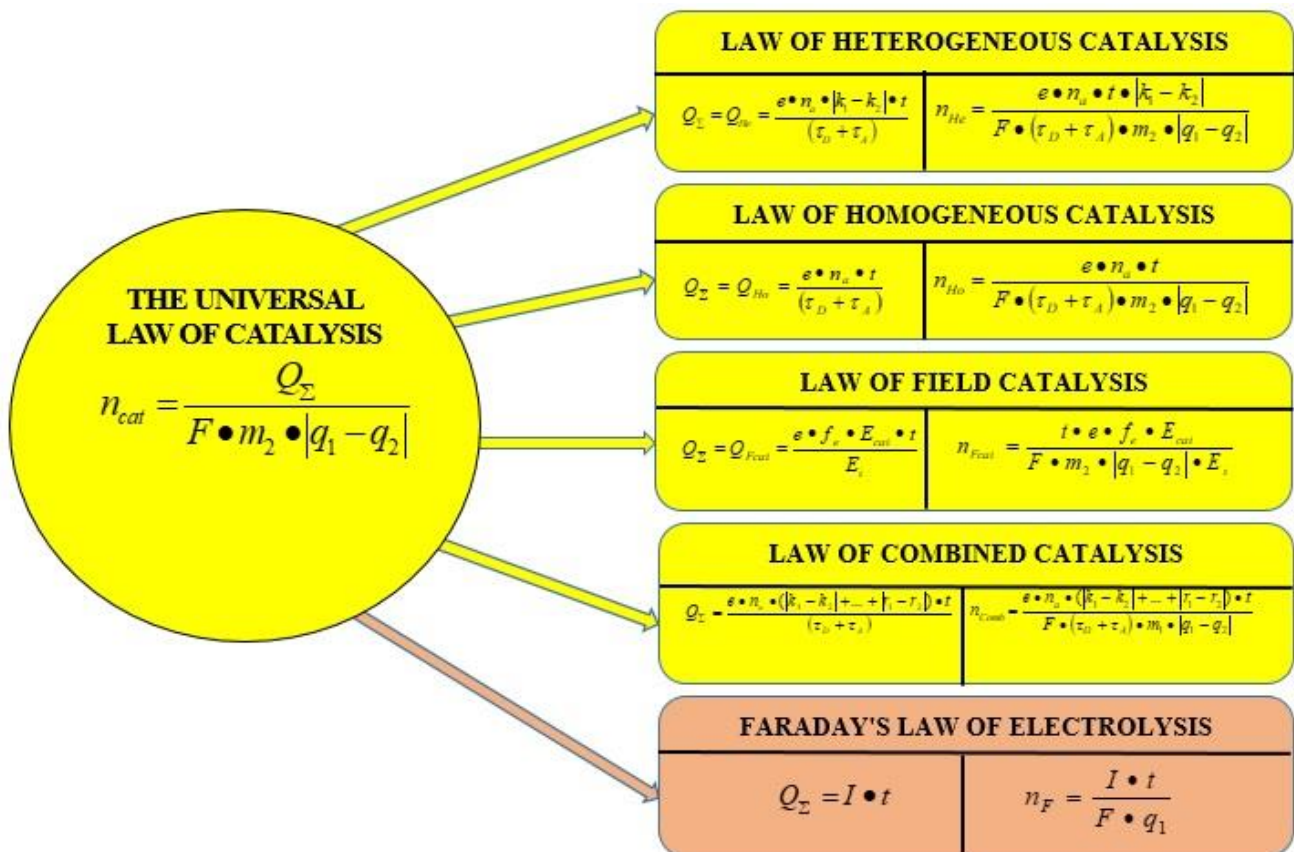


Fig. 13. Unity and interrelation of general and special laws and equations of catalysis.

From the universal law of catalysis, as particular results, follow the laws and equations of heterogeneous, homogeneous, field catalysis, combined catalysis and Faraday's law of electrolysis [88]. This is a confirmation of the unified nature of catalysis and electrolysis. Figure 13 shows equations for calculating the amount of reaction product in the different types of catalysis. These equations follow directly from the generalized equation.

The unity and interrelation of the general and specific laws and equations of catalysis is a confirmation of the unified nature of catalytic reactions. The seeming diversity of catalytic reactions, the seeming diversity of types of catalysis, the seeming difference between them was due to the lack of a unified mechanism and unified laws of catalysis in the current paradigm of catalysis.

14. Characteristics of catalytic reaction participants as parameters in the laws and equations of catalysis

The laws and equations of catalysis directly follow from the mechanism of catalysis. The parameters in the laws and equations of catalysis are the characteristics of the participants in the catalytic reaction (Fig. 14).

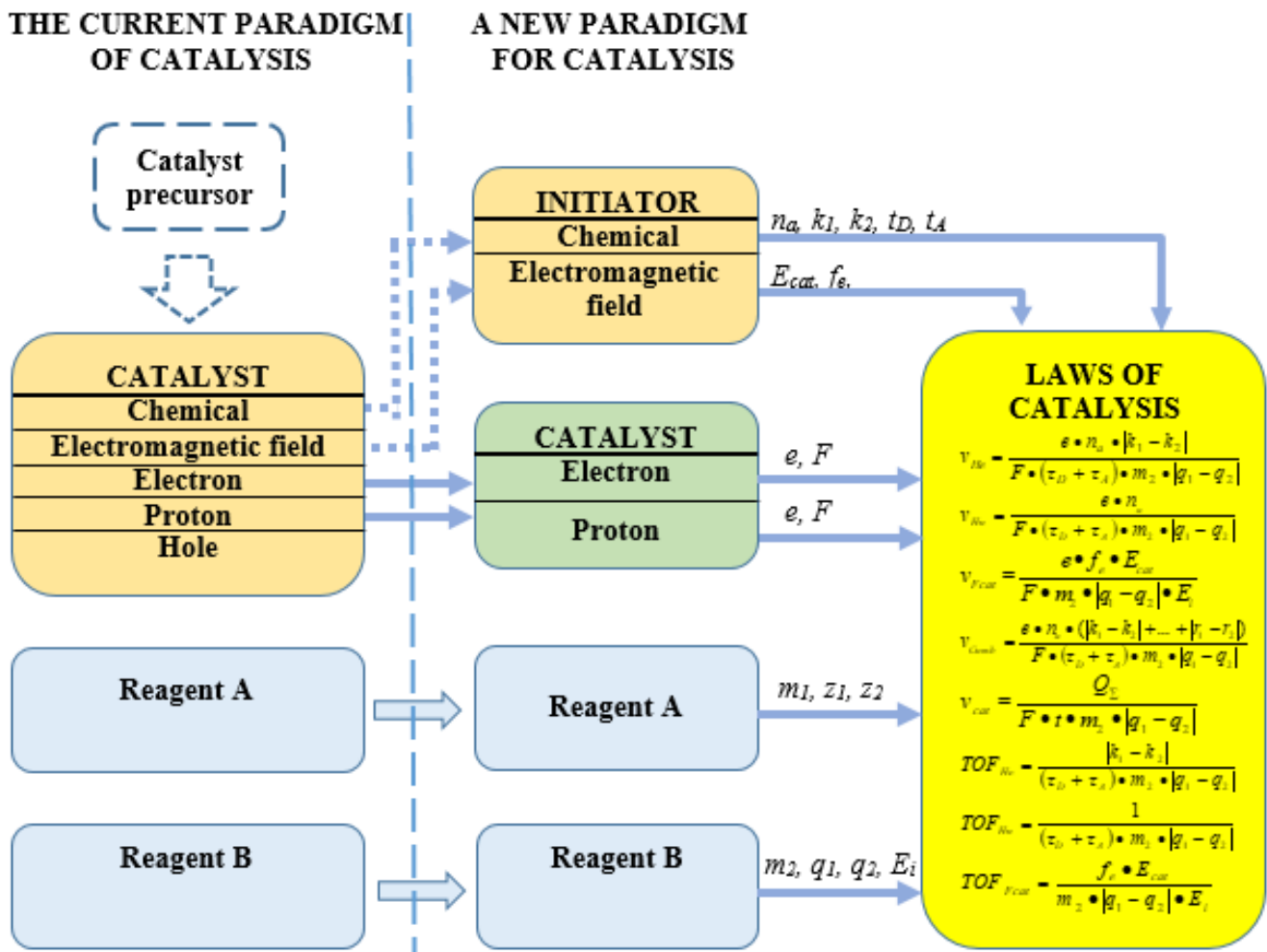


Fig. 14. Redistribution of the roles of the participants in catalysis and characteristics of the participants in the catalytic reaction in the laws and equations of catalysis.

The analytical description of catalytic reactions was obtained as applied to elementary reactions. The substance characteristics of the reaction participants, on which the rate of catalysis depends, were used. The laws and equations of catalysis directly follow from the mechanism of the catalytic reaction and include the characteristics of the substances of the reaction participants as parameters (Fig. 15). The laws of catalysis are the mathematical equivalents of the mechanisms of catalysis.

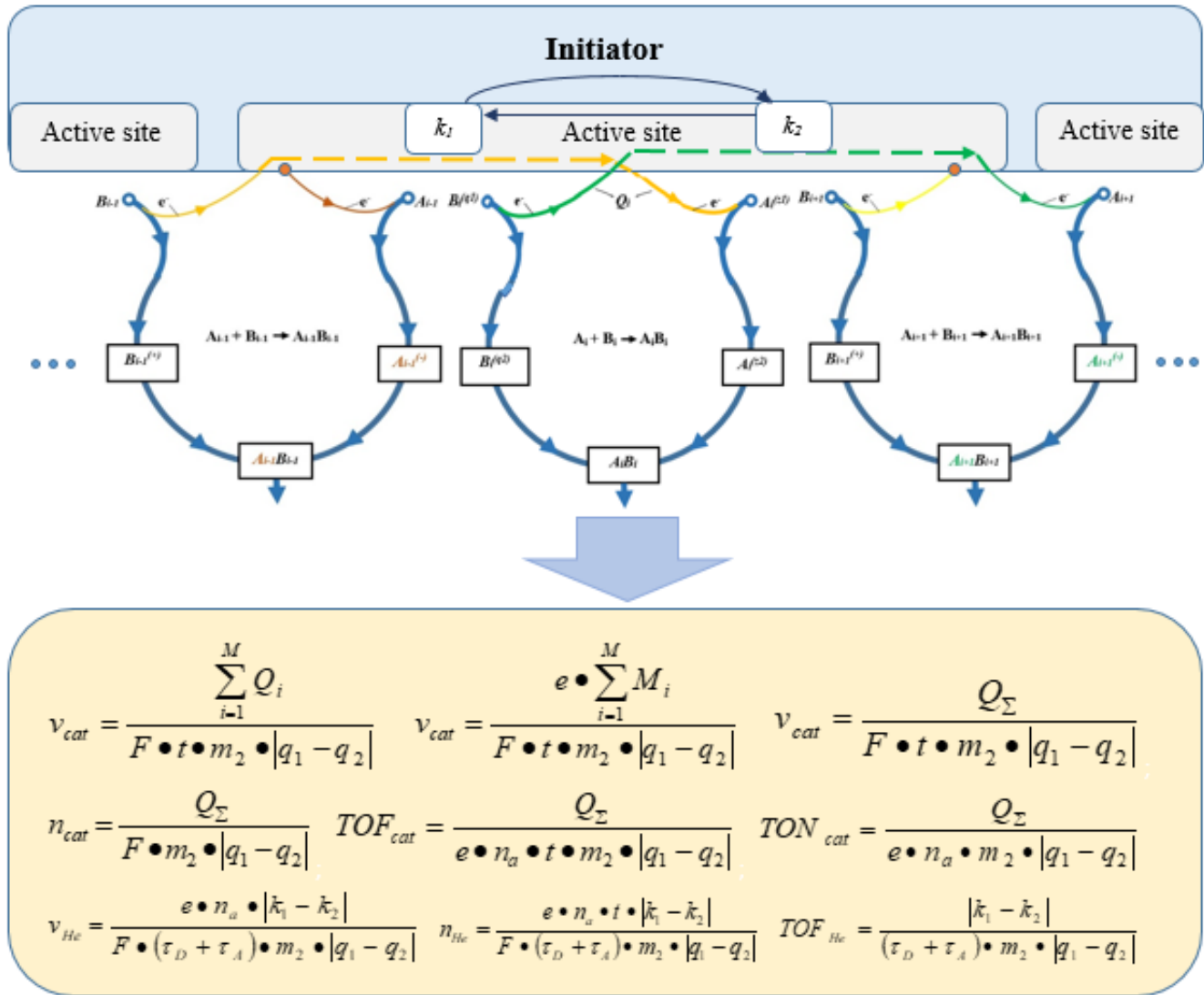


Fig. 15. Obtaining the universal rate law and catalysis equations from the relay donor-acceptor mechanism of catalysis.

15. Catalysis laws as mathematical equivalents of models of catalysis mechanisms

The laws and equations of heterogeneous catalysis are derived from the donor-acceptor mechanism of heterogeneous catalysis. The characteristics of the participants in the catalytic reaction that are included as parameters in the formulas of the laws and equations are shown in Fig. 16. The laws of heterogeneous catalysis are presented as mathematical equivalents of models of the heterogeneous catalysis mechanism.

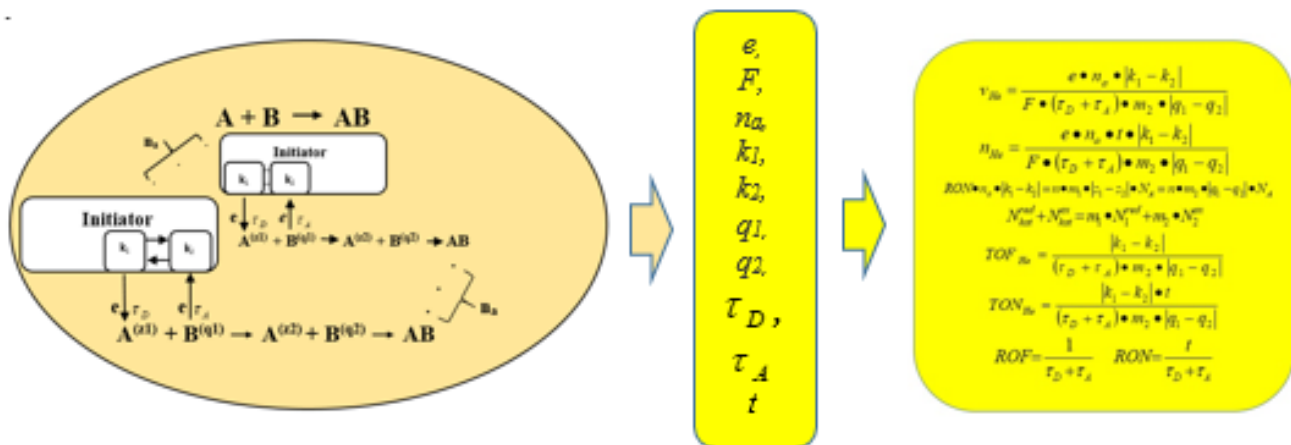


FIG. 16. Laws and equations of heterogeneous catalysis follow from the mechanism of heterogeneous catalysis.

FIG. 17 shows the origin of the heterogeneous catalysis rate law from the heterogeneous catalysis mechanism.

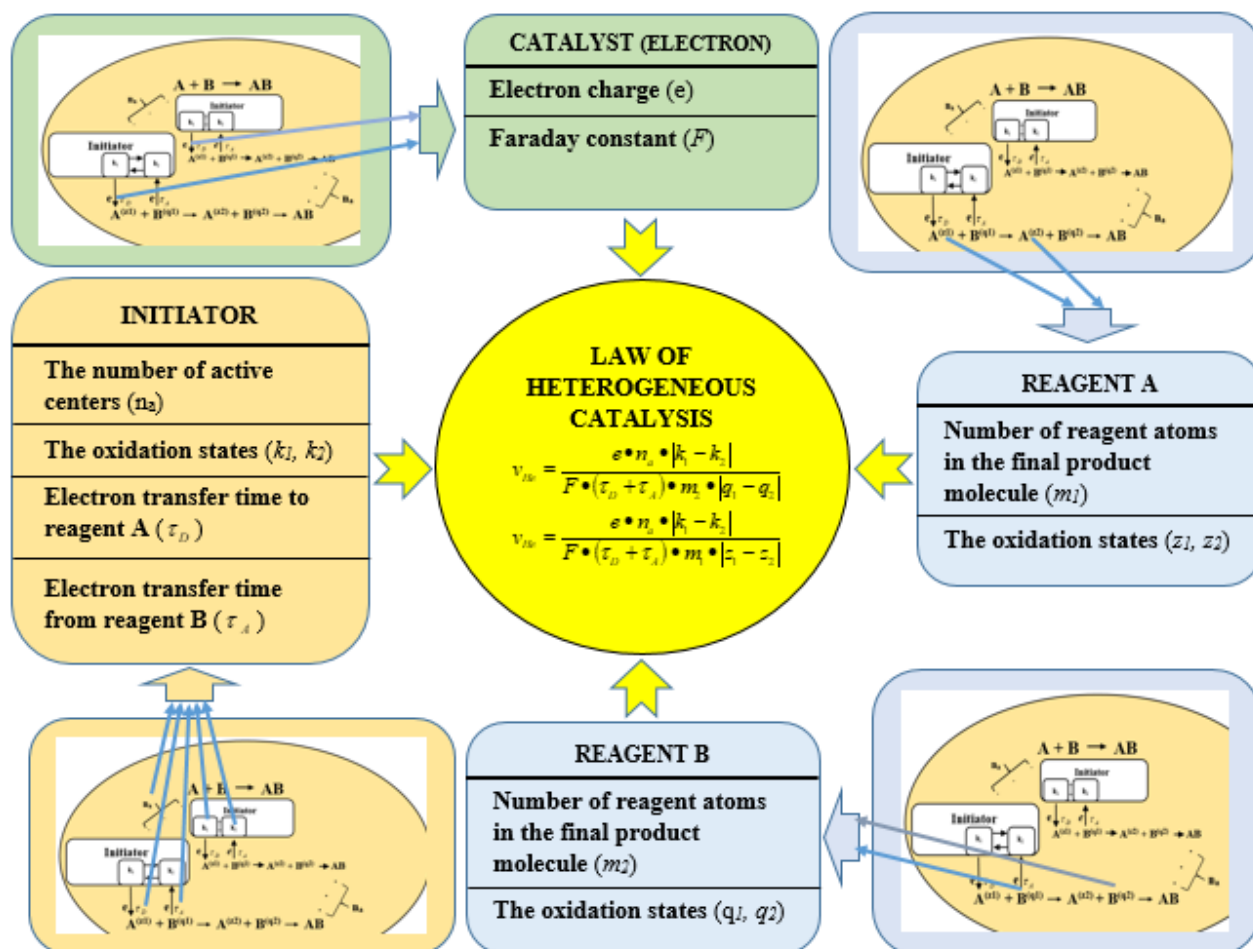


Fig. 17. Origin of the rate law of heterogeneous catalysis from the mechanism of heterogeneous catalysis.

The laws and equations of homogeneous catalysis are derived from the donor-acceptor mechanism of homogeneous catalysis. The characteristics of the participants in the catalytic reaction,

which are included as parameters in the formulas of the laws and equations are shown in Fig. 18. The laws of catalysis are presented as mathematical analogues of the model of the mechanism of homogeneous catalysis.

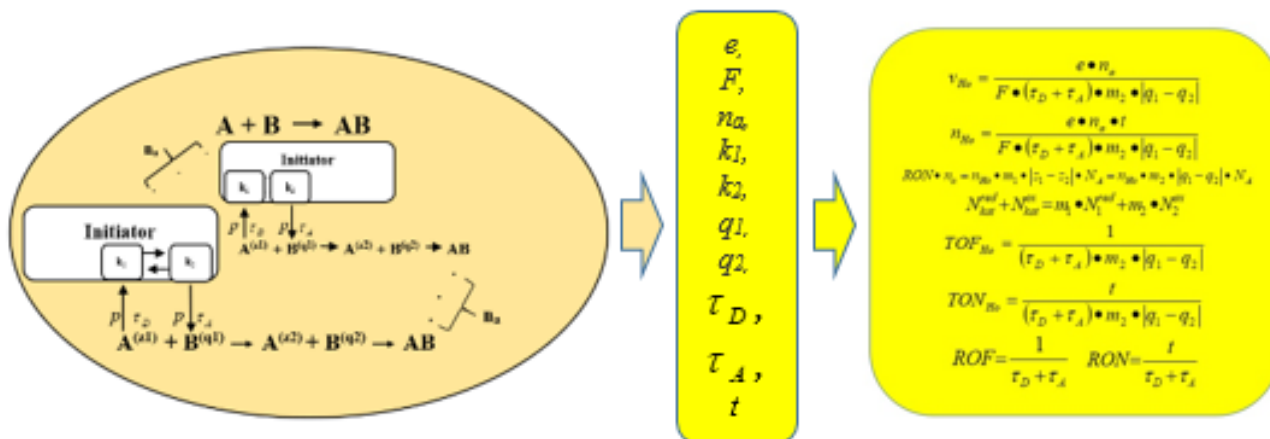


Fig. 18. Laws and equations of homogeneous catalysis follow from the mechanism of homogeneous catalysis

The laws and equations of field catalysis are derived from the donor-acceptor mechanism of field catalysis. Characteristics of the participants in the catalytic reaction, which are included as parameters in the formulas of laws and equations are shown in Fig. 16. The laws of catalysis are presented as mathematical analogues of the model of the mechanism of field catalysis.

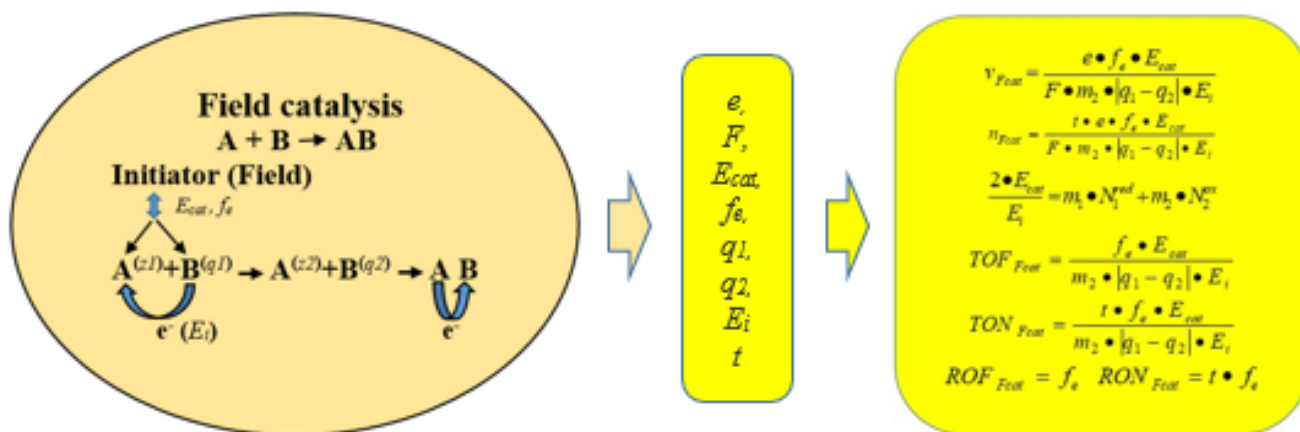


Fig. 19. Laws and equations of field catalysis follow from the mechanism of field catalysis

16. Conclusion

The emergence of the concept of "electron as a catalyst" has become a revolutionary event in catalysis. Unfortunately, it took more than 100 years after the discovery of the electron to come to an understanding of its special role in catalysis - the role of the fundamental catalyst. Unlike the electron, the proton was immediately noticed by Thomas Martin Lowry, and the proton appeared as a catalyst in the donor-acceptor mechanism of homogeneous catalysis a few years after its discovery. The concept of the "electron as a catalyst" opened the way for the transition from empirical equations of the law of the rate of catalysis to analytical equations. The task of searching for analytical models of catalytic reactions

and obtaining laws of catalysis turned out to be closely related to the task of revealing the general mechanism of catalysis.

The unified nature of the various types of catalysis is confirmed:

- the participation in all types of catalysis of elementary particles (electron or proton) in the role of fundamental catalysts;

- a unified mechanism of catalytic reactions based on the transfer of electric charges by the fundamental catalysts;

- the universal law of the rate of catalysis, from which, as particular results, follow the laws and equations of heterogeneous, homogeneous, field, combined catalysis, and Faraday's law of electrolysis.

17. Conclusions

1. The single mechanism of catalytic reactions has been disclosed. In various types of catalysis, the mechanism based on the transfer of electric charges by electrons and protons and on a change in the charge state of the reagents with their participation is realized.

2. The identification of the universal mechanism of catalytic reactions has made it possible to obtain a single universal law of the rate of catalysis.

3. From the universal law of catalysis, the laws of heterogeneous, homogeneous, field catalysis, and Faraday's law of electrolysis follow as particular results.

4. The laws of catalysis are represented by mathematical relations in which the parameters are chemical and physical characteristics of the participants in the catalytic process.

5. The laws and equations of heterogeneous catalysis are represented by the following formulas [84, 87]:

$$\begin{aligned}
 v_{He} &= \frac{e \cdot n_a \cdot |\dot{k}_1 - \dot{k}_2|}{F \cdot (\tau_D + \tau_A) \cdot m_2 \cdot |q_1 - q_2|} & n_{He} &= \frac{e \cdot n_a \cdot t \cdot |\dot{k}_1 - \dot{k}_2|}{F \cdot (\tau_D + \tau_A) \cdot m_2 \cdot |q_1 - q_2|} \\
 RON \cdot n_a \cdot |\dot{k}_1 - \dot{k}_2| &= n \cdot m_1 \cdot |z_1 - z_2| \cdot N_A = n \cdot m_2 \cdot |q_1 - q_2| \cdot N_A & N_{kat}^{red} + N_{kat}^{ox} &= m_1 \cdot N_1^{red} + m_2 \cdot N_2^{ox} \\
 TOF_{He} &= \frac{|\dot{k}_1 - \dot{k}_2|}{(\tau_D + \tau_A) \cdot m_2 \cdot |q_1 - q_2|} & TON_{He} &= \frac{|\dot{k}_1 - \dot{k}_2| \cdot t}{(\tau_D + \tau_A) \cdot m_2 \cdot |q_1 - q_2|} & ROF &= \frac{1}{\tau_D + \tau_A} & RON &= \frac{t}{\tau_D + \tau_A}
 \end{aligned}$$

6. The laws and equations of homogeneous catalysis are represented by the following formulas [86, 87]:

$$\begin{aligned}
 v_{Ho} &= \frac{e \cdot n_a}{F \cdot (\tau_D + \tau_A) \cdot m_2 \cdot |q_1 - q_2|} & n_{Ho} &= \frac{e \cdot n_a \cdot t}{F \cdot (\tau_D + \tau_A) \cdot m_2 \cdot |q_1 - q_2|} \\
 RON \cdot n_a &= n_{Ho} \cdot m_1 \cdot |z_1 - z_2| \cdot N_A = n_{Ho} \cdot m_2 \cdot |q_1 - q_2| \cdot N_A & N_{kat}^{red} + N_{kat}^{ox} &= m_1 \cdot N_1^{red} + m_2 \cdot N_2^{ox} \\
 TOF_{Ho} &= \frac{1}{(\tau_D + \tau_A) \cdot m_2 \cdot |q_1 - q_2|} & TON_{Ho} &= \frac{t}{(\tau_D + \tau_A) \cdot m_2 \cdot |q_1 - q_2|} & ROF &= \frac{1}{\tau_D + \tau_A} & RON &= \frac{t}{\tau_D + \tau_A}
 \end{aligned}$$

7. The laws and equations of field catalysis are represented by the following formulas [87, 88]:

$$v_{Fcat} = \frac{e \cdot f_{\epsilon} \cdot E_{cat}}{F \cdot m_2 \cdot |q_1 - q_2| \cdot E_i} \quad n_{Fcat} = \frac{t \cdot e \cdot f_{\epsilon} \cdot E_{cat}}{F \cdot m_2 \cdot |q_1 - q_2| \cdot E_i} \quad \frac{2 \cdot E_{cat}}{E_i} = m_1 \cdot N_1^{red} + m_2 \cdot N_2^{ox}$$

$$TOF_{Fcat} = \frac{f_{\epsilon} \cdot E_{cat}}{m_2 \cdot |q_1 - q_2| \cdot E_i} \quad TON_{Fcat} = \frac{t \cdot f_{\epsilon} \cdot E_{cat}}{m_2 \cdot |q_1 - q_2| \cdot E_i} \quad ROF_{Fcat} = f_{\epsilon} \quad RON_{Fcat} = t \cdot f_{\epsilon}$$

8. The universal law of catalysis and generalized equations of catalysis are represented by the following formulas [87]:

$$v_{cat} = \frac{Q_{\Sigma}}{F \cdot t \cdot m_2 \cdot |q_1 - q_2|} \quad v_{cat} = \frac{\sum_{i=1}^m Q_i}{F \cdot t \cdot m_2 \cdot |q_1 - q_2|} \quad v_{cat} = \frac{e \cdot \sum_{i=1}^m M_i}{F \cdot t \cdot m_2 \cdot |q_1 - q_2|}$$

$$n_{cat} = \frac{Q_{\Sigma}}{F \cdot m_2 \cdot |q_1 - q_2|} \quad TOF_{cat} = \frac{Q_{\Sigma}}{e \cdot n_a \cdot t \cdot m_2 \cdot |q_1 - q_2|} \quad TON_{cat} = \frac{Q_{\Sigma}}{e \cdot n_a \cdot m_2 \cdot |q_1 - q_2|}$$

9. In the mechanism of catalysis, two stages are distinguished by the type of interaction between the reaction participants. These are the stage of fundamental interaction of the process participants and the stage of chemical interaction of the modified reactants. At the stage of fundamental interaction of the participants, the main scenario of catalysis is played out, which leads to a change in the reactivity of the reactants.

10. The model of the relay donor-acceptor mechanism of catalysis as the unified mechanism of catalytic reactions has been proposed.

11. In the relay donor-acceptor mechanism of catalysis, the fundamental interaction of initiator and catalyst with reagents is realized at the first stage.

12. It follows from the relay donor-acceptor mechanism of catalysis that the rate of catalytic reaction can be controlled by changing the direction of electron or proton transfer to the reagents. The reaction rate control mechanism can be reacted in combined catalysis.

13. The main function of fundamental catalysts in catalytic reactions is to increase the reactivity of the reactants.

14. The electron-catalyst concept, the oxidation state concept, and the concept of two fundamental catalysts were the main missing links in the science of catalysis.

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