The Reaction Mechanisms of H₂S Decomposition into Hydrogen and Sulfur: Application of Classical and Biological Thermodynamics

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Abstract

Four possible pathways of H₂S decomposition into hydrogen and elemental sulfur are considered. In the thermal reversible process, H₂S dissociation results in the formation of diatomic both hydrogen and sulfur in the singlet state according to the rule of spin conservation:

\[ H₂S \quad \text{ads, ambient T°C} \rightarrow H₂ + \frac{1}{2}S₂\text{g(s)} \]  

(i)

On the surface of sulfide catalysts, irreversible H₂S splitting proceeds at low temperature through the stage of disulfane, H₂S₂ 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:

\[ 2H₂S \quad \text{ads, low temperature} \rightarrow \{H₂S₂\}_\text{ads} + H₂ \rightarrow H₂ + \frac{1}{2}S₂\text{g(s)} \]  

(ii)

On metal catalysts, irreversible H₂S decomposition occurs at low temperature through the stage of H₂S₂ 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:

\[ H₂S \quad \text{metal catalyst C} \rightarrow H₂ + \frac{1}{2}S₂\text{g(s)} \]  

(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 H₂S assimilation by sulfur bacteria is suggested to occur in the processes of chemosynthesis resulted in the formation of colorless sulfur globules and activated hydrogen:

\[ H₂S \quad \text{under bacterial ambient conditions} \rightarrow 2H₂ + 1S₂\text{g(s)} \]  

(iv)

Similar to the bacterial process, the hydrogen production from H₂S is realized with the efficiency of 99.6% on metal catalysts immersed into the liquid which is capable well-dissolving H₂S.

Keywords: H₂S 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 unwanted 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, H₂S 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.

H₂S, on the other hand, is a simple molecule which has a structure similar to that of water, however, unlike water, the H₂S 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 H₂S 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 H₂S 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 H₂S Decomposition

Thermal dissociation of H₂S is a well researched route for the hydrogen production:

\[ 2H₂S \quad \text{ΔH: 1000°C} \rightarrow 2H₂ + S₂\text{g(s)} \]  

(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 H₂ yields. To shift the reaction equilibrium to the right, various ways of intermediate use, distribution, and reproduction in any medium, provided the original author and source are credited.

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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]:

\[
S_2(\text{gas}) \neq S_2(\text{gas}) \quad (2)
\]

As is well known, diatomic sulfur is isoelectronic to oxygen [10,11], therefore the \( S_2 \) ground state is a triplet \( X^3\Sigma_- \), and the first excited state is a singlet \( a^3\Delta \), which is above the ground state by \( \sim 4400 \text{ cm}^{-1} \) (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 [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 under 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 and normal pressure, it is not possible for the \( d^7 \) Co(II) ions (∆H\text{f} < 0, ∆S\text{f} > 0) to exist in the gas phase: in the absence of catalyst the H2S decomposition is thermodynamically impossible. The second step -dissociative chemisorption of two \( H_2S \) molecules on two adjacent cobalt atoms (Figures 2 and 4), occurs spontaneously (∆H\text{f} < 0, ∆S\text{f} > 0) on the d(III) ions as well, and does not possible for the d(II) ions (∆H\text{f} > 0, ∆S\text{f} > 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:

\[
2 \text{H}_2\text{S} \neq \text{H}_2\text{S}_2 + \text{H}_2 \quad (3)
\]

\[
\Delta H_{298}^\circ = +13.6 \text{ kcal/mol, } \Delta S_{298}^\circ = -3.9 \text{ cal/mol K, } \Delta G_{298}^\circ = +14.1 \text{ kcal/mol, initial parameters for calculations are taken from [18].}
\]

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 sulfur, is a strongly endothermic process and requires large energy consumption \( \Delta H_{298} = 25.5 \text{ kcal/mol. There is, however, the possibility of terminating the catalytic cycle, which is the recombination (oligomerization) of molecular sulfur } S_2 (\text{gas}) \text{ on the catalyst surface without it’s desorption into the gas phase. This coupled reaction is the highly exothermic process and occurs spontaneously (∆H}_\text{f} = -78.4 \text{ kcal/mol, } ∆S_\text{f} = -116.0 \text{ cal/mol K, } ∆G_\text{f} = -43.6 \text{ kcal/mol [16,17]. Therefore, the overall catalytic reaction:}

\[
2 \text{H}_2\text{S}_2(\text{gas}) \rightarrow 2 \text{H}_2(\text{gas}) + \frac{1}{2} S_8(\text{solid}) \quad (4)
\]
This irreversible gas phase reaction occurs on the platinum catalyst at ambient conditions under steady state regime with the efficiency of ∼15%. Let’s consider the reaction (5) in the light of biological thermodynamics. Adsorption of H$_2$S molecule on the surface of any metals is an exothermic process. In the case of Pt(111) [21], the energy of molecular H$_2$S adsorption is $E_{ads}=-21.0$ kcal/mol. The minimum energy pathway of the adsorbed H$_2$S is then considered for its dissociation in two steps [21]:

$$\text{H}_2\text{S}(ad) \rightarrow \text{SH}(ad) + \text{H}(ad) \quad (6)$$

$$\text{SH}(ad) \rightarrow \text{S}(ad) + \text{H}(ad) \quad (7)$$

The first dissociation step (6) occurs via the reaction barrier of $E_a=1.6$ kcal/mol with the reaction energy $\Delta E_{rxn}=-19.6$ kcal/mol, while for the second step (7) these values are $E_a=0.7$ kcal/mol and $\Delta E_{rxn}=-18.2$ kcal/mol. Hence, the total reaction energy of H$_2$S 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 H$_2$S molecules of the reaction (5). It is very important, that H$_2$S 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 H$_2$S molecule is 92 kcal/mol [18]. In the reaction (5) four HS-H bonds should be cleaved, what is $\Sigma D_o=368$ kcal/mol, while two H-H bonds ($\Sigma D_o=2 \times 104=208$ 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 $\Delta D_o=57.5$ kcal/mol than that of reaction products, therefore H$_2$S molecule is stable and does not convert into H$_2$ and S$_2$ at room temperature. However in the adsorbed state the required energy for H$_2$S splitting can be invested from the surface dissociation energy of H$_2$S 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 S$_2$ species on...
Pt(111) is $\sim 45$ kcal/mol [22], while molecular hydrogen desorbs from the surface even at $230$ K [23]. Undoubtedly, this rough approximation of energy transduction from $\text{H}_2\text{S}$ 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$_2$S 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 $\text{H}_2\text{O}$ [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 $\mu$m, 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 $\text{nm}$. 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 $\text{cm}^{-1}$ 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 $S_8$ condensed phase with sulfur in the ground triplet state.

Surprisingly, the white sulfur globules obtained from $\text{H}_2\text{S}$ on metal catalysts under layer of water bear a great resemblance to colorless globules produced with sulfur bacteria in aqueous medium containing $\text{H}_2\text{S}$ [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 $+95^\circ\text{C}$, 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 $\mu$m 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 $\text{g/cm}^3$ [35] in contrast to density of liquid sulfur 1.80 $\text{g/cm}^3$ and solid 2.07 $\text{g/cm}^3$. 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 $\text{H}_2\text{S}$ along...
a pathway that includes the formation of zero-valent sulfur as a characteristic intermediate [32,34]:

\[ 2 \text{H}_2\text{S} + \text{O}_2 \rightarrow 2\{\text{S}_0\} + 2\text{H}_2\text{O} \quad (8) \]

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. H₂ 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. H₂ is utilized as an energy source by many anaerobic bacteria including sulfate reducers [39]. Therefore, it is not clear how H₂ 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:

\[ 2 \text{H}_2\text{S} \xrightarrow{\text{bio. bacteria}} 2\text{H}_2^* + \{\text{S}_2\} \quad (9) \]

where H₂* is an activated in situ hydrogen participating in chemosynthesis:

\[ \text{H}_2^* + \text{CO}_2 \xrightarrow{\text{bio. bacteria}} \{\text{HCOOH}\} \quad (10) \]

Obviously, the reaction (9) takes place as a result of the nucleation of diatomic sulfur as a condensed hydrophilic S₂ 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].
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 then used to obtain sulfuric acid. Instead of this high temperature procedure of H₂S utilization, the concentrated with H₂S 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 H₂S occurs at room temperature with hydrogen evolution to the gas phase (Figure 7) and sulfur accumulation in solution with efficiency towards H₂S utilization of 97.9% (Table 2) [40]. Efficiency of H₂S decomposition can be improved to 99.6% in the periodical regime (Table 3) [20], when, after solution saturation with H₂S, 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 H₂S decomposition is practically unlimited taking into account a wide range of choice of catalysts, solvents, regimes, etc.

Figure 8: The possible pathways of H₂S decomposition into hydrogen and elemental sulfur. The catalytic pathways are considered from the standpoints of biological thermodynamics.
due to the stable single state of the \( \text{S}_2 \) 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 \( \text{S}_2 \) molecule with that of the diatomic \( \text{S}_2 \) molecule.

The adsorption of hydrogen sulfide decomposition at room temperature over stainless steel chips placed in aqueous solutions. Catalyst mass is 5 g. Reaction temperature is ambient, Ar flow is 10 ml/min, \( \text{H}_2\text{S} \) flow is 3 ml/min.

### Table 3: The periodical regime of hydrogen sulfide decomposition at room temperature over stainless steel chips placed in aqueous 5% MEA solution. Ar gas flow rate, 6 ml/min; \( \text{H}_2\text{S} \) gas flow rate, 1.8 ml/min; catalyst weight, 2 g; solution volume, 150 ml [20]. After saturation with \( \text{H}_2\text{S} \), the reactor inlet and outlet were closed and overnight left the \( \text{H}_2\text{S} \) feeding starts again.

### Table 2: \( \text{H}_2\text{S} \) decomposition over stainless steel chips placed into aqueous solutions. Catalyst mass is 5 g. Reaction temperature is ambient, Ar flow is 10 ml/min, \( \text{H}_2\text{S} \) flow is 3 ml/min.

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### References