

Low-Temperature Catalytic Decomposition of Hydrogen Sulfide into Hydrogen and Diatomic Gaseous Sulfur

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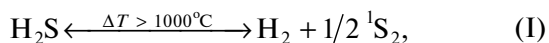
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Abstract—The thermodynamics of three pathways of the hydrogen sulfide decomposition reaction is considered. In the thermal process, the gas-phase dissociation of hydrogen sulfide yields hydrogen and diatomic singlet sulfur. Over sulfide catalysts, the reaction proceeds via the formation of disulfane (H_2S_2) as the key surface intermediate. This intermediate then decomposes to release hydrogen into the gas phase, and adsorbed singlet sulfur recombines into cyclooctasulfur. Over metal catalysts, H_2S decomposes via dissociation into surface atoms followed by the formation of gaseous hydrogen and gaseous triplet disulfur. The last two pathways are thermodynamically forbidden in the gas phase and can take place at room temperature only on the surface of a catalyst. An alternative mechanism is suggested for hydrogen sulfide assimilation in the chemosynthesis process involving sulfur bacteria. To shift the hydrogen sulfide decomposition equilibrium toward the target product (hydrogen), it is suggested that the reaction should be conducted at room temperature as a three-phase process over a solid catalyst under a layer of a solvent that can dissolve hydrogen sulfide and sulfur. In this case, it is possible to attain an H_2S conversion close to 100%. Therefore, hydrogen sulfide can be considered as an inexhaustible source of hydrogen, a valuable chemical and an environmentally friendly energetic product.

Keywords: hydrogen sulfide decomposition, reaction thermodynamics, diatomic sulfur, triplet and singlet sulfur, sulfide and metal catalysts, sulfur bacteria, hydrogen production, hydrogen sulfide utilization, three-phase process

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Hydrogen is among the most demanded chemicals used in multipurpose industrial processes, and demand for hydrogen is growing at an increasing rate because of the predicted prospects of its application as a main energy carrier [1, 2]. There has been a continual search for new hydrogen sources, particularly for renewable ones [3]. One of the practically inexhaustible potential hydrogen sources is hydrogen sulfide [4, 5]. As distinct from hydrogen in the water molecule, hydrogen in the hydrogen sulfide molecule is weakly bonded: $\Delta_f H_{298}^0(\text{H}_2\text{S}) = -4.82$ kcal/mol, while $\Delta_f H_{298}^0(\text{H}_2\text{O}) = -57.80$ kcal/mol. This implies that much less energy will be required to split the hydrogen sulfide molecule. However, the thermal decomposition of hydrogen sulfide into hydrogen and sulfur,



is a very endothermic process and can occur only at a high temperature. Standard methods of separating reaction products are used to increase the conversion in hydrogen sulfide thermolysis, and the reaction temperature is reduced by employing additional energy sources, namely photochemical, plasma chemical, and electrolytic ones [4, 5]. However, none of the

hydrogen sulfide decomposition methods has found wide application because of the high cost of the resulting hydrogen [6].

At the same time, use of sulfide catalysts made it possible to carry out hydrogen sulfide decomposition at room temperature in the batch mode to obtain hydrogen and solid sulfur [7, 8]. Later, it was discovered [9–11] that, over metal catalysts, this reaction can be carried out in the gas phase in a flow reactor with an H_2S conversion of ~15%, and its products are hydrogen and diatomic gaseous sulfur. Since these results are obviously in conflict with the commonly accepted conception that hydrogen sulfide thermally decomposes via reaction (I), we will attempt to elucidate the cause of this inconsistency. Supposedly, this inconsistency is due to the fact that diatomic sulfur obtained in the thermal process and that obtained in the catalytic process have different electronic structures.

THERMODYNAMICS OF THE THERMAL DECOMPOSITION OF HYDROGEN SULFIDE INTO HYDROGEN AND DIATOMIC SULFUR

Diatomic sulfur is known for certain to be an isoelectronic analogue of dioxygen [12]. Its ground

state is the triplet S_2 ($X^3\Sigma_g^-$), and its first excited, singlet state S_2 ($a^1\Delta_g$) is ~ 4700 cm^{-1} (13.4 kcal/mol) higher on the energy scale. Although the electronic spectra of the S_2 molecule have been the object of many studies [13], their interpretation involves numerous contradictions because of experimental difficulties in acquiring these spectra above 650°C , temperatures at which the gas phase is a very complex mixture of various sulfur molecules.

As determined from the energy of dissociation of hydrogen sulfide in the temperature range from 1362 to 1667 K, the enthalpy of formation of diatomic sulfur is 30.8 kcal/mol [14]. A similar value of $\Delta_f H_{298}^0 = 31.2$ kcal/mol was obtained by measuring the partial pressure of diatomic sulfur vapor in the temperature range from 823 to 1273 K [15]. The $\Delta_f H_{298}^0 = 30.7$ kcal/mol value, obtained at high temperatures, was accepted as the standard enthalpy of formation of diatomic sulfur under normal conditions [16]. This approach is often used in thermodynamics when the state of a substance (diatomic gaseous sulfur in this case) at room temperature is unknown. Because experiments in both cases [14, 15] were performed under equilibrium conditions, the following question arises: What is the electronic state of diatomic sulfur in the high-temperature range? Since any system at equilibrium must be in the thermodynamically most stable state, the triplet state of the S_2 molecule was taken to be the ground state by default (see, e.g., [17, 18]), even though there are no direct instructions concerning this issue in the literature [14–16].

Now we will consider the electronic structure of the molecule of diatomic sulfur resulting from thermal processes [10, 11, 19]. In solid sulfur S_8 and in the H_2S molecule, sulfur is in the singlet state. As these compounds are heated to a high temperature, they dissociate to diatomic sulfur (and singlet hydrogen in the case of hydrogen sulfide). Sulfur in the diatomic molecule can, in principle, pass into the ground, triplet state, but, in the absence of a catalyst, this process would violate the spin conservation rule. However, even if this singlet \rightarrow triplet transition took place, then, an abrupt cooling of sulfur vapor to low temperatures would yield triplet sulfur in a condensed state, because the reverse, triplet \rightarrow singlet transition needs energy to be inputted from outside and is forbidden by selection rules. Therefore, there is good reason to believe that the metastable singlet sulfur state 1S_2 (which results from reaction (I)) persists at high temperatures [10, 11, 19]. Accordingly, the experimentally determined thermodynamic parameters of the diatomic gaseous sulfur molecule [16] refer to its excited, metastable, singlet state. This behavior seems to be a unique feature of sulfur—we do not know other diatomic molecules capable of being in a metastable excited state.

CASSCF and Hartree–Fock calculations of the enthalpy of the reaction



give $\Delta_r H_{298}^0 = +46.9$ kcal/mol for the triplet state of S_2 and $\Delta_r H_{298}^0 = -10.4$ kcal/mol for the singlet state of the molecule [10, 11, 19]. This result confirms the possibility of singlet sulfur existing at high temperatures, since it is energetically more favorable for singlet sulfur to aggregate from the gas phase into the S_8 structure. At the same time, it follows from the calculations that the triplet state of the diatomic sulfur molecule is thermodynamically the most favorable and stable one and, therefore, the triplet molecule 3S_2 ($X^3\Sigma_g^-$) cannot turn into solid singlet sulfur 1S_8 ($a^1\Delta_g$).

Thus according to the spin conservation rule, the thermal dissociation of hydrogen sulfide (reaction (I)) yields, along with singlet hydrogen, singlet diatomic sulfur [10, 11, 19], whose standard enthalpy of formation can be found in thermodynamic handbooks [16]. However, a triplet ground state is ascribed to this diatomic molecule [17, 18]. This is, obviously, inconsistent with the value of the standard enthalpy of formation of solid sulfur that is accepted as zero in the same thermodynamic handbooks, since the energy of the triplet state of diatomic sulfur must be lower than the energy of the singlet state, according to molecular orbital theory.

LOW-TEMPERATURE DECOMPOSITION OF HYDROGEN SULFIDE OVER SULFIDE CATALYSTS

The possibility of sulfide-catalyzed hydrogen sulfide decomposition yielding hydrogen at room temperature was discovered in a study of the oxidative addition of hydrogen to an active metal atom (Ni, Co) as part of the active component of a sulfide catalyst involved in hydrodesulfurization and in a study of hydrogen occlusion into an active-component matrix [20, 21]. In these processes, the active ions of the metal are oxidized by hydrogen to Co(III) and Ni(IV) and acquire a d^6 electron configuration (Fig. 1b). It was demonstrated in an earlier study [22] that it is the two unoccupied orbitals of the active metal atom— $3d_{z^2}$ and $3d_{xz}$ —that interact effectively with the n_σ and n_π orbitals of the hydrogen sulfide molecule. In the absence of occluded hydrogen, the hydrogen sulfide molecule is not adsorbed by a Co(II) or Ni(III) atom with a d^7 electron configuration, because the $3d_{z^2}$ orbital is filled. DFT calculations [7, 8] demonstrated that the heat of adsorption of hydrogen sulfide on the Co(III) ion (d^6) is $\Delta H_{298} = -12.7$ kcal/mol, which is well above the enthalpy of adsorption calculated for Co(II) (d^7), $\Delta H_{298} = -2.2$ kcal/mol [20, 21]. It is significant that, in the adsorbed state, two hydrogen sul-

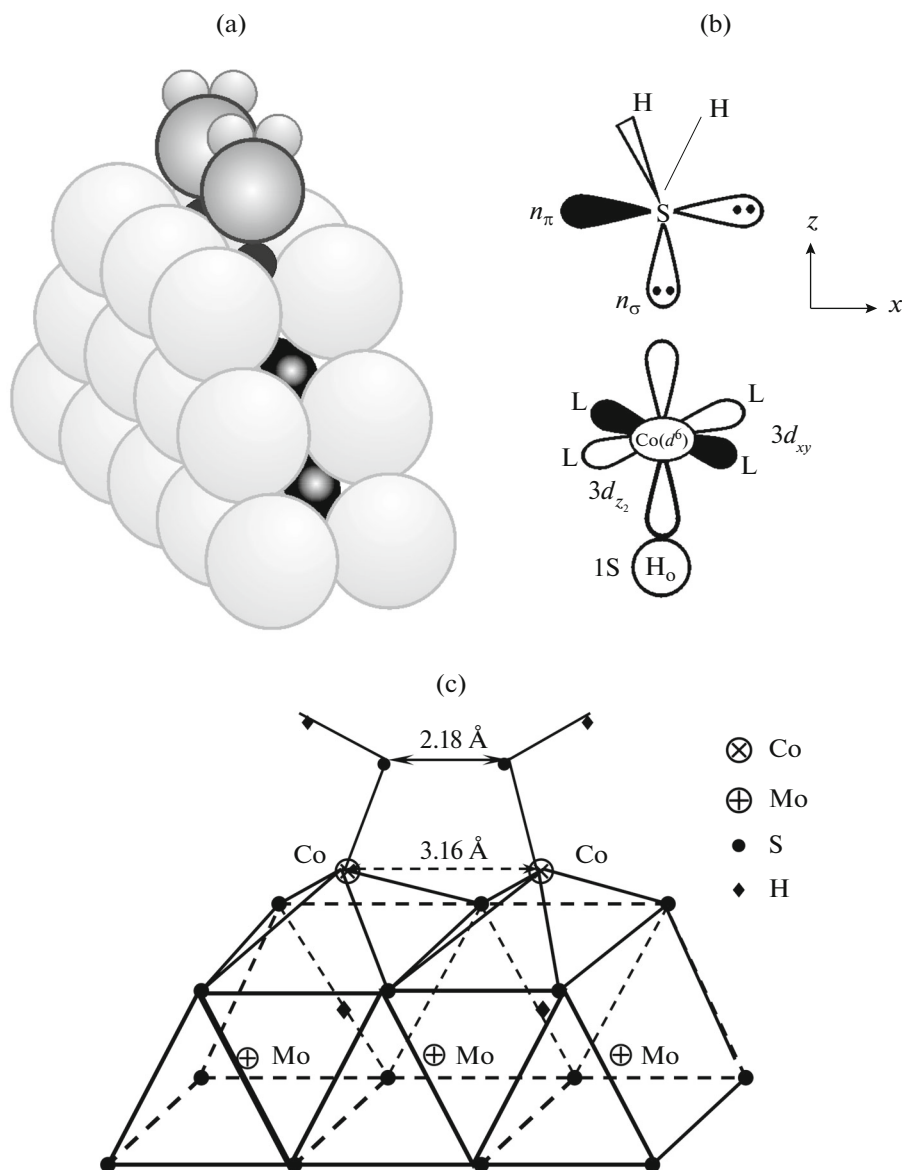
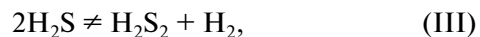


Fig. 1. (a) Fragment of the structure of the electroneutral macromolecule of the active component of sulfide hydrotreating catalysts with two hydrogen sulfide molecules adsorbed on two adjacent Co(III) or Ni(IV) atoms. (b) The latter have a d^6 electron configuration owing to their chemical interaction with an occluded ("hidden") hydrogen atom H_0 (L = electron orbital). (c) Mutual approach of two adsorbed hydrogen sulfide molecules accompanied by the formation of a new sulfur-sulfur chemical bond (adsorbed disulfane molecule) and by the release of a hydrogen molecule into the gas phase.

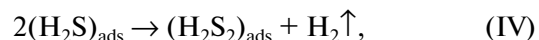
fide molecules interact (Fig. 1a), as is indicated by their coming within a short distance of 2.18 Å of each other (Fig. 1c). As a result, a new sulfur-sulfur chemical bond forms in the surface intermediate, and this process is accompanied by the release of a hydrogen molecule into the gas phase and by the formation of adsorbed disulfane H_2S_2 .

The detailed study of hydrogen sulfide chemisorption on sulfide catalysts was stimulated by the detection of disulfane among the desorption products in a temperature-programmed heating of sulfide catalysts containing adsorbed hydrogen [23, 24]. The point is

that direct disulfane formation from hydrogen sulfide in the gas phase,



is thermodynamically forbidden ($\Delta_r H_{298}^0 = 13.6$ kcal/mol, $\Delta_r S_{298}^0 = -3.9$ cal mol⁻¹ K⁻¹, $\Delta_r G_{298}^0 = 14.1$ kcal/mol [16]). At the same time, it was discovered [7, 8, 23, 24] that the following reaction takes place on the sulfide catalyst surface:



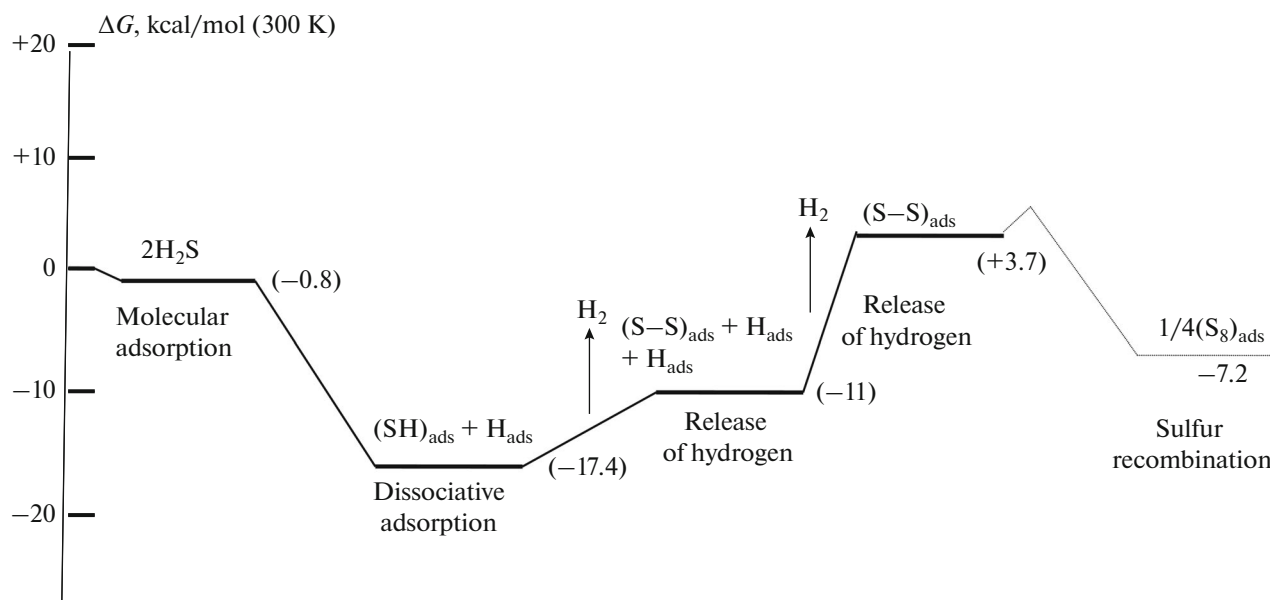


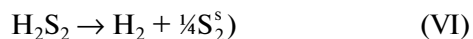
Fig. 2. Energy profile for the hydrogen sulfide decomposition reaction occurring at room temperature over a sulfide catalyst.

which yields disulfane and releases hydrogen into the gas phase. The driving force of this process is the stoichiometric surface reaction between two adsorbed hydrogen sulfide molecules resulting in the formation of a sulfur–sulfur bond in the surface intermediate $(\text{H}_2\text{S}_2)_{\text{ads}}$ (Fig. 1c). This reaction is essentially exothermic ($\Delta H_{298}^0 = -28.9$ kcal/mol) and is characterized by a considerable decrease in Gibbs energy ($\Delta G_{298}^0 = -11.0$ kcal/mol) (Fig. 2). Thus, favorable conditions are established on the catalyst surface for the chemical reaction that is thermodynamically forbidden in the gas phase. This makes the process irreversible, because the products of the surface reaction are separated, the hydrogen molecule leaving the catalyst surface.

Gas-phase disulfane decomposition can proceed via the following two routes:

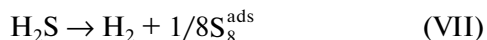


($\Delta_r H_{298}^0 = 27.1$ kcal/mol, $\Delta_r S_{298}^0 = 23.4$ cal mol⁻¹ K⁻¹, $\Delta_r G_{298}^0 = 20.1$ kcal/mol) and

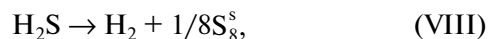


($\Delta_r H_{298}^0 = -3.8$ kcal/mol, $\Delta_r S_{298}^0 = -29.2$ cal mol⁻¹ K⁻¹, $\Delta_r G_{298}^0 = 4.9$ kcal/mol). The initial data for these calculations were taken from Ref. [16].

Reaction (V) is endothermic and needs energy supply from outside, while reaction (VI) can take place even at a low temperature. It is most likely the latter reaction route that is realized with sulfide catalysts. As judged from the energy profile presented in Fig. 2, at room temperature the overall reaction



is accompanied by a decrease in Gibbs energy ($\Delta_r H_{298}^0 = -23.8$ kcal/mol, $\Delta_r S_{298}^0 = -53.2$ cal mol⁻¹ K⁻¹, $\Delta_r G_{298}^0 = -7.2$ kcal/mol); that is, it is a thermodynamically allowable process when it proceeds via the formation of adsorbed disulfane as the key surface intermediate. However, the initiation of this process can be carried out in the gas phase, without involving the catalyst surface,



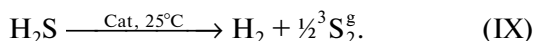
because it is thermodynamically forbidden ($\Delta_r H_{298}^0 = 4.9$ kcal/mol, $\Delta_r S_{298}^0 = -17.0$ cal mol⁻¹ K⁻¹, $\Delta_r G_{298}^0 = 10.0$ kcal/mol).

Thus, hydrogen sulfide decomposition on the surface of sulfide catalysts is an exothermic process and is accompanied by a decrease in Gibbs energy, yielding hydrogen and adsorbed solid singlet sulfur. In other words, favorable conditions for this reaction, which is thermodynamically unfavorable in the gas phase, occur on the catalyst surface. The surface process is irreversible because its products are separated and the hydrogen molecule leaves the catalyst surface.

LOW-TEMPERATURE DECOMPOSITION OF HYDROGEN SULFIDE ON METAL CATALYSTS

An unexpected, unpredictable result was obtained when hydrogen sulfide was decomposed over metal catalysts: the reaction yields, along with hydrogen, diatomic gaseous sulfur (Fig. 3) [9–11, 19]. As hydrogen sulfide was passed through a catalyst, unreacted H_2S was absorbed in absorbers filled with an aqueous

solution of zinc acetate to perform a quantitative analysis. The gaseous products that had passed through the absorbers were chromatographed. Two gaseous products were distinguished after the separation of the gas phase in the chromatographic column (Fig. 3). One of them was hydrogen, and the other was identified as gaseous sulfur by the methods developed by us for this purpose [9–11, 19]:



The reaction was carried out at room temperature in a flow reactor in the gas phase over a platinum catalyst with a hydrogen sulfide conversion of ~15% (Table 1). Without the dispersion of platinum taken into account, the turnover number of the reaction in 1 h was 20–30 (mol H₂S)/(mol Pt), which clearly indicated that the process is a catalytic one (Table 1). The main regularities of the reaction conducted in a flow reactor and in an autoclave were studied, and “fingerprints” of diatomic gaseous sulfur, both adsorbed on a support, and dissolved, were obtained. Gaseous diatomic sulfur S₂ is stable, has a nauseating odor at liquid-nitrogen temperature, crystallizes as white openwork “snowflakes,” and sublimates on being warmed to room temperature [9–11, 19].

Hydrogen sulfide dissociation on the surface of single crystals has been the subject of numerous experimental studies using surface science methods and theoretical calculations mainly based on DFT (see, e.g., [25, 26]). The dissociation of adsorbed hydrogen sulfide on the Pt(111) face takes place even at low temperatures (110 K), and, at low surface coverages ($\theta_{\text{S}} < 0.3 \text{ ML}$), the most stable adsorbed species are atomic sulfur and hydrogen. As the surface is progressively occupied by adsorbed atoms, a tendency to H–H and S–S bond formation in surface intermediates is observed, which markedly reduces the energy of the interaction of the adsorbed diatomic molecules with the single crystal surface [27, 28]. This makes molecular hydrogen desorb from the surface at a low temperature of 230 K, while sulfur remains in the adsorbed state up to 500 K [25]. Here, the determining factor is the weakening of the metal–sulfur bond due to the

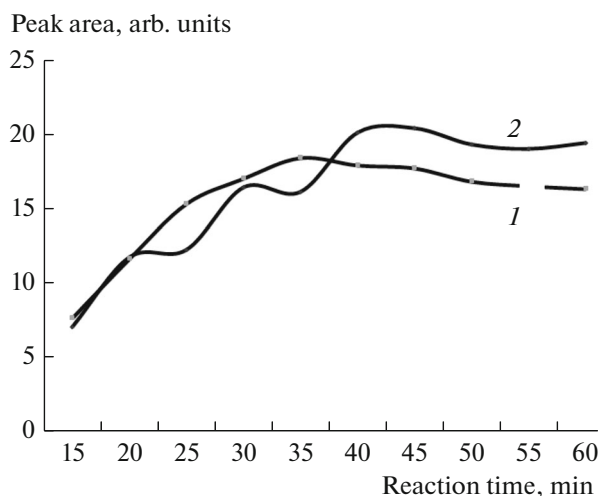
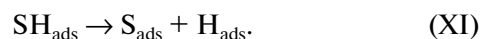


Fig. 3. Typical gaseous product evolution curves for hydrogen sulfide decomposition at room temperature over stainless steel chips: (1) hydrogen and (2) sulfur. The catalyst weight was 2 g. The total hydrogen sulfide conversion throughout the reaction time (60 min) was 4.5%. The reaction products were analyzed by gas chromatography at room temperature using a 5 m × 3 mm column packed with a microporous carbon adsorbent (AG-3 brand). The ordinate axis represents the integral intensity of chromatographic peaks in arbitrary units [9–11].

formation of an S–S bond in the surface intermediate, which leads to the desorption of an S₂ molecule upon heating [28].

As was demonstrated by DFT calculations [26], hydrogen sulfide adsorption on almost all transition metals is an exothermic process: the activation energy of adsorption, E_{a} , is –12 to –20 kcal/mol. The dissociation of adsorbed hydrogen sulfide on the (111) face of metal single crystals occurs in two steps:



Reaction (X) is also exothermic ($\Delta_r E = -3.5$ to -30 kcal/mol) and is opposed by an energy barrier of

Table 1. Hydrogen sulfide decomposition at room temperature over the 0.5%Pt/SiO₂ catalyst [9, 11]

Entry	Amount of H ₂ S introduced into the reaction, mmol	Amount of H ₂ S trapped in the absorber, mmol	H ₂ S conversion, %	Turnover number *, (mol H ₂ S)/(mol Pt)
1	9.8	8.5	13.3	22
2	9.4	8.0	15.0	23
3	10	7.9	21.0	35
4	9.4	8.4	10.6	17

The weight of the catalyst (which was reduced with hydrogen at 400°C) is 2 g; hydrogen sulfide flow rate, 2.5–3.0 mL/min; argon flow rate, 20 mL/min; reaction time, 60 min. The catalyst was not regenerated before the next run.

* The turnover number was calculated without the dispersion of platinum taken into account. In case the dispersion of platinum is 10 to 30% (which is typical of catalysts prepared by impregnation), the actual turnover number associated with surface platinum can be obtained by multiplying the given value by a factor of 3–10.

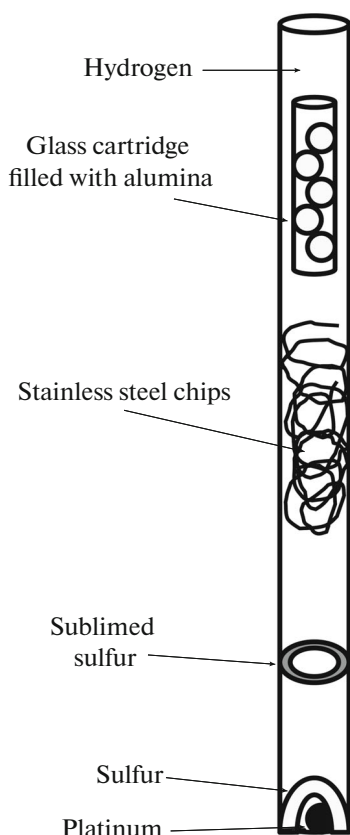


Fig. 4. Simplest setup for obtaining diatomic gaseous sulfur from solid sulfur [11, 19].

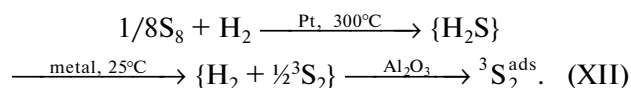
$E_a = 1.5\text{--}5$ kcal/mol. The second step of the dissociation of adsorbed hydrogen sulfide (reaction (XI)) on transition metals takes place almost spontaneously, characterized by an activation energy of $E_a \ll 1$ kcal/mol, and the total energy change in this reaction, $\Delta_r E$, is between -18 and -25 kcal/mol. The energy profile for reactions (X) and (XI) indicates that hydrogen sulfide dissociates readily on metals to yield adsorbed hydrogen and sulfur atoms and this process experiences no thermodynamic or kinetic limitations [26].

Thus, experimental and theoretical studies of hydrogen sulfide dissociation on single crystals demonstrated that H_2S can dissociate into atoms even at low temperatures. The easy elimination of molecular hydrogen from the surface after hydrogen atom recombination and the separation of the H_2S dissociation products suggest that the process is irreversible. It is, therefore, possible to carry out a catalytic cycle provided that adsorbed sulfur is removed from the surface, since the sulfur–surface interaction energy can decrease significantly owing to the formation of S_2 dimers on the surface.

As was noted above, diatomic sulfur is an isoelectronic analogue of dioxygen, in which the ground state of the molecule is a triplet. However, as distinct from

singlet dioxygen, the metastable singlet state of diatomic sulfur, which results from the high-temperature dissociation of elemental sulfur or hydrogen sulfide (see above), is fairly stable, and, as sulfur is cooled to room temperature, it does not pass into the ground, triplet state but turns into solid singlet sulfur. This led us to conclude that reaction (IX) yields singlet hydrogen and diatomic hydrogen in the ground, triplet state [10, 11, 19].

In the isolated disulfur molecule, the direct singlet \rightarrow triplet transition is forbidden by selection rules, but this process was effected in a closed space via the hydrogenation of molten sulfur into hydrogen sulfide followed by H_2S decomposition yielding diatomic gaseous sulfur [11, 19]:



These experiments were performed in the following way (Fig. 4). Solid sulfur samples, each ~ 0.4 g, were placed in three test-tubes ~ 30 cm in length, and pieces of platinum were placed in two of them. Stainless steel chips were mounted at the center of the test-tubes, and a glass cartridge filled with calcined alumina was placed over the chips. All test-tubes were pumped to a residual pressure of 10^{-2} Torr, and hydrogen was then admitted into two of them up to a pressure of about 100 Torr. In the third test-tube, there was no hydrogen and the reaction was conducted in a vacuum. Next, the bottom parts of all test-tubes were simultaneously heated to $\sim 300^\circ\text{C}$ in ~ 2 h. Most of the sulfur sublimed and condensed as a ring of orange-yellow drops. Alumina in the cartridges, which were mounted well above the sulfur condensation zone, did not change its color in the two blank experiments in which either platinum or hydrogen was not involved. In the test-tube containing both platinum and hydrogen, alumina turned yellow and its weight increased by 14.35 mg, or $\sim 1\%$. The color of the granules was uniform both throughout the cartridge height and along the granule radius. The diffuse reflectance IR spectra of these granules showed a single band at ~ 810 cm^{-1} , which was assigned to stretching vibrations of the sulfur–sulfur bond. We did not observe any other bands, e.g., bands assignable to S–H, S–O, or S–S bonds in multiatomic molecules. Therefore, it is diatomic sulfur that was adsorbed on alumina.

According to chemical equation (XII), molten sulfur in the presence of platinum reacts with hydrogen to yield hydrogen sulfide, which, in turn, decomposes at room temperature over stainless steel chips to produce gaseous diatomic sulfur adsorbed on alumina. Therefore, this experiment demonstrates that, in principle, singlet sulfur can be converted into hypothetical triplet form via its intermediate hydrogenation into hydrogen sulfide. Obviously, a necessary condition for this conversion to take place is the formation of adsorbed

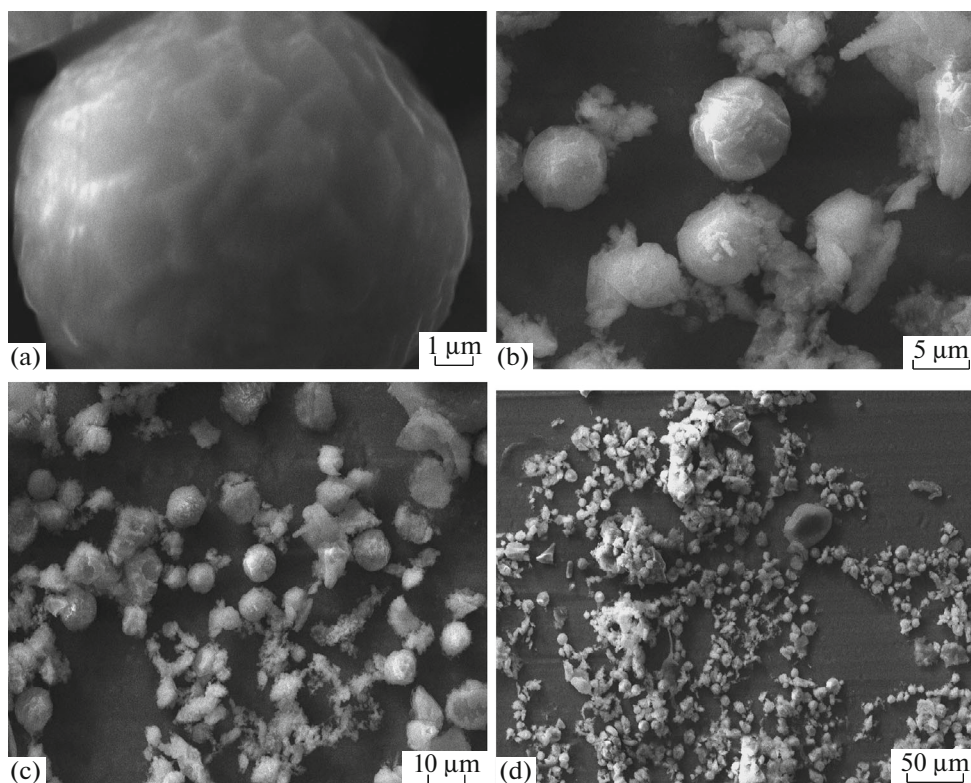


Fig. 5. SEM images of white sulfur [29].

atomic sulfur upon the dissociation of hydrogen sulfide on the metal catalyst.

Thus, the thermodynamic driving force of low-temperature hydrogen sulfide decomposition over metals is the dissociative chemisorption of H_2S on the catalyst surface with the formation of hydrogen and sulfur as adsorbed atoms. The dissociation process occurs spontaneously even at low temperatures and experiences neither thermodynamic nor kinetic limitations. The presence of free electrons in the conduction band of the metal is favorable for the elimination of spin forbiddings and for singlet sulfur passing into the triplet, thermodynamically most stable state, and, after dimerization on the catalyst surface, triplet sulfur desorbs as a diatomic gaseous molecule. In non-catalytic thermal processes, the direct singlet \rightarrow triplet transition in the isolated S_2 molecule is forbidden by selection rules.

HYDROGEN SULFIDE ASSIMILATION IN BIOLOGICAL SYSTEMS INVOLVING COLORLESS SULFUR BACTERIA

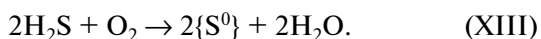
Diatomic gaseous sulfur obtained via reaction (IX) is readily soluble in water, its solubility exceeding 0.5 wt %. The pH value and refractive index of the colorless sulfur solution are the same as those of the initial water, and the Raman spectrum of the solution shows only bands characteristic of water. This situation is

typical of solutions of diatomic gases that do not interact with water (N_2 , O_2 , H_2 , etc.). A white modification of solid sulfur was isolated from saturated sulfur solutions [29]. The morphology of the white sulfur particles is shown in Fig. 5. The size of the parties, which were near-spherical globules, was up to 10 μm . Electron diffraction on a separate white sulfur globule indicated that the globule had a hexagonal structure with interplanar distances of 0.45, 0.29, and 0.15 nm. Among the known allotropes of solid sulfur [30], the white hexagonal modification was not found. It turned out that an electron beam can cause structural changes in the sulfur globules and their evaporation. For this reason, the electron micrographs were obtained using minimum possible radiation intensities ruling out the effect of radiation on the specimen. For the same reason, we failed to obtain a Raman spectrum of hexagonal white sulfur. However, the Raman spectrum of the saturated aqueous solution of sulfur showed a single band at 880 cm^{-1} , which was assigned to stretching vibrations of the sulfur–sulfur bond ($\nu_{\text{S-S}}$) in the colloidal particles—nuclei of the white precipitate [29]. The absence of other absorption band unambiguously indicated that there were no colloidal S_8 particles or other fragments of multiatomic sulfur particles and no S–O or S–H bon vibrations. For this reason, it was hypothesized that globular white hexagonal sulfur is a condensed phase of S_2 .

In 1887, S.N. Vinogradsky demonstrated for the first time that it is possible to generate energy by oxidizing hydrogen sulfide and to use this energy in carbon dioxide assimilation and thus discovered chemosynthesis [31]. He introduced the term *sulfur bacteria* to refer to microorganisms that accumulate elemental sulfur in their cells when they live under suitable conditions in water containing hydrogen sulfide. Chemosynthesis is the kind of autotrophic nutrition in which the source of energy for the synthesis of organic compounds from CO₂ is oxidation reactions of inorganic compounds. This way of generating energy is unique to bacteria.

It is well known [32] that, in H₂S-containing springs and basins, there are plenty of microorganisms whose cells contain sulfur drops. These microorganisms, which are referred to as colorless sulfur bacteria, often form large aggregates appearing as films, white incrustations, or other kinds of coatings. The colorless sulfur bacteria function at temperatures of 4 to 95°C, pH 1.0–10.5, and oxygen concentrations ranging between the level corresponding to saturation and absolutely anaerobic conditions [33, 34]. The existence of a particular microorganism in a given climatic zone is governed by a combination of physical, chemical, and ecophysiological factors. Representatives of colorless sulfur bacteria are widespread in fresh water and seawater bodies, in ocean hydrothermal vent regions, and in anthropogenic ecosystems.

The commonly accepted mechanism of hydrogen sulfide assimilation by sulfur bacteria includes the following reaction [32]:



No experimental evidence of this reaction taking place has been reported; furthermore, as was mentioned above, sulfur bacteria can function under anaerobic conditions as well.

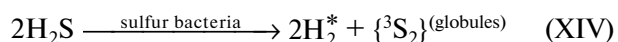
There is controversy about the nature of elemental sulfur produced by sulfur bacteria. Various microorganisms producing transparent intracellular and extracellular drops (globules) have been discovered to date. The drops are up to 1 μm in diameter, have a spherical or ellipsoidal shape, and are hydrophilic. This elemental sulfur (which is commonly called bacterial sulfur S⁰) differs radically in properties from “normal” inorganic sulfur. In particular, the density of the sulfur globules formed by *Chromatium* bacteria is 1.22 g/cm³, lower than the density of orthorhombic sulfur (2.07 g/cm³) [35]. Bacterial sulfur shows hydrophilic properties, as distinct from common, inorganic, hydrophobic, solid sulfur. As globules of bacterial sulfur are dried, they turn into common crystalline sulfur S₈.

Various models of bacterial sulfur S⁰ are considered in the literature [31, p. 289]. The liquid-crystal model was discarded because of the high density of liquid sulfur (1.80 g/cm³ at the triple point, 115°C) and because of its hydrophobicity. The ionic polysulfide and inor-

ganic and organic polysulfane models were also abandoned for some reasons. The polythionate (S_n(SO₃)₂²⁻) model involving up to 140 sulfur atoms was recognized to be most adequate. However, a special-purpose study of the bacterial medium by ion chromatography [36] did not detect polythionates, polysulfides, or any other polysulfur compounds. For this reason, it was hypothesized that the S⁰ globule consists of drops of “normal” sulfur (1/3 of its volume) and water (2/3 of its volume) and each drop is covered with a monolayer of some amphiphile (e.g., polysulfide or polythionate) that cannot be isolated because of its low concentration but imparts hydrophilic properties to the globule. In another model, it is supposed that solid sulfur particles are covered with a monolayer of an organic polymeric surfactant, most likely a protein [32].

Thus, the main distinctive feature of the sulfur globules resulting from hydrogen sulfide assimilation by sulfur bacteria, irrespective of the nature and habitat of the latter, is their spherical shape and the hydrophilicity of their colloidal particles [32–38]. It was also proved that sulfur in these globules is in a zero-valence state, not in oxidized or reduced form [39, 40].

The striking morphological similarity between the hydrophilic globules isolated by us from saturated aqueous solutions upon hydrogen sulfide decomposition (Fig. 5) and the globules of biological sulfur produced by colorless sulfur bacteria suggests that hydrogen sulfide assimilation by these bacteria also results in the formation of diatomic sulfur in the ground, triplet state. This takes place via the reaction



as a result of the nucleation of diatomic sulfur as a condensed hydrophilic S₂ phase. The resulting activated hydrogen participates in chemosynthesis, and diatomic sulfur is in the ground, triplet state, as would be expected for all biological processes occurring at ambient temperature. Since the spherical shape and hydrophilicity of the sulfur globules produced by sulfur bacteria is independent of their nature and habitat, reaction (XIV) can take place both under anaerobic conditions and in the presence of oxygen. Now the role of hydrogen becomes clear. It is commonly believed that the source of hydrogen in lithotrophic sulfur bacteria is hydrogen sulfide; however, sulfur formation via reaction (XIII) is in conflict with this opinion, since hydrogen in this reaction is spent on water formation. In our case, hydrogen resulting from reaction (XIV), activated at the instant it forms, participates in chemosynthesis reactions. Obviously, this hypothesis needs to be thoroughly and comprehensively investigated.

HYDROGEN SULFIDE DECOMPOSITION OVER SOLID CATALYSTS UNDER A SOLVENT LAYER

The above data suggest that, in principle, it is possible to obtain hydrogen by low-temperature hydrogen sulfide decomposition over a heterogeneous catalyst or in a biological system. However, since the initial substance is toxic hydrogen sulfide, it is of primary importance to utilize this substance completely. In other words, the challenging problem of deriving hydrogen from renewable raw materials should be solved in combination with the problem of attaining 100% hydrogen sulfide conversion. One possible way of solving these problems is by carrying out a three-phase hydrogen sulfide decomposition process in which the solid catalyst is placed under a layer of a solvent capable of readily dissolving both hydrogen sulfide and the final and/or intermediate products of the reaction [41–44].

The initial step of hydrogen sulfur removal from exhaust gas is the absorption of the toxicant in a solvent for meeting the existing sanitary regulations. Next, the concentrated absorbent solution is subjected to regeneration, in which hydrogen sulfide is separated out of the solution and is utilized either by using mainly the Claus process or by converting H_2S into sulfuric acid. There are many solvents that are industrially employed in hydrogen sulfide removal from gas streams of various origins. The choice of solvent depends on many parameters, primarily on the chemical composition of the exhaust gas and on the technological problems faced by the given processing enterprise [45].

The basic idea of our study is to carry out hydrogen sulfide decomposition simultaneously with the removal of hydrogen sulfide from the “tail” gas and to obtain the target product, hydrogen, thereby obviating the need for subsequent high-temperature H_2S processing stages.

The experiments were performed at room temperature using a glass absorber fitted with a magnetic stirrer. The solid catalyst was placed in a solvent layer. The

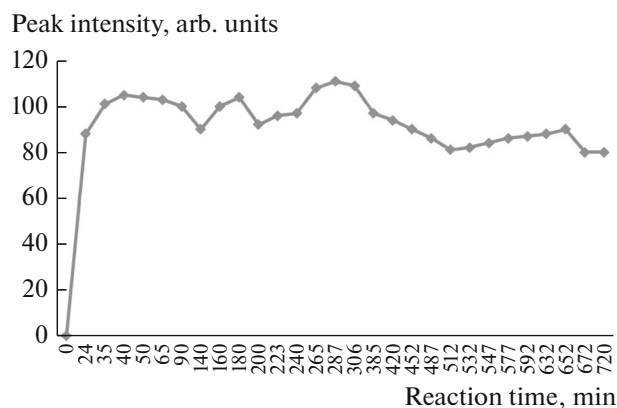


Fig. 6. Release of hydrogen from hydrogen sulfide being passed through stainless steel chips placed in 5% aqueous solution of monoethanolamine.

solvent was purged with argon to remove dissolved air, and an argon–hydrogen sulfide mixture was passed through the absorber under stirring. The unreacted hydrogen sulfide leaving the absorber was extracted from the argon stream with an aqueous solution of zinc acetate to carry out a quantitative analysis. The resulting gaseous products—hydrogen and diatomic sulfur—were quantified at intervals on a gas chromatograph [46].

An aqueous solution of monoethanolamine (MEA), a well-known and widespread hydrogen sulfide adsorbent, turned out to be one of the most appropriate solvents for carrying out reaction (IX) [46]. Hydrogen sulfide decomposition over stainless steel chips, a very simple and readily available catalyst, occurred at room temperature and released hydrogen into the gas phase (Fig. 6), and the resulting sulfur accumulated in the solution (Table 2). In 12 h at a hydrogen sulfide conversion of ~98%, more than 3 g of sulfur accumulated in the solution. This weight of sulfur corresponded to an S : MEA molar ratio of 1.7 and a sulfur concentration of 16 g per liter of solution (Table 2) and was comparable with the weight of the catalyst (5 g), whose specific surface area was very

Table 2. Hydrogen sulfide decomposition over stainless steel chips placed in aqueous solutions

Aqueous solution	Solution volume, mL	Amount of H_2S			Sulfur found in solution*		S : MEA(Na)
		introduced into the reaction, mmol	decomposed, mmol (g)	conversion, %	wt %	g	
5% MEA	200	110.6	108.3 (3.69)	97.9	1.62	3.24	1.7
Na_2CO_3 ([Na] = 0.84%)	100	53.4	42.5 (1.33)	79.6	1.30	1.30	1.17
5% hydrazine	77	19.5	19.2 (0.65)	98.5	0.60**	0.20**	—

Catalyst weight, 5 g; reaction conducted at room temperature; argon flow rate, 10 mL/min; hydrogen sulfide flow rate, 3 mL/min.

* X-ray fluorescence analysis data obtained after removing unreacted H_2S from the solution with bubbling argon.

** Part of the sulfur volatilizes out of the solution as the latter is purged with argon to remove unreacted H_2S .

Table 3. Hydrogen sulfide decomposition at room temperature over stainless steel chips placed in 5% monoethanolamine solution in water

Adsorption run number	Reaction time, min	Amount of H ₂ S, mmol		Conversion, %
		introduced into the reaction	trapped in the absorber	
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

Argon flow rate, 6 mL/min; H₂S flow rate, 1.8 mL/min; catalyst weight, 2 g; solution volume, 150 mL [11].

* Conversion was measured only after the completion of the entire experiment.

small. In a similar experiment, the hydrogen sulfide conversion was 99.6% (Table 3) [11]. Sulfur in the solution was in the form of a diatomic molecule coordinated to an MEA molecule [46]. Accordingly, because of the induced dipole moment, the IR spectrum showed weak bands at 672 cm⁻¹, which were due to vibrations of the sulfur–sulfur valence bond. The spectrum did not indicate S–O or S–H vibrations or S–S stretching or bending vibrations characteristic of dissolved commercial sulfur. The same situation was observed for sulfur in aqueous solutions of hydrazine and sodium carbonate (Table 2) [46].

In order to precipitate sulfur, the aqueous solutions of MEA and hydrazine were neutralized with a 2% hydrochloric acid solution to pH 2. The resulting yellow precipitate was collected on filter paper, washed with water, and dried in air under an IR lamp. X-ray diffraction data demonstrated that the precipitate was orthorhombic α-sulfur with unit cell parameters of $a = 10.45 \text{ \AA}$, $b = 12.84 \text{ \AA}$, and $c = 24.46 \text{ \AA}$ [46]. Hydrazine and MEA are known to be strong bases; accordingly, as their solutions are titrated with hydrochloric acid, large amounts of heat are released as a result of neutralization. This energy is sufficient to bring the diatomic sulfur resulting from reaction (IX), which is in the ground, triplet state, into the excited, singlet state, which then turns spontaneously into common solid sulfur. As the sodium carbonate solution was acidified, no sulfur precipitation took place and sulfur remained in the solution as diatomic molecules even at low pH.

Nevertheless, instead of precipitating the sulfur forming via reaction (IX) from the solution, it is possible to involve this sulfur in the synthesis of organosulfur compounds for various purposes [17, 18, 47, 48]. Various solvents, both aqueous and nonaqueous, can be used in this process. No less attractive is prospective use of diatomic sulfur solutions in making up sulfur deficiency in soils and in the synthesis of new composites [49]. Solid sulfur to be used for these purposes must be preactivated with expensive and toxic reagents [49], while diatomic sulfur that results from reaction (IX) is a fairly reactive substance.

CONCLUSIONS

Hydrogen sulfide is among the few chemicals that, due to their toxicological properties, attract rapt attention from numerous researchers. From the environmental standpoint, hydrogen sulfide needs to be completely utilized, because continually increasing amounts of this gas as a by-product are emitted by mining and processing industries. The results of this study inspire a certain optimism in those who are interested in carrying out low-temperature hydrogen sulfide decomposition for obtaining hydrogen as the target product. Hydrogen sulfide decomposition can proceed via the following four pathways to yield molecular sulfur in different states.

(1) The thermal dissociation of hydrogen sulfide yields diatomic sulfur in the metastable singlet state. It is to this state that the standard enthalpy of formation of sulfur presented in thermodynamic handbooks refers.

(2) Hydrogen sulfide dissociation over sulfide catalysts yields disulfane as the key surface intermediate, whose subsequent decomposition results in the formation of adsorbed solid sulfur. The reaction is accompanied by a decrease in free energy only on the catalyst surface at room temperature and is thermodynamically forbidden in the gas phase.

(3) The decomposition of hydrogen sulfide over sulfide catalysts includes its dissociation yielding adsorbed atomic sulfur, the subsequent passage of the latter into the ground, triplet state with the participation of free electrons from the conduction band of the metal, and the desorption of sulfur as gaseous triplet diatomic molecules. In the isolated disulfur molecule, the singlet → triplet transition is forbidden by selection rules.

(4) It is believed that, in biological systems, hydrogen sulfide dissociates via a similar mechanism in which active hydrogen participates in organic matter chemosynthesis involving carbon dioxide and the resulting sulfur, which is in the ground, triplet state, accumulates in sulfur bacteria as colorless hydrophilic intracellular or extracellular globules.

The thermodynamic inconsistency between the thermal and catalytic methods of hydrogen sulfide decomposition was eliminated by thoroughly analyzing the properties of diatomic sulfur resulting from these processes. This inconsistency turned out to be due to the fact that the standard enthalpy of formation of diatomic sulfur at high temperatures refers to the unexpected, metastable, singlet state of the S₂ molecule, while in the literature the same enthalpy is assigned by default to the ground, triplet state of the molecule. At the same time, it was demonstrated that diatomic gaseous sulfur forming via the catalytic reaction is a new, hitherto unknown, triplet ground state of sulfur that can appear only on the catalyst surface through the dissociation of a hydrogen sulfide molecule into atoms.

The chemical conception of the essence of catalytic action, developed by G.K. Boreskov in the mid-1950s, defines catalysis as “initiation of chemical reactions or changes in their rate under the action of catalytic substances that multiply enter into an intermediate chemical interaction with reaction participants...” [50]. In the case considered here, the catalyst does not shift the chemical equilibrium but initiates hydrogen sulfide decomposition via two new pathways yielding products whose formation in the gas without the participation of the catalyst surface is impossible. We mean the formation of triplet diatomic sulfur as the final product on metal catalysts and the formation of disulfane H₂S₂ as the key surface intermediate in hydrogen sulfide decomposition over sulfide catalysts. In the absence of a catalyst, the thermal decomposition of hydrogen sulfide yields singlet sulfur and hydrogen. Apparently, hydrogen sulfide assimilation by colorless sulfur bacteria proceeds via the same low-temperature hydrogen sulfide decomposition mechanism and the resulting hydrogen is involved in chemosynthesis, while the resulting diatomic sulfur is in the ground, triplet state, in which it must be in all biological processes occurring at ambient temperature.

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