The key role of catalysts in the process of low temperature decomposition of hydrogen sulfide: non-equilibrium thermodynamics of open system

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The reaction mechanisms of low-temperature H_2S decomposition on sulfide and metal catalysts are considered in the framework of thermodynamics of non-equilibrium irreversible biological processes for open systems, since these reactions occur at room temperature without supplying thermal energy from the outside due to the internal chemical energy of substrate molecules – hydrogen sulfide. On sulfide catalysts the irreversible process of H_2S decomposition proceeds through the stage of formation of hydrogen disulfide (disulfane), H_2S_2, as a key intermediate, and the reaction products are hydrogen and solid sulfur. The reaction occurs through a sequence of consecutive exothermic stages of dissociation of H_2S molecules, in which the entropy of the system is reduced due to its dissipation into environment as the bound (waste) energy $T\Delta S$. The remaining part of the free energy ΔG is accumulated on the catalyst surface and is used for the implementation of the energy-intensive step of decomposition of the adsorbed intermediate. Similarly, the metal catalyst provides capture and accumulation of energy from the exothermic processes of adsorption and dissociation of the initial H_2S molecules in the atomic adsorbed species of hydrogen and sulfur. The stored energy is used for chemical conversion of adsorbed intermediates into the final reaction products – molecular hydrogen and diatomic triplet sulfur, followed by it's desorption into the gas phase. When H_2S is decomposed on metal catalysts at room temperature, along with hydrogen, previously unknown diatomic gaseous sulfur in the ground triplet state is obtained, the existence of which is predicted by quantum chemistry. Some properties of the triplet sulfur and the white globular hexagonal sulfur obtained from its saturated aqueous solutions (which is also a previously unknown allotrope of solid sulfur) are considered. Similarity of the morphology of hydrophilic white sulfur globules and bacterial colorless sulfur S^0 obtained by sulfur bacteria in the processes of chemosynthesis of organic matter from CO_2 and H_2S, allowed to develop an alternative hypothesis about the nature of bacterial sulfur S^0 and possible mechanism of chemosynthesis of carbohydrates with the participation of sulfur bacteria.

Key words: H_2S decomposition, reaction mechanism, classical and non-equilibrium thermodynamics, open system, biological thermodynamics, metal and sulfide catalysts, diatomic sulfur, triplet and singlet sulfur, globular white sulfur, sulfur bacteria, chemosynthesis

Non-equilibrium thermodynamics, or thermodynamics of irreversible processes, was formed as an independent scientific discipline in the middle of the last century and one of its creators is I. R. Prigogine [1]. The inevitability of the emergence of this science was due to the understanding that the vast majority of processes occurring in nature and with human activities are irreversible and cannot be described within the existing "classical" equilibrium thermodynamics, which does not take into account the time factor. Currently, non-equilibrium thermodynamics is a rapidly developing branch of science [2].

According to [1], depending on the character of interaction with the environment there are 3 types of thermodynamic systems: 1. Isolated systems do not exchange energy or substance with the environment, i.e. the boundaries of such a system are impenetrable. 2. Closed systems exchange energy with the environment, but not substance. 3. Open systems exchange both energy and matter with the environment.

Classical equilibrium thermodynamics investigate isolated systems, which include all high-temperature catalytic processes. A typical example of an isolated system is the thermal decomposition of hydrogen sulfide, which is a well-researched process for producing hydrogen from a highly toxic substance:

$$2\ H_2S \xrightleftharpoons{\Delta T > 1000\ ^oC} 2\ H_2 + {}^1S_2\ ^{(gas)} \qquad (1)$$

This equilibrium endothermic process (1) starts to begin already at 500 °C, while at 1000 °C the equilibrium conversion of hydrogen sulfide does not exceed 15 % [3]. To increase conversion, you need to increase the temperature. The reversibility of the reaction (1) means that the process proceeds in both directions always near equilibrium. The catalyst does not shift the equilibrium of the reaction, does not change the enthalpy and free energy of the process, but it reduces the energy barrier and increases the reaction rate in both directions equally. The driving force of the process is the growth of entropy to the maximum possible value under the given conditions. To shift the equilibrium to the right in order to increase the yield of hydrogen, various methods of separating the reaction products are used, and to reduce the temperature, alternative energy sources are used [4,5].

An example of a closed system can be a chemical process in an autoclave or calorimeter. Open systems include all biological objects that can exist only due to the constant flow of nutrients and energy obtained during their assimilation, to ensure the life of these organisms. General regularities of energy transformation in biological systams, from the simplest unicellular to higher living organisms, are studying by biological thermodynamics [6,7]. It also addresses the issues of sustainability and evolution of biological systems.

In contrast to the high-temperature process (1), very unexpected and unpredictable results were obtained by passing hydrogen sulfide at room temperature through sulfide [8.9] and metal catalysts [10-16]. Along with hydrogen, the reaction products were either solid sulfur:

$$H_2S \xrightarrow{\text{sulfide catalyst, } 25^oC} H_2\uparrow + 1/8\ (S_8)_{ads} \quad (2)$$

or diatomic gaseous sulfur in the ground triplet state:

$$2\ H_2S \xrightarrow{\text{metal, } 25^oC} 2\ H_2\uparrow + {}^3S_2^{(gas)} \qquad (3)$$

in so doing, the H_2S conversion reaches 100% when the catalyst is placed in a liquid layer of solvent capable of well dissolving H_2S and reaction products [16-18]. Because

irreversible reactions (2) and (3) are carried out without a supply of thermal energy from the outside due to its income in the form of chemical energy of the molecules of hydrogen sulfide, these catalytic system should be attributed to the open systems and considered within the framework of non-equilibrium biological thermodynamics, since all biological processes occur at the constant temperature and pressure of the environment [6,7].

The main objective of this review is to consider the revised version of previously obtained results in the framework of non-equilibrium thermodynamics for open systems in order to justify the thermodynamic possibility of catalytic reactions (2) and (3) at room temperature, since these processes are ***impossible*** in the gas phase without participation of solid catalysts.

EQUILIBRIUM THERMODYNAMICS OF H_2S DECOMPOSITION

One of the obvious reasons for the observed contradiction in the thermal and catalytic processes of H_2S decomposition by reactions (1) and (3) is the formation of diatomic sulfur in a different electronic state. According to the theory of molecular orbitals, it is well known that diatomic sulfur is an isoelectronic analog of oxygen, which, like molecular oxygen, differs from the most diatomic molecules by the presence of the ground triplet state (S_2) ($X^3\Sigma_g^-$), while the first excited singlet state S_2 ($a\ ^1\Delta_g$) is higher in energy by 12.6 kcal/mol (Table 1) [19]. However, the singlet oxygen converts spontaneously to the ground triplet state resulted from the emission of an energy quantum with a half-life of 72 min at normal conditions [20, 21].

At the same time, singlet sulfur obtained at high temperature (1), after quenching sulfur vapors to room temperature, prefers to agglomerate (concatenate) into the solid sulfur S_8 instead of conversion to the ground triplet state. This unusual feature of singlet sulfur was experimentally verified and confirmed by calculations with the methods of CASSCF and Hartree-Fock. It turned out that the enthalpy of reaction

$$4\ S_2^{(gas)} \longrightarrow S_8^{(solid)} \qquad (4)$$

is $\Delta_r H^o_{298}$ = + 46.9 kcal/mol for the triplet S_2 molecule and $\Delta_r H^o_{298}$ = − 10.4 kcal/mol for the singlet state of the initial diatomic sulfur [12 - 14].

The first strongly endothermic process is characterized by a negative change in entropy ($\Delta S < 0$, the number of gaseous molecules decreases), so this process cannot occur under any conditions, since the change in the Gibbs potential is always positive $\Delta G > 0$. In the case of the second exothermic process ($\Delta H < 0$), the direct reaction can occur spontaneously at low temperature, since $\Delta H > T\Delta S$ and $\Delta G < 0$. At high temperature $\Delta H < T\Delta S$, so the direct reaction cannot proceed ($\Delta G > 0$), while the reverse reaction is thermodynamically favorable.

Thus, it follows from the calculations that the triplet molecular state of diatomic sulfur is thermodynamically most favorable and stable (Table 1) [19], so the triplet molecule $S_2(X\ ^3\Sigma^-_g)$ cannot transform into solid singlet sulfur S_8. Therefore, if in the thermal process (1) the triplet sulfur was formed, then, after quenching its vapors to room temperature, we would ***inevitably*** have to obtain a triplet state of sulfur in the condensed phase, but experimentally, solid singlet sulfur is always obtained [12-14].

One of the possible reasons for the existence of a high-temperature metastable state of singlet sulfur could be the kinetic complications of its transition to the ground triplet state, when even at high temperature this process could be very slow and under

experimental conditions of studying the properties of gaseous sulfur equilibrium is not achieved. Formally, this means a prohibition on the spin transition, which could be excluded by metal catalysts.

$$^1S_2 \quad -x\rightarrow \quad ^3S_2 \qquad (5)$$

However, experimental verification of this assumption showed [12-14] that even the presence of platinum catalysts does not reduce the energy barrier and does not accelerate the reaction (5) at a temperature as high as 1000 K.

Thus, in accordance with the rule of spin state conservation, in the thermal equilibrium process of H_2S decomposition (1), the diatomic sulfur is formed in the ***metastable singlet state***, thermodynamic parameters of which are given in the handbooks [22].

H_2S DECOMPOSITION ON SULFIDE CATALYSTS

This story began at the end of the last century, when we observed that an irreversible reaction takes place on the surface of sulfide catalysts at room temperature

$$2\ H_2S \xrightarrow{\text{sulfide catalyst, 25oC}} (H_2S_2)_{ads} + H_2\uparrow \qquad (6)$$

resulted in formation of disulfane H_2S_2 (hydrogen disulfide) and desorption of hydrogen in the gas phase. The fact is that the direct formation of disulfane H_2S_2 from H_2S in the gas phase:

$$2\ H_2S \neq H_2S_2 + H_2 \qquad (7)$$

Is ***impossible*** because of thermodynamic prohibition ($\Delta_r H^o_{298}$ = + 13.6 kcal/mol, $\Delta_r S^o_{298}$ = – 3.9 cal/mol×K, $\Delta_r G^o_{298}$ = + 14.1 kcal/mol). It became obvious that the catalyst performs a very important and specific function: after adsorption of H_2S on the catalyst surface, the conditions are created for the formation of a new chemical bond sulfur – sulfur between two neighboring adsorbed molecules [8,9,14].

In contrast to equilibrium thermal process (1), both reactions (2) and (6) are irreversible because molecular hydrogen desorbs into the gas phase, while the second reaction product – solid sulfur or H_2S_2, remains on the catalyst surface. Hence, let's consider the mechanisms of both reactions (2) and (6) from the stand point of non-equilibrium thermodynamics for open system [1,2]. Owing to all reaction concerned occur at room temperature, our discussion will be based on the principles of biological thermodynamics [6,7], because of all bio-organisms must perform useful action to stay alive, to grow, and to reproduce themselves at the constant temperature and pressure of the environment. A living organism is an open system, able to exchange both matter and energy with its environment. No matter what the type of living species, all bio-organisms must capture, transduce, store, and use energy to live.

As is known, there are two principal forms of energy: kinetic and potential. Kinetic energy is the energy of movement of molecules, which is to be important at the first step of any heterogeneous catalytic reaction – molecule chemisorption by the catalyst surface. The second form of energy, potential energy, or stored energy, is more important in the study of biological or chemical systems. Central of our attention is the potential energy stored in the chemical bonds connecting atoms in molecules. The ability to harness energy from a variety of metabolic pathways and channelize it into activities of organism is a fundamental property of all living systems.

In terms of thermodynamics, the amount of energy capable of doing useful action during a chemical reaction is measured quantitatively by the change in the Gibbs free energy. Owing to all forms of energy are interconvertible, they can be transformed in such a way that the Gibbs free energy of any chemical process must be minimized. At any constant temperature and pressure, two factors determine the ΔG of a reaction and thus whether the reaction will tend to occur: the change in bond energy between reactants and products and the change in entropy of the system.

In accordance with the Gibbs equation ($\Delta G = \Delta H - T\Delta S$), the spontaneous course of an irreversible chemical reaction is provided under the condition when in the exothermic process (the reaction enthalpy decreases, $\Delta H < 0$), the entropy increases ($\Delta S > 0$). However, if in the exothermic reaction ($\Delta H < 0$) the entropy decreases ($\Delta S < 0$), the Gibbs equation determines the boundaries of the spontaneous process. When a certain amount of energy that enters the system resulted from an exothermic process is spent on increasing entropy (which is inevitable for any irreversible processes), then this part of energy is lost to perform a useful action (for example, the formation of new chemical bonds in the reaction products), it dissipates into the environment in the form of heat. Therefore, this part of energy $T\Delta S$ can be defined as a bound (waste) energy. The remaining part of energy can be used to perform a useful action, therefore the Gibbs energy is often called a free energy [6,7]. A chemical mixture at equilibrium is already in a state of minimal free energy: no free energy is being generated or released.

The change in the entropy of an open system results from both its increase due to the spontaneous flow of irreversible processes within the system (d_iS), and due to the processes of exchange of the system with the external environment (d_eS) [1,2]. In the thermodynamics of irreversible processes, it is postulated that the components d_iS and d_eS are independent, and the total change in the entropy of the open system is equal to their sum: $dS = d_iS + d_eS$. In a stationary non-equilibrium process in an open system, the positive production of entropy within the system is compensated by the outflow of entropy into the environment, thereby maintaining the stationary state. Most biological reactions lead to an increase in order, and thus a decrease in entropy ($\Delta S < 0$).

Similar processes of the energy capture and its transformation into the final reaction products seems to occur in the catalytic reaction (2) of H_2S decomposition on sulfide catalysts [8,9,14], Therefore, we will try to revise the previously proposed mechanism of this catalytic reaction from the standpoint of biological thermodynamics for an open system.

Indeed, according to our conception [23,24], the active component of sulfide hydrodesulfurization (HDS) catalysts is an electro neutral macromolecule $(MoS_2)_x$ with Ni(IV) or Co(III) ions in the d^6 electron configuration to be located in its edge plane. A fragment of this macromolecule in real scale with allowance for all interatomic distances and ionic radii is represented in Fig. 1. Under catalysis conditions, the active center contains always an adsorbed H_2S molecule; this favors in stabilization of the ‘‘active state’’ of nickel or cobalt [23,24].

An indispensable element of the active component structure consists of an occluded hydrogen atom that appeared in the active component due to oxidative addition of hydrogen to Ni or Co atoms during the catalyst sulfidation (Fig. 1,2). The occluded hydrogen is located in the matrix of a MoS_2 single slab in the center of an ‘‘empty’’ trigonal prism formed by six sulfur atoms under a nickel (cobalt) atom at the distance of 1.5 Å from it (Fig. 1-3). The occluded hydrogen creates an electronic configuration of Ni (Co) essential for adsorption of the H_2S molecule. The Co(III) or Ni(IV) atoms in the d^6 electronic configuration have two formally vacant (‘‘empty’’) $3d_{z2}$

and $3d_{xy}$ orbitals. Hence, they are strong Lewis acid centers which interact effectively with a lone electron pair of a H_2S molecule to form a chemical bond M–S (Fig. 2). In the case of d^7 configuration, the $3d_{z2}$ orbital appeared to be occupied.

As it follows from DFT calculations [8,9], H_2S molecule adsorption on the Co(III), d^6 atom is characterized with the negative reaction enthalpy because of the capture of kinetic energy of the gas phase molecule movements by the catalyst surface. This exothermic process results in the inevitable decrease of entropy ΔS = – 39.6 cal/mol.K (Table 2). If the bound energy $T\Delta S$, consumed for entropy production, is subtracted from the adsorption enthalpy, we obtain a negative value of Gibbs energy (ΔG = – 0.8 kcal/mol), indicating the spontaneous character of the adsorption process. The free energy is not allowed to dissipate as heat but is captured in chemical bonds formed by other molecules. At the same time, H_2S adsorption on the Co(II), d^7 ion is hardly possible because $\Delta H < 0$ and $\Delta G > 0$ [8,9].

The second step is the dissociation of two adsorbed H_2S molecule on two adjacent cobalt atoms (Table 2). This strongly exothermic process results in formation of two surface S – H species and occurs with a substantial benefit in the Gibbs energy $\Delta G < 0$ meaning spontaneous character of this stage.

The next stage is the formation of a new S – S chemical bond in the surface intermediate (Table 2, Fig. 3). This surface reaction proceeds via pairwise drawing together of two surface species resulting in the S – S bond formation at the distance of 2.18 Å, which is only slightly longer than in the free H_2S_2 molecule 2.06 Å. This highly exothermic process is accompanied with the formation of H – H bond in molecular hydrogen which desorbs in the gas phase making the total process irreversible. Like in the previous steps, after subtracting waste energy $T\Delta S$ from the exothermic processes of S – S and H – H bond formation, we get the negative change in the free Gibbs energy what means the spontaneous character of this stage as well.

A characteristic feature of all biological systems is their ability to store (accumulate) energy obtained in the process of nutrition in the form of chemical compounds for its further use in the processes of chemosynthesis of new chemicals and their removal in environment as products of their vital activity [6,7]. It is obvious that the catalyst can also act as an accumulator of free energy. In our case, the only energy-consuming endothermic step is the stage (4) (Table 2) of splitting two chemical bonds S – H and removing the second hydrogen molecule into the gas phase. However, these energy expenditures are compensated by the energy accumulated in the previous stages of the exothermic dissociation of H_2S. Therefore, one may say that the unfavorable chemical reaction (4) (Table 2) can proceed because it is coupled with the energetically favorable stages (1-3).

At the final stage (5) (Table 2), two chemical bonds M – S must be broken to remove sulfur from the active center. The thermal process requires considerable consumption of energy, however there exists a coupled exothermic reaction of diatomic sulfur recombination into the solid cycloocta-sulfur S_8. Therefore, the step (5) is also exothermic and is characterized with negative change in the free Gibbs energy. Solid sulfur can be removed from the catalyst surface either by heating catalyst to low temperatures [8,9], or by placing catalyst in a liquid solvent of sulfur [16-18].

In general, the catalytic reaction (2) is an exothermic process that occurs spontaneously at room temperature despite a decrease in entropy that is dissipated

from the system into environment as a bound (waste) energy. In the gas phase this process is ***not possible*** (Table 2).

H_2S DECOMPOSITION ON METAL CATALYSTS

In a few experimental works devoted to the study of H_2S interaction with the surface of metals, it is shown that H_2S adsorption on the surface of single crystals Pt(111) results in its dissociation to the atomic species of hydrogen and sulfur even at 110 K. A small warming of the surface to 185 K is accompanied by the release of molecular hydrogen into the gas phase, while sulfur forms Islands on the surface of the single crystal [25]. It is very important that water does not dissociate into atoms on metals. Similar results were obtained in the study of hydrogen sulfide adsorption on model surfaces Pd(111) [26], Ru(110) [27] and InP(100) [28]. However, the interpretation of the results of these studies is complicated by the possibility to destroy the adsorbed surface species under exposure to electromagnetic radiation or an electron beam.

At the same time, a lot of studies are devoted to the DFT calculations of H_2S interaction with the surface of many model systems (see, e.g., [29] and references within). It is well known that any solid body, including catalysts, has an excess of Gibbs surface energy G_S, which characterizes the energy of intermolecular interaction of particles on the interface with the particles of each of the contacting phases. Surface energy can be converted into chemical energy as a result of spontaneous processes determined by the reduction of Gibbs energy, the most important of which (for catalysis) is chemisorption, i.e., the absorption of substances from the environment by the solid body, accompanied by the formation of surface chemical compounds, so chemisorption should be considered as a chemical reaction, the flow area of which is limited to the surface layer. The heats of the exothermic chemisorption process on the surface of many transition metals are in the range of (– 20 to – 30) kcal/mol and above.

So, the solid surface captures of the kinetic energy of molecule movements in the gas phase resulting in H_2S adsorption, and for Pt(111) E_{adc} = – 21 kcal/mol [29]. However, this surface reaction is not terminated with a simple molecular chemisorption of H_2S; there is a further dissociation process of adsorbed H_2S, which occurs on the Pt (111) face in two stages:

$$H_2S_{(ads)} \rightarrow SH_{(ads)} + H_{(ads)} \qquad (8)$$

$$SH_{(ads)} \rightarrow S_{(ads)} + H_{(ads)} \qquad (9)$$

The first dissociation step (8) is energetically favorable over the many different surfaces and for Pt(111) this reaction step is highly exothermic $\Delta E_{rxn(8)}$ = – 19.6 kcal/mol and occurs via very low barrier E_a = 1.6 kcal/mol. The second dissociation step (9) is also highly exothermic $\Delta E_{rxn(9)}$ = – 18.2 kcal/mol with activation energy E_a = 0.7 kcal/mol [29]. The energy profile of the reactions (8) and (9) indicates that H_2S dissociates readily with the formation of atomic hydrogen and sulfur species in the adsorbed state, and this H_2S dissociation has neither thermodynamic nor kinetic limitations [29]. Thus, the overall energy of dissociative adsorption of H_2S on the surface of Pt(111) is

$$\Delta E_{diss\text{-}overall} = (E_{ads} + \Delta E_{rxn(8)} + \Delta E_{rxn(9)}) = -58.8 \text{ kcal/mol} \qquad (10)$$

or for two H_2S molecules in the reaction (3) $\Delta E_{diss\text{-}overall}$ = – 117.6 kcal/mol.

On the other hand, from the point of view of thermo chemistry, the energy of chemical bonds in the molecule is one of the main molecular constants characterizing the structural features and reactivity of chemical compounds [30, 31]. The dissociation energy of chemical bond D_o is defined as the change in the standard enthalpy of formation of the reaction products and the initial chemical substance. In the reaction (1), dissociation energy D_{298} of HS – H bond in the H_2S molecule under standard conditions is 92 kcal/mol (Table 3) [22,30,31], whereas dissociation of the second S – H bond requires only 82.3 kcal/mol. In the reaction (1) of two H_2S molecules, four HS – H bonds must be broken, which gives the total dissociation energy of two molecules ΣD_{298} = (92.0 + 82.3) x 2 = 348.6 kcal/mol. At the same time, two bonds H – H (ΣD_{298} = 2 x 104.2 = 208.4 kcal/mol) and one bond S – S D_{298} = 99.8 kcal/mol are formed (Table 3) [30,31]. From it is followed that the total energy of the bond dissociations in the initial H_2S molecules exceeds this value for the reaction products (1) at

$$\Delta D_{298} = \Sigma D_{298}(H_2S) - \Sigma D_{298}(\text{products}) = 40.4 \text{ kcal/mol} \qquad (11)$$

In other words, this means that the initial H_2S molecule is stable and does not convert into the reaction products H_2 and S_2 at room temperature, therefore the thermal energy is required to initiate the reaction (1).

However, in the catalyst adsorbed state, the required energy for breaking H_2S bonds can be obtained at the expense of adsorption and dissociation energy of the H_2S molecule into the atomic species. Indeed, after dissociation of H_2S molecule into atoms on the Pt(111) surface, the resulted process gives raise in the energy surplus:

$$\Delta E_{\text{surplus}} = \Delta E_{\text{diss-overall}} + \Delta D_{298} = -117.6 + 40.4 = -77.2 \text{ kcal/mol} \qquad (12)$$

which can be spent for desorption of the reaction (3) products into the gas phase.

Actually, the energy of S_2 molecule adsorption on Pt (111) is – 45 kcal/mol [32]. The heat of dissociative adsorption of H_2 on Pt (111) varies within – (9.5 ÷ 12) kcal/mol [33], while molecular hydrogen is desorbed from the surface already at 260 K [34]. Therefore, after removal of diatomic sulfur and two hydrogen molecules from the Pt (111) surface, we obtain a minimum excess of energy $\Delta E_{\text{total.min}}$ = – (8.2 ÷ 13.2) kcal/mol, which means the exothermic process as a whole. Moreover, an additional gain in energy 12.6 kcal/mol should appear as a result of the transition of diatomic sulfur from the excited singlet state to its ground triplet state in the reaction (3) (Table 1). Therefore, the resulted gain in energy can be estimated as $\Delta E_{\text{total.max}}$ = – (20.8 ÷ 25.8) kcal/mol.

Thus, the simplest consideration of the capture by the catalyst surface of the kinetic and potential energy of H_2S molecules with its subsequent transformation and redistribution in the surface chemical reaction (3) provides a positive response to the thermodynamic possibility of this catalytic reaction at room temperature on metal catalysts. In this case, First Law of Thermodynamics is fully realized – the law of energy conservation for opens systems: energy is neither created nor destroyed, but can be converted from one form to another. In other words, the catalyst surface provides conversion of energy from the exothermic processes of adsorption and dissociation of the initial H_2S molecules into the formation of new chemical bonds in the final reaction products – diatomic both hydrogen and sulfur, and their desorption to the gas phase. As a result, after desorption of products into the gas phase, the closure of the catalytic cycle is realized with the exothermic effect of the reaction (3). If we take into account that the entropy of reaction (3) increases $\Delta S > 0$ (the number of molecules in the gas phase increases), then the exothermic nature of this reaction $\Delta H < 0$, the change in the

Gibbs potential is always negative $\Delta G < 0$, which means the ***spontaneous*** flow of the process. In the gas phase this process is ***not possible***.

No doubt, this reaction mechanism requires a comprehensive study by theoretical and experimental methods, taking into account the entropy and determining the Gibbs free energy at all stages of the catalytic cycle, similar to that we have done for sulfide catalysts (see previous section).

H_2S ASSIMILATION BY SULFUR BACTERIA

It has been over 130 years since the opening by S.N. Vinogradsky of the process of chemosynthesis of organic matter involving hydrogen sulfide [35]. At present, there is no doubt that H_2S is the primary source of energy and hydrogen for the synthesis of organic matter from CO_2 for sulfur bacteria. However, the sulfur bacteria studies are very limited, because of experimental difficulties their cultivation and research in the laboratory. In particular, there is no data on the nature of enzymes in numerous genera and types of sulfur bacteria functioning in different habitats, and on the nature of metal atoms catalyzing the processes of chemosynthesis in the composition of these enzymes. Therefore, the mechanisms of chemosynthesis with the participation of sulfur bacteria are not even discussed in the scientific literature.

Bacteria are the simplest creatures with all the most important features of a living organism, for their life they use the ability to capture, transform and store energy of various kinds in accordance with information encoded in their genetic material [6,7]. Sulfur bacteria are autotrophic organisms that synthesize organic substances from simple inorganic compounds [35]. The most widespread scheme of energy production for chemosynthesis implies the occurrence of the following reaction [36]:

$$2\ H_2S + O_2 \rightarrow\ 2\ \{\ S^0\ \} + 2\ H_2O \qquad (13)$$

It is well known that the source of hydrogen in autotrophic sulfur bacteria is H_2S, however, the scheme of sulfur formation by reaction (13) contrary to this assertion, since hydrogen is consumed in the formation of water. Direct experimental evidence for reaction (13) are absent in the literature, while many types of sulfur bacteria function in the completely anaerobic conditions.

The main distinguishing feature of the sulfur globules, formed in the process of chemosynthesis by sulfur bacteria, regardless of their nature, origin and habitat, is their spherical shape and hydrophilic nature of colorless colloidal particles [36-42]. It is also proved that sulfur in these globules is in the zero-valence state, but not in the oxidized or reduced form [43,44]. Regarding the nature of the elemental sulfur produced by sulfur bacteria, there are conflicting opinions. This elemental sulfur (it is commonly referred to as bacterial sulfur S^0) is fundamentally different in properties from the "normal" inorganic sulfur. Various models of bacterial sulfur S^0 are considered in [36,38,39] but none of them finds experimental confirmation.

A white allotrope of solid sulfur was isolated from the saturated solutions of diatomic sulfur [45]. The morphology of the white sulfur particles is shown in Fig. 4. The size of particles, which are near-spherical globules, is up to 10 μm. Electron diffraction on a separate white sulfur globule indicated that the globule has a hexagonal structure with interplanar distances of 0.45, 0.29, and 0.15 nm. Among the known allotropes of solid sulfur, the white hexagonal modification was not found.

The morphology of hydrophilic globules of white sulfur, obtained by us from saturated aqueous solutions of diatomic sulfur as a reaction product of catalytic decomposition of hydrogen sulfide [14,16,45], surprisingly coincides with the morphology of globules of biological sulfur S^0, produced by numerous genera of sulfur bacteria in chemosynthesis [36,38,39]. Taking into account that sulfur in these globules is elemental [43,44], we conclude that the H_2S assimilation by colorless sulfur bacteria at ambient temperature and pressure, causes, most likely, also in formation of diatomic sulfur in the ground triplet state:

$$2\ H_2S \xrightarrow{\text{sulfur bacteria}} 2\ H_2{}^* + \{\ {}^3S_2\ \}^{(\text{globules})} \qquad (14)$$

due to nucleation of diatomic sulfur in the form of condensed hydrophilic phase S_2. The resulting activated hydrogen is involved in the chemosynthesis reactions:

$$H_2{}^* + CO_2 \xrightarrow{\text{bacteria enzymes}} \{\ HCOOH\ \}\ (\text{carbohydrates}) \qquad (15)$$

Because of the spherical shape and hydrophilicity of the colorless sulfur globules produced by sulfur bacteria, do not depend on their nature and habitat, it may be concluded that reaction (14) can occur under anaerobic conditions and in the presence of oxygen. Thus explains the role of hydrogen: activated at the moment of formation, hydrogen is involved in the catalytic reactions of chemosynthesis of carbohydrates with the participation of enzymes of sulfur bacteria (15). Of course, this hypothesis requires careful and comprehensive research.

As shown in the previous section, the spontaneous process of H_2S dissociation into the atomic surface species results in a significant release of the free Gibbs energy. This stored energy can be used to activate the CO_2 molecule in the coupled reaction of chemosynthesis of organic molecules involving activated hydrogen by reaction (15). In the absence of coupling, the interaction of hydrogen with CO_2 requires high temperature and pressure. Therefore, the use of heterogeneous catalysts of H_2S decomposition as model objects of chemosynthesis can offer a promising opportunity to search for and create new catalytic systems of CO_2 molecule activation under mild conditions.

THE ROLE OF CATALYSTS IN LOW-TEMPERATURE PROCESSES OF HYDROGEN SULFIDE DECOMPOSITION

Thus, there are two temperature ranges of H_2S decomposition (Fig. 5). In the high-temperature region, the reaction occurs without catalysts in accordance with the laws of classical equilibrium thermodynamics. The introduction of the catalyst does not change the thermodynamic characteristics of the process, but reduces the energy barrier and the time to achieve equilibrium by increasing the reaction rate in both directions.

In the low-temperature area, the irreversible reaction of hydrogen sulfide decomposition can occur only on the surface of solid catalysts or with the participation of enzymes of biological organisms in accordance with the laws of non-equilibrium thermodynamics for open systems, while the composition of the final reaction products depends on both the type of catalyst and the conditions of the process (Fig. 5).

In the fundamental concept of academician G. K. Boreskov on the unity of the essence of homogeneous, heterogeneous and enzymatic catalysis as a phenomenon of Nature, the definition of catalysis is given as:

"***initiation*** of chemical reactions ***or change of their rate*** under the influence of catalysts repeatedly entering into the intermediate chemical interaction with the reaction participants..." [46].

Our results fully confirm this concept for the catalytic processes occurring at ambient temperature and atmospheric pressure in the absence of external energy sources. Solid catalyst in the open systems:

- Ensures the capture of kinetic energy of the substrate molecule movements – spontaneous exothermic chemisorption;
- Ensures the flow of internal exothermic processes of the substrate molecule dissociation into the atomic adsorbed species;
- Ensures the redistribution of internal energy for the formation of new chemical bonds in the reaction products;
- Provides accumulation of free energy due to entropy dissipation into environment as the bound energy;
- The accumulated free energy, resulted from dissociation of substrate molecules and entropy dissipation into environment, is used for desorption of reaction products into the gas phase.
- The active performance of the system against external forces is provided by the continuous supply of free energy in the form of substrate molecules;

The driving forces of the process are:

- ❖ Formation of the final reaction products in the ground electronic state (i.e., having the minimal free energy) – singlet hydrogen, solid sulfur and diatomic sulfur molecule in the ground triplet state.
- ❖ Concentration gradients at the outlet and inlet of the system, in the absence of the free energy supply, the process stops.

Apparently, the low-temperature catalytic decomposition of hydrogen sulfide is the first example in heterogeneous catalysis, when the principles of non-equilibrium biological thermodynamics of open systems are used to justify the possibility implementing a catalytic reaction.

CONCLUSION

Toxic and "useless " hydrogen sulfide, which has not found any practical application in human activities, turned out to be the very substance that underlies the nature-created process of chemosynthesis of organic matter from CO_2, laid the foundation of biological life on Earth. In contrast to the chemical analogue – water, which is the fundamental basis of the existence of biological organisms, H_2S is a supplier of hydrogen and energy for the processes of life support of these organisms. This extremely important role of hydrogen sulfide is probably due to the unique property of this molecule – the standard enthalpy of formation ($\Delta_f H^o_{298}$= − 4.82 kcal/mol) is the lowest among all known potential sources of hydrogen, which means minimal energy consumption in the splitting of the molecule. The driving force of H_2S decomposition processes in nature is the formation of final products in the ground electronic state (i.e., having minimal free energy) – singlet hydrogen, solid sulfur and diatomic sulfur molecule in the ground triplet state. At the same time, the annual increase in hydrogen sulfide volumes is estimated in hundreds of millions of tons due to the activity of

anaerobic sulfate-reducing bacteria, which provides a continuous circulation of hydrogen sulfide in nature.

Currently, we know the only way to obtain diatomic gaseous sulfur in the ground triplet state, a stable molecule that exists under normal conditions indefinitely, by low-temperature catalytic decomposition of hydrogen sulfide. However, in nature this substance is synthesized for millions of years with the participation of enzymes of sulfur bacteria. These conclusions of the existence of triplet sulfur are based on our experimental but indirect evidence, as well as on the analysis of numerous highly controversial literature data. To obtain direct evidence of our findings and assumptions, systematic, targeted experimental and theoretical studies are required. Therefore, the main goal of this review will be considered to be achieved if the formulated questions arouse interest among readers for the initiation of studies in this new and very attractive field of chemistry of hydrogen sulfide and sulfur.

Of particular interest are the standard thermodynamic parameters of the ground triplet state of diatomic sulfur {(S2) x 3S-g}, which can currently only be obtained by (?) at low temperature catalytic decomposition of hydrogen sulfide. The standard enthalpy of formation of diatomic sulfur given in reference books refers to the excited singlet state {(S2) a 1Dg} of this molecule. However, based on the analogy with molecular oxygen (table. 1), the standard enthalpy of formation of triplet sulfur must be also zero, as for all diatomic gases in the ground electronic state:

$$\Delta_f H^o_{298} (S_2\ X\ ^3\Sigma^-_g) = 0$$

At the same time, the generally accepted thermodynamic reference point is solid orthorhombic α-sulfur. To resolve this very difficult conflict situation, one should compare the total energy of solid α-sulfur with the total energy of 4 molecules of diatomic triplet sulfur. At the Institute of catalysis, attempts were made to calculate the total energy of the cyclooctaser by available quantum chemical methods, but so far without success due to the complexity of the calculations. Therefore, this question remains open.

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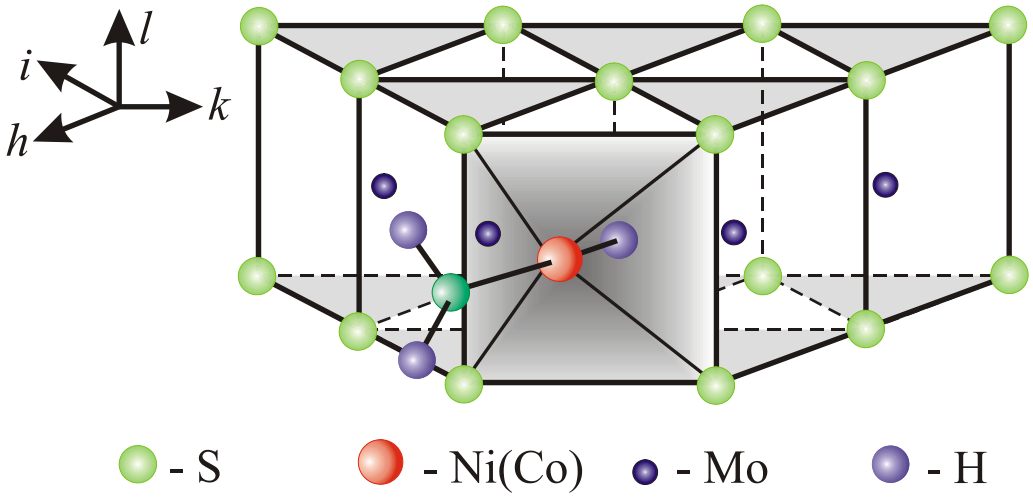

Fig. 1. A fragment of the structure of the electro-neutral macromolecule of the active component of sulfide HDS catalysts with an occluded hydrogen and H_2S molecule adsorbed on the active centers of Co(III) or Ni(IV) atoms [14,23,24].

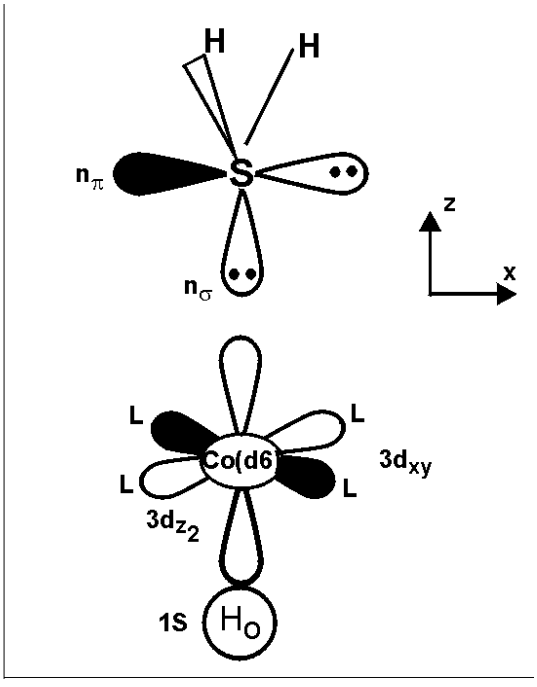

Fig. 2. Scheme of interaction of n_σ and n_π orbitals of H_2S molecule with $3d_{z2}$ and $3d_{xy}$ orbitals of the Co(III) atoms in the d^6 electronic configuration [14,23,24]. H_o – occluded hydrogen, L – electron orbitals.

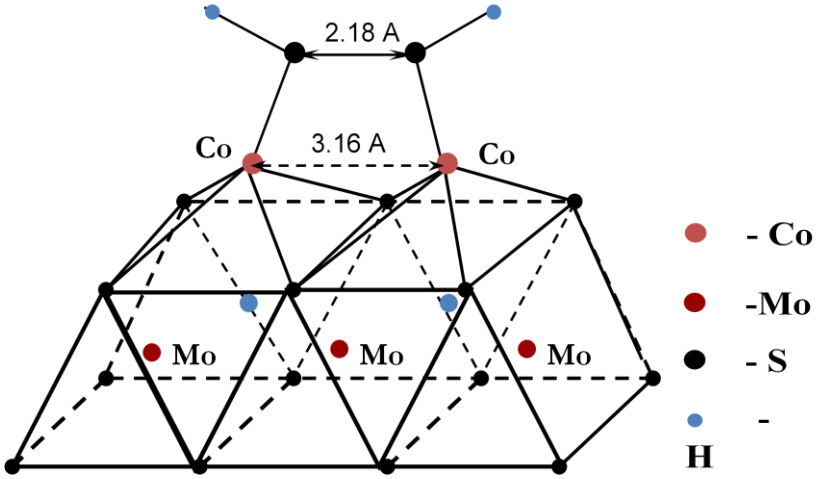

Fig. 3. Coupling two adsorbed molecules of hydrogen sulfide, caused from formation of S - S bond in the adsorbed molecule disulfide and removal of the hydrogen molecule in the gas phase.

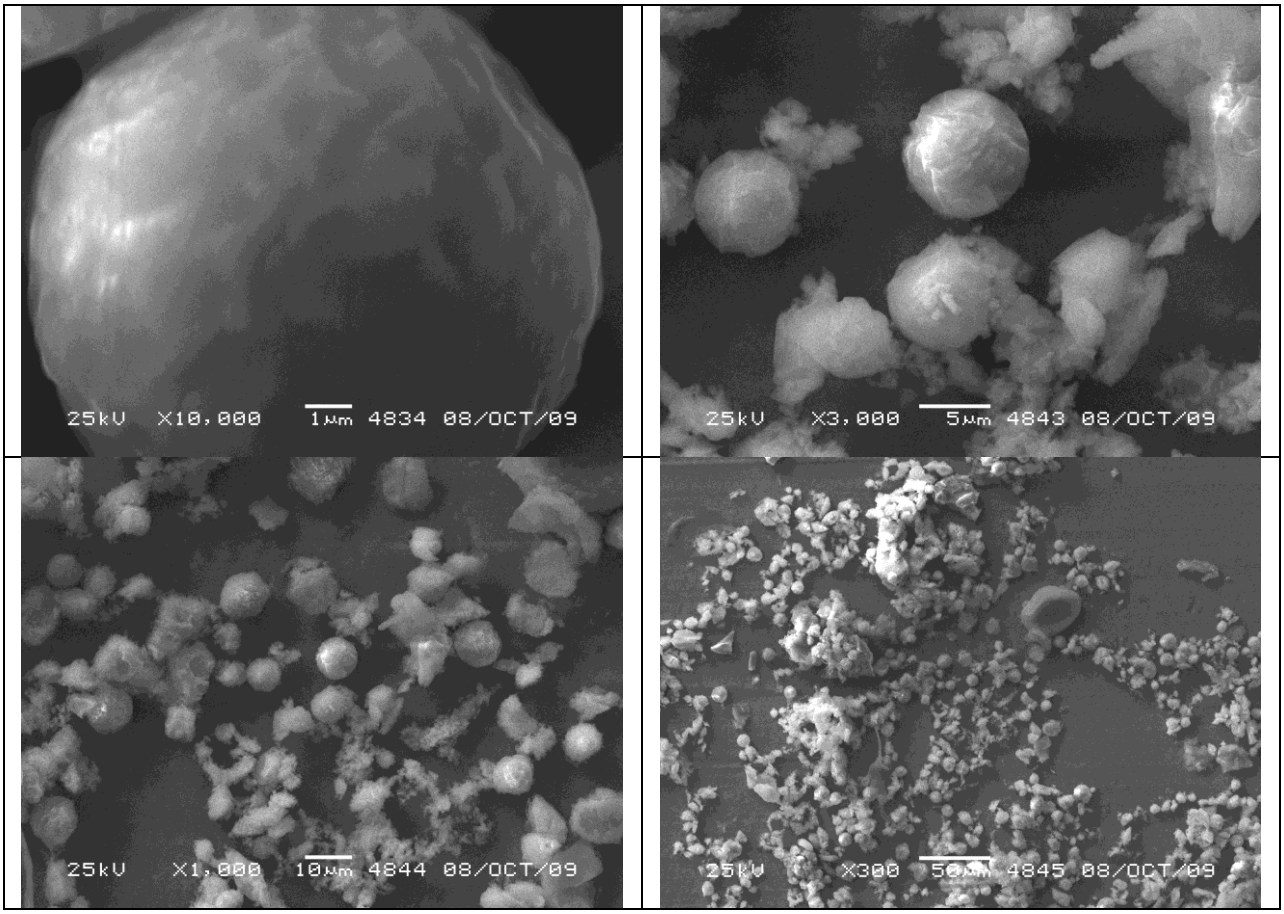

Fig. 4. Electron micrographs of white sulfur globules obtained from saturated aqueous solutions of diatomic sulfur [45].

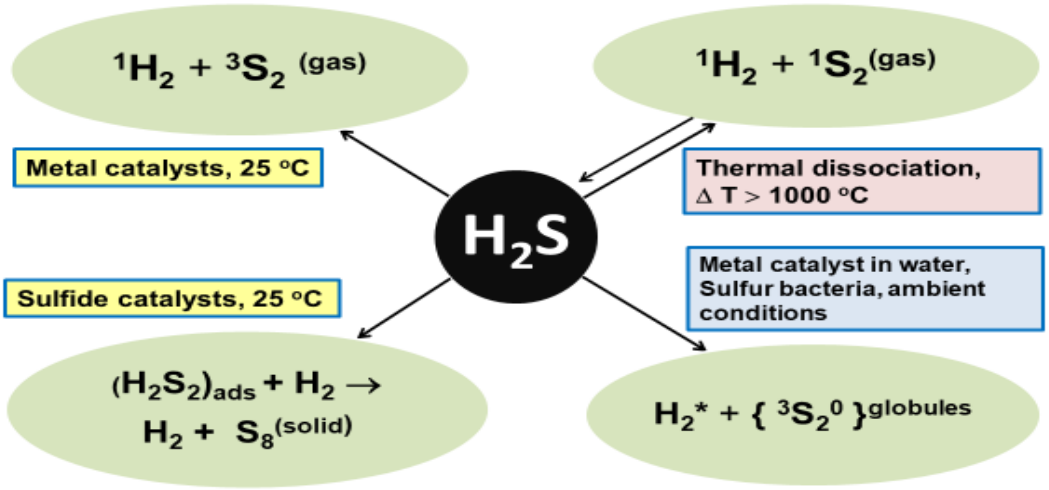

Fig 5. Two temperature ranges of H_2S decomposition. At high temperature, the non-catalytic reaction follows to laws of classical equilibrium thermodynamics. At ambient temperature and pressure, the reaction can occur only on the surface of solid catalysts or with participation of enzymes of sulfur bacteria in accordance with the laws of non-equilibrium thermodynamics of open systems.

Table 1. Comparison of experimentally determined excitation energies (in cm^{-1}) for the electronic states of O_2 and S_2 molecules [19].

T_e – energy of electron term

State	T_e* O_2	T_e* S_2
$c\ ^1\Sigma^-_u$	33 057	20 203
$b\ ^1\Sigma^+_g$	13 195	7 981
$a\ ^1\Delta_g$	7 923	4 395
$X\ ^3\Sigma^-_g$	0	0

Table 3. Dissociation energy of chemical bonds (kcal/mol) at O K and 298 K [30,31].

Bond dissociation	D_o	D_{298}
$S_2 \rightarrow S + S$	98,5	99.8
$H_2 \rightarrow H + H$	103.3	104.2
$H_2S \rightarrow HS + H$	90.7	92.0
$SH \rightarrow S + H$	81.4	82.3

Table 2. DFT calculations of the thermodynamic parameters of sequential stages of the catalytic H_2S decomposition at room temperature [8,9].

M = Co^{3+} or Ni^{4+} - metal ions in d^6 electron configuration, which are the Lewis active centers in the active component of the sulfide HDS catalysts [23].

Step	Reaction	ΔH_{298}, kcal/mol	ΔS_{298}, cal/mol.K	$T\Delta S$, * kcal/mol	ΔG_{298}, kcal/mol
1	Molecular adsorption $2\ M + 2\ H_2S^{(gas)} \rightarrow 2\ (M - H_2S)_{(ads)}$	– 12.7	– 39.6	– 11.8	– 0.8
2	Dissociative chemisorption $2\ (M - H_2S)_{(ads)} \rightarrow 2\ (M - SH)_{(ads)} + 2\ H_{(ads)}$	– 28.7	– 37.8	– 11.3	– 17.4
3	The removal of the first hydrogen molecule $2\ (M - SH)_{(ads)} + 2\ H_{(ads)} \rightarrow 2\ M - (\mu\text{-}S_2)_{(ads)} + 2\ H_{(ads)} + H_2^{(gas)} \uparrow$	– 28.9	– 59.7	– 17.8	– 11.0
4	The removal of the second hydrogen molecule $2\ M - (\mu\text{-}S_2)_{(ads)} + 2\ H_{(ads)} \rightarrow 2\ M - (\mu\text{-}S_2)_{(ads)} + H_2^{(gas)} \uparrow$	+ 25.5	+ 35.9	+ 10.7	+ 14.7
5	Recombination $2\ M - (\mu\text{-}S_2)_{(ads)} \rightarrow 2\ M + ¼\ S_{8(ads)}$	– 19.6	– 29.0	– 8.6	– 10.9
Overall	Catalytic reaction $2\ H_2S^{(gas)} \xrightarrow{\text{catalyst}} 2\ H_2^{(gas)} \uparrow + ¼\ S_{8(ads)}$	– 23.0	– 53.2	– 15.9	– 7.2
Gas phase	$2\ H_2S^{(gas)} \rightarrow 2\ H_2^{(gas)} \uparrow + ¼\ S_{8(solid)}$	+ 15.8	– 10.3		+ 18.9

***** – the bound (waste, lost) energy $T\Delta S$, which is dissipated into the environment, therefore it cannot be used to make useful action (chemical efficiency in generation of target products).