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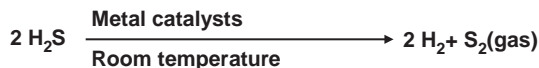
## The reaction thermodynamics of hydrogen sulfide decomposition into hydrogen and diatomic sulfur

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To verify a hypothesis about the electronic state of diatomic gaseous sulfur formed during the low-temperature catalytic decomposition of hydrogen sulfide, we carried out some experiments to examine elemental sulfur dissociation. As shown, after heating at  $\sim 1000$  K, elemental sulfur sealed in quartz ampoules with metal catalysts followed by quenching at room temperature did not produce any visible changes on solid sulfur. However, conversion of solid sulfur into gaseous diatomic sulfur can be realized via intermediate interaction of melted sulfur with hydrogen in the presence of Pt followed by decomposition of  $\text{H}_2\text{S}$  formed on the surface of the metal catalyst at room temperature. It is suggested that the conversion of the singlet sulfur atoms into the ground triplet state becomes feasible only on the surface of metal catalysts resulted from the dissociation of hydrogen sulfide into adsorbed atomic species.

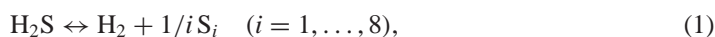


**Keywords:** hydrogen sulfide;  $\text{H}_2\text{S}$  decomposition; hydrogen production; diatomic sulfur; electronic structure; reaction thermodynamics

### 1. Introduction

Hydrogen sulfide attracts the attention of many researchers as an inexhaustible source of hydrogen, high-energy pollution-free fuel and a valuable chemical agent. Hydrogen is only loosely bound to the  $\text{H}_2\text{S}$  molecule, which can be seen from the standard enthalpy of  $\text{H}_2\text{S}$  formation ( $\Delta_f H_{298}^0 = -4.82$  kcal/mol), which is much less than that of methane ( $\Delta_f H_{298}^0 = -17.89$  kcal/mol) and water ( $\Delta_f H_{298}^0 = -57.80$  kcal/mol), the source of most discretionary hydrogen produced today. However, numerous attempts to develop a suitable technology for hydrogen production from  $\text{H}_2\text{S}$  decomposition failed because of the high cost of hydrogen produced.[1–4]

The thermal dissociation of hydrogen sulfide via the gas phase reaction



occurs only at high temperatures, and at 1000 K and 1.0 atm the equilibrium conversion of  $\text{H}_2\text{S}$  is about 5%, giving a composition in the gas phase a mixture of all sulfur molecules from  $\text{S}_2$  to

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S<sub>8</sub>.<sup>[5]</sup> As is well known, the catalyst cannot shift equilibrium (1), but the yield of hydrogen can be upgraded when the reaction (1) runs on a catalyst surface via the intermediate formation of disulfane <sup>[6]</sup>:



Notice that disulfane formation from H<sub>2</sub>S in the gas phase is thermodynamically prohibited.

The S–S bond formation is the key surface reaction (reaction 2) and the thermodynamic driving force of H<sub>2</sub>S decomposition into hydrogen and sulfur on the surface of sulfide catalysts at room temperature.<sup>[7,8]</sup> Studies on metallic catalysts revealed an unexpected experimental fact: along with hydrogen, diatomic gaseous sulfur appeared to be the reaction product of hydrogen sulfide decomposition at ambient conditions.<sup>[9–11]</sup>



In flow systems, conversion of hydrogen sulfide on Pt catalysts at room temperature is about 15%, while removing sulfur from the reaction zone leads to an increase in H<sub>2</sub>S conversion to 30% or more.<sup>[9–11]</sup> These experimental facts are in contradiction with accepted thermodynamical data for thermal H<sub>2</sub>S dissociation, therefore the hypothesis was advanced that the electronic structure of the S<sub>2</sub> molecule formed in the reactions (1) and (3) differs from one another.<sup>[10,11]</sup>

The main objectives of this communication are the comparative analysis of some properties of diatomic sulfur obtained in reactions (1) and (3), and the experimental verification of the possible transmission of solid sulfur into gaseous diatomic sulfur in the presence of metal catalysts.

## 2. Some properties of diatomic sulfur

It is generally recognized that the electronic structure of the diatomic sulfur molecule is quite similar to that of oxygen,<sup>[12]</sup> therefore the S<sub>2</sub> ground state is a triplet  $X^3\Sigma_g^-$  and the first excited state is a singlet  $a^1\Delta_g$  which is above the ground state by about  $\sim 4700 \text{ cm}^{-1}$ . However, the electronic spectra and electronic states of S<sub>2</sub> molecule are less known than that of O<sub>2</sub> as a result of the difficulty associated with studying S<sub>2</sub> vapor at temperatures above 650°C.<sup>[13]</sup>

The standard enthalpy of diatomic sulfur formation  $\Delta_f H_{298}^0 = 30.7 \text{ kcal/mol}$  <sup>[14]</sup> was determined using high-temperature experimental conditions for H<sub>2</sub>S <sup>[15]</sup> and elemental sulfur <sup>[16]</sup> dissociation while no reference data about the electronic state of diatomic sulfur obtained were published. Evidently, the ground triplet state of gaseous S<sub>2</sub> at STP (standard temperature pressure) conditions was assigned by default, although neither gaseous nor condensed phase of the S<sub>2</sub> molecule was isolated in a pure form under the STP conditions. Moreover, on cooling to 500 K S<sub>2</sub> molecules transform into S<sub>5</sub>–S<sub>8</sub> species and in the liquid or solid state sulfur is presumably S<sub>8</sub> molecules with a cyclic structure.<sup>[17]</sup> Hence, the enthalpy of diatomic sulfur formation determined in <sup>[15,16]</sup> seems to be valid only for high temperature, but it cannot be applied for reactions under STP conditions.

The simplest method to produce S<sub>2</sub> consists of heating either solid sulfur or metal sulfides to high temperature above 1000°C where S<sub>2</sub> is the most abundant species.<sup>[17]</sup> After quenching the hot sulfur vapors to low temperatures, deposits of colored sulfur were obtained,<sup>[18,19]</sup> which contained a mixture of various vapor components and after warming to room temperature they are rapidly transformed into plastic sulfur and then into S<sub>8</sub>. No condensed S<sub>2</sub> phase was detected in this procedure as might be expected.<sup>[20]</sup> To estimate a concentration of unpaired electrons in the colored sulfur deposits, the electron spin resonance (ESR) technique was applied.<sup>[21]</sup> As was shown, only one in every 500 sulfur atoms is paramagnetic at 77 K, while by warming to 195 K the characteristic ESR spectrum completely disappeared. Consequently, one may conclude

that the concentration of the paramagnetic  $S_2$  molecules at high temperature in the gas phase is as low as that in the deposits cooled to low temperatures. This gives us reason to believe that a metastable state of the diatomic singlet sulfur is conserved at high temperatures. If the ground triplet state of the  $S_2$  molecule were populated at high temperatures, one should expect its conservation upon quenching sulfur vapor to low temperatures.

The  $S_2$  molecule was isolated in inert gas matrices at 4 and 20 K.[22–25] Ultraviolet spectra of these species [22,23] were tentatively attributed to the ( $X^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ ) transition in the  $S_2$  molecule. However, what happened with these species after warming to room temperature remains unknown, because color and spectral changes were observed.[22]

So, based on the above statement the hypothesis indicates that the diatomic gaseous sulfur formed in reaction (3) is in the ground triplet state, while the  $S_2$  metastable singlet state is realized in the thermal dissociation of hydrogen sulfide (reaction 1) or elemental sulfur.[10,11]

### 3. Results and discussion

In the initial substances, which are generally used for producing gaseous diatomic sulfur thermally – elemental solid sulfur and hydrogen sulfide – the sulfur is in the singlet state. On heating to high temperature and dissociating into diatomic sulfur (and singlet hydrogen in the case of  $H_2S$ , reaction 1), the transition singlet  $\rightarrow$  triplet in the  $S_2$  molecule is hindered by the spin conservation rule. The interaction of  $S_2$  molecule with metal catalysts could remove these restrictions. Therefore, the following experiments were undertaken.

In three of the four quartz ampoules, containing  $\sim 0.2$  g sulfur, black platinum, a piece of metallic platinum, and chip of stainless steel were added. Black platinum was prepared by precipitation from Zeise's acid  $H[PtCl_3(C_3H_6)]$  with hydrazine hydrate. After pumping to  $10^{-2}$  Torr, the ampoules were sealed in vacuum and heated to  $\sim 1000$  K for 5 h. Subsequently, the red substance in the ampoules was quenched to room temperature in a vessel with water and yellow sulfur was found in all the four ampoules. The procedure was repeated three times, but the cooling rate was varied. In all the cases, no change in sulfur in comparison with the reference sample was observed. Hence, the inability to observe the singlet–triplet interconversion in the  $S_2$  molecule at high temperature seems to be consistent with kinetic restrictions and the spin conservation rule, which might be circumvented with metal catalysts sealed into ampoules with sulfur.

From calculation using complete active space self-consistent field and Hartree–Fock methods, the reaction enthalpy for reaction (4)



is  $\Delta_r H_{298}^0 = +46.9$  kcal/mol for the triplet  $S_2$  molecule and  $\Delta_r H_{298}^0 = -10.4$  kcal/mol for the singlet  $S_2$  molecule.[11] This confirms once again the existence of singlet diatomic sulfur at high temperature because condensation of its sulfur vapor into solid sulfur is much more favorable. Besides, it follows from calculations that the triplet molecular state of diatomic sulfur is thermodynamically most favorable, therefore the  $^3S_2$  molecule does not transform into the solid singlet sulfur. Furthermore, if the singlet  $\rightarrow$  triplet transition were to happen at high temperature we can expect conservation of this ground state at low temperature, contrary to the experimental observation.

A participant in reaction (3) is hydrogen, therefore it was decided to test its role in the formation of gaseous sulfur. For this purpose, to three long (30 cm) glass test tubes 0.4 g of solid sulfur was added and pieces of metallic platinum were placed at the bottom of two test tubes (Figure 1). A chip of stainless steel [9–11] was placed in the center of all the test tubes, and just above it glass cartridges with alumina were kept to trap gaseous sulfur. The entire system was

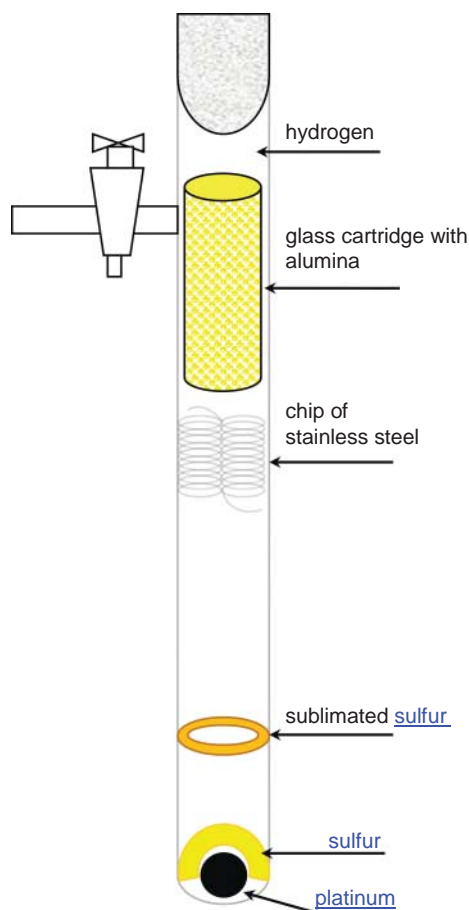


Figure 1. Apparatus to observe transition of solid sulfur into gaseous diatomic sulfur.

pumped with  $10^{-2}$  and  $\sim 100$  Torr of hydrogen. In one of two parallel experiments, no platinum was introduced into the test tube, while in the second case hydrogen was absent and the reaction was carried out in vacuum. After that all three test tubes were heated at  $300^{\circ}\text{C}$  for 2 h. The main part of the sulfur was sublimated and condensed on the cold walls of the test tubes in the form of a ring of bright orange-yellow droplets. Cartridges with alumina were significantly above the sulfur condensation zone at room temperature (Figure 1). This eliminated the possibility of sublimated sulfur reaching the alumina which was confirmed with control experiments where coloration and increase in weight of alumina have not been detected. However, the alumina in the test tube with platinum and hydrogen was colored yellow and it increased in weight by 14.35 mg or  $\sim 1$  wt.%. A diffuse reflectance infrared spectrum of this alumina (Figure 2) exhibits a band at  $\sim 810\text{ cm}^{-1}$ , which was attributed to the  $\nu_{(\text{S-S})}$  stretching mode of the adsorbed diatomic sulfur.[9–11] Because no other bands such as S–H, S–O and S–S were found in the IR spectra, one may conclude that the adsorbed diatomic species appeared on the alumina surface via the gas phase transfer of  $\text{S}_2$  molecule from the stainless steel chip in accordance with reaction (3). In control experiments, in the absence of Pt no interaction of boiling sulfur with hydrogen can occur, while in the absence of hydrogen the sulfur vapors cannot reach alumina surface because of very low partial pressure of  $\text{S}_2$  gaseous molecule vapor at  $300^{\circ}\text{C}$ .[17]

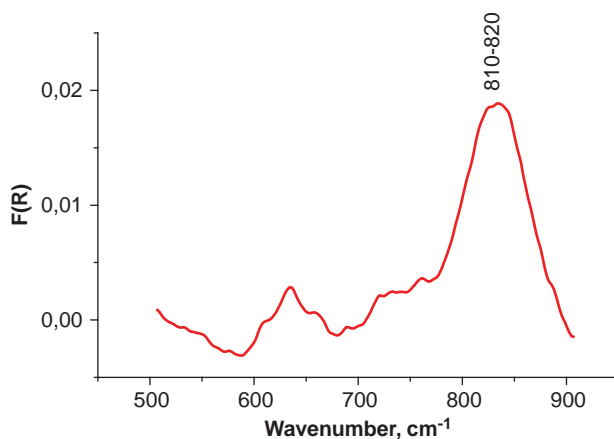


Figure 2. IR spectrum of diffuse reflectance of 1 wt% S<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

Thus, in the experiments described melted sulfur in the presence of platinum reacts with hydrogen to form H<sub>2</sub>S, which, in turn, decomposes on a stainless steel chip to form gaseous diatomic sulfur via reaction (3). Dissociative adsorption of H<sub>2</sub>S on the surface of many transition metals occurs via three exothermic steps.[26] For Pt(111), the molecular H<sub>2</sub>S adsorption is characterized by a  $\Delta E_{\text{ads}} = -21$  kcal/mol, while dissociation into adsorbed SH and atomic H species occurs with a gain of overall reaction energy of  $-39$  kcal/mol. Minimum energy pathways and energy profiles predict that on the surface of many metal catalysts H<sub>2</sub>S dissociation into adsorbed atomic species occurs with a gain in free energy and do not have any thermodynamic or kinetic restrictions.[26] These conclusions are in good agreement with experimental data: dissociative adsorption of H<sub>2</sub>S into adsorbed atomic species occurs on the Pt(111) surface even at 110 K.[27] Therefore, we may presuppose that the dissociative H<sub>2</sub>S adsorption on the metal catalysts is the first step of the low-temperature decomposition of hydrogen sulfide. After pairing adsorbed atoms, the diatomic sulfur molecule can be desorbed into the gas phase in the ground triplet state. In other words, the process of low-temperature decomposition of hydrogen sulfide (3) occurs on the surface of metal catalysts via H<sub>2</sub>S dissociation into adsorbed atomic species resulting in the desorption of both diatomic reaction products in the ground states – singlet hydrogen and triplet sulfur.

In summary, one may conclude that the reaction thermodynamics of low-temperature decomposition of hydrogen sulfide (3) are best explained by the assumption that the diatomic gaseous sulfur in the ground triplet state is the reaction product along with the singlet hydrogen. In the process of thermal decomposition (1) H<sub>2</sub>S dissociates into singlet hydrogen and singlet diatomic sulfur in accordance with the spin conservation rule. The metastable singlet diatomic sulfur seems to be the unique molecule existing only at high temperature and this phenomenon must be carefully investigated.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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