

# Diatomic Gaseous Sulfur Obtained at Low Temperature Catalytic Decomposition of Hydrogen Sulfide

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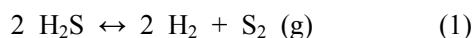
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**Abstract:** Experimental evidences of occurrence of gaseous diatomic sulfur produced in the low temperature catalytic decomposition of hydrogen sulfide  $2 \text{H}_2\text{S} \leftrightarrow 2 \text{H}_2 + \text{S}_2 (\text{g})$  are summarized. The  $\text{S}_2$  molecule is suggested to be in the ground triplet state. Analysis of literature data allows concluding that the  $\text{S}_2$  metastable singlet state is realized in the thermal dissociation of hydrogen sulfide and solid sulfur. Arguments in favor of the hypothesis are been discussed.

**Key words:** Diatomic gaseous sulfur,  $\text{H}_2\text{S}$  decomposition, sulfur electronic structure, reaction thermodynamics, standard enthalpy formation.

## 1. Introduction

Experimental evidences of catalytic decomposition of hydrogen sulfide according to reaction (1) were recently presented in Ref. [1].



Reaction (1) occurs on metal catalysts at room temperature with  $\text{H}_2\text{S}$  conversion about 15%, what is in the clear contradiction with the generally accepted thermodynamical data for thermal decomposition (dissociation) of hydrogen sulfide. In addition to hydrogen, diatomic gaseous sulfur was detected as a reaction (1) product. Because  $\text{S}_2$  molecule was observed only in sulfur vapors at temperature above 200 °C [2], the question arises of whether  $\text{S}_2$  molecule obtained in reaction (1) is a new form of elemental sulfur or rather an experimental artifact. In the paper, the authors summarize experimental evidences and literature date to prove existence of diatomic gaseous sulfur at room temperature and thereafter we discuss a possible electronic structure of  $\text{S}_2$  molecule. The objective of the present work was to understand

distinctions of two diatomic sulfur molecules obtained at both thermal dissociation and low temperature catalytic decomposition of hydrogen sulfide.

## 2. Experiments

The gas-flow experimental setup to study hydrogen sulfide decomposition is shown in Fig. 1. Argon is mixed with  $\text{H}_2\text{S}$  in a definite proportion and fed to the catalyst. In the reactor outlet, two absorbers (the second one for control) with aqueous zinc acetate solution are served as a trap for unreacted hydrogen sulfide collection and are used for quantitative analysis of hydrogen sulfide conversion. After  $\text{H}_2\text{S}$  separation, composition of reaction products is analyzed with a gas chromatograph "Zwet-500". Quadrupole mass spectrometer RGA-100 (Stanford research systems) is used to analyze gas phase composition.

Bulk catalysts used in this work are chips made from stainless steel pig.

## 3. Results

Along with hydrogen, a substance with mass  $m/z = 64$  is always presented in stainless steel vessels for  $\text{H}_2\text{S}$  storage (Fig. 2). This served us as a basis for

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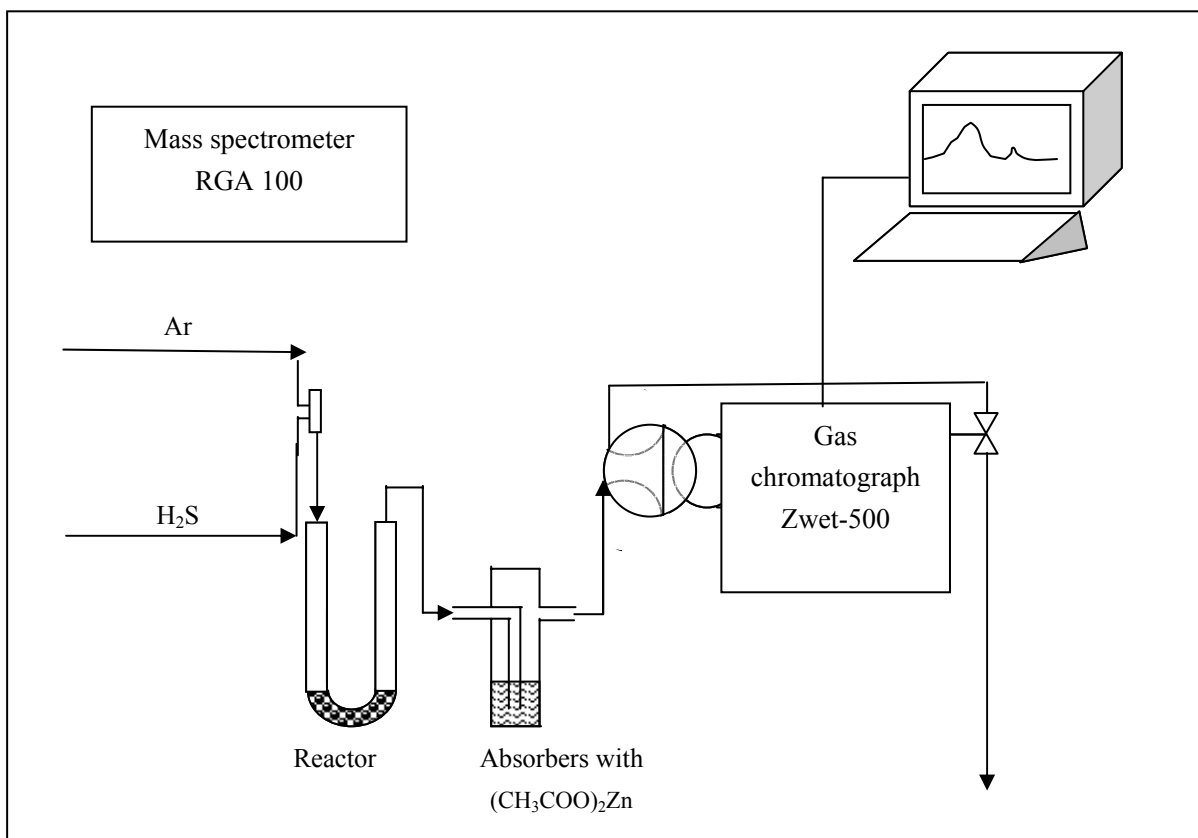


Fig. 1 Experimental setup to study hydrogen sulfide decomposition at room temperature.

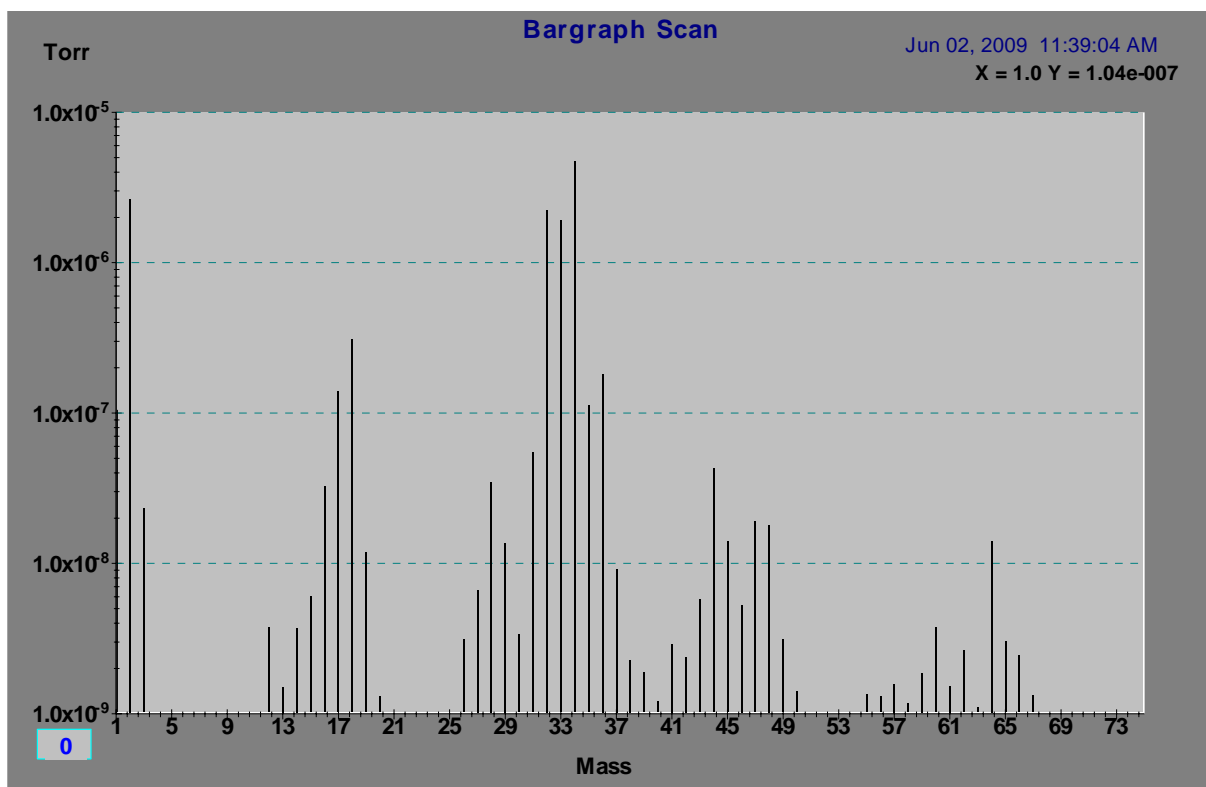
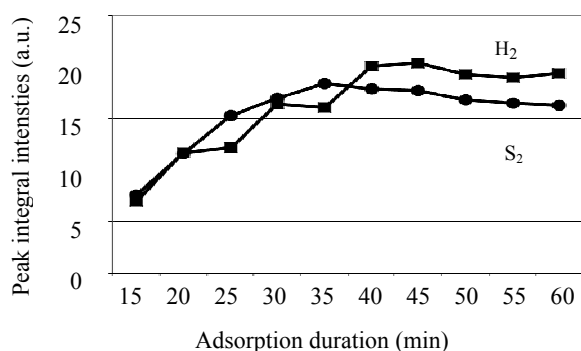


Fig. 2 Typical mass spectrum of hydrogen sulfide stored in a stainless steel vessel.



**Fig. 3** Evolution of gaseous products during H<sub>2</sub>S decomposition over metal catalysts at room temperature.

**Table 1** Hydrogen sulfide decomposition on the bulk stainless steel chips at room temperature.

Catalyst mass (g)	2.7
Argon feeding (mL/min)	10
Hydrogen sulfide feeding (mmol/min)	0.0803
Amount of H <sub>2</sub> S supplied (mmol)	4.82
Amount of H <sub>2</sub> S non-reacted (mmol)	4.69
H <sub>2</sub> S conversion (%)	2.7
Amount of H <sub>2</sub> S converted (mmol)	0.13
Volume of 5% MEA solution (mL)	100
Concentration of sulfur in MEA solution (mass %)*	0.0042
Amount of sulfur in MEA solution (mmol)	0.13

\*—X-ray fluorescent analysis.

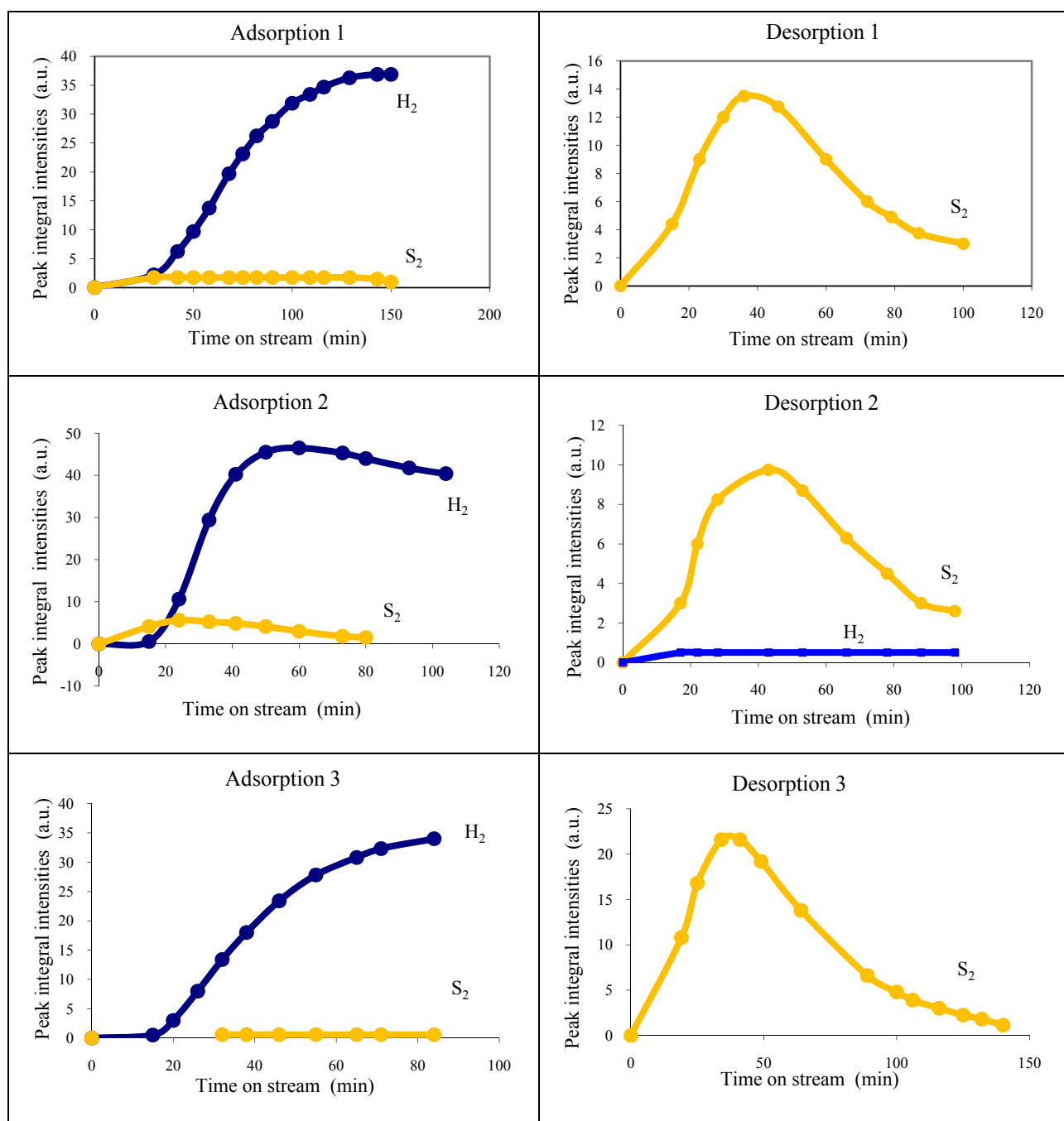
assumption that the equilibrium reaction (1) occurs on the vessel walls, therefore, stainless steel chips (shavings) were selected as the main catalyst for our research work. To extract gaseous sulfur, H<sub>2</sub>S can be merely passed through calcined alumina and “fingerprints” of S<sub>2</sub> adsorbed can be identified with known methods.

As shown in Ref. [1], on passing H<sub>2</sub>S through metal catalysts at room temperature, two gaseous reaction products were detected with a chromatograph (Fig. 3), both products traveled through absorbers with aqueous zinc acetate solution while non-reacted H<sub>2</sub>S was trapped in. The first product is true hydrogen whereas the nature of the second product was identified as gaseous sulfur after being trapped in either MEA (monoethanolamine) solution or pyridine placed just after the first zinc acetate absorber [1]. In this case, only hydrogen was detected with a

chromatograph in gas phase, and the second product was absent. The material balance has shown that the amount of sulfur trapped in a MEA solution is exactly the same as H<sub>2</sub>S decomposed (Table 1). Gaseous sulfur obtained in the reaction (1) has very unpleasant sickening smell.

By use of alumina as a carrier for supported metal catalysts, separation of both reaction products was fortunately to be obtained (Fig. 4). On passing H<sub>2</sub>S through the alumina supported metal catalyst [1], evolution of hydrogen is increasing in time, while gaseous sulfur evolution is very slight and comes down (Fig. 4). After 3 h of time-on-stream, the catalyst was isolated in a closed space, i.e., the reactor inlet and outlet were shut off. Overnight later, the reactor was blown through with argon, in gas phase gaseous sulfur was detected, and evolution of hydrogen was negligible (Fig. 4). The total conversion of hydrogen sulfide in the adsorption-desorption cycle is 27.5% what is essentially higher in comparison with bulk catalysts (Table 1). The experiment is well reproducible (Fig. 5) what means that alumina may serve as a reservoir to accumulate gaseous sulfur, which can be removed by argon blowing through the catalyst. According to X-ray fluorescent analysis, surface concentration of sulfur adsorbed is ~0.5% mass [1].

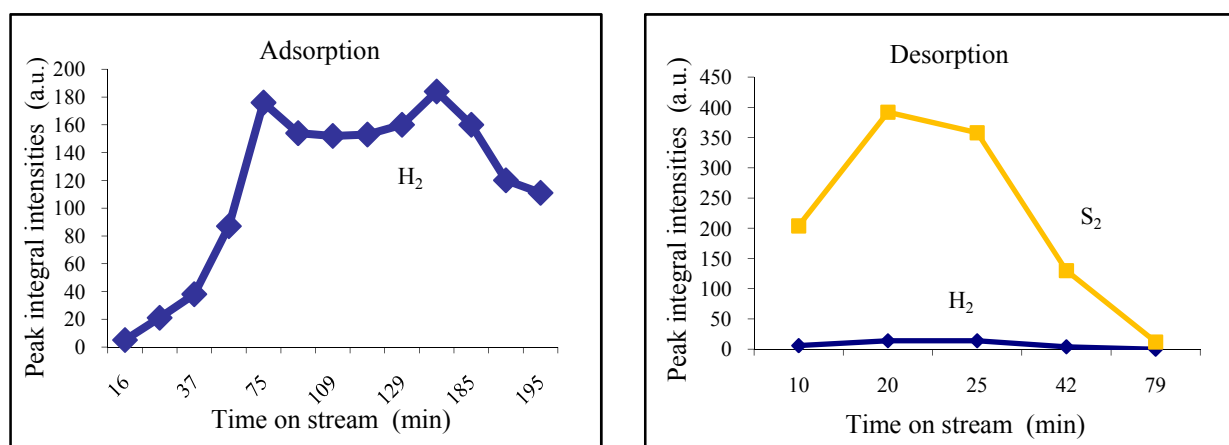
According to equation, reaction (1) occurs with a volume increasing, therefore to shift equilibrium to the right, one or both reaction products should be removed from the gas phase. The main idea to employ autoclave implies in use of alumina to accumulate gaseous sulfur at the equilibrium conditions. For this purpose, a high pressure cylinder of 300 cm<sup>3</sup> was used. On the bottom of autoclave, 55 g of a freshly-calcined alumina was loaded and from above through a partition made of fiberglass, 5 g of stainless steel chips were placed. After evacuation till 10<sup>-2</sup> tor, 4 g of H<sub>2</sub>S was introduced by autoclave cooling. Overnight later, autoclave was open to atmosphere, and color of alumina was found to be yellow with sickening smell



**Fig. 4** Three consecutive cycles of  $\text{H}_2\text{S}$  adsorption and desorption of reaction products on alumina supported metal catalysts at room temperature [1].

of gas phase. All alumina granules were colored uniformly among themselves and along the grain radius as well. After blowing with argon, sulfur content on alumina was found to exceed 2 mass % (Table 2), that means  $\text{H}_2\text{S}$  conversion came to near 30%. In IR (infra red) spectra of diffuse reflectance of alumina, the only strong band at  $809\text{ cm}^{-1}$  was

observed, which is lacking in spectra of solid sulfur [1]. This band was attributed to the sulfur-sulfur stretching mode in the adsorbed species  $\nu_{\text{S-S}}$ . Because no other bands like S-H, S-O and S-S were found in the IR spectra, one may evidently conclude that the adsorbed diatomic species appeared on the alumina surface via gas phase transfer of  $\text{S}_2$  molecule from the catalyst in



**Fig. 5** Separation of reaction products of low temperature decomposition of hydrogen sulfide in a “sulfur generator”. A glass vessel equipped with two stop cocks is charged with stainless steel chips and calcined alumina. On passing  $\text{H}_2\text{S}$  at room temperature only hydrogen is detected in gas phase, color of alumina turns yellow. After saturation, the vessel is isolated in a closed space. Few days later, the apparatus is flowing with argon at room temperature and gaseous sulfur is detected with a gas chromatograph.

**Table 2**  $\text{H}_2\text{S}$  decomposition in autoclave at room temperature over the bulk stainless steel chips and alumina as a sulfur accumulator, which is separated from the catalyst with a fiberglass spacer.

Catalyst mass (g)	5
Alumina mass (g)	54.6
Hydrogen sulfide mass (g)	4
$\text{H}_2\text{S}$ conversion (%)	28.2
Sulfur content on alumina (mass %) *	2.07
Sulfur mass on alumina (g)	1.13

\*—X-ray fluorescent analysis.

accordance with the reaction (1).

After exposure to air in several days, ( $\text{S}_2 + \text{alumina}$ ) sample became colorless, while sulfur surface concentration did not change in this period. After 1.5 year storage of this sample in closed vessel, but under air blanket, 25 g of this colorless sample was blown down with argon at room temperature. During blowing, gaseous sulfur was detected with a chromatograph. X-ray fluorescent analysis has shown that the sulfur surface concentration was decreased from 1.006% mass in the initial sample to 0.7021% mass in the final sample, i.e., 0.076 g of sulfur was sublimated [1]. The understated sulfur surface concentration in comparison with the freshly prepared sample means that the adsorbed sulfur is still sublimated from the surface; however, it does react with neither

oxygen nor water of the air. Therefore, alumina can be used as an accumulator of gaseous sulfur, which might be easily claimed in case of need. It is very important that both ( $\text{S}_2 + \text{alumina}$ ) sample and sulfur desorbed from alumina are odor free in contrast to gaseous sulfur obtained directly in the reaction (1).

The apparatus to produce hydrogen and gaseous sulfur consists of glass vessel equipped with two stop cocks. This vessel is charged with calcined alumina and stainless steel ships. On passing  $\text{H}_2\text{S}$  through this apparatus, only hydrogen is detected in gas phase with a chromatograph (Fig. 5), colorless alumina turns yellow. After  $\sim 3$  h of time-on-stream, the “sulfur accumulator” is isolated in close space, i.e., stop cocks are closed. To desorb gaseous sulfur, argon is passing through this apparatus at room temperature. The procedure (adsorption-desorption) is usable many times, amount of sulfur collected on alumina depends on the catalyst-alumina proportion and  $\text{H}_2\text{S}$  time-on-stream adsorption. The procedure is very well reproducible and clearly demonstrated that sulfur appeared on the alumina surface via gas phase transfer.

When the catalyst is immersed into water,  $\text{H}_2\text{S}$  conversion increases remarkable (Table 3) in comparison with gas phase (Table 1) because of good

**Table 3** H<sub>2</sub>S decomposition on the stainless steel chips immersed into water.

Catalyst mass (g)	2.0
Water volume (mL)	100
Time-on-stream (min)	45
H <sub>2</sub> S fed (mmol)	7.26
H <sub>2</sub> S non-reacted (mmol)	3.93
H <sub>2</sub> S conversion (%)	45.6

solubility in water (up to 0.5%) of gaseous sulfur obtained in reaction (1). Aqua sulfur solutions are colorless, they have a neutral pH = 7, refractive index corresponds to one of water. All these features are typical for dissolved diatomic gases which do not react with water.

Gaseous sulfur is often presented in natural gas pipelines in concentrations ranging from a few to several tens of ppm, where it creates a lot of problems being deposited in solid form on valves, flow meters, fittings, filters and control equipments [3]. The sulfur vapor becomes supersaturated due to the quick cooling of the gas mixture that is rapidly flowing through these apparatus resulted in condensation of solid sulfur.

#### 4. Discussion

We assume that arguments in favor of existing diatomic gaseous sulfur would suffice to discuss its possible electronic structure. In our presentation [1] we suggested that S<sub>2</sub> molecule formed in the reaction (1) is in the excited singlet state. This presumption was based on the thermodynamical reference data for diatomic sulfur produced in the thermal process of H<sub>2</sub>S decomposition, where sulfur, by definition, should be in the ground triplet state. However, the suggestion taken in Ref. [1] aggravates barely the conflict in thermodynamics of the final and initial states of the reaction (1). Therefore, now the authors suggest an alternate proposal that the S<sub>2</sub> ground triplet state is realized in the catalytic reaction (1), while the “classical” thermodynamical data are referred to the S<sub>2</sub> excited singlet state produced in the thermal dissociation of hydrogen sulfide and solid sulfur. This

assumption seems to be reasonable if we consider literature data on determination of the standard enthalpy formation  $\Delta_f H^0_{298}$  of the diatomic gaseous sulfur.

Actually, the enthalpy formation of S<sub>2</sub> molecule, determined from the H<sub>2</sub>S dissociation energy in the temperature range of 1,362-1,667 K, was found to be  $\Delta_f H^0_{298} = 30.8$  kcal/mol [4]. The close value of  $\Delta_f H^0_{298} = 31.2$  kcal/mol [5] was obtained from measurements of partial pressure of S<sub>2</sub> vapors at 823-1,273 K. Namely, the value of  $\Delta_f H^0_{298} = 30.7$  kcal/mol, obtained at high temperature, was generally accepted as the standard enthalpy formation of diatomic sulfur molecule at normal STP (standard temperature and pressures) conditions [6] presumably due to the fact that the gaseous state of diatomic sulfur at room temperature was unknown at that time. So far as experiments were performed in both cases [4, 5] at the equilibrium conditions, the question arises about the electronic state of S<sub>2</sub> molecule at these high temperature circumstances. Because any system at the equilibrium must be in the most thermodynamically stable state, the ground triplet state of S<sub>2</sub> gaseous molecule was evidently assigned by default, although no direct indication on this subject can be found in the original papers [4-6].

The simplest methods to produce diatomic gaseous sulfur consist in heating either solid sulfur or metal sulfides to high temperature [7]. Depending on temperature and pressure, sulfur vapors constitute of complex mixture of different sulfur molecules S<sub>x</sub> (x = 2-8). It is very difficult to assess the reliance of the sulfur vapor compositions determined at various temperature and pressure by different investigators. Obviously these do not describe the complicated system in details. As follows from Ref. [2], at 1,000 K and pressure as low as 1 tor, S<sub>2</sub> is almost 99% pure. After suddenly cooling sulfur vapors to below liquid air temperatures, deposits of colored sulfur were obtained which are not in thermodynamic equilibrium, therefore, after warming they are rapidly transformed

into plastic sulfur and then into  $S_8$  [2]. No condensed  $S_2$  phase was detected at this procedure as might be expected [8].

In the initial substances to produce gaseous sulfur-solid sulfur and hydrogen sulfide, sulfur is in the singlet state. On heating to high temperature and dissociating into diatomic sulfur (and singlet hydrogen in the case of  $H_2S$ ), the transition singlet  $\rightarrow$  triplet in  $S_2$  molecule is basically possible, but, in the absence of catalyst, this process is forbidden because of the spin conservation rule. But even it is yet happened; we should expect conservation of the ground triplet state of sulfur after suddenly cooling to low temperature. However, the highest concentration of unpaired electrons in the colored sulfur deposits was about one per 500 sulfur atoms, while the lowest concentration was over a thousand times smaller [9]. Therefore, only solid sulfur in different allotrope modifications was experimentally observed in all the cases described in literature. Consequently, one may, evidently, conclude that the concentration of the triplet  $S_2$  molecules at high temperature in gas phase is as low as that in the deposits cooled to low temperatures. This serves as a guide to believe that a metastable state of diatomic singlet sulfur is conserved at high temperatures. The metastable excited state of diatomic molecule seems to be inherent only to sulfur, because we do not know other examples of this unusual stable state. Undoubtedly, this principal and far from obvious question demands careful investigation.

## 5. Conclusions

Based on experimental and literature data one may conclude that the diatomic gaseous sulfur produced in the catalytic decomposition of hydrogen sulfide at room temperature is more likely to exist as a new

unknown form of elemental sulfur. This diatomic sulfur must be distinct from that obtained in high temperature processes of  $H_2S$  or  $S_8$  dissociation. The most probable electronic configuration of  $S_2$  molecule produced in the reaction (1) is the ground triplet state, while metastable excited singlet state of  $S_2$  molecule seems to be realized in thermal processes of  $H_2S$  and  $S_8$  dissociation. However, we can not exclude that diatomic singlet sulfur may be formed on the alumina surface resulted from  $^3S_2 \rightarrow ^1S_2$  conversion at the sacrifice of adsorption energy.

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