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Diatomic sulfur: a mysterious molecule

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ABSTRACT

Diatomic gaseous sulfur obtained in thermal processes of elemental sulfur dissociation and hydrogen sulfide decomposition is considered. It is shown that the thermodynamic parameters of this substance formation accepted in literature refer to its metastable singlet state $\{S_2 a^1 \Delta_g\}$. Since diatomic sulfur is an isoelectronic analog of oxygen, its ground state must be a triplet $\{S_2 X^3 \Sigma_g^-\}$. As it turned out, this ground triplet state of S_2 molecule can be obtained at low temperature catalytic decomposition of H_2S . The reaction mechanism is considered in terms of non-equilibrium thermodynamics for open systems. The process occurs at room temperature due to internal energy of H_2S molecules without using external energy sources. As shown, metal catalyst provides the capture and inter-conversion of energy from exothermic processes of adsorption and dissociation of H_2S molecules resulted in their chemical transformation on the catalyst surface into the final reaction products - molecular hydrogen and diatomic triplet sulfur. Some properties of gaseous triplet sulfur and white solid globular sulfur obtained from its saturated aqueous solutions are considered. A hypothesis about the nature of bacterial sulfur S^0 and possible mechanism of chemosynthesis of carbohydrates from H_2S and CO_2 is proposed.

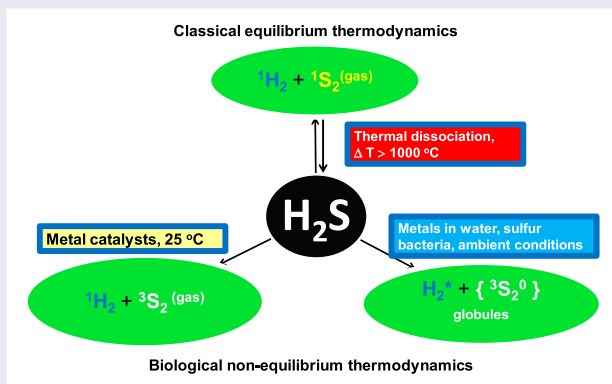
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1. Introduction

Solid Sulfur is the first chemical element known to mankind in its native status for several millennia. In nature, sulfur is in a free state and in the form of various inorganic and organic compounds. The most comprehensive bibliography of scientific reviews and monographs for the period 1938–2015 in the chemistry of sulfur and its compounds is collected in [1]. There are more than 30 solid allotropes of solid sulfur, which are various molecular forms of sulfur in the form of linear, branched or cyclic structures with a molecular weight of up to 10^6 atoms. The thermodynamically most stable modification – orthorhombic $S\alpha$ – sulfur, is crystallized in the form of a crown cyclooctasulfur [2,3].

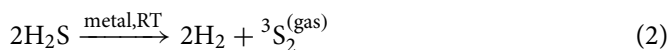
When heating solid sulfur to high temperature, the composition of the liquid and gas phase is extremely diverse and contains, depending on the temperature, from two to more than 30 atoms in the molecule. Above the boiling point, concentration of low-chain molecules in the gas phase increases sharply, and at a temperature above 1000 °C, S_2 molecules prevail [4]. On cooling to ambient temperature, the reversible condensation of sulfur vapor into solid state is observed [2].

Diatomic sulfur can be also obtained by thermal decomposition of hydrogen sulfide at temperature as high as $\Delta T > 1000^\circ\text{C}$:



This endothermic process (1) begins to occur already at a temperature of 500°C, and at 1000°C the equilibrium H_2S conversion does not exceed 15% [5]. To increase conversion, temperature should be raised. Reaction reversibility means that the process proceeds in both directions always near the equilibrium. The catalyst does not shift the reaction equilibrium, but it reduces the energy barrier and increases the reaction rate in both directions. To shift the equilibrium to the right in order to increase the yield of hydrogen, various methods of separating reaction products are well researched, and alternative energy sources (solar energy, electrochemical, photochemical and plasma methods, etc.) are used to reduce the temperature [6,7].

Meanwhile, a very unexpected and unpredictable result was obtained by passing hydrogen sulfide through a platinum catalyst at room temperature (RT, 25°C), because, along with hydrogen, the reaction product appeared to be diatomic gaseous sulfur [8–14]:



This irreversible reaction proceeds at room temperature on metal catalysts in the gas-phase steady-state regime with the conversion of hydrogen sulfide $\sim 15\%$, however, the H_2S conversion reaches 100% when placing the catalyst in a layer of liquid capable of well-dissolving hydrogen sulfide and products of reaction (2) [15]. In our studies, we used a chip of stainless steel as a simplest, stable and active catalyst.

The purpose of this review is to analyze the electronic state and some properties of diatomic sulfur obtained in the thermal and catalytic processes of elemental sulfur dissociation and hydrogen sulfide decomposition as the simplest chemical compound of sulfur.

2. Classical thermodynamics of sulfur dissociation and H₂S decomposition

According to molecular orbital theory, it is well known that diatomic sulfur is an iso-electronic analog of oxygen, which, like molecular oxygen, differs from most diatomic molecules by the presence of the triplet ground state (S₂) ($X^3\Sigma_g^-$), and the first excited singlet state S₂ ($a^1\Delta_g$) is higher in energy by 12.6 kcal/mol (Table 1) [16]. The theory predicts two low-lying excited singlet states, which differ only in spin and population density of the degenerated antibonding π_g – orbitals. Despite the fact that the S₂ electron spectra have been studied many times, there are many contradictions in the interpretation of the electronic state of the molecule, due to the experimental difficulties in studying the electronic spectra of sulfur at temperatures above 700 °C, when the gas phase is a very complex mixture of various sulfur molecules and, possibly, radicals.

Thermodynamic properties of elemental sulfur vapor are considered in [4]. The enthalpy of S₂ molecule formation ($\Delta_f H^\circ_{298} = 30.7$ kcal/mol) was determined at the high temperature of sulfur vapor dissociation [17] and H₂S decomposition [18] and was accepted as the standard enthalpy of the formation of the S₂ molecule [19]. Such approach is often used in thermodynamics, if the state of the substance (in this case, diatomic sulfur gas) is not known at room temperature. Moreover, since experimental measurements of the enthalpy of formation of diatomic sulfur were carried out under equilibrium conditions [17,18], which means the thermodynamically most stable state of the system, it becomes clear why the literature is dominated by the view that at high temperature the molecule S₂ is in the ground triplet state (See *e.g.* [20,21]), although neither in the original works nor in the reference literature the electronic state of this molecule is indicated.

This conclusion was based, obviously, on the analogy with singlet oxygen [22,23]. The difference between the energy of O₂ in the singlet and triplet state is ($T_e(a^1\Delta_g \leftarrow X^3\Sigma_g^-) = 22.5$ kcal/mol) (Table 1) and the transition singlet \rightarrow triplet, occurs spontaneously in the gas phase at room temperature as a result of a bimolecular reaction with the release of an energy quantum [22,23]. Therefore singlet oxygen in the gas phase is extremely long-lived – the half-life of the singlet state in the ground triplet state under normal conditions is 72 min. Interaction with solvents, however, reduces the lifetime of singlet oxygen to microseconds.

However, unlike oxygen, diatomic sulfur obtained at high temperature as a result of dissociation of elemental sulfur vapor or decomposition of hydrogen sulfide, after quenching to room temperature, prefers to agglomerate (concatenate) into solid sulfur S₈ instead of conversion to the ground triplet state. This unusual feature of singlet sulfur was experimentally verified and confirmed by calculations by the methods of CASSCF and Hartree–Fock.

Table 1. Comparison of excitation energy (in cm⁻¹) of the three most reliably studied low-lying molecular orbitals of the S₂ molecule with a molecule of oxygen O₂.

| State | $T_e^* O_2$ | $T_e^* S_2$ |
|-----------------|-------------|-------------|
| $c^1\Sigma_u^-$ | 33,057 | 20,203 |
| $b^1\Sigma_g^+$ | 13,195 | 7981 |
| $a^1\Delta_g$ | 7923 | 4395 |
| $X^3\Sigma_g^-$ | 0 | 0 |

Note: T_e^* – energy of electronic term (cm⁻¹) [16].

It turned out that enthalpy of the reaction



is $\Delta_r H_{298}^\circ = +46.9$ kcal/mol for the triplet state S_2 and $\Delta_r H_{298}^\circ = -10.4$ kcal/mol for the singlet state of the initial diatomic sulfur [10–13].

The first strongly endothermic process is characterized by a negative change in entropy ($\Delta S < 0$, the number of gaseous molecules decreases), so this process cannot occur under any conditions, since the change in the Gibbs free energy is always positive $\Delta G > 0$. In the case of the second exothermic process ($\Delta H < 0$), the direct reaction can occur spontaneously at low temperature, since $\Delta H > T\Delta S$ and $\Delta G < 0$. At high temperature $\Delta H < T\Delta S$, thus the direct reaction cannot proceed ($\Delta G > 0$), while the reverse reaction is thermodynamically favorable. This confirms once again the possibility of the existence of singlet sulfur at high temperatures, since it is more profitable to agglomerate the singlet sulfur into the S_8 structure from the gas phase. At the same time, it follows from the calculations that the triplet molecular state of diatomic sulfur is the most thermodynamically advantageous and stable, therefore the triplet 3S_2 ($X^3\Sigma^-_g$) molecule cannot be transformed into solid singlet sulfur S_8 .

One of the possible reasons for the existence of a high-temperature metastable state of singlet sulfur may be the kinetic problems of its transition to the ground triplet state, when even at high temperature this process can be very slow and under experimental conditions of studying the properties of gaseous sulfur equilibrium is not achieved. Formally, this means prohibition on the spin of this transition, which could be enabling by metal catalysts.



However, experimental verification of this assumption showed [10–12] that even the presence of platinum catalysts does not reduce the energy barrier and does not accelerate the reaction (4) at a temperature of 1000 K.

As a consequence, in accordance with the rule of spin conservation, in the thermal processes of elemental sulfur dissociation and hydrogen sulfide decomposition, diatomic sulfur is formed in the metastable singlet state, the thermodynamic parameters of which are given in the handbooks [19]. Its reference to the ground triplet state [20,21] should be recognized as *erroneous*. Direct experimental evidence of the existence of diatomic sulfur in the ground triplet state in the form of an isolated chemical substance has not been found in the literature.

3. Low-temperature catalytic decomposition of hydrogen sulfide

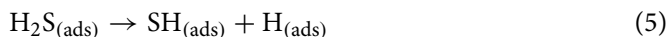
At ambient temperature and pressure, the H_2S molecule is stable indefinitely in the absence of external influences. However, if H_2S is passed through a metal catalyst at room temperature, the output is hydrogen and diatomic gaseous sulfur in accordance with the reaction (2) [8–15]. Since in this case, there is no energy supply from the outside, but this system can be exchanged both with substance and energy with the environment, therefore, the reaction can occur due to the free and chemical energy of hydrogen sulfide. Let's try to justify this thesis.

Experimental investigation of the interaction of H₂S with the surface of single crystals of metals testifies to the easy dissociation of H₂S at the majority of metals at temperatures usually below 185 K. In particular, the adsorption of H₂S on the surface of Pt(111) at 110 K leads to the complete dissociation of H₂S into the surface atomic S and H species [24]. At low coverage with adsorbed H₂S ($\theta_{\text{H}_2\text{S}} = \sim 0.5$ arbitrary units, a.u.), molecular hydrogen appears in the gas phase after heating to 230 K, while a new peak of hydrogen desorption appears already at 185 K with an increase in H₂S coverage to 1.0 a.u.

At low coverage of a single crystal surface with H₂S ($\theta_{\text{H}_2\text{S}} = 0.2$ a.u.) in HREELS¹ spectra a band at 375 cm⁻¹ appears corresponding to oscillations of the Pt–S bond. By increasing coverage with H₂S to 0.5 a.u. and above, two additional bands appear in the spectra at 585 and 685 cm⁻¹, which are attributed to two forms of vibrations of S–H bonds in surface species. Both of these bands disappear after heating the surface to 185 K, while molecular hydrogen H₂ is desorbed and a single band appears, attributed to Pt–S stretching as a result of the growth of sulfur islands [24]. It is very important that water does not dissociate into atoms on metals.

Similar studies on model surfaces show that H₂S dissociates, for example, on single crystals of Pd(111) [25], Ru(110) [26] and InP(100) [27] resulting in the formation of surface atomic H and S species. In other words, S–H bonds in the H₂S molecule are easily broken below 200 K as a result of dissociation on metal atoms, sulfur atoms remain on the surface, and hydrogen H₂ is desorbed into the gas phase.

As follows from the DFT studies [28], adsorption of H₂S on transition metals is an exothermic process, and for Pt(111) it is $E_{\text{ads}} = -21$ kcal/mol. The dissociation of adsorbed H₂S on the Pt (111) surface proceeds in two stages:



The reaction (5) is also an exothermic process $\Delta E_{\text{rxn}(5)} = -19.6$ kcal/mol and proceeds with an energy barrier $E_a = 1.6$ kcal/mol. The second dissociation step of adsorbed H₂S (6) proceeds almost spontaneously with the activation energy of $E_a \leq 1$ kcal/mol and the change in the total energy $\Delta E_{\text{rxn}(6)} = -18.2$ kcal/mol for Pt (111). The energy profile of the reactions (5) and (6) indicates that H₂S easily dissociates with the formation of atomic hydrogen and sulfur species in the adsorbed state and this process has neither thermodynamic nor kinetic restrictions [28].

Thus, the total energy of dissociative adsorption of hydrogen sulfide on the surface of Pt (111) is $\Delta E_{\text{diss-total}} = (E_{\text{axc}} + \Delta E_{\text{rxn}(5)} + \Delta E_{\text{rxn}(6)}) = -58.8$ kcal/mol or for two H₂S molecules in the reaction (2) $\Delta E_{\text{diss-total}} = -117.6$ kcal/mol.

On the other hand, from the point of view of thermochemistry, the energy of chemical bonds is one of the main molecular constants characterizing the structural features of chemical compounds [19,29,30]. The dissociation energy of the chemical bond D_0 is defined as the change in the standard enthalpy of formation of the reaction products and the initial chemical compound. In reaction (1), the dissociation energy D_{298} of the HS–H bond in the H₂S molecule under normal conditions is 92 kcal/mol (Table 2) [19,29,30], whereas the dissociation of the second S–H bond requires only 82.3 kcal/mol. In the reaction (1) of two H₂S molecules, four HS–H bonds must be broken, which gives the total dissociation energy of two molecules $\Sigma D_{298} = (92.0 + 82.3) \times 2 = 348.6$ kcal/mol. At the

Table 2. Bond dissociation energy (BDE), kcal/mol at 0 and 298 K [19,29,30].

| Reaction of bond dissociation | D_0 | D_{298} |
|-------------------------------|-------|-----------|
| $S_2 \rightarrow S + S$ | 98.5 | 99.8 |
| $H_2 \rightarrow H + H$ | 103.3 | 104.2 |
| $H_2S \rightarrow HS + H$ | 90.7 | 92.0 |
| $SH \rightarrow S + H$ | 81.4 | 82.3 |

same time, two bonds H–H ($\sum D_{298} = 2 \times 104.2 = 208.4$ kcal/mol) and one bond S–S $D_{298} = 99.8$ kcal/mol are formed (Table 2) [19,29]. This gives the enthalpy of reaction (1) as shown in Equation (7).

$$\Delta H_{\text{rxn}(1)} = \sum D_{298}(\text{H}_2\text{S}) - \sum D_{298}(\text{products}) = 40.4 \text{ kcal/mol} \quad (7)$$

In other words, the total energy of dissociation of bonds in the initial H_2S molecule exceeds this value for the reaction products by $\Delta H_{\text{rxn}(1)} = 40.4$ kcal/mol. This means that the original H_2S molecule is stable and does not transform into H_2 and S_2 reaction products at room temperature, therefore the reaction (1) needs to be provided with thermal energy.

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

$$\Delta E_{\text{surplus}} = \Delta E_{\text{diss} - \text{total}} + \Delta H_{\text{rxn}(1)} = -117.6 + 40.4 = -77.2 \text{ kcal/mol} \quad (8)$$

which can be spent for desorption of the reaction (2) products into the gas phase.

Actually, adsorption energy of S_2 molecule on Pt (111) is -45 kcal/mol [31]. The heat of dissociative adsorption of H_2 on Pt (111) varies within $-(9.5/12)$ kcal/mol [32], while molecular hydrogen is desorbed from the surface already at 260 K [33]. Therefore, after removal of diatomic sulfur and two hydrogen molecules from the surface of Pt (111), we obtain a minimum excess in energy $\Delta E_{\text{total.min}} = -(8.2/13.2)$ kcal/mol, which means exothermism of the process as a whole. Moreover, an additional gain in the energy of 12.6 kcal/mol should appear as a result of the transition of diatomic sulfur from the excited singlet state to its ground triplet state in the reaction (2) (Table 1). Therefore, the resulted gain in energy can be estimated as $\Delta E_{\text{total.max}} = -(20.8/25.8)$ kcal/mol.

Thus, the simplest consideration of the capture of free and internal energy of H_2S molecules by the catalyst surface resulting in subsequent transformation and redistribution of the stored energy in the surface chemical reaction (2) gives raise a positive response to the thermodynamic possibility of this catalytic reaction at room temperature on metal catalysts. In other words, the catalyst surface provides the transformation of energy from the exothermic steps of adsorption and dissociation of the original H_2S molecules into chemical conversion to final products of the reaction – hydrogen and diatomic sulfur, and their desorption to the gas phase. As a result of the closure of the catalytic cycle after desorption of products into the gas phase, an exothermic effect is obtained. Such mechanisms of initiation of the process of chemosynthesis and energy conversion are carried out in biological objects (see below). In gas phase this process is impossible.

Without any doubt, this conclusion requires a comprehensive study by theoretical and experimental methods, taking into account the entropy factor and determining the free

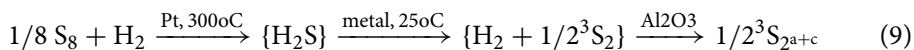
Gibbs energy at all steps of the catalytic cycle. If we take into account that the entropy of the reaction (2) increases (the number of molecules in the gas phase increases), then with the exothermic nature of this reaction $\Delta H < 0$, the change in the free Gibbs energy will be always negative $\Delta G < 0$, which means the *spontaneous* character of the process. Previously, such a study was performed by us on sulfide catalysts of low-temperature decomposition of hydrogen sulfide [34,35].

4. Some properties of diatomic triplet sulfur

The diatomic sulfur obtained in the catalytic reaction (2) is most likely in the ground triplet state. This conclusion was made on the basis of the exclusion from consideration of diatomic singlet sulfur obtained in the thermal processes of elemental sulfur dissociation and hydrogen sulfide decomposition. To the extent of our experimental and financial capabilities, we tried to study the properties of this unique chemical substance where we hypothesized it was in the triplet state.

The gaseous state of diatomic sulfur under normal conditions was discovered by us for the first time more than 10 years ago and is now beyond doubt [8–15]. Gaseous diatomic sulfur S_2 is stable at temperatures up to 200°C and above, it has a sharp nauseating smell, at a temperature of liquid nitrogen crystallizes in the form of openwork white snowflakes, and after heating to room temperature sublimates. An additional argument can serve as a gas-chromatographic-mass spectrometric (GC-MS) analysis of the gaseous substance, where it was proved that the molecule is diatomic with a mass $m/e = 64$ amu., which in the decay gives two identical particles with a mass of 32 amu. This completely excludes its assignment to the SO_2 molecule.

A very simple and illustrative experiment, which can be performed in any laboratory, demonstrates the possibility of obtaining diatomic gaseous sulfur from solid sulfur in a closed glass tube without the use of special equipment [11,12]. As noted above, the direct transition of diatomic singlet sulfur into the expected triplet sulfur is impossible. However, this process of singlet \rightarrow triplet conversion is made possible through the intermediate stage of hydrogenation of molten sulfur to hydrogen sulfide, followed by its decomposition on metal catalysts at room temperature:



The gaseous sulfur obtained in this experiment is adsorbed on the alumina surface. In the IR spectra of diffuse reflection of yellow Al_2O_3 granules, a single band at 810 cm^{-1} was found which was attributed to the stretching mode of S–S bond vibrations in accordance with the previously made assignments [10,11]. Other bands, such as vibrations of S–H and S–O bonds, as well as vibrations of S–S bonds in polyatomic sulfur molecules [36], were not found. Consequently, it was concluded that the diatomic sulfur was adsorbed on aluminum oxide. This singlet \rightarrow triplet conversion became possible due to the decomposition of H_2S on chip stainless steel at room temperature resulted from H_2S dissociative adsorption to the sulfur atomic species according to reactions (2), (5) and (6). Under other conditions, discussed above, the dissociation of sulfur or hydrogen sulfide into adsorbed atomic species does not occur.

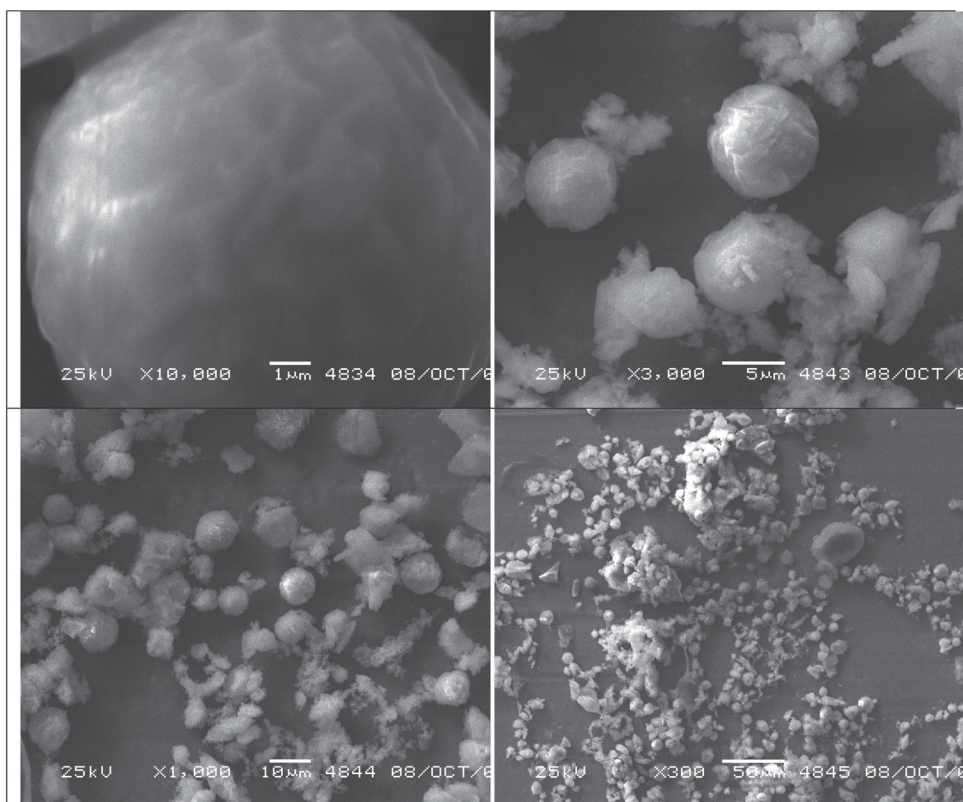


Figure 1. Scanning electron microscope images of white hexagonal sulfur obtained from saturated aqueous solutions of diatomic sulfur [39].

It is well known that solid sulfur is insoluble in water under normal conditions; there are only some data of its interaction with boiling water [37]. However, there are colloidal hydrophobic sulfur sols S_8 of size 0.1–1.0 microns, which are thermodynamically unstable with respect to their transformation into orthorhombic sulfur S_8 [38].

One of the most important characteristic features of the diatomic sulfur obtained in the reaction (2) is its good solubility in water above 5 g of sulfur per liter [39]. The aqueous solution of sulfur (5.1 g of S per liter of H_2O , X-Ray fluorescent analysis data) is colorless, has a neutral pH as in the source water, has no absorption bands in the IR and Raman spectra, the refractive index corresponds to that of water. Therefore we conclude that in aqua solution sulfur is a diatomic molecule. This is typical for many dissolved diatomic gases that do not interact with water.

From saturated aqueous solutions of diatomic sulfur, white globular modification of solid sulfur was obtained, electron microscopic images of which are shown in Figure 1 [39]. The size of white spherical globules is up to 5–10 microns, whereas smaller particles are transparent and colorless. In the energy dispersion spectrum obtained from the 10-micron globule, only intense peaks from sulfur and weak signals from the substrate material were found. No other elements from F to U, including metals of catalyst, were found in the electron micrographs.

Images of transmission electron microscopy and electron diffraction were obtained on a device JEM 2010 (JEOL, Japan) with a lattice resolution of 0.14 nm [39]. It has been observed that the electron beam can cause structural changes and evaporation of the sulfur sample. Therefore, the extremely low radiation intensities excluding the impact on the sample were used to obtain the images. The diffraction of electrons on a separate sulfur globule indicates its hexagonal structure with interplanar distances of 0.45, 0.29 and 0.15 nm. Currently, there is known more than 30 allotropic modifications of solid sulfur [2,3] with color change from red to black, but white hexagonal sulfur is not found in this list.

When recording Raman spectra of white sulfur, it was observed that the laser beam causes irreversible changes of samples, resulting in 'normal' solid yellow sulfur. However, in the Raman spectrum of aqueous sulfur saturated solution, the only band at 880 cm^{-1} is presented which attributed to the stretching mode of sulfur-sulfur bond vibrations (ν_{s-s}) in colloidal particles – the precursors of a white precipitate [39]. The absence of other absorption bands clearly indicates the absence of colloidal S_8 particles [38] or other fragments of multi atomic sulfur species [36], as well as the S–O and S–H bond vibrations. Therefore, it was suggested that white hexagonal globular sulfur is the condensed phase S_2 .

It is well known that the diatomic sulfur molecule is not active in the IR spectra due to the lack of dipole moment. In the Raman spectra of its aqueous solution, no new bands were found in comparison with the initial water. The absence of S–H and S–S vibrations clearly indicates that in the solution there is no hydrogen sulfide and polyatomic sulfur fragments, and in the solution there is a diatomic molecule that does not chemically interact with water. Vibrations of diatomic gases are active in Raman spectra, but in some cases, they have a rather small Raman cross-section, so the sensitivity of the standard Raman spectrometer is often not enough to measure the lines related to such vibrations. In the case of S_2 the Raman spectrum can be measured, apparently, only when the spectrum is excited by certain lines of some lasers [36].

However, by dissolving diatomic sulfur in aqueous solutions of some substances it is possible to register both Raman and IR spectra. In particular, in an aqueous 5% solution of hydrazine containing 0.6% by weight of sulfur, single absorption bands were found at 679 cm^{-1} in Raman spectra and at 662 cm^{-1} in IR spectra [15]. The absence of other absorption bands clearly proves the diatomic nature of the solute. The DFT calculation of the valence vibration frequency of the S_2 molecule gives a value of 682 cm^{-1} in the gas phase, which shifts to 669 cm^{-1} when dissolved in aqueous hydrazine [15]. Note that in Raman spectra of diatomic gaseous sulfur this band is at 716 cm^{-1} [36].

It is well known that monoethanolamine (MEA) is widely used in industrial processes for the extraction of H_2S from gas streams, so we used aqueous solutions of MEA as solvents for H_2S decomposition in the three-phase mode. In this case, it was possible to achieve the H_2S conversion 99.6%, the hydrogen formed was released into the gas phase, and diatomic sulfur was accumulated in the solution [15]. In the IR spectra of the solution containing 1.62% sulfur and 5% MEA, a weak band was found at 660 cm^{-1} , which is attributed to the valence vibrations of the S–S bond. It is obvious that, as in the case of aqueous hydrazine, the appearance of this band is due to the induced dipole moment of diatomic sulfur, which appeared due to formation of a coordination complex of a sulfur molecule with a solvent molecule as a result of partial transfer of electron density from a nitrogen atom of hydrazine or MEA to sulfur atoms [15].

To precipitate sulfur from aqueous solutions of MEA and hydrazine, the solution was neutralized with hydrochloric acid to $\text{pH} = 2$, the resulting yellow precipitate was filtered out on a paper filter, washed with water and dried in air under an IR lamp. X-ray phase analysis showed that the precipitate is an orthorhombic modification of α – sulfur with cell parameters $a = 10.45 \text{ \AA}$, $b = 12.84 \text{ \AA}$, $c = 24.46 \text{ \AA}$ [15]. Apparently, the energy released during the neutralization of the solutions is sufficient to transfer the diatomic sulfur formed in the reaction (2) in the ground triplet state to the excited singlet state, which lies above the ground state by 12.6 kcal/mol (Table 1), and which, in turn, spontaneously agglomerates into ‘normal’ solid sulfur in reaction (3).

Thus, diatomic gaseous sulfur, first obtained by us at the low-temperature catalytic decomposition of hydrogen sulfide by reaction (2), is a stable chemical substance, highly soluble in water and forming a new unknown modification of white hexagonal sulfur from saturated aqueous solutions. Direct experimental evidence for its reference to the ground triplet state of the diatomic molecule has not yet been obtained, which is primarily due to the lack of targeted experimental studies of this unusual substance.

5. Assimilation of hydrogen sulfide by sulfur bacteria

In 1887, S. N. Vinogradsky first proved the possibility of using energy released during conversion of hydrogen sulfide to assimilate carbon dioxide, thus opening chemosynthesis in contrast to photosynthesis well known at that time. He suggested using the term ‘sulfur bacteria’ for microorganisms that accumulate elemental sulfur in the cell, if they live in suitable conditions in water containing hydrogen sulfide. Chemosynthesis is a method of autotrophic feeding of microorganisms, in which the energy source for the synthesis of organic substances from CO_2 is the oxidation reactions of inorganic compounds. Autotrophic bacteria are organisms that synthesize organic substances from simple inorganic compounds [40].

It is well known [41] that in aqueous natural H_2S sources and reservoirs, there are a large number of unpainted microorganisms in the cells of which sulfur droplets are found. These microorganisms, called colorless sulfur bacteria, often form massive accumulations in the form of films, white deposits and other fouling on underwater objects. Colorless sulfur bacteria function at temperatures from 4°C to 95°C , in the pH range from 10.5–1.0, and the oxygen concentration can vary from air saturated to fully anaerobic level [42–44]. The combination of physical, chemical and physiological factors determine the existence of a particular microbiological organism in a given climatic region. Colorless sulfur bacteria specimens widely distributed in water reservoirs of different types – freshwater, marine, in the areas of oceanic hydrothermal springs and anthropogenic ecosystems. This is reflected in the multitude and diversity of different types of sulfur bacteria, systematic in their classifications [43,44].

The predominated mechanism of hydrogen sulfide assimilation by sulfur bacteria includes the following reaction [41]:



It is generally accepted that the source of hydrogen in the autotrophic sulfur bacteria is hydrogen sulfide, however, the scheme of formation of sulfur by reaction (10) contrary to this assumption, since hydrogen is consumed in the formation of water, while, as noted

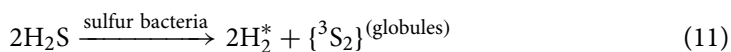
above, sulfur bacteria can function under fully anaerobic conditions. Direct experimental evidence for reactions (10) is absent in the literature.

Regarding the nature of the elemental sulfur produced by sulfur bacteria, there are conflicting opinions. Currently found many microorganisms that form transparent droplets (globules) both inside (intracellular) and outside (extracellular) bacteria cells. Colorless drops reach a diameter of 1 micron, have a spherical or ellipsoidal shape and are hydrophilic. This elemental sulfur (it is commonly referred to as bacterial sulfur S^0) is fundamentally different in properties from the 'normal' inorganic sulfur. In particular, the density of sulfur globules 1.22 g/cm^3 obtained by bacteria is lower than the density of orthorhombic sulfur 2.07 g/cm^3 , and they exhibit hydrophilic properties in contrast to the well-known hydrophobicity of inorganic solid sulfur [45]. In the process of drying globules turn into ordinary crystalline sulfur S_8 .

Various models of bacterial sulfur S^0 are considered in [46]. The liquid crystal model is rejected due to the high density of liquid sulfur 1.80 g/cm^3 at the triple melting point of 115°C and its hydrophobicity. For various reasons, ionic polysulfides, inorganic and organic polysulfane are also rejected. The most suitable model is the $S_n(\text{SO}_3)_2^{2-}$ polythionates, in which the number of sulfur atoms in the chain can reach 140. However, a purposeful study of bacterial sulfur using ion chromatography [47] found neither polythionates nor polysulfides, nor any other polysulfide compounds. Therefore, it is suggested that the globule S^0 consists of drops of 'normal' sulfur (1/3 volume) and water (2/3 volume). Each drop of sulfur is covered with a monolayer of some amphiphilic compound (for example, polysulfides or polythionates), which cannot be isolated due to low concentration, but it gives the globule hydrophilic properties. In another model, it is assumed that the particles of sulfur coated with monolayer of organic surface-active polymer material, most likely – protein [41]. Other exotic forms of bacterial sulfur are considered in [44].

Thus, the main distinguishing feature of the sulfur globules, formed in the process of chemosynthesis in the assimilation of hydrogen sulfide by sulfur bacteria, regardless of their nature, origin and habitat, is their spherical shape and hydrophilic nature colorless colloidal particles [41–47]. It is also proved that sulfur in these globules is in the zero-valence state, but not in the oxidized or reduced form [48,49].

The similarity of the morphology of hydrophilic globules of white sulfur obtained by us from saturated aqueous solutions in the decomposition of hydrogen sulfide (Figure 1), with biological sulfur globules produced by sulfur bacteria [41–47], is to allow the definite conclusion that in the process of H_2S assimilation by colorless sulfur bacteria at ambient temperature the diatomic sulfur in the ground triplet state is also formed (see previous section):



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



Because of the spherical shape and hydrophilicity of the colorless sulfur globules produced by sulfur bacteria, do not depend on their nature and habitat, it may be concluded that reaction (11) can occur under anaerobic conditions and in the presence of oxygen.

Thus explains the role of hydrogen: activated at the moment of formation, hydrogen is involved in the catalytic reactions of chemosynthesis of carbohydrates with the participation of enzymes of sulfur bacteria (12). Of course, this hypothesis requires careful and comprehensive research.

It has been 130 years since the opening chemosynthesis by S.N. Vinogradsky. Currently no doubt that hydrogen sulfide is the primary source of energy and hydrogen to synthesize organic compounds from CO_2 . However, unlike other chemosynthetic microorganisms (methanobacteria, iron bacteria, cyanobacteria, etc.), sulfur bacteria is studied very little, due to experimental difficulties of their cultivation and research in the laboratory. In particular, there is no data on the nature of enzymes in numerous species and types of sulfur bacteria functioning in different habitats, and on the nature of metal atoms catalyzing the processes of chemosynthesis in the composition of these enzymes. Therefore, the mechanisms of chemosynthesis with the participation of sulfur bacteria do not even discussed in the scientific literature. In this regard, the presented material allows us to propose an alternative to study thermodynamics and mechanisms of biological processes of chemosynthesis involving H_2S on the example of model heterogeneous catalysts decomposing H_2S at ambient temperature. Unlike sulfur bacteria, the structure of the active component of solid catalysts can be studied in detail with modern methods; it does not require the creation of any specific conditions for their functioning in catalysis. At the same time, calorimetry and kinetic methods of research are fully applicable for them, which is very important for the study of thermodynamics of chemosynthesis. Therefore, the use of heterogeneous catalysts as model objects of chemosynthesis may open a promising opportunity to create new catalytic systems of CO_2 molecule activation under mild conditions.

6. Conclusion

Currently, We know the only way to obtain diatomic gaseous sulfur is in the ground triplet state, a stable molecule that exists under normal conditions indefinitely, by the low-temperature catalytic decomposition of hydrogen sulfide. However, in nature this enzymatic reaction appears to occur for millions of years with the participation of sulfur bacteria (Figure 2). Toxic and 'useless' H_2S , which has not found any practical application in human activities, turned out to be the very substance that underlies the nature-created process of chemosynthesis of organic matter from CO_2 , laid the foundation of biological life on Earth. In contrast to the chemical analogue – water, which is the fundamental basis of the existence of biological organisms, H_2S is a supplier of hydrogen and energy for the processes of life sustenance of these organisms. This extremely important role of H_2S is probably due to the unique property of this molecule – the standard enthalpy of formation ($\Delta_f H^\circ_{298} = -4.82 \text{ kcal/mol}$) is the lowest among all known potential sources of hydrogen, which means minimal energy consumption in the splitting of the molecule. The driving force of H_2S decomposition in nature is the formation of final products in the ground electronic state (*i.e.* having minimal free energy) – singlet hydrogen, solid sulfur and diatomic sulfur molecule in the ground triplet state. At the same time, the annual increase in hydrogen sulfide volumes is estimated in hundreds of millions of tons due to the activity of anaerobic sulfate-reducing bacteria, which provides a continuous cycle of hydrogen sulfide in nature.

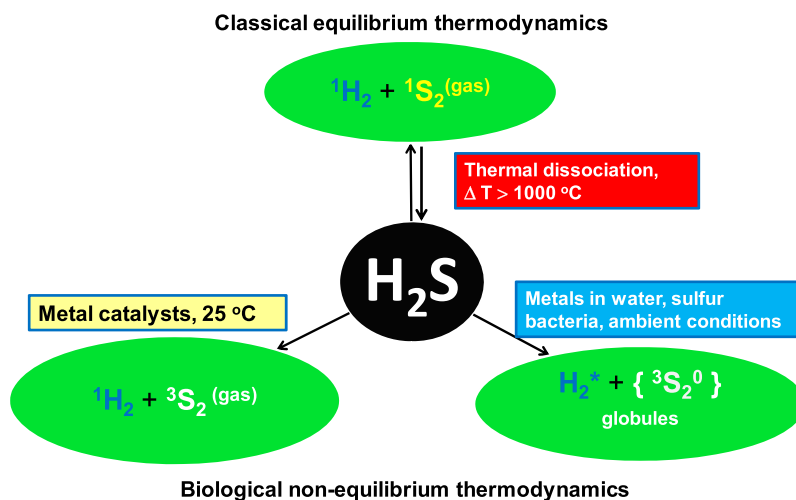


Figure 2. Principal scheme of the diatomic gaseous sulfur production from H_2S .

These conclusions of the existence of triplet sulfur are based on our experimental but indirect evidence, as well as on the analysis of numerous highly controversial literature data. To obtain additional evidence of our findings and assumptions, systematic, targeted experimental and theoretical studies are required. Therefore, the main goal of this review will be considered to be achieved if the formulated questions arouse interest among readers for the initiation of studies in this new and little-known field of sulfur chemistry.

Of particular interest are the standard thermodynamic parameters of the ground triplet state of diatomic sulfur $\{\text{S}_2X^3\Sigma_g^-\}$, which seems to be obtained during the low-temperature catalytic decomposition of H_2S . The standard enthalpy of formation of diatomic sulfur given in handbooks refers to the excited singlet state $\{\text{S}_2a^1\Delta_g\}$ of this molecule. However, based on the analogy with molecular oxygen (Table 1), the standard enthalpy of formation of triplet sulfur must also be zero, as for all diatomic gases in the ground electronic state:

$$\Delta_f H_{298}^\circ \left(\text{S}_2X^3\Sigma_g^- \right) = 0$$

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

Note

1. HREELS – high resolution electron energy-loss spectroscopy

Disclosure statement

No potential conflict of interest was reported by the author.

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