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## **THERMOELECTRONIC PHENOMENA IN HETEROGENEOUS CATALYSIS: POSITIVE FEEDBACK LOOP ON TEMPERATURE IN THE CATALYTIC CYCLE**

***Abstract.** The mechanism of heterogeneous catalysis taking into account the influence of temperature is briefly considered in the development of the concept "electron as a catalyst". Here the catalytic cycle includes the heat transfer and electron generation besides the mass transfer. The mechanism of temperature influence in heterogeneous catalysis is realised through the generation of electrons in a positive feedback loop. This mechanism involves the Edison and Seebeck thermoelectronic effects. The catalytic cycle of heterogeneous catalysis is supplemented with a thermoelectronic stage. The thermoelectronic stage of catalysis involves heat transfer and electron generation. Energy transfer to the active centre of the catalyst is an integral part of the catalytic cycle. Energy transfer is considered as a positive temperature feedback loop. The generation of electrons in the positive feedback loop and their transfer to the reactants leads to an increase in reactivity of the reactants. The positive temperature feedback loop leads to an exponential (sigmoidal) dependence of the reaction rate.*

***Keywords:** "electron as a catalyst" concept, thermoelectronic stage of catalysis, positive feedback loop, donor-acceptor mechanism of catalysis, Seebeck effect, Edison effect.*

### **1. Introduction**

The emergence of the "electron as a catalyst" concept [1 - 12] and the discovery of electric field catalysis [13 - 33] allow us to reveal the role of electrons in the mechanism of heterogeneous catalysis. The essential role of electrons in heterogeneous catalysis is indicated by the high sensitivity of catalytic activity to the Seebeck effect and to the electrical surface potential [34 - 45]. This is indicated by the high sensitivity to other external stimuli, which are in one way or another connected with the electron transfer and lead to the modulation of the electron density on the catalyst surface [34 - 45].

Thermal and non-thermal effects in catalysis have a close resemblance. Therefore, thermal effects can be masked by non-thermal effects and remain unnoticed [46 - 47]. Thermal-stimulated catalysis based on the Seebeck effect shows high efficiency [34 - 36]. At the same time, thermoelectric phenomena in catalysis have been little studied [48]. The high sensitivity of heterogeneous catalysis to thermoelectric stimulation [34-36] is evidence that the Seebeck effect organically fits into the mechanism of heterogeneous catalysis. We assume that thermoelectric effects are an integral part of the mechanism of heterogeneous catalysis.

In the "electron as a catalyst" conception, the main task is to reveal the mechanism of electron regeneration in a catalytic cycle. It is necessary to find out how in an elementary reaction the catalyst is

regenerated for the next elementary reaction. Here we set out to find out the mechanism of the influence of temperature on the catalytic activity and on the mechanism of electron regeneration.

## 2. Temperature gradients on the active catalyst centres

It is known that heterogeneous catalytic reactions occur on the surface of the active catalytic centres. Heat release of exothermic reaction occurs in local areas of space on the catalyst surface. Local heating effects and temperature gradients are observed on the catalyst surface [46].

The thermal energy of the exothermic reaction leads to a significant increase in the temperature of the active centres of the catalyst. The heating of a local area of the catalyst surface occurs in a very small volume of space. This results in a high temperature gradient at the active centres where the chemical reaction takes place (Fig. 1a). In the local area where the reaction occurs, the temperature exceeds the temperature in the reactor (Fig. 1a). After the high temperature gradient occurs, the heat energy dissipates. If the rate of heat energy dissipation is low, the temperature of the active centre may be much higher than the catalyst carrier temperature and the reactor temperature (FIG. 1b).

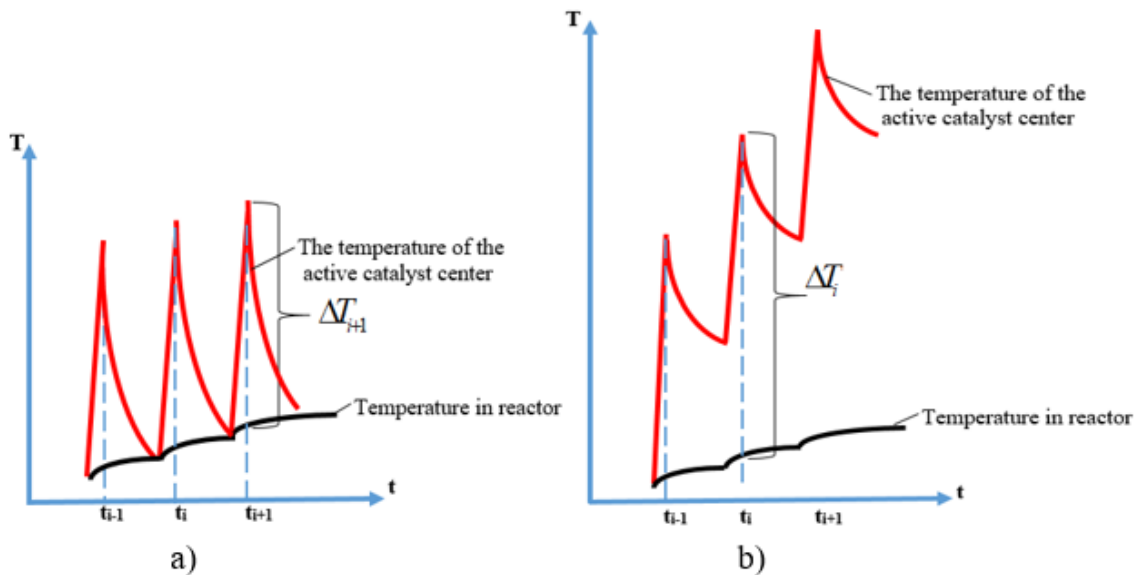


Fig. 1. Temperature gradients on the catalyst active centres. a) - at high rate of energy dissipation; b) - at low rate of energy dissipation;  $T$  - temperature;  $t$  - time;  $t_{i-1}$ ,  $t_i$ ,  $t_{i+1}$  - time of  $(i-1)$ -th,  $i$ -th,  $(i+1)$ -th elementary reaction;  $\Delta T_i$ ,  $\Delta T_{i+1}$  - temperature gradients of the catalyst active centre for the  $i$ -th,  $(i+1)$ -th elementary reaction.

Two oppositely directed processes work on the catalyst's active centre temperature. One process leads to an increase in the temperature of the active centre of the catalyst due to the energy of the exothermic reaction. The second process is the dissipation of thermal energy. The dissipation leads to a decrease in the temperature of the active centre of the catalyst. Increasing the temperature gradient allows the use of nanocatalysts, while reducing the heat energy dissipation can be achieved by using substances with low thermal conductivity as the catalyst carrier.

## 3. Thermoelectronic phenomena in heterogeneous catalysis

In electric circuits, where Edison and Seebeck thermoelectric effects occur, there are high temperature gradients, electron transfer and contact of dissimilar substances. Conditions similar to these are created on the

catalyst surface. There are also high temperature gradients on the active centres of the catalyst and the interaction of dissimilar substances and electron transfer. The general features are shown in Fig. 2. Both thermoelectric phenomena (Edison effect and Seebeck effect) and catalysis are kinetic phenomena. These phenomena are accompanied by electron transfer. In the Seebeck effect, electrons are transported by contact between heterogeneous conductors. In catalysis, electrons are transported by contact of heterogeneous substances on the catalyst surface. Electron transfer in heterogeneous catalysis, by analogy with electric current in an electric circuit, can be regarded as a local diffusion electric current. The Seebeck effect is realised in the presence of a temperature gradient in the electric circuit section. In catalysis, there is also a high temperature of the active centre of the catalyst and high temperature gradients between the electron donor and electron acceptor. In the Seebeck effect, electrons are generated and transferred between heterogeneous conductors. In the mechanism of heterogeneous catalysis, electrons are also generated and transferred between heterogeneous substances participating in the reaction.

In a catalytic reaction, the process of attaching an electron to an acceptor results in the release of energy by the acceptor and the creation of a temperature gradient. Energy is expended in the transfer of the electron by the donor. This results in a temperature gradient between the donor and the acceptor.

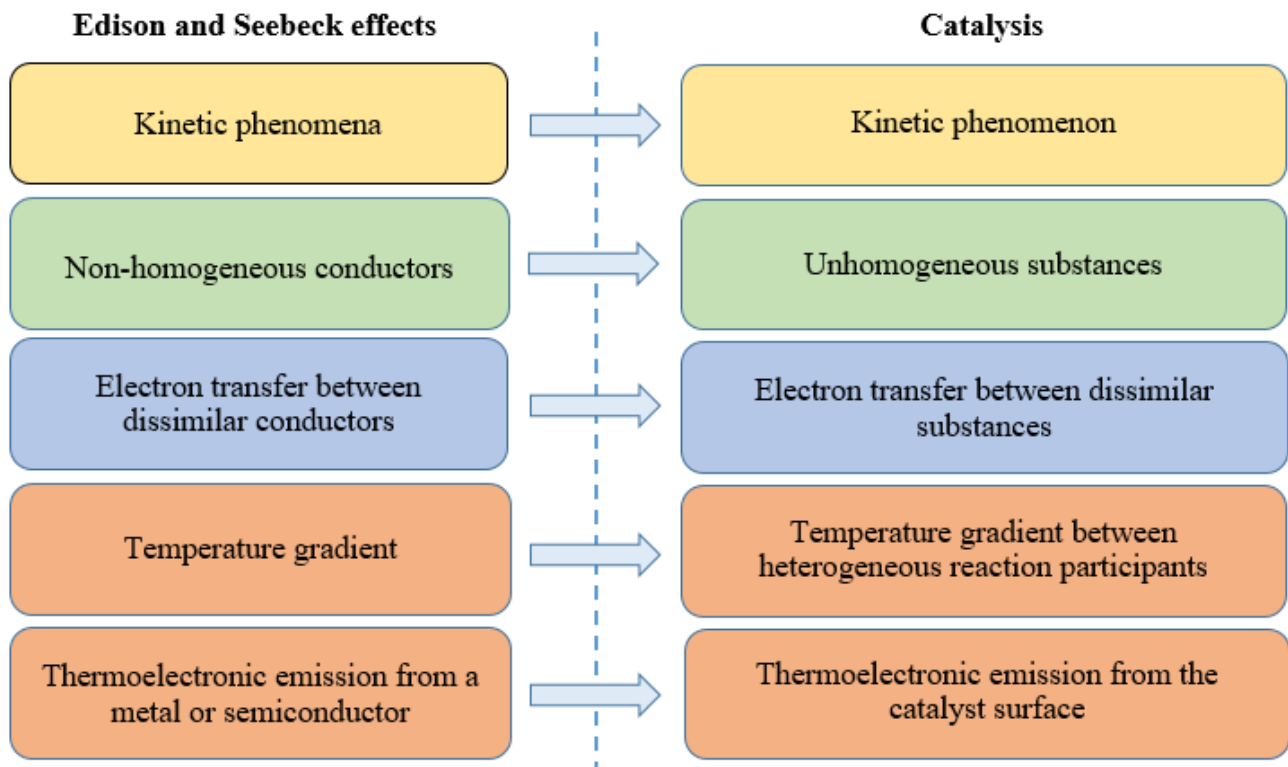
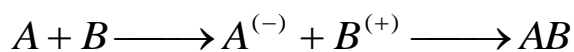


Fig. 2. Common signs of thermoelectric phenomena in electrical circuits and thermoelectric phenomena in catalysis.

Thus, such signs as electron transfer, contact of dissimilar substances on the catalyst surface, high temperature gradients indicate the reality of thermoelectric effects in heterogeneous catalysis.

#### 4. Catalytic cycle with mass transfer and heat transfer in heterogeneous catalysis

In catalysis a complicated combined catalytic cycle with the mass transfer and heat transfer is realized (Fig. 3). Combining the "electron as catalyst" concept with the oxidation degree concept [49 - 61] makes it possible to present the catalytic reaction in the following scheme:



In a catalytic reaction, reagents A and B change their charge state by the action of electrons and are transformed into modified reagents  $A^{(-)}$  and  $B^{(+)}$ . The reactants and the catalyst are affected by the reactor temperature  $T_2$ . The catalyst active sites are additionally affected by exothermic reaction temperature  $T_1$  (Fig. 3). Temperature gradient and thermoelectronic effects are realized on the active catalyst centres under the influence of heat transfer. The charge state of the reactants changes under the influence of electrons (Fig. 3).

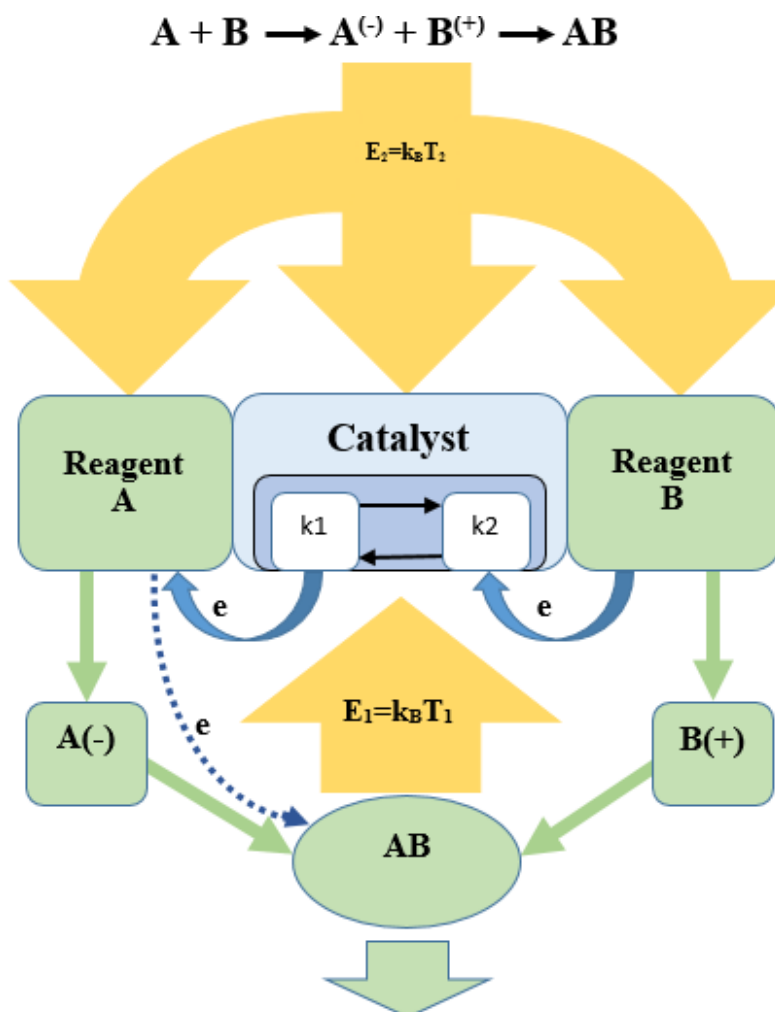


Figure 3. Mass transfer and heat transfer in a heterogeneous catalytic reaction.  $A^{(-)}$  - reagent A in altered charge state;  $B^{(+)}$  - reagent B in altered charge state; AB - reaction product substance;  $E_1$  - exothermic reaction energy;  $k_1$ ,  $k_2$  - oxidation degrees of catalyst;  $k_B$  - Boltzmann constant;  $T_1$  - exothermic reaction temperature;  $T_2$  - reactor temperature;  $E_2$  - external energy.

Electrons that participated in the current elementary reaction are included in the final product and do not participate in the next elementary reaction (Fig. 3). The second reaction product, thermal energy, completes the catalytic cycle and leads to an increase in the temperature of the active centre of the catalyst. The temperature in the local area on and near the surface of the catalyst increases. The

temperature gradient creates a condition for the implementation of Edison and Seebeck effects on the catalyst surface. Through realization of thermoelectronic effects on the catalyst surface the thermal energy of exothermic reaction  $E_1$  fulfils a function of generation of new electrons for the next elementary reaction.

### 5. Thermoelectronic stage as an integral part of the catalytic cycle of heterogeneous catalysis

An additional stage (Fig. 4) is introduced into the mechanism of heterogeneous catalysis. At this stage, the heat energy of the exothermic reaction is transferred to the active centre of the catalyst. Under the influence of thermal energy, the Seebeck and Edison effects are realized in this stage. We called this stage *the thermoelectronic stage*. In this stage the heat transfer and generation of electrons for the next elementary reaction takes place. This stage forms a positive temperature feedback loop.

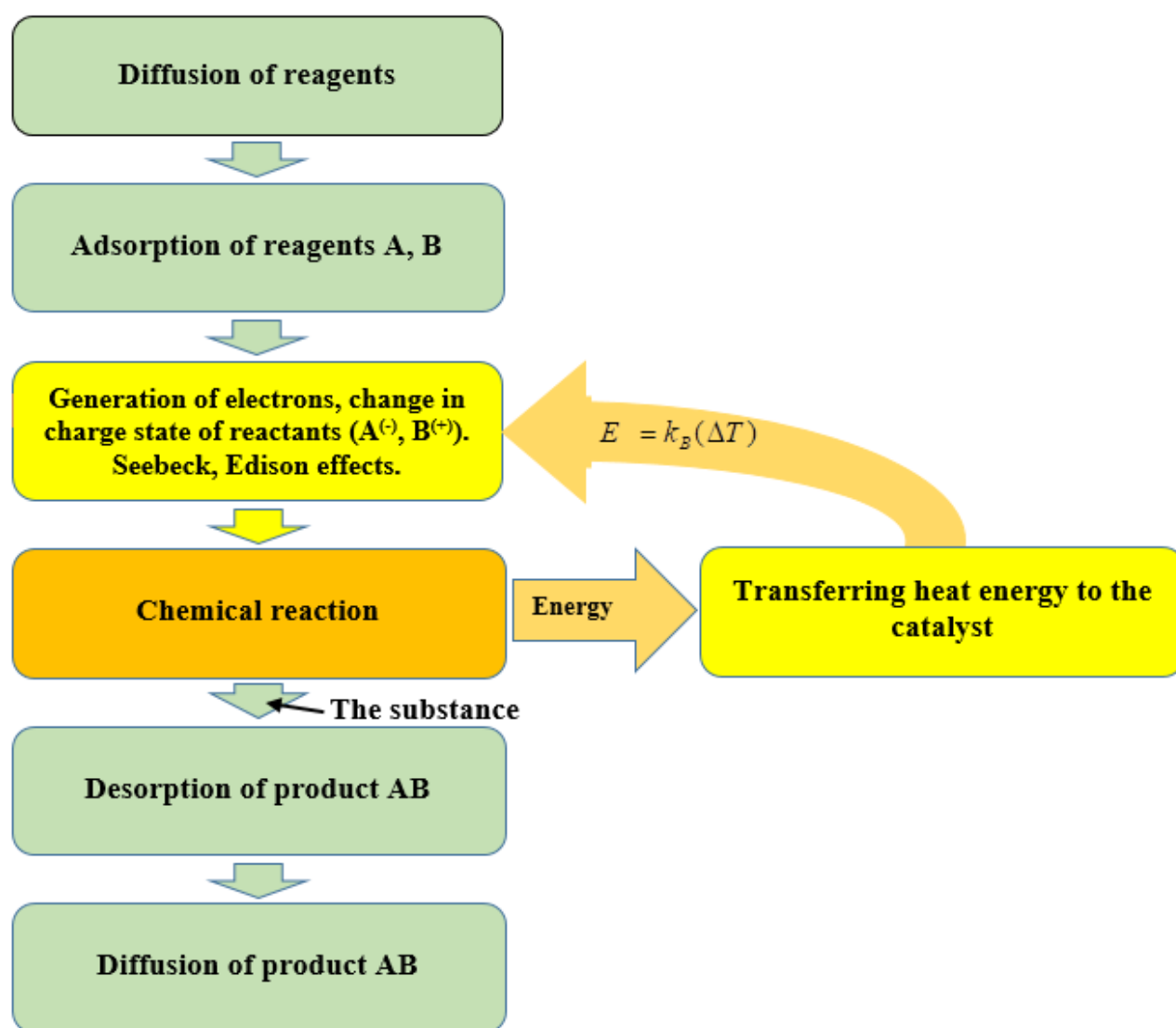


Figure 4. Heat transfer stage and electron generation stage (thermoelectronic stage) in the mechanism of heterogeneous catalysis.  $E$  - energy of exothermic reaction;  $A^{(-)}$  - reagent A in final charge state;  $B^{(+)}$  - reagent B in final charge state; AB - reaction product.

Through the positive feedback loop, the chemical stage affects the fundamental interaction stage of the reactants (Fig. 5).

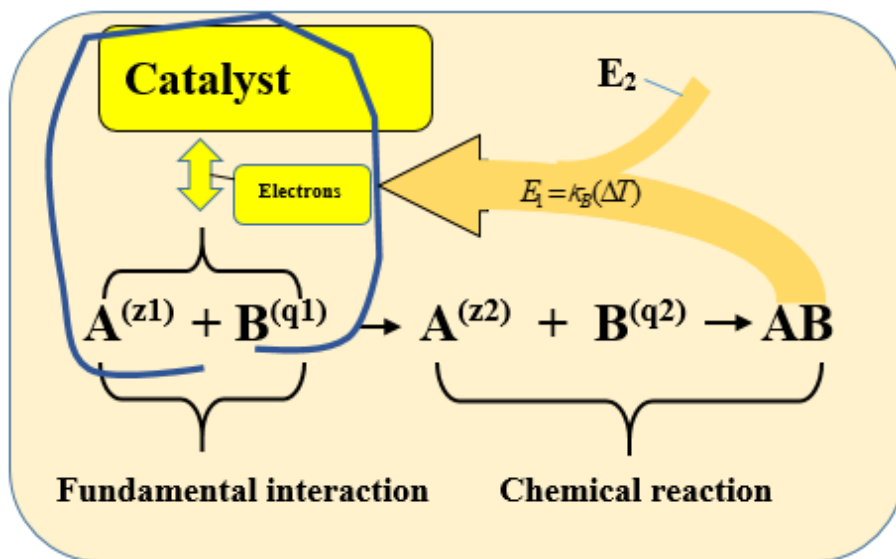


Fig. 5. Schematic of the influence of the chemical stage on the fundamental interaction stage along the positive feedback loop.  $A^{(z_1)}$  - reagent A in initial charge state;  $B^{(q_1)}$  - reagent B in initial charge state;  $A^{(z_2)}$  - reagent A in final charge state;  $B^{(q_2)}$  - reagent B in final charge state; AB - reaction product;  $q_1, z_1$  - oxidation degree of reactants in initial product;  $q_2, z_2$  - degrees of oxidation of reactants in final product;  $k_B$  - Boltzmann constant;  $\Delta T$  - temperature gradient of active centre of catalyst;  $E_1 = k_B(\Delta T)$  - energy, transferred through positive feedback loop;  $E_2$  - external energy.

## 6. Thermal energy as one of the "products" of an exothermic reaction and the positive feedback loop in a catalytic cycle.

In an exothermic catalytic reaction, there are two types of catalytic reaction products. One is the substance as the target product of the reaction. In addition to the material product of the catalytic reaction, another intermediate "product" of the reaction is the thermal energy of the exothermic reaction. Under the influence of thermal energy, electrons are generated for the next elementary reaction. Thermal energy is involved in the catalytic cycle. The heat transfer stage completes the catalytic cycle and is the positive feedback loop in the catalysis mechanism (Fig. 6). Thermoelectronic effects similar to Edison and Seebeck effects are realized on the catalyst surface in conditions of temperature gradient  $\Delta T$ . The peculiarity of these effects in the catalysis is that the electron transfer does not occur in a closed circuit, but between the participants of the process. The electrons change the charge state of the reactants and take part in the catalytic cycle as a substance. Thus, one of the end products of the elementary catalytic reaction (thermal energy ( $E = k_B(\Delta T)$ )) activates the next elementary reaction. This results in a positive feedback in the mechanism of heterogeneous catalysis (Fig. 6).

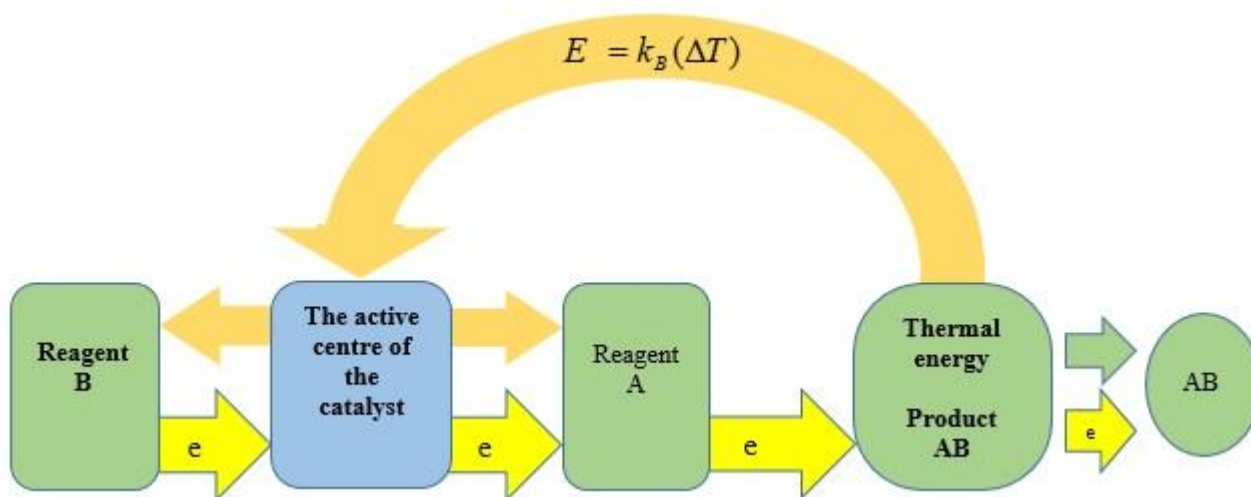


Figure 6. Transfer of electrons ( $e$ ) and heat energy ( $E = k_B(\Delta T)$ ) in a heterogeneous catalytic reaction

## 7. Peculiarities of electrons' behaviour in electric circuits and in catalytic reactions

The behaviour and fate of free electrons in the Seebeck effect in electric circuits and in catalysis have both similarities and differences. In a conductor, the electrons behave like an electric current, while in a catalytic reaction they create a product flux. There is some formal similarity and similarity. But further processes involving electrons in conductors and in chemical reactions are radically different.

In the Seebeck effect, free electrons show themselves. This manifests itself as an electric current in a circuit. Free electrons act as energy carriers. In thermoelectronic phenomena in catalysis the electrons do not remain free, but form part of the final product (Fig. 3, Fig. 6). This manifests itself as the formation of a new chemical substance, which includes in its composition the electrons generated in the thermoelectronic effects. This is how heat energy in a catalytic reaction is involved in the synthesis of a chemical. If in electric circuits the transfer of electrons is an electric current, then in the catalytic reaction the transfer of electrons is associated with the flux of a new substance containing acceptor electrons.

## 8. Mechanism of heterogeneous catalysis with positive temperature feedback

There are many examples when positive feedback results in exponential growth of a quantity. Examples are chemical chain reactions, population explosion, industrial growth, population growth, growth of bacteria in a colony, etc. Exponential growth is due to positive feedback [62]. Positive feedback is present in autocatalytic chemical reactions.

In heterogenic catalysis, the essence of positive feedback is that the number of electrons in the reactant interaction zone increases with increasing temperature. The mechanism of heterogeneous catalysis involves a positive temperature feedback loop that closes on the active site of the catalyst (Fig. 7).

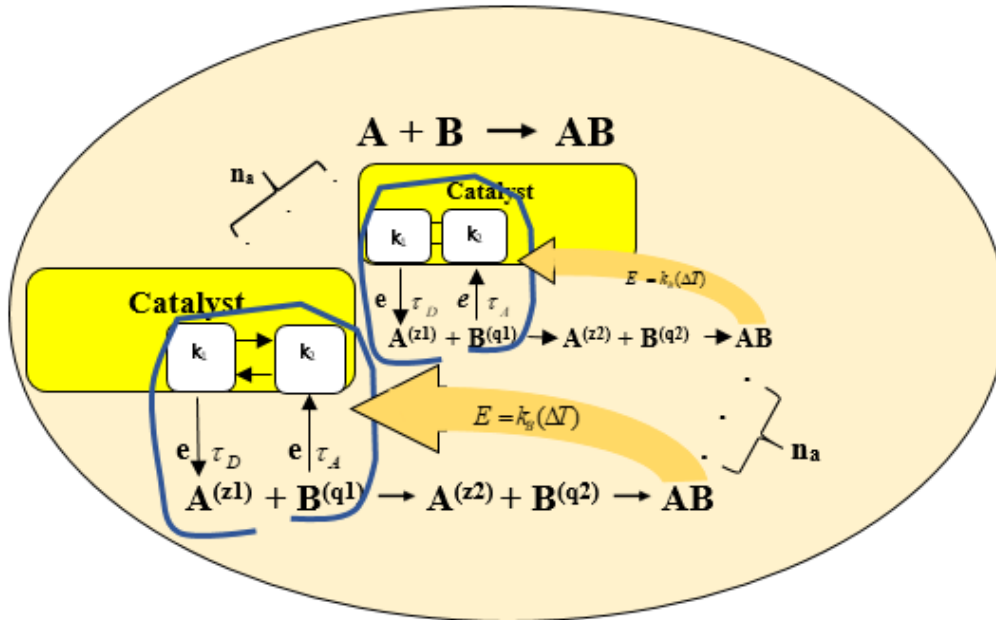


Figure 7. Mechanism of heterogeneous catalysis with positive temperature feedback loop.  $A$ ,  $B$  - reactants;  $AB$  - reaction product;  $A^{(z_1)}$  - reagent  $A$  in initial charge state;  $B^{(q_1)}$  - reagent  $B$  in initial charge state;  $A^{(z_2)}$  - reagent  $A$  in final charge state;  $B^{(q_2)}$  - reagent  $B$  in final charge state;  $k_1$  - initial catalyst oxidation degree;  $k_2$  - final catalyst oxidation degree;  $e^-$  - electrons;  $n_a$  - number of active sites;  $\tau_D$  - time of donor stage;  $\tau_A$  - time of acceptor stage;  $q_1$ ,  $z_1$  - oxidation degree of reactants in initial product;  $q_2$ ,  $z_2$  - oxidation degree of reactants in final product;  $k_B$  - Boltzmann constant;  $E = k_B(\Delta T)$  - energy, transferred along positive feedback loop.

In the presence of positive feedback, three variants of catalytic reaction behaviour are possible. If the thermal energy along the positive feedback loop in the  $i$ -th elementary reaction leads to the generation of more electrons than in the  $(i-1)$ -th elementary reaction, this leads to an acceleration of the reaction.

If the thermal energy in the positive feedback loop leads to the generation of the same number of electrons, then the process either slowly decays or builds up to a limit.

If the thermal energy in the positive feedback loop leads to the generation of fewer electrons, then the reaction will decay.

The first option is a typical case of self-catalysis. This is catalysis by the reaction product. In heterogeneous catalysis, the reaction product that leads to the generation of electrons is thermal energy. Self-catalysis is characterized by a sigmoidal kinetics [63 - 64].

## 9. Sigmoidal kinetics of heterogeneous catalysis

The effect of temperature on the chemical reaction rate is usually given by the exponential multiplier in the Arrhenius equation:

$$\exp(-E_a/RT)$$

where:  $R$  - gas constant;  $E_a$  - activation energy,  $T$  - absolute temperature.

This formula does not take into account the temperature gradient in the reaction zone.



In heterogeneous catalysis the reaction rate increases as the number of generated electrons in the positive feedback loop increases. In the role of activation energy the characteristics relating to the electron must be introduced into the exponent. This is either the ionisation energy or the electron affinity energy  $\mathcal{E}$ . An exponential sigmoid of the form may serve as a function describing such a process:

$$\frac{\exp(k_B \Delta T / \mathcal{E})}{1 + \exp(k_B \Delta T / \mathcal{E})}$$

where:  $k_B$  is Boltzmann constant;  $\Delta T$  - temperature gradient of the active centre of the catalyst;  $\mathcal{E}$  - electron affinity energy.

### 10. The positive temperature feedback loop in the mechanism of heterogeneous catalysis

The positive feedback loop begins with the transfer of thermal energy of the exothermic reaction to the catalyst and ends with the generation of electrons for the next elementary reaction (Fig. 8).

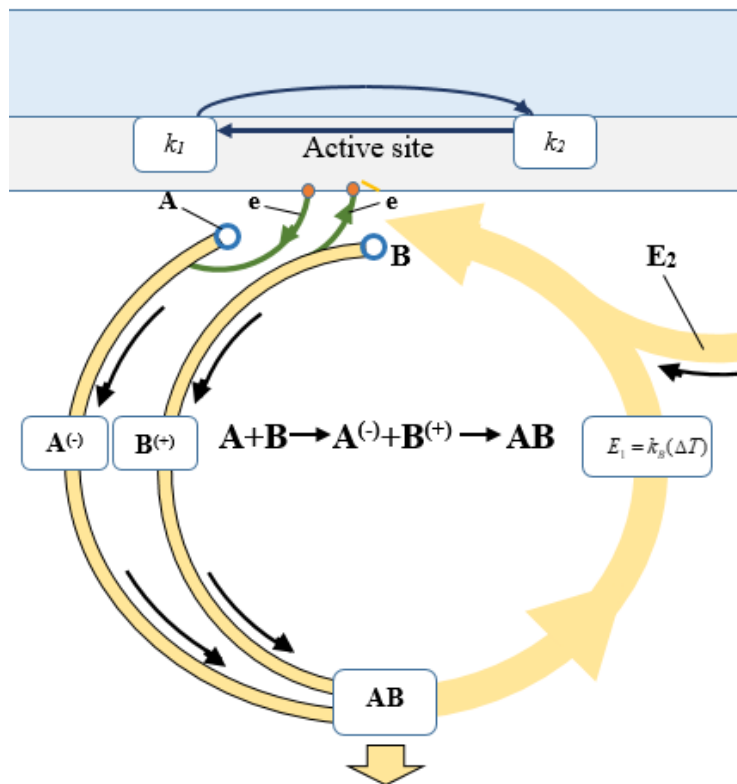


Fig. 8. Catalytic cycle with positive temperature feedback loop.

Schematic of the relay donor-acceptor mechanism of heterogeneous catalysis with a positive temperature feedback loop is shown in Fig. 9

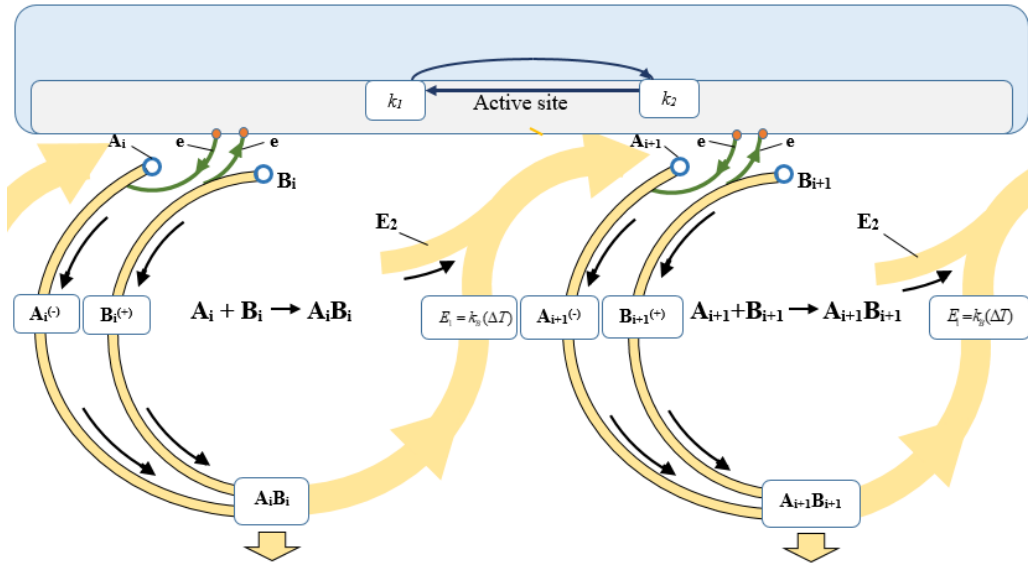


Figure 9. Relay donor-acceptor mechanism of heterogeneous catalysis with a positive temperature feedback loop.

The generation of electrons for the next elementary reaction takes place under the influence of the heat energy generated in the current elementary reaction. The presence of a heat transfer step in the catalysis mechanism is the main distinguishing feature of the relay donor-acceptor mechanism of heterogeneous catalysis.

Scheme of the relay donor-acceptor mechanism of heterogeneous catalysis with a positive temperature feedback loop on the example of ammonia synthesis from nitrogen and hydrogen is shown in Fig. 10.

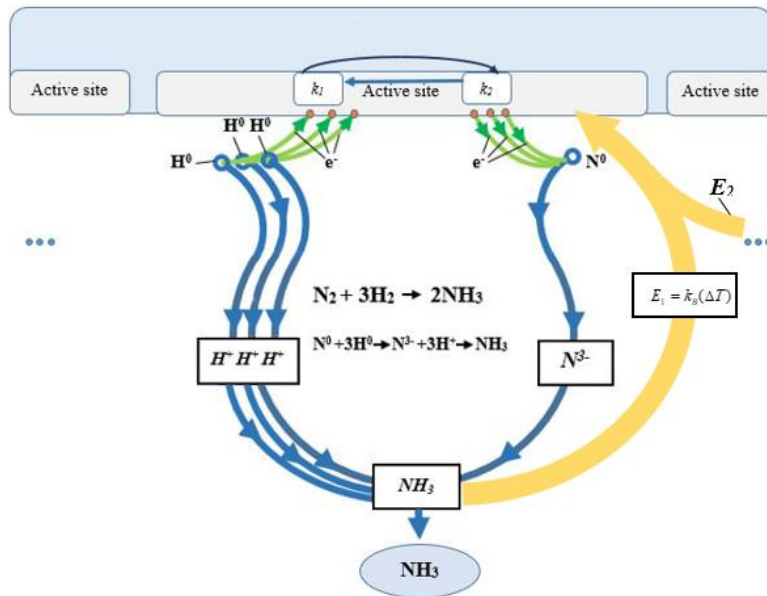


Fig. 10. Mechanism of heterogeneous catalysis with positive feedback loop by the example of ammonia synthesis from nitrogen and hydrogen.  $H^0$  - hydrogen atom in initial charge state;  $N^0$  - nitrogen atom in initial charge state;  $H^+$  - hydrogen atom in final charge state;  $N^{3-}$  - nitrogen atom in final charge state;  $k_1$  - initial oxidation degree of the active initiator site;  $k_2$  - final oxidation degree of the active

initiator site;  $e^-$  - electrons;  $E_1 = k_B(\Delta T)$  - energy transferred through the positive feedback loop;  $E_2$  - external energy.

## 11. Conclusion.

Heterogeneous catalysis is a complicated multi-stage chemical and physical phenomenon. In it, besides the mass transfer stage, the thermal transfer stage and the electron generation stage are realised. A direct chemical reaction is preceded by thermoelectronic physical phenomena. These thermoelectronic physical phenomena are the Edison and Seebeck effects. Thermoelectronic effects allow for the regeneration of electrons in the catalytic cycle. Thermoelectronic effects are caused by high temperature gradients in local halls on the catalyst surface, the transfer of electrons between the reaction participants and the contact of dissimilar substances. The contact of dissimilar substances occurs when the reagents adsorb on the catalyst surface. The electrons change the charge state of the reactants, which increases their reactivity. The heat transfer stage is an integral part of the catalytic cycle and an integral part of the mechanism of heterogeneous catalysis. It is the final stage of the catalytic cycle. It is also a positive feedback loop in the catalysis mechanism. It is also the stage of electron regeneration in the catalytic cycle. The positive feedback loop transfers the thermal energy of the elementary exothermic reaction to the active centres of the catalyst. The electrons generated in the Edison and Seebeck effects act as catalysts in the next elementary catalytic reaction.

## 12. Conclusions

1. The complexity of the mechanism of heterogeneous catalysis is due to the fact that the phenomena of mass transfer, heat transfer, electron generation and transfer, and the Seebeck and Edison thermoelectronic effects are implemented in it.

2. One of the "products" of an exothermic reaction is thermal energy. Thermal energy realises a positive feedback loop in the catalytic cycle. The catalytic cycle of heterogeneous catalysis is a combination of the mass transfer, heat transfer and electron generation stages.

3. The relay donor-acceptor mechanism of heterogeneous catalysis is supplemented with a thermoelectronic stage. This stage is a positive feedback loop in the catalysis mechanism. In this stage the transfer of thermal energy and the generation of electrons for another elementary reaction takes place.

4. In the positive feedback loop, a conversion of the form: "thermal energy"- "electrons". This conversion takes place due to the implementation of physical effects - the Edison effect and the Seebeck effect.

5. Electrons play a major role in the mechanism of heterogeneous catalysis.

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