The Reaction Mechanisms of H$_2$S Decomposition into Hydrogen and Sulfur: Application of Classical and Biological Thermodynamics

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Abstract

Four possible pathways of H$_2$S decomposition into hydrogen and elemental sulfur are considered. In the thermal reversible process, H$_2$S dissociation results in the formation of diatomic both hydrogen and sulfur in the singlet state according to the rule of spin conservation:

$$H_2S \xleftrightarrow{\Delta\hat{O} > 1000°\tilde{N}} H_2 + \tfrac{1}{2}{}_1 S_{2(gas)} \qquad \text{(i)}$$

On the surface of sulfide catalysts, irreversible H$_2$S splitting proceeds at low temperature through the stage of disulfane, H$_2$S$_2$ formation as a key surface intermediate, followed by its decomposition due to release of hydrogen into the gas phase and recombination of the adsorbed singlet sulfur into cyclooctasulfur:

$$2H_2S \xleftrightarrow{sulfide\ catalyst\ 25°C} \{H_2S_2\}_{ads} + H_2 \rightarrow H_2 + \tfrac{1}{4}S_{8(ads)} \qquad \text{(ii)}$$
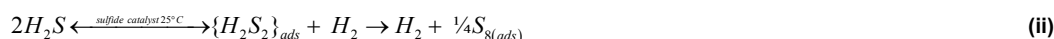
On metal catalysts, irreversible H$_2$S decomposition occurs at low temperature through the stage of H$_2$S dissociation into the adsorbed atomic surface species resulted in the formation of both diatomic reaction products in the ground electronic state -the singlet hydrogen and the triplet diatomic sulfur:

$$H_2S \xrightarrow{Metal\ catalyst\ 25°C} H_2 + \tfrac{1}{2}{}_3 S_{2(gas)} \qquad \text{(iii)}$$

The reactions (**ii**) and (**iii**) are considered to be realized under the principles of biological thermodynamics, in the absence of catalyst both reactions are thermodynamically prohibited in the gas phase. The mechanism of H$_2$S assimilation by sulfur bacteria is suggested to occur in the processes of chemosynthesis resulted in the formation of colorless sulfur globules and activated hydrogen:

$$H_2S \xrightarrow{sulfur\ bacteria,\ ambient\ conditions} 2\ H_2{}^* + \{{}_3S_2\}_{(globules)} \qquad \text{(iv)}$$

Similar to the bacterial process, the hydrogen production from H$_2$S is realized with the efficiency of 99.6% on metal catalysts immersed into the liquid which is capable well-dissolving H$_2$S.

Keywords: H$_2$S decomposition; Hydrogen production; Classical and biological thermodynamics; Reaction mechanism; Diatomic sulfur; Triplet and singlet sulfur; Sulfide and metal catalysts; Sulfur bacteria

Introduction

Hydrogen sulfide is one of the most toxic substances produced as an obligatory and unavoidable by-product in the mining and processing industries in the total annual amount of tens and hundreds of millions of tons. The reserves of hydrogen sulfide in the entrails and water reservoirs of the Earth are estimated by the billions of tons, its contents in the explored deposits of natural gas may be more than 50%. At the same time, it is the "useless" matter, which did not find any commercial application. Therefore, H$_2$S must be removed from waste gases and waters to the level of sanitary norms. Processes of hydrogen sulfide utilization are implemented worldwide by the Claus method, developed in the 19th century; as a result, the final products of its disposal are water and solid sulfur.

H$_2$S, on the other hand, is a simple molecule which has a structure similar to that of water, however, unlike water, the H$_2$S molecule is much less stable and is decomposed into elements even at temperatures as low as 500°C [1]. This means that hydrogen can be released from H$_2$S by an array of techniques including simple heating, irradiation, electrolysis, photolysis etc. [2,3]. Several of these processes have been demonstrated on a significant scale, but none of them has yet achieved commercial success because of high cost of hydrogen produced [4,5]. The goal of this article aims to consider the processes of H$_2$S decomposition from two opposite standpoints. For high-energy, reversible processes, when the system is continuously supplied with energy in the form of heat, the decomposition of hydrogen sulfide is subject to the laws of classical equilibrium thermodynamics for isolated systems, which are permeable neither to heat nor matter. For processes at room temperature, an external source of energy is absent, so the decomposition of hydrogen sulfide is examined from the standpoint of biological thermodynamics, when exchanges of both matter and energy take place in an open system [6].

Thermal Processes of H$_2$S Decomposition

Thermal dissociation of H$_2$S is a well researched route for the hydrogen production:

$$2\ H_2S \xleftrightarrow{\Delta\hat{O} > 1000°\tilde{N}} 2\ H_2 + {}_1 S_{2(gas)} \qquad (1)$$
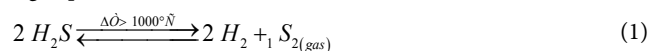
Since conversion is very low, only 15% at 1000 °C and 1 atm., it is beneficial to increase the reaction temperature. Rapid quenching the reaction products is important to maximize H$_2$ yields. To shift the reaction equilibrium to the right, various ways of intermediate

removing the reaction products have been presented [2,3]. Reversibility of the reaction (1) means that process runs equally well forwards and backwards and is always in a near equilibrium state. In accordance with the rule of spin conservation, diatomic sulfur formed in the reaction (1) is in the metastable singlet state which does not convert into the ground triplet state even at high temperature and in the presence of metal catalysts [7-9]:

$$_1S_{2\,(gas)} \quad \neq \quad _3S_{2\,(gas)} \tag{2}$$

As is well known, diatomic sulfur is isoelectronic to oxygen [10,11], therefore the S_2 ground state is a triplet $X\,^3\Sigma_g^-$ and the first exited state is a singlet $a_1\Delta_g$ which is above the ground state by ~4400 cm^{-1} (Table 1). However, unlike to singlet oxygen which is spontaneously converted into the ground triplet state [12], the diatomic singlet sulfur prefers to aggregate from the gas phase into the solid S_8 structure. Another high-energy processes of H_2S decomposition reviewed in [2,3] resulted in the formation of solid sulfur as well.

Application of Biological Thermodynamics to the Catalytic Systems

Biological thermodynamics is the quantitative study of the energy transductions that occur in and between living organisms, structures, and cells and of the nature and function of the chemical processes underlying these transductions. All biological organisms require energy to survive. No matter what the type of living species, all living organisms must capture, transduce, store, and use energy to live. In application of thermodynamics to biological systems functioning at ambient conditions, the following peculiarities of organization of living systems are accepted [6]:

• biological systems are open to flows of matter and energy;

• processes in living systems are irreversible and far from equilibrium;

• biological systems are heterogeneous, structured, and individual phases may have a small ultimate number of molecules.

All these features distinguish biological systems from the isolated and close to equilibrium systems in the classical thermodynamics. It is well recognized that for an adequate description of the properties of living systems it is necessary to apply the thermodynamics of irreversible processes which deals with the processes in time. A fundamental concept in classical thermodynamics is the notion of equilibrium state. In thermodynamics of irreversible processes an important concept is the notion of a steady state of the system [6]. Unlike thermodynamic equilibrium, the steady state is characterized by a constant flow of substances in and removing the reaction products out of the system, a continuous expenditure of free energy, which maintains the constancy of the concentrations in the system and the constancy of the thermodynamic parameters (including the internal energy and entropy). It is important that an open biological system can exist only due to the inflow of energy from outside and outflow of energy in the environment [6]. Catalytic reactions, which run at ambient conditions (room temperature and normal pressure) and do not obtain energy from the surroundings (solar energy is excluded, we consider only dark processes), seem to be referred to the open systems which are permeable to heat and matter flows [6]. Actually, H_2S is a stable molecule at ambient conditions and exists for a long period of time in the absence of action of external forces. However, on passing H_2S over metal catalysts at room temperature, two reaction products are observed which are hydrogen and gaseous sulfur [7-9]. Hence, the reaction is likely to occur at the expense of the molecule free energy. The energy stored in H_2S can be released through the molecule dissociation on the catalyst surface.

H2S Decomposition on Sulfide Catalysts

The initial step of any heterogeneous catalytic reaction is an adsorption of substrate molecules on the surface of solid catalyst. The active component of the sulfide hydrodesulfurization (HDS) catalysts consists of a single slab of MoS_2 with Ni or Co atoms being located in its edge plane in the center of a square pyramid made of sulfur atoms (Figure 1). The active sites for H_2S adsorption are Co(III) or Ni(IV) atoms in the d_6 electronic configuration (Figures 2 and 3) [13-15]. The essential element of the active component is hydrogen occluded into the MoS_2 matrix (Figures 1 and 3). The occluded hydrogen appeared in the active component during the catalyst sulfiding as a result of its oxidative addition to the Ni (Co) atoms. It localizes in the center of "empty" trigonal prism of a MoS_2 matrix made from six sulfur atoms under Ni (Co) atom at the distance of 1.5 Å (Figure 1). The active metal ions are oxidized by the occluded hydrogen to Co(III) and Ni(IV) and acquired d_6 electron configuration (Figure 3) [13-15]. Two unoccupied orbitals of the active metal atom, $3d_{z^2}$ and $3d_{xz}$ interact effectively with the n_σ and n_π orbitals of the H_2S molecule (Figure 3). In the absence of occluded hydrogen, H_2S molecule is not adsorbed by a Co(II) or Ni(III) atom with d_7 electron configuration, because the $3d_{z^2}$ orbital is occupied. The molecular H_2S adsorption on the d_6 Co(III) ion is an exothermic process (ΔH_{298}=-12.7 kcal/mol) and occurs spontaneously (ΔG_{298}=-0.8 kcal/mol) [16,17], while H_2S adsorption on the d_7 Co(II) ion is hardly possible (ΔH_{298}=-2.2 kcal/mol, ΔG_{298}=+6.6 kcal/mol).
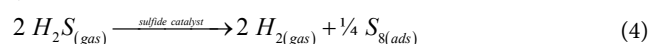
The second step -dissociative chemisorption of two H_2S molecules on two adjacent cobalt atoms (Figures 2 and 4), occurs spontaneously (ΔH_{298}=-28.7 kcal/mol, ΔG_{298}=-17.4 kcal/mol) on the d_6 Co(III) ions as well, and does not possible for the d_7 Co(II) ions (ΔH_{298}>0, ΔG_{298}>0) [16,17]. It is significant that, in the adsorbed state, two H_2S molecules interact to one another, as is indicated by their coming together within a short distance of 2.18 Å of each other (Figure 4). As a result, a new sulfur–sulfur chemical bond is formed in the surface intermediate, and this process is accompanied by the release of a hydrogen molecule into the gas phase and by the formation of adsorbed disulfane H_2S_2 (Figures 4 and 5).
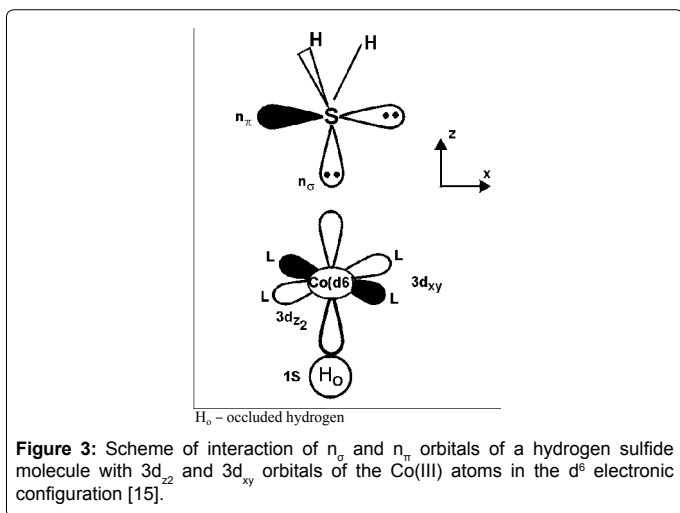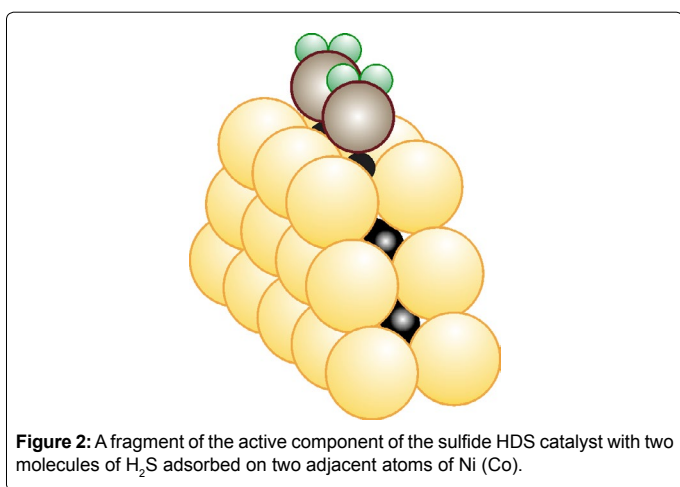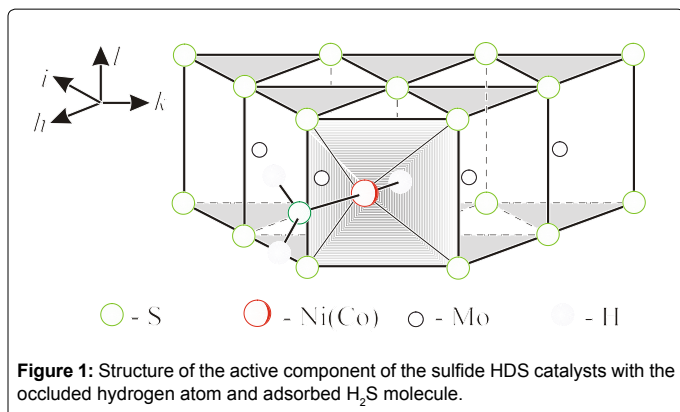
It is very important, that formation of disulfane, H_2S_2 from H_2S in the gas phase in the absence of catalyst is thermodynamically prohibited:

$$2\,H_2S \neq H_2S_2 + H_2 \tag{3}$$

($\Delta_r H_{o298}$=+13.6 kcal/mol, $\Delta_r S_{o298}$=-3.9 cal/mol. K, $\Delta_r G_{o298}$=+14.1 kcal/mol, initial parameters for calculations are taken from [18]). Disulfane was also established in the gas phase during the high temperature metal-catalyzed reaction of H_2S decomposition [19].

The next step of surface reaction -decomposition of adsorbed disulfane into molecular hydrogen and adsorbed disulfur, is a strongly endothermic process and requires large energy consumption ΔH_{298}=25.5 kcal/mol. There is, however, the possibility of terminating the catalytic cycle, which is the recombination (oligomerization) of molecular sulfur S_2 into cyclooctasulfur S_8 on the catalyst surface without it's desorption into the gas phase. This coupled reaction is the highly exothermic process and occurs spontaneously (ΔH_{298}=-78.4 kcal/mol, ΔS_{298}=-116.0 cal/mol. K, ΔG_{298}=-43.6 kcal/mol [16,17]). Therefore, the overall catalytic reaction:

$$2\,H_2S_{(gas)} \xrightarrow{\text{sulfide catalyst}} 2\,H_{2(gas)} + \tfrac{1}{4}\,S_{8(ads)} \tag{4}$$

Figure 1: Structure of the active component of the sulfide HDS catalysts with the occluded hydrogen atom and adsorbed H₂S molecule.

Figure 2: A fragment of the active component of the sulfide HDS catalyst with two molecules of H₂S adsorbed on two adjacent atoms of Ni (Co).

Figure 3: Scheme of interaction of n_σ and n_π orbitals of a hydrogen sulfide molecule with $3d_{z^2}$ and $3d_{xy}$ orbitals of the Co(III) atoms in the d^6 electronic configuration [15].

Figure 4: The key surface intermediate $\{H_2S_2\}^{ads}$ resulted from H₂S dissociation on the surface of sulfide catalysts after H₂ molecule being released in the gas phase [16,17].

Atoms of the active component of the sulfide HDS catalysts:

• - sulfur, • - molybdenum, • - cobalt, • - occluded hydrogen, hydride ion H⁻.

Atoms of the adsorbed species:

• sulfur, • hydrogen ion, proton H⁺.

$$2\,H_2S \xrightarrow{\;metal\;catalyst,\;25°C\;} 2\,H_2 +_3 S_{2(gas)} \qquad (5)$$

This irreversible gasphase reaction occurs on the platinum catalyst at ambient conditions under steady state regime with the effivency of ~15%. Let's consider the reaction (5) in the light of biological thermodynamics. Adsorption of H₂S molecule on the surface of any metals is an exothermic process. In the case of Pt(111) [21], the energy of molecular H₂S adsorption is E_{ads}=-21.0 kcal/mol. The minimum energy pathway of the adsorbed H₂S is then considered for its dissociation in two steps [21]:

$$H_2S_{(ad)} \rightarrow SH_{(ad)} + H_{(ad)} \qquad (6)$$

$$SH_{(ad)} \rightarrow S_{(ad)} + H_{(ad)} \qquad (7)$$

The first dissociation step (6) occurs via the reaction barrier of E_a=1.6 kcal/mol with the reaction energy ΔE_{rxn}=-19.6 kcal/mol, while for the second step (7) these values are E_a=0.7 kcal/mol and ΔE_{rxn}=-18.2 kcal/mol. Hence, the total reaction energy of H₂S dissociation on Pt(111) into the adsorbed S and H atoms is $\Delta E_{diss.total}$=-58.8 kcal/mol or $\Delta E_{diss.total}$=-117.6 kcal/mol for two H₂S molecules of the reaction (5). It is very important, that H₂S dissociation is a facile process which is kinetically and thermodynamically favorable [21]. On the other hand, from the point of view of thermo-chemistry, the bond dissociation energy D_o of HS‑H bond in H₂S molecule is 92 kcal/mol [18]. In the reaction (5) four HS‑H bonds should be cleaved, what is ΣD_o=368 kcal/mol, while two H‑H bonds (ΣD_o=2 x 104=208 kcal/mol) and one S‑S bond D_o=102.5 kcal/mol [18] are formed. From this it follows that the total energy of bond dissociation of initial substance is over ΔD_o=57.5 kcal/mol than that of reaction products, therefore H₂S molecule is stable and does not convert into H₂ and S₂ at room temperature. However in the adsorbed state the required energy for H₂S splitting can be invested from the surface dissociation energy of H₂S adsorption. The resulted energy surplus ($\Delta E_{diss.total} + \Delta D_o$)=-117.6+57.5=-60.1 kcal/mol seems to be consumed for desorption of the reaction (5) products into the gas phase. Actually, the adsorption energy of S₂ species on
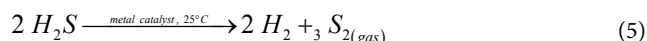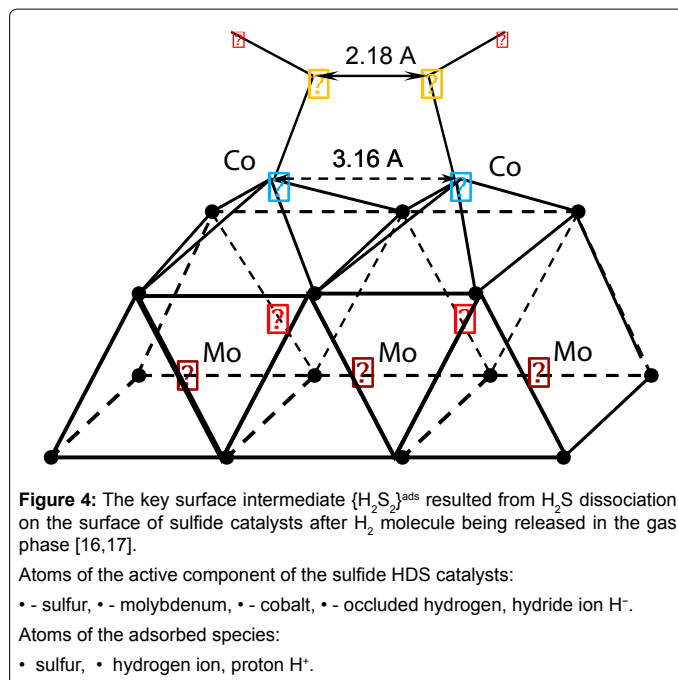
runs also spontaneously at room temperature (ΔH_{298}=-23.0 kcal/mol, ΔS_{298}=-53.2 cal/mol. K, ΔG_{298}=-7.2 kcal/mol [16,17]) (Figure 5). Removal of adsorbed sulfur from the catalyst surface can be realized by immersing solid catalyst into liquid solvent (see next sections).

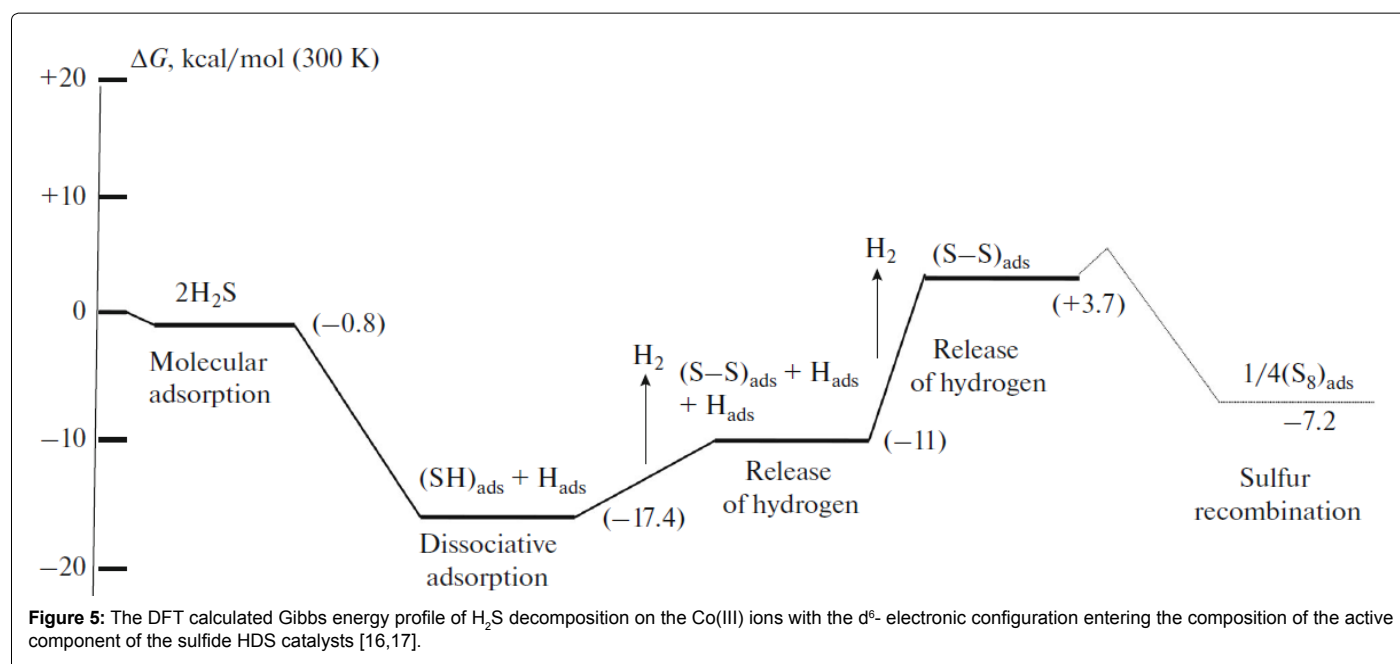## H₂S Decomposition on Metal Catalysts

An unexpected, unpredictable phenomenon was observed when hydrogen sulfide was passed through metal catalysts at room temperature: along with hydrogen, diatomic gaseous sulfur was discovered as a reaction product [7-9,20].

Figure 5: The DFT calculated Gibbs energy profile of H_2S decomposition on the Co(III) ions with the d^6- electronic configuration entering the composition of the active component of the sulfide HDS catalysts [16,17].

Pt(111) is ~45 kcal/mol [22], while molecular hydrogen desorbs from the surface even at 230 K [23]. Undoubtedly, this rough approximation of energy transduction from H_2S dissociation into the surface catalytic reaction should be carefully investigated with both theoretical and experimental methods similar to that made for sulfide catalyst (see above). However, this approach seems to offer new opportunity to understand mechanisms of the low temperature catalytic reactions by means of biological thermodynamics on the atomic scale.

H_2S Assimilation with Sulfur Bacteria

As distinct from solid sulfur, the diatomic sulfur formed in the reaction (5) is well soluble in water, over 5 g of sulfur per liter of H_2O [24]. The pH value and refractive index of the colorless sulfur solution are the same as those of the initial water, and the Raman spectrum of the solution exhibits only bands characteristic of water. It is typical of solutions of diatomic gases that do not interact with water (N_2, O_2, H_2, etc.). When the reaction (5) is carried out on metal catalyst immersed into water, white sulfur globules were obtained from the saturated solutions (Figure 6) [24]. The size of the white spherical globules is up to 10 μm, while the smallest globules are practically transparent and colorless. The elemental analysis of the single globule obtained with the energy dispersive spectroscopy evidences in the only element -sulfur [24]. Electron diffraction on the separate sulfur globule indicates a hexagonal structure of the sulfur crystallites with the interplanar spacing of 0.45, 0.29, and 0.15 nm. More than 30 allotropic modifications of solid sulfur are currently known [25,26] with changes in color from red to black, but no white hexagonal sulfur was found in the database. The only single absorption band at 880 cm_{-1} was observed in the Raman spectra of saturated water solution over precipitate of white globules, while the globules themselves are irreversible transferred into the solid S_8 under the laser beam of a Raman spectrometer. Taking into account the hydrophilic character of white globules, we suggest that this substance is obviously composed of S_2 condensed phase with sulfur in the ground triplet state.

Surprisingly, the white sulfur globules obtained from H_2S on metal catalysts under layer of water bear a great resemblance to colorless globules produced with sulfur bacteria in aqueous medium containing H_2S [27-34]. The role of autotrophic (self-feeding) bacteria in the biosphere was first recognized by Winogradsky at the end of 19 century on the example of sulfur bacteria used hydrogen sulfide as an energy source in the chemosynthesis [27]. Bacteria are the simplest living cells which exhibit all the essential features of a living organism. The ability to harness energy from various sources and to channel it into growth and biological work is a fundamental property of these organisms. The bacteria carry out a remarkable variety of energy transductions, conversions of one form of energy to another [6].

There is a wide range of different types of colorless sulfur bacteria with very diverse properties and with equally diverse environmental habitats. The colorless sulfur bacteria are found in marine and freshwater sediments, soils, and waste water treatment systems. They are growing in aqueous media from acid to alkaline pH values, at temperature ranging from +4 to +95°C, in both aerobic and completely anaerobic conditions [30,32-34]. Many of the properties of "biological sulfur" S_0 produced with sulfur bacteria do not match the properties of any known chemical allotrope of elemental sulfur [25,26]. S_0 forms transparent droplets in diameter of up to 1 μm which are deposited inside or outside of the bacteria cells. S_0 is hydrophilic and of white or pale-yellow color. The buoyant density of S_0 has been determined as 1.22 g/cm_3 [35] in contrast to density of liquid sulfur 1.80 g/cm_3 and solid S_8 2.07 g/cm_3. Therefore, the question was raised of whether S_0 is a new form of elemental sulfur or rather sulfur-rich compound [28].

To answer this question, several models of known sulfur compounds were critically evaluated and it was concluded that S_0 most likely consists of long-chain polythionates [28]. However, the purposeful searching experiments have shown complete absence of polythionates and a new model was proposed where S_0 globules were composed of spherical sulfur droplets, each covered by a monomolecular layer of an amphiphilic compound [36]. Later [32,37] some other models were considered. S_0 was also found in the phototrophic organisms under aerobic conditions [38].

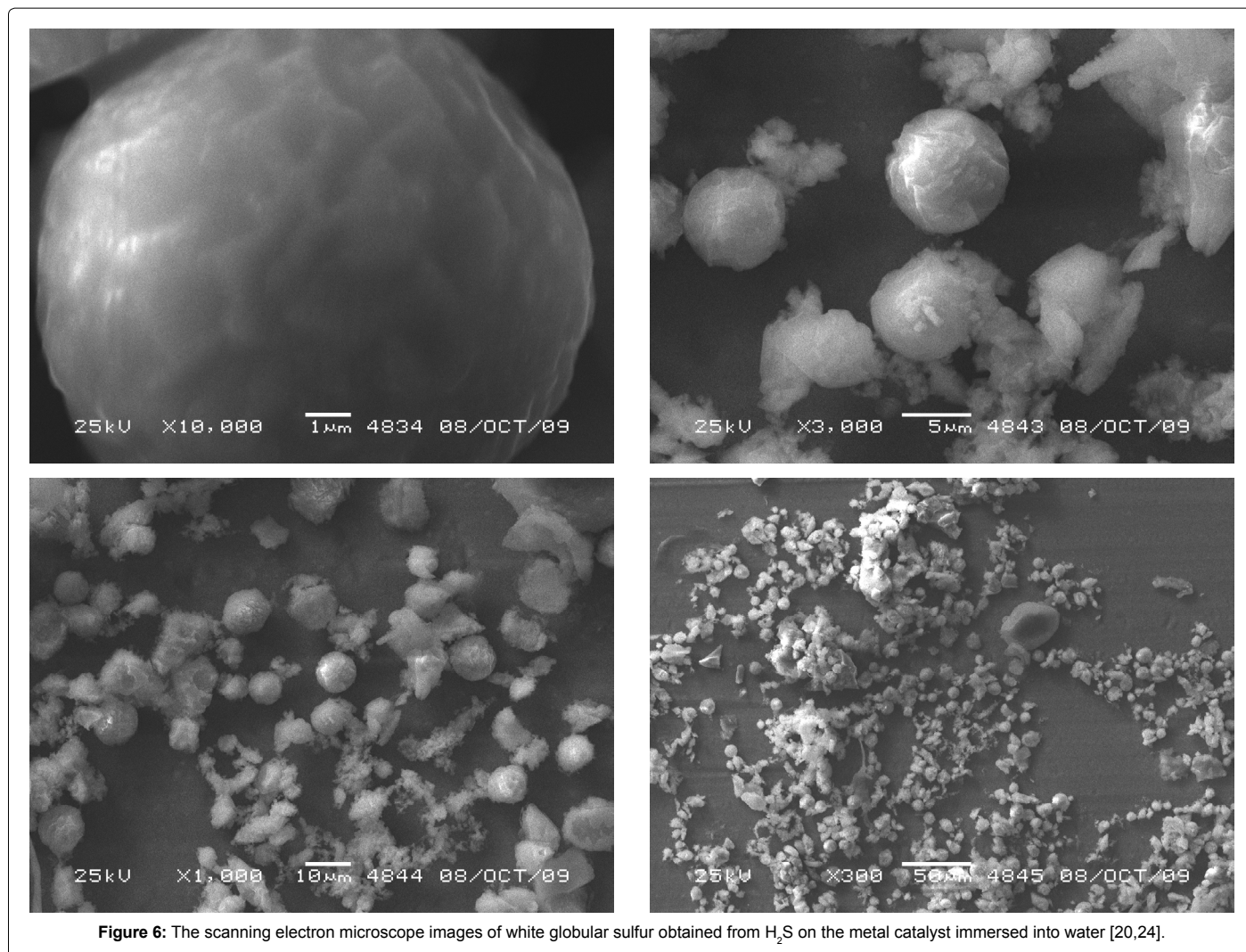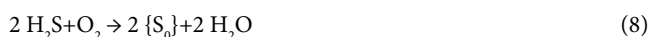It is generally accepted that sulfur bacteria oxidize H_2S along

Figure 6: The scanning electron microscope images of white globular sulfur obtained from H₂S on the metal catalyst immersed into water [20,24].

a pathway that includes the formation of zero-valent sulfur as a characteristic intermediate [32,34]:

$$2\ H_2S + O_2 \rightarrow 2\ \{S_0\} + 2\ H_2O \tag{8}$$

As believed, the energy from this reaction is used to reduce carbon dioxide to create carbohydrates. However, following this reaction (8), hydrogen is irreversibly bound into water and can't participate in the chemosynthesis. At the same time, it is well recognized that hydrogen is the most important inorganic energy carrier in anaerobic pathways in nature. H_2 can be detected in all environments including waters and the atmosphere. Hydrogen does not accumulate but is rapidly recycled where it is produced, and remains at very low concentrations in aquatic environments. H_2 is utilized as an energy source by many anaerobic bacteria including sulfate reducers [39]. Therefore, it is not clear how H_2 is produced in oxidic waters from H₂S if it follows to the reaction (8).

The astonishing resemblance between the hydrophilic globules isolated by us from saturated aqueous solutions upon hydrogen sulfide decomposition (Figure 6) and the globules of biological sulfur produced by colorless sulfur bacteria [27-34,38] suggests that hydrogen sulfide assimilation by these bacteria can be also resulted in the formation of diatomic sulfur in the ground triplet state via the reaction:
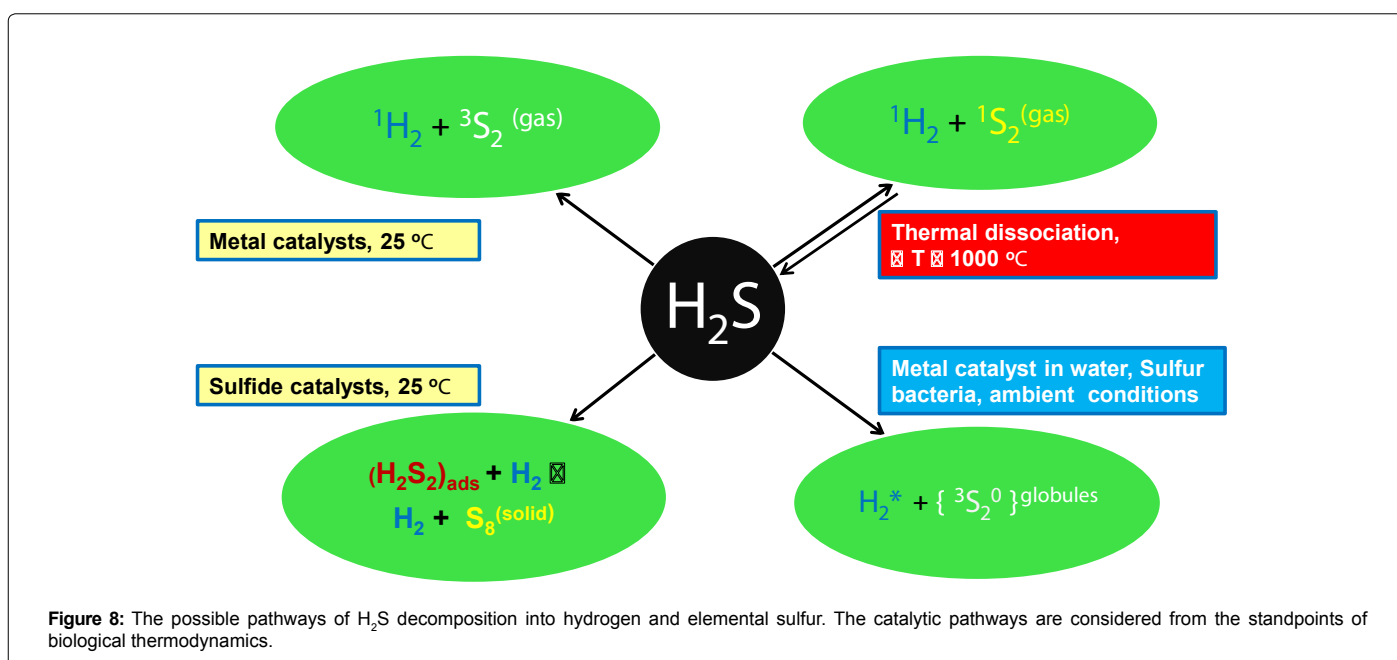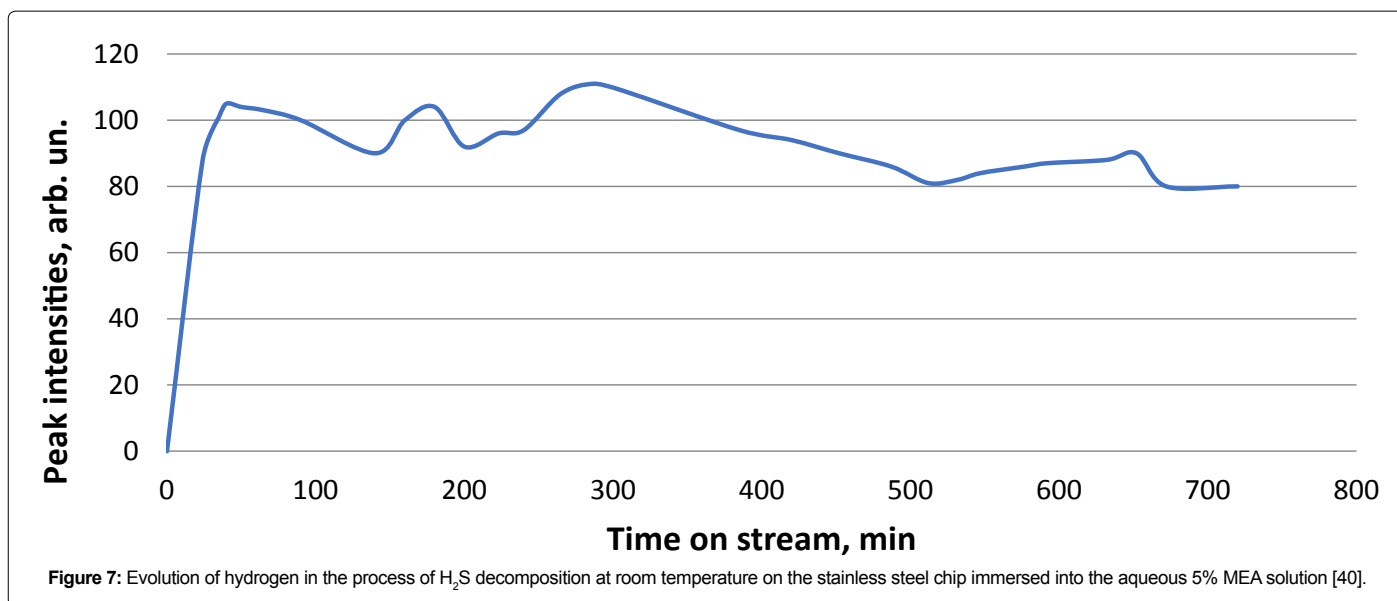
$$2\ H_2S \xrightarrow{\text{sulfur bacteria}} 2\ H_2{}^* + \left\{ {}_3S_2 \right\}_{(globules)} \tag{9}$$
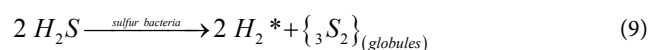
where $H_2{}^*$ is an activated *in situ* hydrogen participating in chemosynthesis:

$$H_2{}^* + CO_2 \xrightarrow{\text{sulfur bacteria}} \left\{ HCOOH \right\} \tag{10}$$

Obviously, the reaction (9) takes place as a result of the nucleation of diatomic sulfur as a condensed hydrophilic S_2 phase. Since the spherical shape and hydrophilic nature of the globules produced by sulfur bacteria is independent of their nature and habitat [27-34,38], reaction (9) seems to occur both under anaerobic conditions and in the presence of oxygen. Doubtless this hypothesis should be comprehensively verified as well.

H₂S Decomposition on Metal Catalysts Under Layer of Solvents

Similar to the biological processes of H₂S assimilation with sulfur bacteria in aqueous medium, the efficiency of H₂S decomposition can be essentially improved (compared to the gas phase process) when solid catalyst is being immersed into a solvent capable of readily dissolving both hydrogen sulfide and the final products of the reaction (5) [20,40].

Figure 7: Evolution of hydrogen in the process of H$_2$S decomposition at room temperature on the stainless steel chip immersed into the aqueous 5% MEA solution [40].

Figure 8: The possible pathways of H$_2$S decomposition into hydrogen and elemental sulfur. The catalytic pathways are considered from the standpoints of biological thermodynamics.

The use of liquids significantly increases the volumetric and surface concentration of hydrogen sulfide compared with the gas phase. This, in turn, leads to a substantial increase in the overall rate of chemical transformation due to the increasing coverage of the catalyst surface by adsorbed molecules of hydrogen sulfide. Moreover, the reaction product -diatomic sulfur, accumulates in the solvent thereby freeing the catalyst surface for adsorption of new molecules of hydrogen sulfide.

As is well known, purification of any wastes from hydrogen sulfide begins with its extraction from gas streams in absorbers with liquid solvent to the required sanitary standards. Concentrated solutions of the absorbers are thereupon directed to the regeneration stage where H$_2$S is recovered by solvent boiling and is utilized mainly with the Claus method or is used to obtain sulfuric acid. Instead of this high temperature procedure of H$_2$S utilization, the concentrated with H$_2$S solutions could be passed through the metal catalyst at ambient conditions to provide the reaction (5) and to get hydrogen as the target product, while sulfur is accumulated in solution.

Indeed, the aqueous monoethanolamine (MEA) solution, a well-known and widespread hydrogen sulfide absorber, is turned out one of the most suitable solvent for the reaction (5) realization. Decomposition of H$_2$S occurs at room temperature with hydrogen evolution to the gas phase (Figure 7) and sulfur accumulation in solution with efficiency towards H$_2$S utilization of 97.9% (Table 2) [40]. Efficiency of H$_2$S decomposition can be improved to 99.6% in the periodical regime (Table 3) [20], when, after solution saturation with H$_2$S, the reaction is allowed to be completed in a closed system. No doubt, the possibilities of this process to achieve close to 100% efficiency of H$_2$S decomposition is practically unlimited taking into account a wide range of choice of catalysts, solvents, regimes, etc.

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 1: Comparison of excitation energy (in cm⁻¹) of the three most reliably studied low-lying molecular orbitals of the S_2 molecule with a molecule of oxygen O_2. T_e - energy of electronic term (in cm⁻¹) [11].

Solution	5 % MEA	Na₂CO₃ [Na] = 0.84 %
Volume, ml	200	100
Fed H₂S , mmol	110.6	53.4
H₂S decomposed, mmol (g)	108.3 (3.69)	42.5 (1.33)
H₂S conversion, %	**97.9**	**79.6**
Sulfur content in solution*, % mass	1.62	1.30
Sulfur content in solution*, g	3.24	1.30

* - X-ray fluorescent analysis data after removal of non reacted H₂S from solution with Ar flow

Table 2: H₂S decomposition over stainless steel chips placed into aqueous solutions. Catalyst mass is 5 g. Reaction temperature is ambient, Ar flow is 10 ml/min, H₂S flow is 3 ml/min.

Adsorption No	Time on stream, min	H₂S, mmol Fed	H₂S, mmol Non-reacted	Conversion, %
1	130	10.45	traces	
2	111	8.91	traces	
3	120	9.64	traces	
4	270	21.7	traces	
Σ	631	50.7	0.2	**99.6**

Table 3: The periodical regime of hydrogen sulfide decomposition at room temperature over stainless steel chips placed in aqueous 5% MEA solution. Argon flow rate, 6 ml/min; H₂S flow rate, 1.8 ml/min; catalyst weight, 2 g; solution volume, 150 ml [20]. After saturation with H₂S, the reactor inlet and outlet were closed and overnight later the H₂S feeding starts again.

Analysis of technologies of H₂S disposal has shown that the method proposed can be adapted to the existing industrial technologies of H₂S utilization. The implementation of this method on an industrial scale actually means the gradual replacement of the metal- and energy-intensive Claus processes for a new mode of operation at ambient conditions to produce hydrogen -a recognized energy resource of the future and a valuable chemical reagent. As liquid absorbers, it is proposed to use the known commercially available solvents of hydrogen sulfide with well proven technology of their operation.

Conclusion

"Useless" and hazardous hydrogen sulfide, which in nature is inexhaustible and renewable, plays a very important role in chemosynthesis as an energy and hydrogen source. Due to the sulfur bacteria, H₂S is easily refined into the vitally important substances under ambient conditions in the natural springs, so it is not accumulated in the atmosphere. However it creates a lot of problems in the refinery of petroleum, natural gas and coal, requiring the energy- and metal-intensive processes of H₂S utilization. Therefore, the catalytic reaction of low-temperature decomposition of H₂S into hydrogen and sulfur seems to offer new opportunity to use the biologically-similar process at the

industrial scale. The stumbling block of our researches was to explain experimental data in the framework of classical thermodynamics, because it is hardly possible to understand formation of hydrogen and gaseous diatomic sulfur in the ground triplet state from H₂S at room temperature. In terms of biological thermodynamics, the role of solid catalysts becomes clear as an energy transducer from the exothermic processes of molecule adsorption to the surface chemical reactions, which are impossible to be done in the gas phase. Therefore, there exist two regions of the reaction of H₂S decomposition (Figure 8). At high temperature this reaction follows to the laws of the classical equilibrium thermodynamics and results in formation of both diatomic reaction products in the singlet state. At the ambient conditions, this reaction occurs either on the surface of solid catalysts or in the bacteria cells. However, the final reaction products are different depending on the catalyst and the reaction conditions. Of the special interest is the diatomic sulfur in the ground triplet state $X \, _3\Sigma_{-g}$, which can be obtained in the gas phase only (?) on the surface of metal catalysts via H₂S decomposition [7-9,20]. The standard thermodynamical reference data [18] are concerned with the metastable single state $a \, _1\Delta_g$ of this molecule (Table 1). Following the analogy with oxygen, the standard enthalpy of the $_3S_2$ molecule formation should be equal to zero as well. However, the generally accepted thermodynamical reference point is the orthorhombic solid sulfur. Therefore, to solve this conflicting problem, it should be necessary to compare the full energy of the S_8 molecule with that of the diatomic triplet sulfur. We made attempts to calculate full energy of cyclooctasulfur by the available computational methods, but unsuccessfully. So, the problem is open for discussion.

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