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Entropy of the surface catalytic reaction: Expansion of the advanced H_2S paradigm to novel catalytic systems

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ABSTRACT

The main provisions of the recently developed concept of the crucial role of catalysts in the process of low-temperature decomposition of H_2S to produce hydrogen and elemental sulfur are considered. The concept is based on the non-equilibrium thermodynamics of an irreversible process in an open system. It is shown that irreversible chemical reactions prohibited in the gas phase take place on the catalyst surface under conditions of non-equilibrium thermodynamics at ambient temperature and pressure. This became possible due to the Gibbs free energy accumulated on the catalyst surface as a result of exothermic processes of chemisorption and dissociation of H_2S molecules and the dissipation of entropy in the form of bound energy into the environment. The innovative proposed method of H_2S utilization will replace the long-outdated Claus method of H_2S disposal with the production of water and sulfur (up to 100 million tons per year, more than 1,000 units in the world) with advanced technology to produce hydrogen and diatomic gaseous sulfur. Various types of solid catalysts have been developed to implement advanced technology. The advanced H_2S paradigm of catalytic processing allows unexpected chemical reactions to be realized that cannot be carried out by traditional methods under normal conditions. Atomically adsorbed hydrogen and sulfur species formed as a result of H_2S dissociation can react with chemically inert molecules of methane, CO_2, nitrogen, and argon. It is concluded that at the moment all prerequisites have been created for initiating full-scale scientific, technological, and commercial projects to implement the innovative idea of using the toxic substance H_2S to serve humanity.

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1. Introduction

The problem of predicting the chemical properties of solid catalysts for a specific reaction has been exciting the minds of scientists since the understanding of the essence of catalysis as a natural phenomenon and since the selection of highly active and selective catalysts has always been based on the intuition of the researcher. However, if for a gas-phase chemical process "resolved" by equilibrium classical thermodynamics, the problem boils down to a simple empirical selection of a suitable catalyst, then for irreversible processes occurring in nature within the framework of non-equilibrium thermodynamics, such an approach is hardly possible in principle, since it requires knowledge of the detailed mechanism of interaction of substrate molecules not only among themselves but also knowledge of the elementary stage mechanisms of their interaction with active centers of biocatalysts (enzymes), taking into account thermodynamics of all these stages [1].

This is exactly the situation in the case of H_2S assimilation by sulfur bacteria. Indeed, at the end of the nineteenth century, Sergey Vinogradsky discovered an amazing process of chemosynthesis of organic molecules using sulfur bacteria that catalyze the reaction of H_2S interaction with carbon dioxide. This process, unlike photosynthesis known at that time, did not require sunlight as an energy source [2]. It would seem that this scientific discovery will allow mankind to solve not only the problem of recycling toxic H_2S, but also to use it for the synthesis of the chemicals demanded. However, on the way to the realization of this idea, numerous problems arose with the cultivation of sulfur bacteria in the laboratory, which did not allow us to solve the main task - to study the nature of the catalytically active centers of these bacteria and, as a result, the mechanisms of chemosynthesis.

As is well known, hydrogen sulfide, H_2S is one of the most toxic substances produced as a forced and unavoidable byproduct in the extractive and processing industries in volumes of up to one hundred million tons per year, while its content in the bowels and reservoirs of the Earth is estimated at tens of billions of tons. Unlike its chemical counterpart, water, hydrogen sulfide is a "useless" substance that has not found practical application in human life.

In the interim, the toxicological properties of hydrogen sulfide required taking all necessary measures to destroy this substance to the level of safety standards. The processes of H_2S utilization (more than 1000 installations worldwide) are carried out by the Claus method, discovered back in the 19th century; as a result, the purification products are water and solid sulfur. Thus, hydrogen H_2, a constituent element of hydrogen sulfide H_2S, is irreversibly "lost" in the form of water H_2O, thereby eliminating the possibility of its use as an environ-

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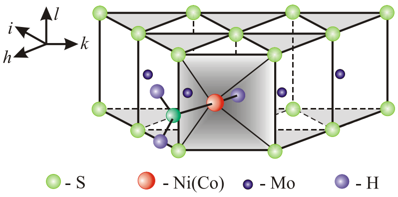

Figure 1. A fragment of the structure of the electroneutral macromolecule of the active component of sulfide HDS catalysts with an occluded hydrogen and H_2S molecule adsorbed on the active centers of the Co(III) or Ni(IV) atoms [13,14].

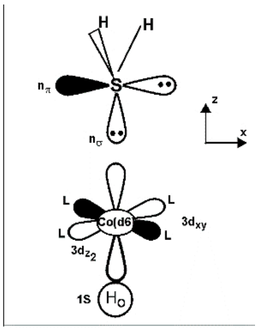

Figure 2. Scheme of interaction of n_σ and n_π orbitals of H_2S molecule with the $3d_{z^2}$ and $3d_{xy}$ orbitals of the Co(III) atoms in the d^6 electronic configuration [13,14]. H_o – occluded hydrogen, L – electron orbitals.

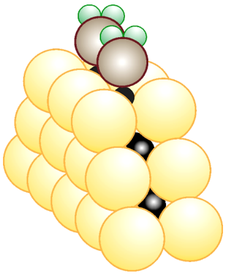

Figure 3. A fragment of the molecular structure of the active component of HDS catalyst with two adsorbed H_2S molecules.

mentally friendly "green" energy carrier. Therefore, many generations of scientists and researchers have tried to obtain products in demand from this substance, hydrogen and sulfur [3-8].

Until recently, all numerous attempts to implement this very relevant and promising process on an industrial scale were undertaken within the framework of classical equilibrium thermodynamics, using a variety of external energy sources to activate the substrate molecule H_2S. However, so far none of these approaches has reached the level of readiness for commercial application in terms of optimal combination of the four E's - Energy, Ecology, Economics and Efficiency [9].

Meanwhile, an original solution to this problem using heterogeneous catalysts has recently been found, which is based on the fundamental principles of biological thermodynamics [10,11]. In this case, we are talking about creating non-equilibrium conditions for the H_2S decomposition at ambient temperature and pressure, which simulate irreversible processes of chemosynthesis occurring in Nature. We have shown that catalytic H_2S decomposition can occur exclusively on the surface of solid catalysts due to the internal (kinetic and potential) energy of the substrate molecules, H_2S, without the use of external energy sources. The result of our research was the creation of a concept on the decisive role of solid catalysts in the irreversible process of low-temperature H_2S decomposition [10]. Taking into account the exceptional practical and scientific significance of this concept, we have stated our claim to replace the existing paradigm of H_2S decomposition using external energy sources with a new paradigm of low temperature H_2S decomposition due to the internal energy sources accumulated in the chemical bonds of H_2S molecules [11]. Experimental details of our research are summarized in [12].

In this analytical review, we will try to substantiate the thermodynamic possibility of low-temperature H_2S decomposition on heterogeneous catalysts within the framework of an irreversible non-equilibrium process, by analogy with chemosynthesis implemented in nature by enzymatic catalysts of sulfur bacteria. The main purpose of this paper can be formulated as follows: is it possible to predict the catalytic activity of solid catalysts based on previously published numerous experimental and theoretical DFT studies of the interaction of an H_2S molecule with the surface of solid catalysts using non-equilibrium thermodynamics for this purpose?

2. Initial data for reflection: Sulfide catalysts

This story began at the end of the twentieth century, when we studied the structure of the active component and the mechanism of action of sulfide hydrodesulfurization (HDS) catalysts (Figure 1) [13,14].

According to our view [13,14], the active centers of the sulfide catalysts are Ni(IV) or Co(III) ions with a d^6 electronic configuration (Figure 2), which were formed as a result of the oxidative addition of hydrogen in the process of catalyst sulfiding. This occluded hydrogen is located inside the active component in an "empty" trigonal prism of six sulfur atoms (Figure 1) and stabilizes an unusually high oxidation state of the

Table 1. DFT calculations of the thermodynamic parameters of sequential stages of catalytic H_2S decomposition at room temperature [13,14]. M = Co^{3+} or Ni^{4+} - metal ions in the d^6 electron configuration, which are the Lewis active centers in the active component of the sulfide HDS catalysts [10-12].

Stage	Reaction	ΔH_{298}, kcal/mol	ΔS_{298}, cal/mol.K	$T\Delta S$ *, kcal/mol	ΔG_{298}, kcal/mol
I	Molecular adsorption $2\ M + 2\ H_2S^{(gas)} \rightarrow 2\ (M - H_2S)_{(ads)}$	−12.7	−39.6	−11.8	−0.9
II	Dissociative chemisorption $2\ (M - H_2S)_{(ads)} \rightarrow 2\ (M - SH)_{(ads)} + 2\ H_{(ads)}$	−16.0	+2.2	+0.7	−16.6
III	The removal of the first hydrogen molecule $2\ (M - SH)_{(ads)} + 2\ H_{(ads)} \rightarrow 2\ M - (\mu\text{-}S_2)_{(ads)} + 2\ H_{(ads)} + H_{2(gas)} \uparrow$	−0.2	−21.9	−6.5	+6.3
IV	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	+35.1	+10.5	+15.0
V	Recombination $2\ M - (\mu\text{-}S_2)_{(ads)} \rightarrow 2\ M + \frac{1}{4}\ S_{8(ads)}$	−19.6	−29.0	−8.6	−11.0
Overall	Catalytic reaction $2\ H_2S^{(gas)} \rightarrow 2\ H_2^{(gas)} \uparrow + \frac{1}{4}\ S_{8(ads)}$	−23.0	−53.2	−15.9	−7.2
Gas phase	$2\ H_2S^{(gas)} \rightarrow 2\ H_2^{(gas)} \uparrow + \frac{1}{4}\ S_{8(solid)}$	+4.9	−17.1		+10.0

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

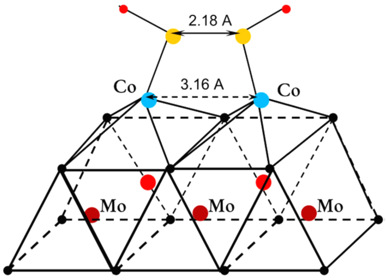

Figure 4. Structure of the key surface intermediate obtained as a result of the coupling of adsorbed H_2S molecules and the removal of molecular hydrogen in the gas phase [10,11].

active metal atom, preventing its reduction under catalysis conditions. Figure 3 shows a fragment of the active component with two adsorbed H_2S molecules on two adjacent atoms of the active center.

After H_2S adsorption on the surface of sulfide catalysts at room temperature, we observed a stoichiometric reaction of hydrogen release into the gas phase by Reaction 1:

$$2\ H_2S \xrightarrow{\text{Sulfide catalyst, 25 }^{o}\text{C}} (H_2S_2)_{ads} + H_{2\ (g)} \qquad (1)$$

which results from the formation of disulfane H_2S_2 (hydrogen disulfide) (Figure 4). The problem is that the direct formation of disulfane H_2S_2 from H_2S in the gas phase (Reaction 2):

$$2\ H_2S \not\longrightarrow H_2S_2 + H_2 \qquad (2)$$

Is *impossible* because of prohibition by the equilibrium thermodynamics ($\Delta_rH^o{}_{298}$ = +13.6 kcal/mol, $\Delta_rS^o{}_{298}$ = -3.9 cal/mol×K, $\Delta_rG^o{}_{298}$ = +14.1 kcal/mol). Thus, we have shown for the first time that a solid catalyst performs a very specific function - a process thermodynamically forbidden in the gas phase is realized on the catalyst surface [10,11]. This became possible due to the interaction (coupling) of two H_2S molecules adsorbed on neighboring atoms of the active centers (Ni or Co in d^6 electronic configuration) of the sulfide catalysts (Figure 4) [10,11].

This unusual surface chemical reaction has become the subject of our thermodynamic studies by DFT calculations (Table 1) [10-14]. Since Reaction 1 is irreversible and proceeds at room temperature without the use of external energy sources, a fair question arises: Where does the energy come from to carry out this chemical reaction? It is known that in biological systems, the main source of energy for ensuring the vital activity of organisms is the potential energy stored in chemical bonds [1]. Therefore, to answer this question, we have developed the concept of the decisive role of solid catalysts in the framework of an irreversible process for an open system that occurs under non-equilibrium conditions [10].

The distinctive features of thermodynamics of non-equilibrium processes are that the systems considered by it are open to flows of matter and energy, and the processes occurring in open systems are far from equilibrium and irreversible. In the thermodynamics of irreversible processes, an important concept is the stationary state of the system. Unlike thermodynamic equilibrium, the stationary state is characterized by a constant influx of substances into the system and the removal of reaction products, continuous expenditure of free energy, which maintains a constant concentration of substances in the system, and the constancy of thermodynamic parameters (including internal energy and entropy). It is important that an open system can exist only due to the influx of energy from the outside and the outflow of energy into the environment [15].

The main task of the thermodynamics of irreversible processes is to determine the value of the increase and the outflow of entropy in a reaction system based on the Gibbs equation [15]. In a stationary non-equilibrium process in an open system, the positive production of entropy inside the system is compensated by the outflow of entropy into the environment, in other words, the non-equilibrium state "dumps" the entropy generated inside the system into the environment, thereby maintaining a stationary state. Thus, the change in entropy of an open system occurs not only due to its increase and the spontaneous course of irreversible processes within the system itself (d_iS), but also due to processes of exchange of the system with the external environment (d_eS) [15]. In the thermodynamics of irreversible processes, it is postulated that the components d_iS and d_eS are independent and that the total change in the entropy of an open system is equal to their sum: $dS = d_iS + d_eS$.

In accordance with the Gibbs equation $\Delta G = \Delta H - T\Delta S$, the spontaneous pathway of an irreversible chemical reaction is ensured provided that in the exothermic process (the enthalpy of the reaction decreases, $\Delta H < 0$) the entropy increases ($\Delta S > 0$).

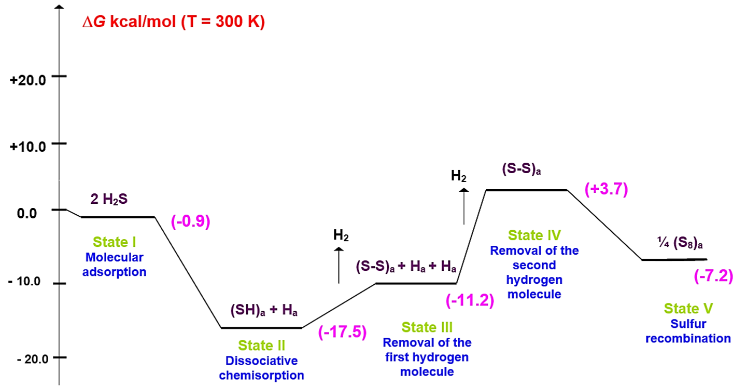

Figure 5. The energetic profile of hydrogen sulfide decomposition on sulfide catalysts at room temperature [11].

However, if the entropy decreases as a result of an exothermic reaction ($\Delta H < 0$) ($\Delta S < 0$), then the Gibbs equation defines the boundaries of the spontaneous pathway of the process. Therefore, if a certain amount of energy entered the system as a result of an exothermic process is spent on the entropy growth (which is inevitable for any irreversible processes), then this part of the energy is lost to perform a useful action (for example, the formation of new chemical bonds in reaction products), it dissipates into the environment in the form of heat. Therefore, this $T\Delta S$ part of the energy is called bound (lost, waste) energy. The remaining part of the energy can be used to perform a useful action; therefore, Gibbs energy is called free energy [1].

So, the first stage of the process under consideration is the chemisorption of H_2S molecules on the active centers of sulfide catalysts. According to our idea, the active centers are Co(III) or Ni(IV) ions with a d^6-electron configuration, which results from the oxidative addition of hydrogen [13,14,16,17]. Formally, the "vacant" molecular orbitals d_{z^2} and d_{xy} of the metal atom effectively interact with the occupied orbitals n_σ and n_π of the H_2S molecule, respectively (Figure 2). Consequently, Co(III) is a Lewis acid center with vacant orbitals that accept an electron pair from a hydrogen sulfide donor molecule, the Lewis base, to form a new chemical bond [13]. This exothermic process (Table 1) results in a decrease in the entropy of the system, which dissipates into the environment in the form of bound energy; however, the remaining part of the Gibbs free energy can be used to maintain a chemical reaction.

In the second stage, dissociation of the adsorbed H_2S molecule occurs resulting as a result of the formation of new chemical bonds with the surface of the catalyst. This exothermic process occurs with an increase in entropy and a significant gain in the Gibbs free energy. In the next stage, a new sulfur-sulfur chemical bond is formed in the key surface intermediate (Figure 4), while the hydrogen molecule leaves the surface of the catalyst. This stage proceeds through a small energy barrier; therefore, it requires the expenditure of free energy (Figure 5, [11]) accumulated in the previous stages.

The most energy-consuming stage (IV) (Table 1) is the decomposition of a key surface intermediate to form reaction products. This stage has an energy barrier (Figure 5) and to overcome it, the free energy accumulated in the previous stages is used, as well as the free energy obtained as a result of the recombination of diatomic sulfur into a cycloocta sulfur and the removal of bound energy in the environment. To remove solid sulfur from the surface of the catalyst, a very simple technique is used, placing the catalyst in a liquid layer capable of dissolving both the initial and final products of the reaction [18,19].

Thus, the decomposition of H_2S on sulfide catalysts at room temperature is an exothermic process that proceeds spontaneously with a decrease in the entropy of the system, which is dissipated in the environment in the form of waste energy (Reaction 3):

$$2\,H_2S \xrightarrow{\text{Sulfide catalyst, 25 °C}} 2\,H_{2\,(g)} + 1/4\,(S_8)_{ads} \qquad (3)$$

The driving force of the process is the formation of reaction products in the ground electronic state, singlet hydrogen and solid singlet sulfur, having a minimum of free energy. In the gas phase, this process is *impossible*.

3. Initial data for reflection: Metal catalysts

The starting point for reflection is an article published in 1986 [20], in which the behavior of H_2S on the surface of a platinum single crystal Pt(111) was experimentally studied. After H_2S adsorption at 110 K, bands appear in the High Resolution Electron Energy-Loss Spectroscopy (HREELS) spectra at 375 and 585 cm^{-1}, which indicates the chemisorption of H_2S with the formation of a Pt–S bond. After heating to 155 K, two additional bands appear in the spectra at 585 and 685 cm^{-1}, which are attributed to two forms of deformation vibrations of the S-H bonds in the surface structures. Both of these bands disappear after heating the surface to 185 K, while the molecular hydrogen H_2 is desorbed into the gas phase; however, a single band 375 cm^{-1} remains in the spectra, attributed to the Pt-S stretching mode of the adsorbed sulfur.

The chemical state of this monatomic sulfur is not discussed in the article [20], so let us try to understand its nature based on the well-known chemical properties of H_2S. The fact is that the appearance of molecular hydrogen in the gas phase should be caused by the decomposition reaction of H_2S, leading to the formation of surface monatomic sulfur (Reaction 4)

$$H_2S \xrightarrow{\text{Pt, 185 K}} H_{2\,(g)} + [S^0]_{ads} \qquad (4)$$

which should be resulted in the formation of the surface platinum sulfide {PtS}, as required by the stoichiometric chemical reaction of platinum *oxidation* with H_2S. However, it is well known that H_2S exhibits *only reducing* properties (as, indeed, all metals) since sulfur is in the lowest oxidation state, hence the reaction above *must be a catalytic* one with the formation of atomic *zero-valence sulfur* as a product of H_2S decomposition. This applies to all transition metals.

At ambient temperature and pressure, the H_2S molecule is stable indefinitely for a long time in the absence of external influences. However, we found [21-23] that if H_2S passes through a metal catalyst at room temperature, then hydrogen and gaseous diatomic sulfur are produced at the outlet.

Table 2. DFT calculation of energy adsorption and dissociation of H_2S molecules on the surface of selected metals (kcal/mol).

No	Stage	Pt(111)	Ni(111)	Ni(111)	(Ni-Mo)	Pd(111)	Pd(111)	Cu(111)	Fe(100)	Cu(111)	Ni(110)	Fe(110)
I	$H_2S \rightarrow H_2S_{(ads)}$	−21.0	−12.9	−12.6	−18.4	−16.4	−12.0	−6.0	−10.6	−5.3	−15.9	−13.6
II	TS*, E_a	+1.6	+4.8	+5.1	+8.1	+8.5	-	+9.9	+5.8	+5.1	+2.1	+4.6
III	$H_2S_{(ads)} \rightarrow SH_{(ads)}+H_{(ads)}$	−19.6	−28.8	−28.7	−27.5	−20.3	−23.3	−18.5	−30.0	−19.8	−25.6	−27.7
IV	TS*, E_a	+0.6	+0.2	+0.3	+0.5	+0.9	-	+9.2	+ 6.5	+7.1	+4.8	+2.8
V	$SH_{(ads)} \rightarrow S_{(ads)}+H_{(ads)}$	−18.2	−20.8	−20.5	−26.8	−16.8	−20.3	−13.9	−30.0	−27.7	−28.6	−43.6
VI	$\Delta E_{diss.total}$	−58.8	−62.5	−61.8	−72.2	−53.5	−55.6	−34.8	−70.6	−52.8	−70.1	−85.1
References		[25]	[25]	[26]	[26]	[27]	[28]	[29]	[30]	[31]	[28]	[32]

TS*, E_a - transition state, activation barrier, kcal/mol.

Since in this case there is no energy supply from the outside, but at the same time both matter and energy are exchanged with the environment, therefore, the H_2S decomposition reaction proceeds due to the free and internal energy of the H_2S molecule, as is the case in biological systems (Reaction 5):

$$2\ H_2S \xrightarrow{\text{Metal catalyst, 25 } ^{o}\text{C}} 2\ H_{2\ (g)} + {}^{3}S_{2(g)} \qquad (5)$$

The process is irreversible; in a stationary state in the gas phase at room temperature and atmospheric pressure on metal catalysts, the H_2S conversion may reach 100%.

The unexpected product of Reaction 5 turned out to be diatomic gaseous sulfur. A thorough analysis of the extensive data in the literature has shown that we have obtained diatomic sulfur for the first time in the ground triplet state $\{S_2X\ {}^3\Sigma^-_g\}$ [22,23], predicted earlier in quantum chemistry as an isoelectronic chemical analog of triplet oxygen. In turn, it was shown that the thermodynamic parameters of diatomic sulfur given in the reference books refer to its metastable singlet state $\{S_2\ a^1\Delta_g\}$, which can exist in free state only at high temperature; upon cooling, this substance inevitably turns into "normal" solid sulfur.

Reaction 5 was discovered by us using platinum as a catalyst. However, it later turned out that stainless steel chips of chemical composition (Fe, Ni, and Cr) turned out to be an excellent catalyst. In addition, we have prepared highly dispersed metal catalysts of a similar chemical constituent supported on various carriers - silica, alumina, carbon support Sibunit, *etc*. For all catalytic systems mentioned, we observed similar patterns of H_2S decomposition. Moreover, we have discovered a number of new catalytic compositions that also follow general rules; therefore, they are registered in our patent [24].

In recent times, numerous experimental and theoretical studies of the H_2S interaction with the surface of various metals have appeared. These works primarily aim to understand the mechanisms of deactivation and inhibition of the properties of metal catalysts as well as their toxic effects on membranes. The main conclusion from all these studies is that H_2S easily dissociates on most metals already at very low temperatures (generally below 185 K) [25].

Table 2 presents the results of the DFT studies of H_2S dissociation on the surface of some metals [25-32]. A characteristic feature of H_2S adsorption on the surface of transition metals is that the chemisorption stage is accompanied by a further process of its dissociation, leading to the formation of surface atomic species. Dissociation occurs in two stages; each of these exothermic stages occurs through a small energy barrier and leads to energy accumulation on the metal surface. It is very important that H_2S dissociation into atoms has neither thermodynamic nor kinetic limitations. Attention is drawn to the good reproducibility of the calculation results for the same systems performed by different authors.

As already noted, metals like hydrogen sulfide are reducing agents; therefore, the process of adsorption and H_2S dissociation on the surface of metals cannot be attributed to traditional redox chemical processes, as is the case in a closed thermochemical cycle of hydrogen production using sulfides of multivalent metals. However, a significant accumulation in energy during H_2S dissociation and the formation of atomic surface species of sulfur and hydrogen suggest that this process can be catalytic, provided that the energy stored in the processes of adsorption and H_2S dissociation will be sufficient for the synthesis of reaction products and their desorption into the gas phase. Of course, it would be necessary to calculate the *entropy* at all elementary stages of the H_2S dissociation process, as we did for sulfide catalysts (Table 1, Figure 5). This would allow us to determine the *Gibbs free energy* of both individual stages and the catalytic process as a whole. In the absence of such an opportunity, we will try to solve this problem (Reaction 5) within the framework of the laws of thermochemistry, using the basic provisions of the concept of the decisive role of catalysts in non-equilibrium thermodynamics [10,11].

In our discussion, we will use the properties of platinum catalysts, since it was on platinum that we discovered the reaction of low-temperature H_2S decomposition [21], and in the literature there is information about the energy of the interaction of reaction products with the surface of a single platinum crystal. As is known, the energy of a chemical bond is an important molecular constant, one of the main characteristics of a molecule [33-35]. The energy of breaking a chemical bond is the minimum energy that must be communicated to a molecule for it to split into appropriate parts. The dissociation energy of a chemical bond D_o or D_{298} is defined as a change in the standard enthalpy of formation of reaction products and the initial chemical compounds. In our case, for Reaction 6,

$$2\ H_2S \leftrightharpoons 2\ H_2 + S_2 \qquad (6)$$

The dissociation energy D_{298} of the HS–H bond in the H_2S molecule under standard conditions is 92 kcal/mol [33], while the dissociation of the second S–H bond requires only 82.3 kcal/mol. In Reaction 6, two H_2S molecules have four HS–H bonds to be broken, which gives the total dissociation energy of the two molecules $\Sigma D_{298} = (92.0 + 82.3)\times 2 = 348.6$ kcal/mol. At the same time, two bonds H–H ($\Sigma D_{298} = 2\times 104.2 = 208.4$ kcal/mol) and one bond S–S $D_{298} = 99.8$ kcal/mol are formed [33]. From this it follows that the total energy of bond dissociation in the initial hydrogen sulfide exceeds this indicator for the products of the Reaction 6 to $\Delta D_{298} = \Sigma D_{298}(2\ H_2S) - \Sigma D_{298}(2\ H_2 + S_2) = 40.4$ kcal/mol.

In other words, this means that the initial H_2S molecule is stable and does not turn into reaction products H_2 and S_2 at room temperature; therefore, additional energy is needed to carry out Reaction 6. Since there is no external energy source in Reaction 5, therefore, to carry out Reaction 6 on the surface of the catalyst, this energy can be obtained due to the adsorption and dissociation energy of the H_2S molecule. Subtracting from the total dissociation energy of two H_2S molecules $\Delta E_{diss\text{-}total} = -117.6$ kcal/mol, the energy necessary for the implementation of Reaction 6, we obtain some excess energy $\Delta E_{surplus} = -77.2$ kcal/mol that can be spent to close the catalytic cycle, *i.e.*, for desorbing reaction products into the gas phase.

Taking into account that on the surface of platinum, the stabilization energy of the S_2 molecule is −45 kcal/mol [36], while for hydrogen it varies within −(9.5÷12) kcal/mol [37,38], we conclude that after desorption of the reaction products in the gas phase, we have a small excess of energy $\Delta E_{\text{total.min}}$ = –(8.2÷13.2) kcal/mol, which means the exothermic nature of the catalytic cycle. However, in catalytic Reaction 5, a spontaneous transition of diatomic sulfur to the ground triplet state is carried out with the release of energy of 12.6 kcal/mol [23], therefore, this energy should be added to the exothermic effect of the reaction under consideration, which corresponds to $\Delta E_{\text{total.max}}$ = –(20.8÷25.8) kcal/mol. The driving force of the process is the formation of reaction products in the ground electronic state: singlet hydrogen and diatomic triplet sulfur, having a minimum of free energy. Of course, a similar analysis can be done for other metals from Table 2, however, this requires to know the interaction energies of molecules with the surface of the corresponding metal.

A very important conclusion follows from the consideration of the energy redistribution of the dissociation of the H_2S molecule on the surface of the metal catalysts. In this case, the First Law of Thermodynamics of energy conservation is fully realized: energy does not appear out of nothing and does not disappear into nowhere, but turns from one form into another. In other words, the surface of the catalyst provides the possibility of transferring the internal energy of the H_2S molecule to create new chemical bonds in the reaction products and their desorption into the gas phase, thus closing the catalytic cycle.

The second important conclusion is that since the entropy of Reaction 5 increases $\Delta S > 0$ (the number of gaseous molecules increases), and the reaction itself is exothermic $\Delta H < 0$, the Gibbs free energy will always be *negative*, which means the *spontaneous* course of catalytic Reaction 5. However, the paradox lies in the fact that the increase in entropy in combination with the exothermic effect will inevitably lead to heating of the catalytic system, and therefore, in order to maintain the stationary state of the system, the heat must be removed. For this reason, we observed an abnormal temperature dependence of H_2S decomposition on metal catalysts [21] – the efficiency of the process increases with decreasing temperature. An even more convincing example is that hydrogen is already formed from H_2S on the Pt surface already at 185 K (–88 °C), while water on Pt does not dissociate into atoms [20].

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).

4. Entropy of the surface catalytic reaction: Why is it important and necessary?

It is quite obvious that the First Law of Thermodynamics, which we used to analyze the possibility of H_2S decomposition on platinum, cannot give an unambiguous answer to the key question: Is it possible in the system (H_2S–metal) noted in Table 2 a spontaneous catalytic process to occur? To answer the question, these systems should be considered within the framework of the Second Law of Thermodynamics. First of all, this problem seems to be very relevant in connection with the possibility of avoiding time-consuming experimental work with toxic and fetid H_2S. Secondly, the prediction of the possibility of carrying out unusual catalytic reactions involving H_2S may be of the highest scientific and practical interest.

Having considered the necessary background, let us look at the problem of predicting the catalytic activity for the (H_2S–metal) system, some examples of which are shown in Table 2. This very attractive task should begin with calculating the *entropy* of the successive stages of H_2S dissociation, as we have done for sulfide catalysts (see above). In this case, it is necessary to consider the isothermal isobaric process occurring on the surface of the catalyst within the framework of non-equilibrium thermodynamics for an open system, *i.e.* with continuous supply with H_2S and removal of reaction products from the catalyst surface [10,11]. Therefore, knowing the entropy change of each elementary stage of the H_2S dissociation, the Gibbs free energy value for the descending branch of the process energetic profile will be obtained (see Figure 2).

The desorption (ascending) branch of the energy profile does not seem to have any thermodynamic or kinetic limitations. Indeed, molecular hydrogen easily leaves the surface of the catalyst because of the low heat of adsorption compared to the potential energy accumulated on the surface. The limiting stage of the surface reaction is apparently the formation of diatomic sulfur, which occurs through a low energetic barrier due to the need for migration of atomic zero-valence sulfur along the catalyst surface. However, singlet sulfur, which initially forms a H_2S molecule, spontaneously transmits to the ground triplet state, since the presence of free electrons in the metal conduction band helps to lift the ban on electronic transitions of singlet sulfur to the thermodynamically most stable ground triplet state. In an isolated S_2 molecule, the direct singlet-triplet transition is prohibited by the selection rules. Recall that the entropy of Reaction 5 is always positive because the number of gaseous reaction products increases.

Thus, if the thermodynamic calculations of the surface reaction turn out to be favorable for the implementation of the catalytic process in the system (H_2S–metal) (Table 2), then this will mean confirmation of our concept on the decisive role of catalysts in the process of low-temperature H_2S decomposition [10,11]. These metals are also mentioned in the patent [24].

However, in this case, we will be interested in catalytic reactions in which atomic hydrogen and sulfur, obtained on the surface of solid catalysts in the process of low-temperature H_2S decomposition, may interact with chemically inert molecules of methane, carbon dioxide, molecular nitrogen, and argon. So, it should be expected that the atomically dispersed surface species of hydrogen and sulfur produced in Reaction 7,

$$H_2S \xrightarrow{\text{Metal catalyst, 25 °C}} 2\,\{H^*\} + \{S^*\} \qquad (7)$$

have an extremely high reactivity; therefore, they can enter into coupling reactions with chemically inert molecules [11,12]. For example, a methane molecule dissociates very weakly on the surface of Pt(111) at room temperature [39], however, in the presence of adsorbed atomic sulfur species, the following chemical reaction (Reaction 8) is apparently possible.

$$2\,\{S^*\} + CH_4 \xrightarrow{\text{Metal, 25 °C}} CS_2 + 2H_2 \qquad (8)$$

Reaction 8 is attractive because methane hydrate and H_2S, whose reserves, for example, in the Black Sea, are practically inexhaustible [40], can be involved in joint processing to produce the target product, hydrogen.

A similar coupling of reactions can occur in the case of carbon dioxide, which also weakly dissociates on the surface of solid catalysts (Reaction 9) [41]:

$$2\,\{H^*\} + CO_2 \xrightarrow{\text{Metal, 25 °C}} \{HCOOH\}\ \text{(carbohydrates)} \qquad (9)$$

Apparently, it is this Reaction 9 that underlies the process of chemosynthesis by sulfur bacteria [2]. However, to activate the CO_2 molecule, a second metal should be selected, as suggested by the results of the work [41].

All biological reactions of nitrogen fixation are catalyzed by enzymes called nitrogenases with Fe as a catalytic active center [42], which convert a strong triple N–N bond into ammonia NH_3 under normal conditions. However, the industrial process requires high pressures (around 200 atm) and high temperatures (at least 400 °C). Meanwhile, in our case, this reaction occurs at room temperature and pressure if there is a source of active hydrogen produced from H_2S on stainless steel chips (7) [11].

Finally, an absolutely incredible result has been obtained when the stream (Ar + H_2S) was passed through a platinum catalyst or stainless steel chips at room temperature. Along with sulfur gas, a new substance was obtained at the reactor outlet instead of the expected hydrogen, to which the formula was attributed - hydrogen argonide H_2Ar [11,12]. Since the heat of adsorption of argon on platinum is only 3 kcal/mol [43], it can be assumed that the hydrogen activated in the Reaction 7, even in this case, effectively interacts with the adsorbed argon atom. The answer to this question can probably be obtained from thermodynamic calculations of the entropy of the surface reaction and, as a result, the Gibbs free energy. If our experimental observations are confirmed, it will mean that stable under normal conditions, the hydrogen argonide molecule H_2Ar can be used for the accumulation, storage, and transportation of hydrogen. Moreover, when hydrogen argonide is burned in fuel cells or in the presence of oxygen, water and argon are released, which returns to the atmosphere without damaging the environment. There is also a reason to assume that the chemical analogues H_2Ne–hydrogen neonide and H_2He–hydrogen helionide can be obtained in a similar way.

To verify and substantiate this hypothesis, targeted experimental studies using modern physicochemical methods involving theoretical calculations of the non-equilibrium thermodynamics of an open system and the mechanism of the catalytic stages of the interaction of atomic hydrogen with adsorbed argon and nitrogen molecules are necessary. Currently, the author does not have such an opportunity, so the author will be very grateful for any expression of interest from the scientific community and is ready to share all available information to achieve his goals.

5. Conclusion

Entropy of the surface catalytic reaction: Why is it important and necessary?

Based on the concept of the decisive role of solid catalysts in the process of low-temperature decomposition of H_2S, we conclude that under conditions of non-equilibrium thermodynamics, reactions prohibited in the gas phase are carried out on the catalyst surface. This was made possible by using the internal energy of H_2S molecules to accumulate the free energy obtained as a result of exothermic processes of chemisorption and dissociation of H_2S molecules to an atomically adsorbed species and dissipation of entropy in the form of bound energy in the environment. To obtain data on the Gibbs free energy, knowledge of the *entropy* of all stages of the surface catalytic reaction is necessary.

The generally accepted paradigm of H_2S decomposition into constituent elements using external energy sources has not yet allowed to create an acceptable technology for producing hydrogen and sulfur from the point of view of finding the optimal combination of the four 'E': ecology, economy, efficiency and energy. The advanced paradigm of low-temperature catalytic decomposition of H_2S is apparently the very tool for solving the extremely urgent problem of not only the disposal of toxic H_2S with the production of demanded products, but also opens up a wide prospect of using atomic hydrogen and sulfur for the implementation of unexpected chemical reactions and the production of new, previously unknown chemicals. The development potential of the paradigm is limited by the volume of processed H_2S, which, in turn, is limited by the amount of sulfur consumed. The situation may change if new unexpected solutions are found for the use of triplet sulfur as a reagent for the synthesis of new substances and materials in chemistry, industry, mechanical engineering, medicine, pharmacology, *etc*.

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

At the moment, apparently, all prerequisites have been created for initiating full-scale scientific, technological, and commercial projects to implement the innovative idea of using the toxic substance H_2S created by nature to serve humanity. Today we have a unique opportunity to use this "gift" of nature to solve scientific and technological problems that cannot be implemented within the existing paradigm of H_2S processing. For this purpose, we have actually reproduced biological processes carried out in nature by biocatalysts–enzymes, using heterogeneous catalytic systems. In turn, we have discovered a new phenomenon in heterogeneous catalysis, the use of the internal energy of the chemical bonds of the H_2S molecule to carry out chemical reactions that cannot be carried out in the gas phase in the absence of solid catalysts, which undoubtedly models biological processes.

It should be emphasized the special role of catalysis for chemistry as a science in general, and for many biological processes occurring under the action of biocatalysts, enzymes. Currently, the role of catalysis in human activity is significantly increasing due to the purposeful search for and creation of highly active and selective catalysts capable of effectively solving the economic and environmental problems of chemical processes. However, the possibilities of catalysis are far from being exhausted, since NATURE has created unique biocatalysts that, under environmental conditions, are capable of performing processes that cannot yet be implemented on an industrial scale. In our opinion, a qualitative shift to a new paradigm of the *science of catalysis* can be achieved if we direct our efforts to create "man-made" irreversible catalytic processes operating in thermodynamically non-equilibrium conditions characteristic of all biological processes.

The author really hopes that the relevance of the raised scientific problem and the prospect of obtaining new knowledge in previously unknown fields of science will allow us to overcome all obstacles in our very difficult time to solve the problem of sustainable human development.

Disclosure statement DS

Conflict of interest: The author declares that I have no conflict of interest.
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