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Estimates of the second dissociation constant of H₂S from the surface sulfidation of crystalline sulfur

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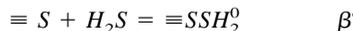
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Abstract—The adsorption of hydrogen sulfide ($\Gamma_{\text{H}_2\text{S}}$) and protons (Γ_{H^+}) on the surface of crystalline sulfur was investigated experimentally in H₂S-bearing solutions at temperatures of 25, 50, and 70°C, NaCl concentrations of 0.1 and 0.5 mol/dm⁻³ and log C_H⁺ values in the range -2.3 to -5. At all temperatures, the dominant process on the surface of the sulfur was deprotonation, and the average values of $\Gamma_{\text{H}_2\text{S}}$ were very close to the highest values determined for Γ_{H^+} . This finding, combined with the lack of detectable proton adsorption in H₂S-free solutions, suggests that proton adsorption/desorption on the surface of sulfur occurs through formation of $\equiv S - H_2S$ complexes in the presence of H₂S.

We propose that this complexation represents sulfidation of the sulfur surface, a process analogous to hydroxylation of oxide surfaces, and that the sulfidation can be described by the reaction:



The deprotonation of the $\equiv SH^0$ complex occurs via the reaction:



Values of 2.9, 2.8, and 2.9 (± 0.23) were obtained for $-\log \beta^-$ at 25, 50, and 70°C, respectively. These data were employed to estimate the second dissociation constant for hydrogen sulfide in aqueous solutions using the extrapolation method proposed by Schoonen and Barnes (1988) and yielded corresponding values for the constant of 17.4 ± 0.3 , 15.7, and 14.5, respectively. The value for 25°C is in very good agreement with the experimentally determined values of Giggenbach (1971) at 17 ± 0.1 ; Meyer et al. (1983) at 17 ± 1 ; Licht and Manassen (1987) at 17.6 ± 0.3 ; and Licht et al. (1990) at 17.1 ± 0.3 . Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

Hydrogen sulfide is one of most important components of ore-forming hydrothermal solutions, and its activity commonly controls the solubility of sulfide ore minerals. However, H₂S is a weak diprotic acid and dissociates in aqueous solutions, forming HS⁻ and then S²⁻. Unfortunately, only pK₁ has been reliably determined. Despite the long history of experimental investigation (Dickson, 1966; Ellis and Milestone, 1967; Giggenbach, 1971; Ellis and Giggenbach, 1971; Kremer and Zarechenskii, 1971; Kryukov et al., 1974; Rao and Hepler, 1977; Sretenskaya, 1983; Meyer et al., 1983; Licht and Manassen, 1987; Schoonen and Barnes, 1988; Licht et al., 1990; Eckert, 1998), there is still little agreement on the value of pK₂, even at 25°C, and proposed values differ by several orders of magnitude (12.5–18.5). For example, in the three most recent papers on the subject, Schoonen and Barnes (1988) reported a value of 18.51 ± 0.56 , Licht et al. (1990) a value of 17.1 ± 0.3 , and Eckert (1998) a value of 13.86 at this temperature.

Because of the large uncertainty in pK₂, the Gibbs free energy for S²⁻ is poorly known, and this affects evaluation of aqueous sulfur speciation and sulfide solubility products. The S²⁻ ion is generally assumed to be insignificant in sulfur-

bearing solutions due to its alkaline properties and is conventionally ignored in most solution models. However, even though S²⁻ displays extremely alkaline behavior at room temperature, we cannot exclude the possibility that this species may be significant in natural solutions at elevated temperatures. To evaluate this possibility, we need to refine the value of pK₂ for H₂S at 25°C and estimate its value at higher temperatures.

Possible reasons for the large variation in the published values of pK₂ are the extremely low concentrations of S²⁻ at experimentally realistic values of pH and the tendency of bisulfide solutions to oxidize rapidly (Ellis and Giggenbach, 1971; Sretenskaya, 1983). In cases like this, where experimental difficulties prevent reliable data from being obtained, experimentalists commonly turn to indirect methods in which the properties of the species of interest are predicted by determining the properties of their chemical homologues. Schoonen and Barnes (1988) used this approach to estimate pK₂ for H₂S by extrapolating the published values of pK₂ for a set of H₂S homologues (polysulfanes; H₂S_n), which dissociate to form polysulfides. The higher stability of polysulfide complexes S_n²⁻ ($n > 1$) relative to S²⁻ makes it possible to experimentally determine the corresponding values of pK₂ to a much higher level of confidence than is possible for S²⁻. Assuming that the surface of crystalline sulfur is the endmember of this series of homologues and that sulfur suspensions prepared from acidified polysulfane solutions have the structures of aqueous poly-

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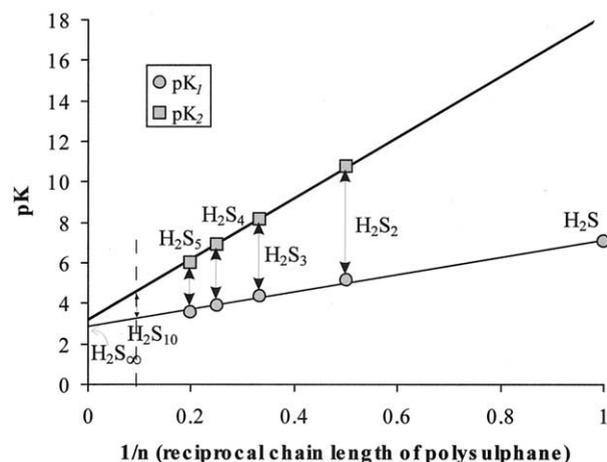


Fig. 1. Dissociation constants for polysulfanes (H_2S_n) vs. reciprocal chain length ($1/n$). Lines represent least squares fits to the data for pK_1 and pK_2 . Data for pK_1 and pK_2 at 25°C are from Schoonen and Barnes (1988). The value of $pK_1(H_2S_\infty) = pK_2(H_2S_\infty)$ was estimated by linear extrapolation of the pK_1 values for the other polysulfanes. The value of $pK_2(H_2S)$ was estimated by linear extrapolation of the pK_2 values.

sulfanes, Schoonen and Barnes (1988) determined the dissociation constant for the sulfur surface and using the values published for H_2S_5 and H_2S_4 , extrapolated these data linearly to obtain a value of 18.51 for $pK_2^{298} H_2S$. However, as discussed below, the suspensions employed by Schoonen and Barnes (1988) probably consisted of a mixture of polysulfane-like chain and ring-structured sulfur, thereby potentially invalidating their results.

We believe that the problem of mixed structures can be overcome and that polysulfane-like complexes can be stabilized on sulfur surfaces by exposing the latter to aqueous H_2S . In this paper, we report results of an experimental study of the surface complexation of sulfur in the presence of $H_2S(aq)$ and use them to obtain a revised value for $pK_2^{298}(H_2S)$ and new values of $pK_2(H_2S)$ at 50 and 70°C .

1.1. The Polysulfane Approach

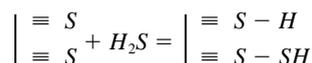
Polysulfanes are planar, zigzag chains of polymerized sulfur that have the common stoichiometry of H_2S_n (Pickering and Tobolsky, 1972). Hydrogen sulfide is the polysulfane having an n equal to 1, and its chemical properties are governed by the rules of homologues, as are those of all other higher order ($n > 1$) polysulfanes. It has been shown experimentally (Maronny, 1959; Schwartzenbach and Fischer, 1960) and from molecular orbital calculations (Meyer et al., 1977) that the values of pK_1 and pK_2 for polysulfanes have a retrograde dependence on sulfur chain length (n). Schoonen and Barnes (1988) suggested that, in the case of an infinite chain length (H_2S_∞), the two terminal protonated sulfane groups would become completely independent, and differences between pK_1 and pK_2 would be eliminated. These researchers obtained a value of pK_1 for H_2S_∞ (2.78) by linear extrapolation of pK_1 values for H_2S , H_2S_4 , and H_2S_5 reported in the literature (Maronny, 1959; Schwartzenbach and Fisher, 1960) with the reciprocal chain length ($1/n$; Fig. 1). Assuming that a molecule with the form H_2S_∞ is effectively the same as the protonated surface of crystalline sulfur, they also

suggested that the closest analog of the dissociation constant of H_2S_∞ is the deprotonation constant (K_{in}) for the sulfur surface. Schoonen and Barnes (1988) argued that this value is close to the zero point of charge (ZPC) of sulfur and supported this hypothesis with data derived from an experimental investigation of the turbidity of a sulfur suspension (pH of ZPC = 2.6–3.1). They also suggested that the dissociation of a protonated surface group can be expressed as:



where \equiv is the sign of the surface complex. The values of ZPC obtained by Schoonen and Barnes (1988) are higher than those reported in the literature, e.g., the value of 2.0 of Ney (1973). However, the experiments of Ney (1973) employed crystalline sulfur, which has a ring structure comprising eight polymerized atoms. By contrast, Schoonen and Barnes (1988) used sulfur formed from acidified polysulfide solutions and assumed that the planar structure of the chain-like aqueous polysulfanes was maintained by the suspension. However, it has been shown experimentally that the dominant structure of sulfur at temperatures up to at least 200°C is a ring comprising eight polymerized atoms (Steudel and Mausle, 1978). Polymerized chains first appear in sulfur melts at temperatures $> 116^\circ\text{C}$, but even at 200°C , their concentration does not exceed 5% (Steudel et al., 1985). Thus, chain-structured sulfur molecules are predicted to be unstable at the experimental conditions, and if precipitated with a polysulfane-like structure, they would tend to recrystallize to the more stable ring-structured form of sulfur. As a result, the suspensions investigated by Schoonen and Barnes (1988) are likely to have comprised a mixture of chain- and ring-structured sulfur, thereby invalidating the assumption that the data obtained can be related to a single form with a polysulfane-like structure.

As mentioned in the introduction, we believe that this problem can be overcome by using hydrogen sulfide to stabilize the polysulfane-like structure of complexes on sulfur surfaces. It is known that interaction between sulfur and hydrogen sulfide in aqueous solutions results in the rupture of S_8 sulfur rings and formation of $>S-H$ thiol groups (Meyer et al., 1977). This process is widely accepted as the principal mechanism responsible for the formation of aqueous polysulfanes. However, the disruption of cyclic $>S = S<$ groups by hydrogen sulfide associated with the formation of polysulfanes also occurs in sulfur melts and in processes involving solid sulfur. For example, Hyne et al. (1966) demonstrated, using nuclear magnetic resonance, that dissolution of H_2S in molten S at 127°C produces a solution of polysulfanes with an average stoichiometry of H_2S_{27} . Long-chain polysulfanes $H_2S_{12} - H_2S_{20}$ were likewise produced by Wiewiorowski (1970) in experiments interacting liquid hydrogen sulfide with crystalline sulfur at -80 to $+80^\circ\text{C}$. Finally, Feher and Berthold (1952) reported the formation of polysulfane oil (average composition H_2S_{354}) and sulfur during the decomposition of $Na_2S_2O_3$ at 40°C . It is therefore clear that sulfur can interact with hydrogen sulfide to form long-chained polysulfanes, such as H_2S_{12} , H_2S_{27} , and even H_2S_{354} , and it is logical to suggest that if hydrogen sulfide in aqueous solutions can be adsorbed by sulfur surfaces, it will also interact with sulfur, rupturing sulfur rings and forming polysulfane-like structures. Such sulfidation of sulfur surfaces (analogous to hydroxylation) can be described by the reaction:



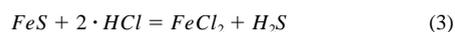
To emphasize the polysulfane-like structure of the surface complex, this equation can be rewritten as:



Owing to the fact that polysulfanes associated with both solid and liquid sulfur are characterized by long chains of polymerized sulfur (> 10 atoms), we predict that this surface complex also has a sufficient concentration of S = S bonds to be a reasonable analog of H₂S_∞. As can be seen from Figure 1, deprotonation constants (pK₁) determined for compounds with the stoichiometry H₂S_{>10} are indistinguishable from the value of pK₁(H₂S_∞) within realistic experimental error. Thus we suggest that by investigating the surface properties of sulfur in solutions with and without H₂S, it should be possible to determine the surface deprotonation constants for ≡SSH₂⁰ and, in turn, pK₁(H₂S_∞) = pK₂(H₂S_∞).

1.2. Experimental Method

Experiments were conducted at temperatures of 25, 50, and 70°C (Tables 1, 2, 3) on aqueous NaCl-H₂S solutions containing dispersed sulfur in sealed, thick-walled Teflon cells (50-cm³ internal volume), equipped with glass pH, platinum (redox) and sulfide (Ag/Ag₂S) electrodes, and a magnetic stirrer. The cells were heated in an electric oven, and temperature was controlled to an accuracy of ± 0.3°C. Solutions employed in the experiments contained 0.1- and 0.5-mol dm⁻³ NaCl and were prepared using triply-distilled water, which was purged by boiling under a stream of nitrogen gas. Quartz-distilled HCl was added in quantities that yielded solutions with pH values of 2.3 to 5 (no HCl was required to produce a pH of 5). Hydrogen sulfide was introduced by adding aliquots of an H₂S-saturated solution, which was prepared by bubbling pure H₂S gas through the 0.1- and 0.5-mol dm⁻³ NaCl solutions at 25°C and P_{total} = 1 atm. The H₂S gas was generated by the reaction



and purified by passing it through a gas-washing bottle containing distilled water (the final H₂S purity was measured to be 99.8% using a GasoChrom 3101 gas chromatograph). The hydrogen sulfide concentrations in the solutions were determined by iodometric titration (Szekeres, 1974).

Taken later were 15 mL of H₂S-bearing solution (20 mL, if a 5-mL sample to analyze the H₂S concentration) and 0.5 g of dispersed sulfur (1 m²/g) were heated in the cell at the temperature of the experiment and stirred vigorously. The electrode potentials were recorded continuously until the system stabilized, which was assumed to have occurred when the drift of the potential was < 0.3 mV per hour. However, sulfur is not inert in hydrogen sulfide solutions, and a large number of chemical reactions occur, not only on the surface of the solid, but also in the H₂S-bearing aqueous solution, forming such species as H₂S_n⁻, HS_n⁻ (aqueous polysulfanes), S₂O₃²⁻, and HS₂O₃⁻ (thiosulfates). We found that the addition of dispersed sulfur to the H₂S-bearing solutions caused an immediate and rapid decrease in the concentration of H₂S. After a few hours, the concentration of H₂S reached a minimum and then slowly increased, but never returned to its original level. This phenomenon can be explained by two processes occurring in parallel, namely, the adsorption of H₂S on the sulfur surface and the formation of aqueous species like H₂S_n in concentrations exceeding equilibrium values. The latter subsequently re-equilibrated with the dispersed sulfur, decomposing into sulfur and hydrogen sulfide, and reached a steady-state concentration after 15 to 20 h.

It should be pointed out that such active interaction between the dispersed sulfur and H₂S-bearing solutions may cause errors in the estimation of H₂S adsorption. The error due to the formation of the equilibrium concentrations of H₂S_n and related species is predicted to

Table 1. Results of experiments designed to measure the adsorption of H⁺ and H₂S on crystalline sulfur in H₂S-bearing solutions at 25°C. S is the mass of sulfur, X is the concentration of adsorption centers, C_H⁺ and C(H₂S) are the proton and H₂S concentrations, respectively, and Γ (H⁺) and Γ (H₂S) are the values of proton and hydrogen sulfide adsorption on the sulfur surface.

NaCl = 0.5 mol/dm ⁻³					
S, g	X · 10 ³ , mol/dm ⁻³	log C _H ⁺ , free	C(H ₂ S), free mol/dm ⁻³ · 10 ³	Γ (H ⁺), mol/m ² · 10 ⁷	Γ (H ₂ S), mol/m ² · 10 ⁷
5.464	5.46	-3.78	1.41	-3.9	3.6
5.286	5.29	-3.76	1.41	-3.7	4.0
5.679	5.68	-3.49	1.42	-3.4	3.7
5.343	5.34	-3.47	1.41	-3.5	3.6
5.633	5.63	-3.46	1.43	-3.1	3.5
5.508	5.51	-3.40	1.39	-2.6	3.0
5.690	5.69	-3.34	1.42	-2.5	3.4
5.667	5.67	-3.30	1.41	-2.0	3.4
5.088	5.09	-3.29	1.35	-2.3	3.5
5.213	5.21	-3.21	1.42	-1.2	3.7
5.298	5.30	-3.18	1.40	-1.2	4.0
5.524	5.52	-3.18	1.41	-0.8	3.8
5.844	5.84	-3.08	1.42	-0.5	3.1
5.877	5.88	-2.98	1.45	0.0	4.1
5.701	5.70	-2.93	1.43	0.0	3.4
5.469	5.47	-2.89	1.46	0.8	3.0
5.973	5.97	-2.85	1.41	0.0	3.5
5.966	5.97	-2.82	1.45	0.0	3.0
5.575	5.58	-2.80	1.46	0.0	3.8
5.041	5.04	-2.80	1.43	0.0	3.3
5.794	5.79	-2.62	1.43	0.0	3.9
5.640	5.64	-2.49	1.46	0.0	3.2
5.372	5.37	-3.80	1.19	-3.9	3.9
5.816	5.82	-3.76	1.19	-3.7	4.1
5.367	5.37	-3.50	1.18	-3.5	3.1
5.947	5.95	-3.50	1.19	-3.1	4.3
5.552	5.55	-3.40	1.19	-2.8	3.8
5.700	5.70	-3.39	1.18	-2.8	3.9
5.296	5.30	-3.35	1.19	-2.6	3.7
5.017	5.02	-3.32	1.19	-2.1	3.6
5.236	5.24	-3.32	1.18	-2.0	4.3
5.105	5.11	-3.30	1.19	-2.2	2.9
5.884	5.88	-3.28	1.18	-1.7	3.3
5.598	5.60	-3.19	1.19	-0.8	3.8
5.517	5.52	-3.18	1.19	-0.8	3.8
5.923	5.92	-3.08	1.19	-0.5	3.3
5.737	5.74	-3.08	1.18	-0.5	4.2
5.664	5.66	-3.00	1.19	0.0	3.7
5.114	5.11	-2.94	1.20	0.0	4.1
5.449	5.45	-2.92	1.20	0.0	3.6
5.067	5.07	-4.01	1.10	-2.0	3.3
5.192	5.19	-4.00	1.06	-2.5	3.5
5.143	5.14	-3.77	1.10	-2.6	2.6
5.768	5.77	-3.76	1.10	-2.1	2.9
5.512	5.51	-3.68	1.10	-2.1	3.0
5.755	5.76	-3.65	1.10	-1.9	3.4
5.336	5.34	-3.58	1.10	-2.3	3.4
5.235	5.24	-3.48	1.10	-1.6	2.9
5.783	5.78	-3.38	1.06	-1.4	2.9
5.113	5.11	-3.33	1.06	-1.2	2.3
5.219	5.22	-3.27	1.10	-1.7	3.7
5.764	5.76	-3.24	1.06	-1.3	3.1
5.124	5.12	-3.19	1.06	-1.3	3.5
5.823	5.82	-3.12	1.10	-1.3	3.3
5.121	5.12	-3.11	1.10	-0.5	2.6
5.283	5.28	-3.04	1.06	-0.6	3.7
5.938	5.94	-3.00	1.06	-0.6	3.0
5.520	5.52	-2.98	1.06	-1.3	3.5
5.044	5.04	-2.91	1.06	-0.8	3.3

(continued)

Table 1. (Continued)

NaCl = 0.5 mol/dm ⁻³					
S, g	X · 10 ³ mol/dm ⁻³	log C _{H⁺} , free	C(H ₂ S), free mol/dm ⁻³ · 10 ³	Γ (H ⁺), mol/m ² · 10 ⁷	Γ (H ₂ S), mol/m ² · 10 ⁷
5.761	5.76	-2.82	1.06	0.0	3.1
5.984	5.98	-2.77	1.10	0.0	2.8
5.478	5.48	-2.62	1.06	0.0	3.8
5.225	5.23	-2.54	1.10	0.0	3.2
5.067	5.07	-4.05	1.26	-2.5	3.3
5.301	5.30	-3.96	1.26	-3.0	2.8
5.421	5.42	-3.84	1.31	-2.6	2.5
5.338	5.34	-3.69	1.26	-2.3	2.5
5.363	5.36	-3.64	1.26	-2.2	2.2
5.337	5.34	-3.62	1.31	-2.4	2.8
5.624	5.62	-3.62	1.31	-1.8	2.4
5.767	5.77	-3.52	1.26	-1.9	2.3
5.783	5.78	-3.42	1.31	-1.8	2.3
5.481	5.48	-3.35	1.26	-1.8	2.7
5.699	5.70	-3.31	1.31	-1.4	2.1
5.385	5.39	-3.29	1.26	-1.3	2.2
5.151	5.15	-3.23	1.31	-1.5	2.3
5.483	5.48	-3.18	1.26	-0.8	2.7
5.393	5.39	-3.14	1.26	-1.8	2.8
5.407	5.41	-3.10	1.31	-1.0	2.2
5.363	5.36	-3.05	1.31	-1.1	2.5
5.678	5.68	-2.89	1.26	-0.8	3.2
5.188	5.19	-2.83	1.26	0.0	2.9
5.818	5.82	-2.82	1.31	0.0	2.3
5.675	5.68	-2.82	1.31	0.0	2.4
5.709	5.80	-2.74	1.31	0.0	2.1
5.668	5.67	-2.71	1.26	0.0	2.6

be small because of their low stability at the experimental conditions. However, the formation of excessive amounts of aqueous polysulfanes and their subsequent decomposition during re-equilibration should cause considerable dissolution and then reprecipitation of the dispersed sulfur. This process could not be controlled during the experiments and may have significantly changed the specific surface area of the suspended sulfur. However, we found that after re-equilibration, addition of dispersed sulfur did not result in a fluctuation of H₂S concentration but rather a small gradual decrease. We therefore conclude that once the system had re-equilibrated, the composition of the solution was independent of the mass of crystalline sulfur. To a first approximation, the solution was assumed to be in a steady state with respect to the dispersed sulfur. The concentrations of H₂S and H⁺ obtained at this stage are referred to below as the "blank" or "total concentration" of the respective species.

Following stabilization of the electrode potential, a further aliquot of dispersed sulfur (5 g) was introduced into the cell and stirred at the experimental temperature. The electrode potentials stabilized after ~7 to 15 h, and the concentrations of H⁺ and H₂S were obtained from the potentiometric measurements and iodometric titration (free concentration). The differences in the composition of the solutions between initial equilibration (total concentration) and that following the addition of a second aliquot of dispersed sulfur (free concentration) were attributed to adsorption on the newly added sulfur surface. This was the final step in each of the experiments. Owing to the high volatility of hydrogen sulfide at the experimental conditions and the high possibility that it would be lost from the system, we did not make the stepwise additions of HCl normally carried out during conventional potentiometric titrations. The method employed in this study can therefore be considered as a titration of solution with different H⁺ and H₂S concentrations by a single aliquot of sulfur surface.

The same method was used in experiments with H₂S-free solutions. These experiments were conducted under a nitrogen atmosphere at 50°C (adsorption was not investigated at other temperatures for the reasons discussed below). However, the solutions took a much longer time to equilibrate as indicated by the fact that the electrode potentials took several days to stabilize (~100 h for each equilibration).

Table 2. Results of experiments designed to measure the adsorption of H⁺ and H₂S on crystalline sulfur in H₂S-bearing solutions at 50°C. S is the mass of sulfur, X is the concentration of adsorption centers, C_{H⁺} and C(H₂S) are the proton and H₂S concentrations, respectively, and Γ (H⁺) and Γ (H₂S) are the values of proton and hydrogen sulfide adsorption on the sulfur surface.

NaCl = 0.5 mol/dm ⁻³					
S, g	X · 10 ³ mol/dm ⁻³	log C _{H⁺} , free	C(H ₂ S), free mol/dm ⁻³ · 10 ³	Γ (H ⁺), mol/m ² · 10 ⁷	Γ (H ₂ S), mol/m ² · 10 ⁷
5.373	5.37	-3.95	1.44	-2.9	3.6
5.646	5.65	-3.93	1.64	-2.8	4.0
5.951	5.95	-3.90	1.62	-2.7	3.5
5.916	5.92	-3.85	1.57	-3.5	3.3
5.854	5.85	-3.69	1.58	-2.5	4.1
5.672	5.67	-3.38	1.64	-1.9	3.4
5.256	5.26	-3.52	1.45	-2.5	4.3
5.844	5.84	-3.44	1.45	-1.9	3.6
5.833	5.83	-3.49	1.54	-2.2	3.6
5.386	5.39	-3.24	1.58	-1.4	3.3
5.824	5.82	-3.38	1.56	-1.4	3.3
5.620	5.62	-3.16	1.60	-1.2	3.2
5.919	5.92	-3.20	1.63	-1.1	3.0
5.349	5.35	-3.23	1.51	-1.5	3.4
5.669	5.67	-3.16	1.46	-1.2	3.2
5.320	5.32	-3.04	1.58	-0.6	3.1
5.930	5.93	-3.05	1.58	-0.5	4.3
5.801	15.80	-2.78	1.54	0.0	4.1
5.239	5.24	-2.77	1.50	0.0	3.4
5.898	5.90	-2.71	1.42	0.0	4.1
5.452	5.45	-2.79	1.40	0.0	3.6
5.408	5.41	-2.50	1.61	0.0	3.1
5.836	5.84	-2.60	1.46	0.0	3.9
5.155	5.16	-3.93	1.45	-3.1	4.1
5.679	5.68	-3.84	1.51	-3.6	3.4
5.117	5.12	-3.60	1.54	-3.3	3.2
5.833	5.83	-3.38	1.57	-1.8	3.3
5.075	5.08	-3.57	1.59	-2.8	3.5
5.706	5.71	-3.43	1.63	-2.4	3.7
5.880	5.88	-3.48	1.59	-2.0	3.8
5.001	5.00	-3.24	1.54	-1.9	3.6
5.129	5.22	-3.48	1.51	-2.0	3.7
5.929	5.93	-3.17	1.63	-0.8	3.8
5.962	5.96	-3.21	1.50	-1.0	3.0
5.190	5.19	-3.22	1.46	-1.5	3.5
5.863	5.86	-3.21	1.49	-1.7	3.1
5.951	5.95	-3.12	1.64	-0.9	3.0
5.100	5.10	-3.04	1.63	-1.2	3.2
5.113	5.11	-2.84	1.52	0.0	3.2
5.360	5.36	-2.71	1.49	0.0	3.1
5.907	5.91	-2.72	1.60	0.0	3.8
5.473	5.47	-2.72	1.56	0.0	3.0
5.591	5.59	-2.46	1.51	0.0	3.2
5.943	5.94	-2.64	1.63	0.0	3.5
5.479	5.48	-2.62	1.51	0.0	3.0

NaCl = 0.1 mol/dm ⁻³					
S, g	X · 10 ³ mol/dm ⁻³	log C _{H⁺} , free	C(H ₂ S), free mol/dm ⁻³ · 10 ³	Γ (H ⁺), mol/m ² · 10 ⁷	Γ (H ₂ S), mol/m ² · 10 ⁷
5.376	5.38	-3.92	1.24	-3.0	3.6
5.225	5.23	-3.88	1.30	-3.4	4.0
5.420	5.42	-3.60	1.21	-2.4	3.9
5.403	5.40	-3.42	1.21	-2.0	3.6
5.644	5.64	-353	1.25	-2.2	3.5
5.867	5.87	-3.49	1.30	-2.0	3.1
5.353	5.35	-3.47	1.27	-2.6	3.4
5.285	5.29	-3.24	1.27	-1.8	3.4
5.086	5.09	-3.44	1.31	-2.2	3.5
5.681	5.68	-3.15	1.27	-1.2	3.7
5.333	5.33	-3.15	1.23	-1.8	3.9

(continued)

Table 2. (Continued)

NaCl = 0.1 mol/dm ⁻³					
S, g	X · 10 ³ mol/dm ⁻³	log C _{H⁺} , free	C(H ₂ S), free mol/dm ⁻³ · 10 ³	Γ (H ⁺), mol/m ² · 10 ⁷	Γ (H ₂ S), mol/m ² · 10 ⁷
5.779	5.78	-3.26	1.25	-1.6	3.9
5.581	5.58	-3.15	1.27	-1.7	3.2
5.322	5.32	-3.03	1.27	-1.8	4.2
5.737	5.74	-2.97	1.25	-1.3	3.4
5.897	5.90	-2.76	1.23	0.0	3.1
5.428	5.43	-2.70	1.27	0.0	3.6
5.890	5.89	-2.68	1.32	0.0	3.1
5.651	5.65	-2.74	1.30	1.1	3.7
5.311	5.31	-2.46	1.29	0.0	3.4
5.602	5.60	-2.66	1.28	0.0	4.0
5.721	5.72	-3.91	1.24	-3.0	3.1
5.572	5.57	-3.87	1.35	-3.1	3.8
5.703	5.70	-3.63	1.23	-2.5	3.9
5.057	5.06	-3.38	1.25	-2.3	3.0
5.796	5.80	-3.54	1.27	-2.6	4.1
5.954	5.95	-3.49	1.32	-2.0	3.8
5.719	5.72	-3.43	1.30	-2.0	3.9
5.157	5.16	-3.29	1.21	-1.9	3.8
5.572	5.57	-3.42	1.28	-1.9	3.8
5.248	5.25	-3.16	1.20	-1.7	4.3
5.371	5.37	-3.15	1.30	-1.7	3.1
5.923	5.92	-2.23	1.23	-1.6	3.3
5.100	5.10	-3.20	1.29	-1.6	3.8
5.953	5.95	-3.04	1.24	-1.0	3.8
5.762	5.76	-2.95	1.28	-1.3	3.4
5.053	5.05	-1.79	1.28	0.0	4.2
5.920	5.92	-2.71	1.32	0.0	3.8
5.678	5.68	-2.72	1.30	0.0	4.2
5.079	5.08	-2.80	1.26	0.0	3.5
5.658	5.66	-2.47	1.22	0.0	3.2

The concentrations of H⁺ and H₂S in the experimental solutions were measured potentiometrically and controlled by acid-base and iodometric titration. To avoid poisoning the Ag/AgCl reference electrode with H₂S, the electrode was removed from the cell and was connected to the solution by a capillary salt bridge. The salt bridge was filled with a solution having the same concentration of NaCl as that of the cell. The reference electrode and the salt bridge were maintained at the same temperature as the experimental solution. Potentiometric measurements were performed to an accuracy of ± 0.2 mV. Concentrations of H⁺ in the experimental solutions were measured using ESL-11G and Beckman-Micro pH glass electrodes, which were calibrated before and after each run at the temperature of the experiment. Two sets of solutions with the same NaCl concentrations (0.1- or 0.5-mol dm⁻³ NaCl) as those of the experimental runs were used for calibration. As NaCl is the major component of both the experimental solutions and those used in the calibration, and NaCl concentrations exceeded those of the sulfur species by more than one order of magnitude, we assumed that junction potentials could be ignored. The initial calibration of the glass electrodes was performed in the solutions with quartz-distilled HCl concentrations of 0.1-, 0.01-, and 0.001-mol dm⁻³ at 25, 50, and 70°C. The solutions were prepared by successive dissolution of 0.1-mol dm⁻³ stock solution in the solutions with the corresponding NaCl concentrations. The concentrations of HCl in the 0.1- and 0.01-mol dm⁻³ calibration solutions were monitored using acid-base titration with a 0.1-mol dm⁻³ NaOH solution. To perform the calibration at lower H⁺ concentrations, we used 0.05-mol dm⁻³ biphthalate and 0.05-mol dm⁻³ phosphate buffer solutions prepared using the 0.1- or 0.5-mol dm⁻³ NaCl solutions. As these solutions buffer the activity of H⁺, activity coefficients of the H⁺ ion were obtained using the extended Debye-Hückel equation:

$$\log \gamma = \frac{-(A \cdot z^2 \cdot \sqrt{I})}{1 + B \cdot a \cdot \sqrt{I}} + \text{GAMMA} + b - \text{dot} \cdot I \quad (4)$$

Table 3. Results of experiments designed to measure the adsorption of H⁺ and H₂S on crystalline sulfur in H₂S-bearing solutions at 70°C. S is the mass of sulfur, X is the concentration of adsorption centers, C_{H⁺} and C(H₂S) are the proton and H₂S concentrations, respectively, and Γ (H⁺) and Γ (H₂S) are the values of proton and hydrogen sulfide adsorption on the sulfur surface.

NaCl = 0.5 mol/dm ⁻³					
S, g	X · 10 ³ mol/dm ⁻³	log C _{H⁺} , free	C(H ₂ S), free mol/dm ⁻³ · 10 ³	Γ (H ⁺), mol/m ² · 10 ⁷	Γ (H ₂ S), mol/m ² · 10 ⁷
5.060	5.06	-3.88	1.21	-3.6	3.6
5.680	5.68	-3.84	1.21	-3.3	5.0
5.470	5.47	-3.77	1.23	-3.8	3.8
5.140	5.14	-3.51	1.20	-3.9	4.7
5.650	5.65	-3.32	1.20	-3.1	4.0
5.150	5.15	-3.51	1.17	-3.2	4.4
5.330	5.33	-3.42	1.20	-2.4	4.8
5.960	5.96	-3.36	1.17	-3.0	4.3
5.960	5.96	-3.23	1.18	-2.2	4.0
5.610	5.61	-3.34	1.16	-3.2	4.0
5.790	5.79	-3.14	1.19	-1.7	4.4
5.950	5.85	-3.19	1.18	-1.8	4.1
5.780	5.78	-3.24	1.17	-2.2	4.2
5.780	5.78	-3.19	1.22	-2.2	4.2
5.400	5.40	-3.08	1.17	-1.5	5.0
5.130	5.13	-3.02	1.23	-1.3	4.1
5.150	5.15	-2.77	1.20	0.0	4.1
5.780	5.78	-2.74	1.21	0.0	4.2
5.680	5.68	-2.74	1.21	0.0	3.7
5.960	5.96	-2.76	1.17	0.0	4.0
5.510	5.51	-2.49	1.18	0.0	4.6
5.390	5.39	-2.65	1.20	0.1	4.2
5.550	5.55	-2.61	1.18	0.0	4.6
5.130	5.13	-3.81	1.29	-4.2	3.5
5.410	5.41	-3.76	1.26	-4.3	4.2
5.070	5.07	-3.74	1.27	-4.3	4.4
5.270	5.72	-3.54	1.25	-3.6	3.7
5.260	5.26	-3.36	1.29	-3.4	3.7
5.450	5.45	-3.45	1.28	-4.0	4.4
5.990	5.99	-3.39	1.28	-3.1	3.5
5.200	5.20	-3.39	1.27	-3.8	4.3
5.940	5.94	-3.20	1.28	-2.1	3.0
5.380	5.38	-3.37	1.25	-3.5	3.9
5.800	5.80	-3.19	1.25	-2.2	3.1
5.020	5.02	-3.15	1.29	-2.3	4.8
5.020	5.02	-3.18	1.26	-2.1	3.9
5.020	5.02	-3.18	1.26	-2.1	3.9
5.550	5.55	-3.15	1.28	-1.7	3.5
5.710	5.71	-3.05	1.28	-1.1	3.4
5.150	5.15	-3.02	1.29	-1.3	4.4
5.910	5.91	-2.80	1.29	-0.9	4.6
5.370	5.37	-2.71	1.30	1.3	3.1
5.650	5.65	-2.82	1.25	0.0	3.7
5.800	5.80	-2.48	1.26	0.0	3.6
5.430	5.43	2.62	1.25	0.0	3.6
5.690	5.69	-2.55	1.29	0.0	3.7

NaCl = 0.1 mol/dm ⁻³					
S, g	X · 10 ³ mol/dm ⁻³	log C _{H⁺} , free	C(H ₂ S), free mol/dm ⁻³ · 10 ³	Γ (H ⁺), mol/m ² · 10 ⁷	Γ (H ₂ S), mol/m ² · 10 ⁷
5.400	5.40	-3.95	1.22	-2.8	3.3
5.410	5.41	-3.92	1.26	-2.8	3.6
5.730	5.73	-3.88	1.26	-2.6	3.4
5.420	5.42	-3.64	1.22	-2.3	3.9
5.980	5.98	-3.36	1.24	-1.4	3.5
5.570	5.57	-3.56	1.33	-2.3	3.5
5.840	5.84	-3.45	1.26	-1.7	4.1
5.220	5.22	-3.47	1.33	-2.0	3.7
5.370	5.37	-3.30	1.34	-1.5	3.6
5.940	5.94	-3.38	1.22	-1.6	3.8

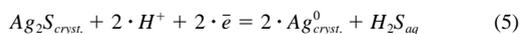
(continued)

Table 3. (Continued)

NaCl = 0.5 mol/dm ⁻³					
S, g	X · 10 ³ mol/dm ⁻³	log C _{H⁺} free	C(H ₂ S), free mol/dm ⁻³ · 10 ³	Γ (H ⁺), mol/m ² · 10 ⁷	Γ (H ₂ S), mol/m ² · 10 ⁷
5.640	5.64	-3.17	1.21	-0.8	3.5
5.280	5.28	-3.13	1.40	-0.9	3.7
5.440	5.44	-3.24	1.36	-1.4	3.9
5.860	5.86	-3.20	1.24	-1.1	3.3
5.520	5.52	-3.06	1.34	-0.5	3.8
5.920	5.92	-3.06	1.33	-0.5	3.5
5.590	5.59	-2.83	1.26	0.0	3.8
5.390	5.39	-2.78	1.27	0.0	3.6
5.540	5.54	-2.67	1.23	0.0	3.8
5.090	5.09	-2.76	1.26	0.0	3.5
5.590	5.59	-2.51	1.33	0.0	3.5
5.840	5.84	-2.64	1.32	0.0	3.1
5.460	5.46	-2.60	1.40	0.0	3.6
5.630	5.63	-3.98	1.34	-2.5	3.2
5.000	5.00	-3.95	1.29	-2.7	3.3
5.220	5.22	-3.90	1.40	-2.5	3.7
5.710	5.71	-3.66	1.40	-1.8	3.4
5.930	5.93	-3.38	1.41	-1.1	3.3
5.880	5.88	-3.56	1.32	-2.1	3.3
5.420	5.42	-3.45	1.28	-1.5	3.0
5.850	5.85	-3.46	1.35	-1.5	3.1
5.240	5.24	-3.31	1.37	-1.2	2.9
5.220	5.22	-3.44	1.34	-2.0	3.2
5.670	5.67	-3.14	1.26	-0.9	2.9
5.390	5.39	3.19	1.25	-0.4	3.1
5.230	5.23	-3.23	1.27	-1.1	3.2
5.950	5.95	-3.17	1.24	-0.8	3.0
5.020	5.02	-3.13	1.29	-0.5	3.0
5.150	5.15	-3.06	1.40	-0.6	2.9
5.860	5.86	-2.79	1.29	0.0	3.3
5.680	5.68	-2.75	1.35	0.0	3.4
5.820	5.82	-2.67	1.25	0.0	3.1
5.810	5.81	-2.80	1.31	-0.0	2.8
5.810	5.81	-2.80	1.31	0.0	2.8

where GAMMA is the mol fraction to molality conversion factor given by $GAMMA = -\log(1 + 0.0180153 \cdot m')$, m' is the sum of the molalities of all solute species, and $b\cdot$ represents the extended term for NaCl-dominated solutions, which is a function of temperature (Helgeson, 1969; Helgeson et al., 1981; Oelkers and Helgeson, 1990). To obtain a pH calibration of the electrode (required for potentiometric measurements of H₂S concentration), H⁺ ion activities were also calculated for the HCl solutions used in the calibration. The final step of the calibration involved titrating 15 mL of the experimental solution (0.1- and 0.5-mol dm⁻³ NaCl, and ~0.005-mol dm⁻³ H₂S), which did not contain dispersed sulfur, with 0.05- and 0.5-mol dm⁻³ solutions of HCl. The titration was performed at the experimental temperatures and yielded HCl concentrations in the titrated solution ranging from 0.0015- to 0.01-mol dm⁻³. Unfortunately, parallel checks of H₂S concentrations showed that there were losses of H₂S (~10–15%) from the solutions during titration. Although these losses were too small to have significantly affected calibration of the glass electrodes, they might have introduced serious errors in our determination of the adsorption of H₂S. Thus, as discussed above, we did not carry out this titration on experimental solutions containing dispersed sulfur.

The activity of H₂S in the experimental solution was measured using an Ag/Ag₂S electrode. The electrodes were built from silver wire covered by an emulsion of Ag₂O (Bates, 1964) and sulfidized by electrolysis in an H₂S solution at 0.4 mA. As the measurements were made for pH conditions at which H₂S_{aq} is dominant over HS⁻, the potential of the Ag/Ag₂S electrode was expressed via the equations:

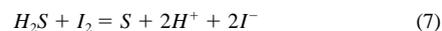


$$E = E_T^0 + \frac{R \cdot T}{n \cdot F} \ln K_r = E_T^0 - \frac{R \cdot T}{2 \cdot F} \ln a_{H_2S} - \frac{2.3026 \cdot R \cdot T}{F} pH \quad (\text{the Nernst equation})$$

where E is the potential of Ag/Ag₂S electrode, $E_T^0 = -\frac{\Delta_r G}{n \cdot F}$ is the standard potential of this electrode, K_r is the constant of the above reaction, $\Delta_r G$ is the Gibbs free energy of this reaction, n is the number of electrons involved in the reaction ($n = 2$), a_{H_2S} is the activity of H₂S in the solution, T is the temperature, R is the Gas constant, and F is the Faraday constant. Before each isothermal series of runs, the sulfide electrode was calibrated at the temperature of the experiments using the standard solutions described above having pH values (25°C) of 2.01, 3.00, and 6.86, and H₂S concentrations varying from 0.005 to 0.1 mol/L. The electrodes used in the runs were selected to be consistent with the Nernst equation (± 0.5 mV) and the theoretically calculated standard potentials (± 1 mV). Consistency with the Nernst equation was also checked before and after each run in two or three solutions with different pH and H₂S concentrations. To calculate the concentration of H₂S in the solutions, the activity coefficients of neutral H₂S_{aq} species were calculated according to the Setchenow equation (cf., Oelkers and Helgeson, 1990):

$$\log \gamma = GAMMA + b - setch \cdot I \quad (6)$$

where $b\cdot$ is the Setchenow coefficient, which is equivalent to $b\cdot$ in the extended Debye-Hückel equation (Eqn. 4). The total concentration of H₂S was corrected by adding the concentration of HS⁻, which was calculated using the dissociation constant of H₂S (Suleimenov and Seward, 1997) and the extended Debye-Hückel equation. To check the results of the potentiometric measurements, the concentrations of H₂S in ~60% of the runs were analyzed by iodometric titration:



Possible losses of hydrogen sulfide were avoided by adding excess iodine to a 5-mL sample, which was then titrated using an Na₂S₂O₃ solution (Szekeres, 1974).

A platinum electrode was used as a sensor to confirm saturation of the system with respect to sulfur. As has been shown by Migdisov et al. (2001), the potential of the platinum electrode at the conditions investigated is governed by the reaction:



Thus, stabilization of the platinum electrode potential can be taken as a criterion for saturation of the aqueous solution by sulfur and attainment of a steady state in the H₂S – S system.

2. RESULTS

As noted above, experiments with H₂S-free solution were conducted at 50°C and an NaCl concentration of 0.1-mol dm⁻³. The potentiometric method did not permit us to obtain any reliable results on proton adsorption or desorption on the sulfur surface, because the differences in the concentrations of H⁺ after the first (blank run) and subsequent stages of sulfur addition were close to the detection limit. An attempt was made to measure the adsorption effect by direct potentiometric titration but was unsuccessful. Owing to the absence of a measurable adsorption effect, we therefore decided to discontinue experiments using the H₂S-free solution and concluded that formation of a ≡ S – H complex was suppressed in this system.

In contrast to the experiments with H₂S-free solutions, there was a measurable and significant adsorption effect at all temperatures and ionic strengths investigated in the experiments with H₂S-bearing solutions. The results are illustrated in Figures 2, 3, and 4, and summarized in Tables 1, 2, and 3. The

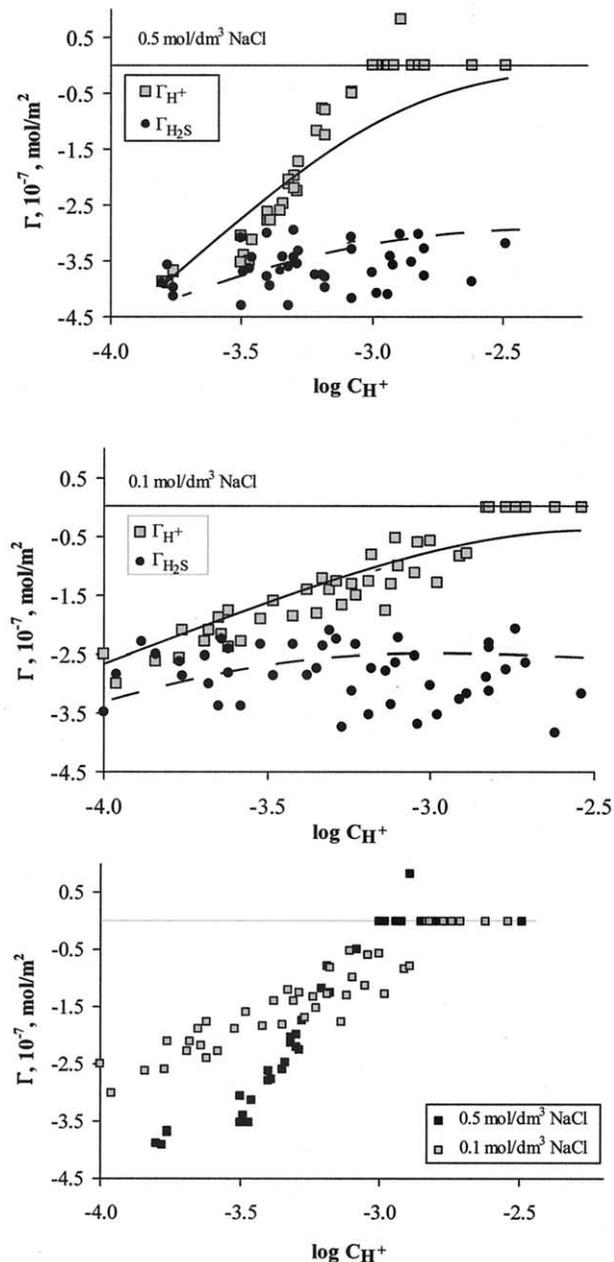


Fig. 2. Experimentally determined concentrations of adsorbed hydrogen sulfide and proton on the surface of crystalline sulfur at 25°C vs. total proton concentration (free H⁺) in H₂S-bearing solutions of ionic strength (NaCl) 0.1 and 0.5. $\Gamma_{\text{H}_2\text{S}}$ is the hydrogen sulfide adsorption in mol/m², Γ_{H^+} is the proton adsorption in mol/m², and C_{H^+} is the free concentration of proton in mol/L. Solid and dashed lines represent the predictions of Model B (see text) for Γ_{H^+} and $\Gamma_{\text{H}_2\text{S}}$, respectively.

proton adsorption (Γ_{H^+} mol·m⁻²) was calculated using the relationship:

$$\Gamma_{\text{H}^+} = \frac{(C_{\text{H}^+}^{\text{total}} - C_{\text{H}^+}^{\text{free}} - [C_{\text{OH}^-}^{\text{total}} - C_{\text{OH}^-}^{\text{free}}]) \cdot V}{m \cdot S} \quad (9)$$

where the superscripts *total* and *free* refer to the states before and after addition of the 5-g aliquot of dispersed sulfur, respec-

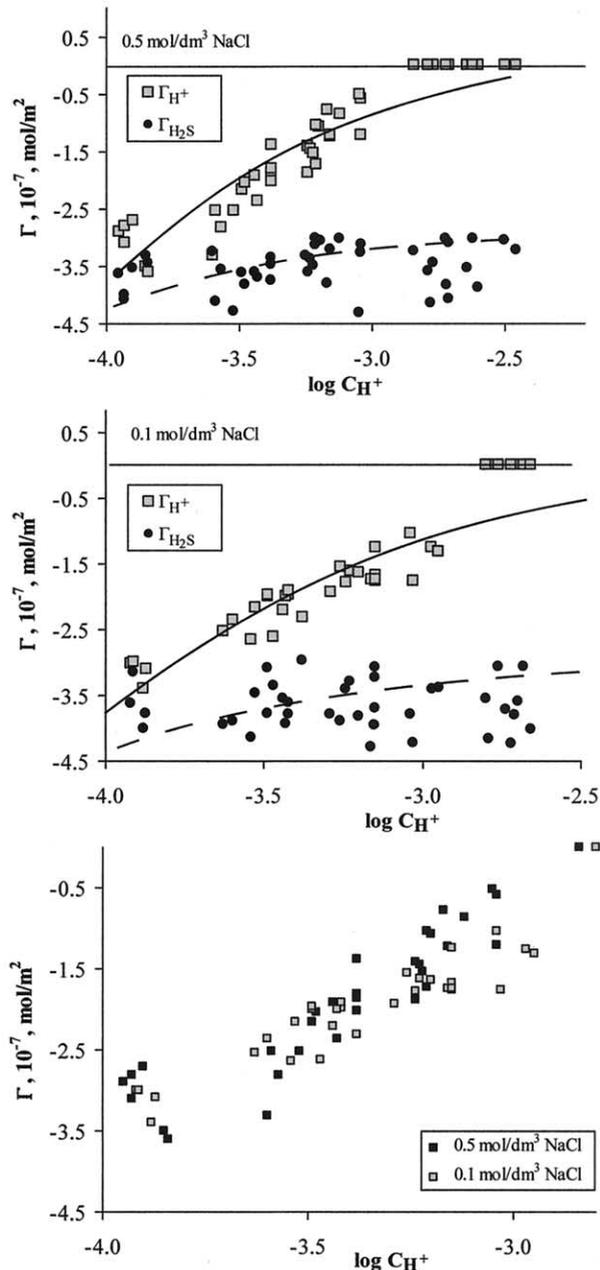


Fig. 3. Experimentally determined concentrations of adsorbed hydrogen sulfide and proton on the surface of crystalline sulfur at 50°C vs. total proton concentration (free H⁺) in H₂S-bearing solutions of ionic strength (NaCl) 0.1 and 0.5. $\Gamma_{\text{H}_2\text{S}}$ is the hydrogen sulfide adsorption in mol/m², Γ_{H^+} is the proton adsorption in mol/m², and C_{H^+} is the free concentration of proton in mol/L. Solid and dashed lines represent the predictions of Model B (see text) for Γ_{H^+} and $\Gamma_{\text{H}_2\text{S}}$, respectively.

tively, C_{H^+} is the proton concentration, C_{OH^-} is the OH⁻ concentration, V is the solution volume (15 mL), m is the mass of the sulfur aliquot (~5 g), and S is the specific surface area of sulfur (1 m²/g), which was determined using the BET argon adsorption method. Although values of $[C_{\text{OH}^-}^{\text{total}} - C_{\text{OH}^-}^{\text{free}}]$ were calculated for each experiment, in most cases they were insignificant. As is evident from Figures 2 to 4 and Tables 1 to 3, most of the Γ_{H^+} values obtained were negative, which means

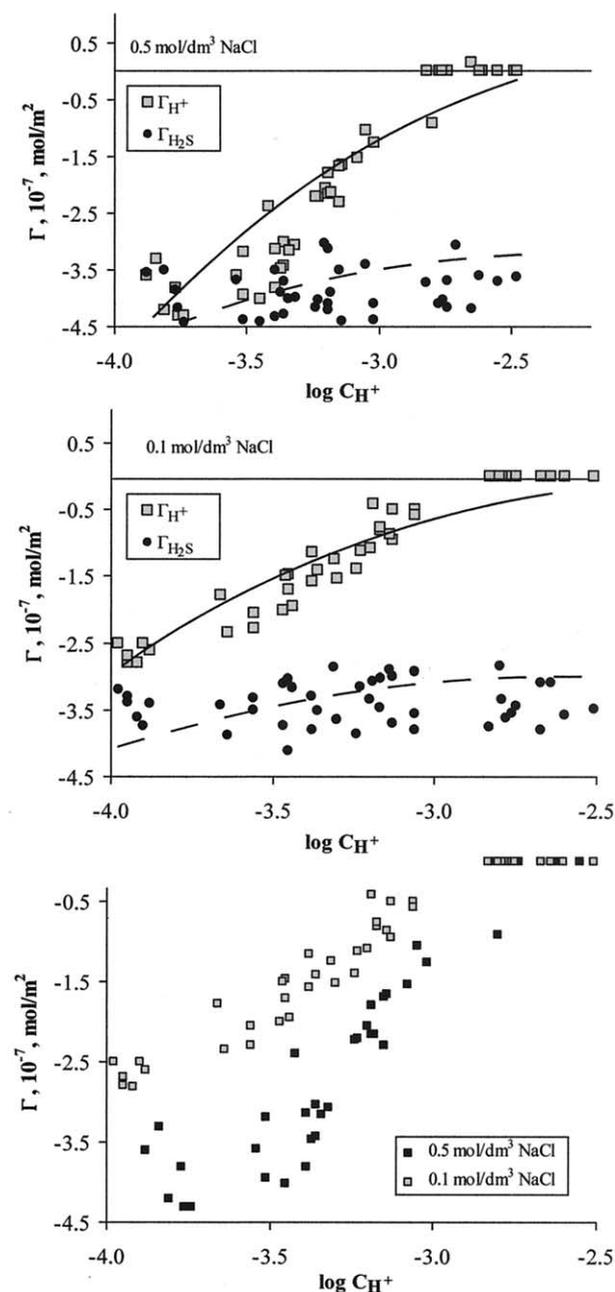


Fig. 4. Experimentally determined concentrations of adsorbed hydrogen sulfide and proton on the surface of crystalline sulfur at 70°C vs. total proton concentration (free H^+) in H_2S -bearing solutions of ionic strength (NaCl) 0.1 and 0.5. Γ_{H_2S} is the hydrogen sulfide adsorption in mol/m^2 , Γ_H^+ is the proton adsorption in mol/m^2 , and C_H^+ is the free concentration of proton in mol/L . Solid and dashed lines represent the predictions of Model B (see text) for Γ_H^+ and Γ_{H_2S} , respectively.

that deprotonation dominated on the sulfur surface (Figs. 2–4; Tables 1–3). It should be noted, however, that reliability of the Γ_H^+ determinations decreases progressively with increasing C_H^+ . At low values of C_H^{+free} ($\log C_H^{+free} < -3.5$), the difference between C_H^{+total} and C_H^{+free} commonly reaches one order of magnitude and Γ_H^+ can be determined to an accuracy of $< 1\%$. By contrast, at $-3.5 < \log C_H^{+free} < -3.2$, an accuracy of one

decimal place for the $\log C_H^+$ values is required to yield Γ_H^+ values that are accurate to the first decimal place and at $\log C_H^{+free} > -3.0$, the measurements of C_H^+ must be accurate to two decimal places to maintain the same accuracy for Γ_H^+ values. Thus, while the calculated values of Γ_H^+ never exceeded $4 \cdot 10^{-7} \text{ mol}/\text{m}^2$, the error in Γ_H^+ varied from $\pm 10^{-10}$ at $\log C_H^{+free} = -3.5$, to $\pm 10^{-8}$ at $\log C_H^{+free} = -3.0$. At proton concentrations $> 1.6 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ($\log C_H^{+free} > -2.7$), proton adsorption on the surface of sulfur could not be detected, and the results of these runs were not analyzed.

The H_2S concentrations ($C_{\Sigma H_2S} = C_{H_2S, aq} + C_{HS^-}$) and H_2S adsorption values ($\Gamma_{H_2S} \text{ mol} \cdot \text{m}^{-2}$) were calculated from the sulfide electrode measurements and the results of iodometric titration using the following relationship:

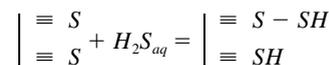
$$\Gamma_{H_2S} = \frac{(C_{H_2S}^{total} - C_{H_2S}^{free}) \cdot V}{m \cdot S} \quad (10)$$

where, as for Γ_H^+ , the indices *total* and *free* refer to the states before and after addition of the 5 g aliquot of dispersed sulfur, C_{H_2S} is the H_2S concentration ($\text{mol} \cdot \text{dm}^{-3}$), and V , S , and m are as defined above. It is interesting to note that for all three temperatures investigated, average values of Γ_{H_2S} were close to the highest values determined for Γ_H^+ (Tables 1–3; Figs. 2–4). The difference between the values of $C_{H_2S}^{free}$ and $C_{H_2S}^{total}$, due to adsorption of H_2S on the surface of the dispersed sulfur, varied from 9 to 11%, and assuming that these concentrations were determined to an accuracy of $\pm 2\%$ (Szekeeres, 1974), the corresponding error in the determination of Γ_{H_2S} was $\pm 25\%$.

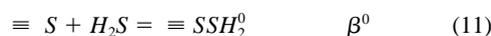
3. DISCUSSION

3.1. Complexation on the Sulfur Surface

The similarity of the highest values of Γ_H^+ to the average value of Γ_{H_2S} , combined with the absence of detectable proton adsorption in H_2S -free solutions, suggests that proton adsorption/desorption on sulfur surfaces occurs through protonation and deprotonation of $\equiv S - H_2S$ complexes:

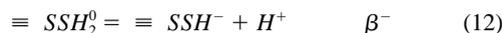


or



where β^0 is the equilibrium constant of the reaction. We suggest that this reaction forms chemical bonds, similar to those of polysulfane molecules.

The process of deprotonation of the $\equiv SSH_2^0$ complex can be described by the reaction:



The value of β^- was obtained by fitting the experimental data as a function of surface charge. This yielded an intrinsic constant, i.e., β^- , calculated for the conditions of the uncharged surface, the negative logarithm of the equilibrium constant of which is effectively equivalent to $\text{p}K_1(H_2S_{aq})$. If our assumption about the formation and deprotonation of $\equiv SSH_2^0$ are correct, then it is also reasonable to suggest that in acidic

solutions ($-\log C_H^+ < 2.7$) this complex participates in proton adsorption via the reaction:

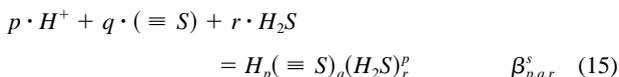


Unfortunately, the lack of experimental data in this C_H^+ range does not permit us to confirm this hypothesis.

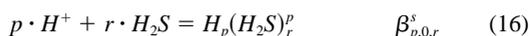
3.2. Data Treatment

As was discussed above, H^+ , $\equiv S$, and H_2S are interpreted to be the main components involved in the reactions in our system. Dissolved sulfur species, as well as surface complexes, were represented as products of reactions between the main components. Owing to the fact that H^+ and H_2S were determined directly during the experiments, only the concentration of $\equiv S$ needs to be estimated. The latter was accomplished by assuming that the sulfur structure is dominated by S_8 rings and that surface adsorption centers form due to the rupture of covalent sulfur-sulfur bonds. The following five molecular parameters of α - S_8 were used in this estimation: a space group of Fddd, an S-S bond length of 2.046 to 2.052 Å, bond angles of 107.3 to 109°, and a torsional angle of 98.5° (Encyclopedia of Inorganic Chemistry, 1994). The calculations were made for a spherical surface of an idealized sulfur particle and showed that $\equiv S$ concentrations ranged from $4.5 \cdot 10^{-3}$ to $6 \cdot 10^{-3}$ mol/L, representing a density of one adsorption center per 5 to 7 Å².

Each equilibrium reaction in the system investigated was described by the general equation:



The associated reactions in the solution were represented as follows:



Dissociation constants used to describe the solution equilibria were calculated from the model of Kestin et al. (1984) of pK_w and the data compiled by Johnson et al. (1992). Activity coefficients of aqueous species were calculated using the extended Debye-Huckel Eqn. 4 and the Setchenow Eqn. 6.

The term $\beta_{p,q,r}^{s,a,r}$ of Eqn. 15 refers to "apparent" constants, which must be corrected for the electrostatic energy of the charged surface to obtain the corresponding intrinsic constants:

$$\beta_{p,q,r}^{s,(inf)} = \beta_{p,q,r}^s \cdot \exp(pF\psi/RT) \quad (17)$$

where ψ is the surface potential at the plane of adsorption, R is the Gas constant, and F is the Faraday constant. Values of $\beta_{p,q,r}^{s,a,r}$ and $\beta_{p,0,r}^{s,a,r}$ were obtained by solving mass-action Eqn. 18 to 20 in which total concentrations (mol dm⁻³) of H^+ , $\equiv S$, and H_2S are represented by H , S , and C , respectively, and $h = [H^+]$, $s = [\equiv S]$, and $c = [H_2S]$.

$$H = h - K_w \cdot h^{-1} + \sum p \cdot \beta_{p,q,r}^{s,a,r} \cdot \exp(-p \cdot F \cdot \psi/RT) \cdot h^p \cdot s^q \cdot c^r + \sum p \cdot \beta_{p,0,r}^{s,a,r} \cdot h^p \cdot c^r \quad (18)$$

$$S = s + \sum q \cdot \beta_{p,q,r}^{s,a,r} \cdot \exp(-p \cdot F \cdot \psi/RT) \cdot h^p \cdot s^q \cdot c^r \quad (19)$$

$$C = c + \sum r \cdot \beta_{p,q,r}^{s,a,r} \cdot \exp(-p \cdot F \cdot \psi/RT) \cdot h^p \cdot s^q \cdot c^r + \sum r \cdot \beta_{p,0,r}^{s,a,r} \cdot h^p \cdot c^r \quad (20)$$

The surface charge (mol dm⁻³) is obtained from Eqn. 21:

$$\Gamma_\sigma = \sum p \cdot \beta_{p,q,r}^{s,a,r} \cdot \exp(-p \cdot F \cdot \psi/RT) \cdot h^p \cdot s^q \cdot c^r \quad (21)$$

or in electrostatic quantities (C m⁻²):

$$\sigma = \Gamma_\sigma \cdot F/A \cdot a \quad (22)$$

where F is the Faraday constant, A is the specific surface area (m² g⁻¹), and a is the concentration of solid (g dm⁻³). The surface potential ψ was related to the surface charge density (σ) using the Constant Capacitance model:

$$\sigma = \kappa \cdot \psi \quad (23)$$

where κ is the specific capacitance (C V⁻¹ m⁻²).

The stoichiometric compositions and corresponding equilibrium constants for the reactions at the sulfur-solution interface were evaluated with the aid of the FITEQL code, Version 3.1 (Herbelin and Westall, 1994), which was modified to permit calculations at 50 and 70°C. Evaluation of the equilibrium model involved minimization of the errors in the mass balances for H^+ (Y_H) and H_2S (Y_C):

$$Y_H = H_{calc} - H_{exp} \quad (24)$$

$$Y_C = C_{calc} - C_{exp} \quad (25)$$

$$Y = Y_H | Y_C \quad (26)$$

where H_{calc} and C_{calc} are the total proton and hydrogen sulfide concentrations calculated according to Eqn. 18 and 20, respectively, H_{exp} and C_{exp} are the corresponding experimentally known total concentrations, and Y is the total error sum. In FITEQL, the weighted error sum of Y over all m titration points, SOS, is minimized:

$$SOS = \sum_{Y^m} (Y/\sigma)^2 \quad (27)$$

The term Y^m symbolizes the summation overall data points and overall components for which both the free concentration (h , c) and the total concentration (H , C) are known. The quality of the fit obtained was evaluated from the overall variance in Y , $V(Y)$:

$$V(Y) = \frac{SOS}{n_p \cdot n_{II} - n_u} \quad (28)$$

where n_p denotes the number of titration points, n_{II} is the number of components for which both the total and the free concentrations are known, and n_u is the number of adjustable parameters (equilibrium constants). The details of the data treatment are given in Table 4.

Two models of surface complexation were tested. These comprised formation of a single complex, $\equiv SSH^-$ (model A), and two complexes, $\equiv SSH^-$ and $\equiv SSH_2^0$ (model B). Although both models provided reasonably good fits to the experimental data, the fit using model B is superior (Table 4). We therefore concluded that our experimental data are best explained by model B:

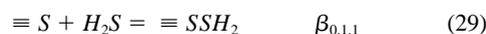
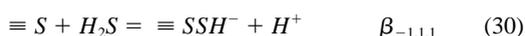


Table 4. Optimized formation constants (β) for sulfur surface complexes. The goodness of fit is given by the value of $V(Y)$. Model A represents formation of a single complex, $\equiv SSH^-$. Model B represents formation of $\equiv SSH^-$ and $\equiv SSH_2^0$ complexes. I is the ionic strength and κ is the specific capacitance ($C\ V^{-1}\ m^{-2}$).

I T°C	0.5 25	0.1 25	0.5 50	0.1 50	0.5 70	0.1 70
Parameter	Model A					
κ	0.8	0.2	0.3	0.3	0.2	0.2
Log $\beta_{-1,1,1}^{in}$	-1.69	-1.22	-1.39	-1.64	-0.08	-1.21
$V(Y)$	2.89	2.78	3.18	3.39	3.72	2.91
	Model B					
κ	1.3	0.5	0.5	0.4	0.8	0.4
Log $\beta_{0,1,1}$	0.93	0.64	0.91	1.02	1.04	1.03
Log $\beta_{-1,1,1}^{in}$	-1.98	-2.33	-1.93	-1.84	-1.82	-2.00
$V(Y)$	1.53	1.78	1.87	0.63	2.69	0.86



As can be seen from Table 4, there are no regular changes in the values of the formation constants with temperature or ionic strength ($\beta_{-1,1,1}$ and $\beta_{0,1,1}$). Taking into account the errors in the determination of these constants, we conclude that the values obtained are statistically indistinguishable. Errors for the constants were calculated from the uncertainties in proton and H_2S adsorption values, and the estimates of $\equiv S$ concentrations. Owing to the fact that the reported errors for Γ_{H_2S} and the concentrations of $\equiv S$ are ~ 25 to 30% and $\sim 15\%$, respectively, the uncertainties in the values of $\log \beta_{0,1,1}$ are ± 0.23 . Errors for Γ_H^+ increase appreciably with increasing proton concentration. Based on calculations for a range of Γ_H^+ , we estimated the error for $\beta_{-1,1,1}$ as ± 0.14 . The model predictions are compared with the experimental data in Figures 2, 3, and 4.

The dissociation constant for the surface complex $\equiv SSH_2^0$ (Eqn. 12) was calculated at different ionic strengths from the values of $\beta_{-1,1,1}(I)$ and $\beta_{0,1,1}(I)$ (Table 5):

$$\log \beta^-(I) = \log \beta_{-1,1,1}(I) - \log \beta_{0,1,1}(I) \quad (31)$$

The value of $\beta_{0,1,1}$ was taken as β^0 (Eqn. 11). Owing to the fact that the $\equiv S$ complex does not participate in Eqn. 12, the value of $\beta^-(I)$ is independent of adsorption center density. The changes in the concentrations of $\equiv S$ resulted in corresponding changes of $\beta_{-1,1,1}$ and $\beta_{0,1,1}$ values, while $\beta^-(I)$ remained constant. The values of $\beta^-(I)$ were found to be independent of

Table 5. A proposed model for the surface complexation of H_2S on elemental sulfur. I is the ionic strength, and $\log \beta_{0,1,1}$, $\log \beta_{-1,1,1}^{in}$, and $\log \beta^-$ are formation constants for the reactions (30), (31), and (12), respectively.

I	T°C	Log $\beta_{0,1,1}$	Log $\beta_{-1,1,1}^{in}$	Log β^-
0.5	25	0.93	-1.98	-2.91
0.1	25	0.64	-2.33	-2.97
0.5	50	0.91	-1.93	-2.84
0.1	50	1.02	-1.84	-2.97
0.5	70	1.04	-1.82	-2.86
0.1	70	1.03	-2.00	-3.03

Table 6. Dissociation constants for polysulfanes at 25, 50 and 70°C.

		25°C	50°C	70°C
	1/n		pK ₁	
H_2S	1	7.05	6.7	6.56
H_2S_2	0.5	4.93	4.79	4.72
H_2S_4	0.25	3.92	—	—
H_2S_5	0.2	3.58	—	—
$H_2S_\infty^{[1]}$	0	2.9	2.8	2.9
	1/n		pK ₂	
H_2S_2	0.5	10.06	9.19	8.68
H_2S_4	0.25	6.66	—	—
H_2S_5	0.2	6.02	—	—
H_2S_∞	0	2.8 ^[2]	2.8	2.9
$H_2S^{[3]}$		17.40	15.7	14.5

^[1] Experimental data.

^[2] Refined by linear extrapolation of the pK₁ values for the other polysulfanes.

^[3] Estimated by linear extrapolation of the pK₂ values for the other polysulfanes.

ionic strength and averaged -2.9 , -2.8 , and -2.9 at 25, 50, and 70°C, respectively.

The value of $\log \beta^-$ is thus also independent of temperature within an error of ± 0.23 log units. This confirms an earlier conclusion (Migdisov, 1993) based on the extrapolation of pK₁ values of polysulfanes at 25, 50, and 70°C. However, we must caution that this apparent temperature independence of β^- means only that differences among the values of β^- at the different temperatures are within experimental and estimation errors. It should also be noted that the conclusion about the temperature independence of $\log \beta$ applies only to the range of temperatures investigated.

3.3. Estimation of pK Values

When we suggested earlier that $-\log \beta^-$ at $I = 0$ is effectively the same as pK₁(H_2S_∞), we noted that for this to be true its value must be linearly dependent on the reciprocal chain length. We also pointed out that this linear fit could be used to correct the experimentally determined values of pK₁(H_2S_∞) and optimize the theoretical value of pK₁(H_2S_∞), thereby reducing experimental error. To refine the sulfur deprotonation constant ($\log \beta^-$), we extrapolated the available pK₁ values vs. reciprocal chain length. We included in the set of analyzed data the value of $-\log \beta^-$ calculated for $I = 0$ (pK₁(H_2S_∞)), pK₁(H_2S_2), obtained in the earlier study of Migdisov (1993), the values of pK₁²⁹⁸ obtained from the data of Schwartzbach and Fisher (1960) for H_2S_4 and H_2S_5 , and the first dissociation constant for hydrogen sulfide (Barbero et al., 1982) (Table 6). A least squares regression for the available experimental pK₁²⁹⁸ values yields a refined value of pK₁²⁹⁸(H_2S_∞) of 2.9 at 25°C. By comparison, Schoonen and Barnes (1988) obtained a value for pK₁²⁹⁸(H_2S_∞) of 2.78. The same extrapolation was performed for the data obtained at 50 and 70°C. Unfortunately, there are few data available for elevated temperatures, and the least squares regression fits for 50 and 70°C were limited to the values of pK₁³²³³⁴³(H_2S) (Johnson et al., 1992), pK₁³²³³⁴³(H_2S_2)

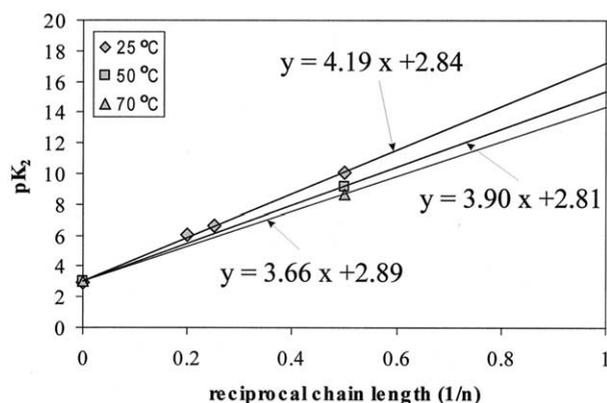


Fig. 5. Calculated (this study) and previously reported values for the second dissociation constant (pK_2) of several polysulfanes vs. reciprocal chain length ($1/n$) and estimates of these values for H_2S and H_2S_∞ at 25, 50, and 70°C. The data for H_2S_4 and H_2S_5 are those of Schwartzbach and Fisher (1960), while the values for H_2S_2 were calculated from the data of Giggenbach (1974) for the stability of S_n^{2-} ions in aqueous solutions, and Gibbs free energy and pK_1 values for $H_2S_2^{aq}$ determined by Migdisov (1993).

(Migdisov, 1993), and $pK_1^{298}(H_2S_\infty)$ (this study). These regressions yield $pK_1(H_2S_\infty)$ corrected values of 2.7 and 2.9 at 50 and 70°C, respectively.

To estimate the value of pK_2^{298} for H_2S , we repeated the extrapolation performed earlier by Schoonen and Barnes (1988). However, the set of analyzed pK_2 values was expanded to include values of $pK_2^{298}(H_2S_2)$ and $pK_2^{298}(H_2S_\infty)$. The latter value was taken to be equal to $pK_1^{298}(H_2S_\infty)$ on the assumption that at infinite chain length pK_1 and pK_2 are indistinguishable (Schoonen and Barnes, 1988). Values of $pK_2(H_2S_2)$ were calculated for 25, 50, and 70°C from the data of Giggenbach (1974) for the stability of S_n^{2-} ions in aqueous solutions and values of Gibbs free energy and pK_1 determined for $H_2S_2^{aq}$ by Migdisov (1993). Extrapolation of these data yielded a value of 17.4 ± 0.3 for the second dissociation constant of hydrogen sulfide at 25°C (Fig. 5). This value differs significantly from that estimated by Schoonen and Barnes (1988) at 18.51 ± 0.56 but is in very good agreement with the experimentally determined values of Giggenbach (1971) at 17.0 ± 0.1 , Meyer et al. (1983) at 17 ± 1 , Licht and Manassen (1987) at 17.6 ± 0.3 , and Licht et al. (1990) at 17.1 ± 0.3 . We therefore conclude that, given an adequate data set, the extrapolation method proposed by Schoonen and Barnes (1988) can be used successfully to estimate pK_2 for H_2S .

The same approach was used to estimate the values of $pK_2(H_2S)$ at 50 and 70°C. Unfortunately, published data on the temperature dependence of the thermodynamic properties for polysulfanes in aqueous solutions are limited to those of Giggenbach (1974) and Migdisov (1993). There are no experimental data available on the temperature dependence of pK_2 for polysulfanes, except H_2S_2 , and even for H_2S_2 , the value of the second dissociation constant has not been measured directly at elevated temperatures. To obtain values at 50 and 70°C, we combined data on S_2^{2-} stability (Giggenbach, 1974) and our values for $H_2S_2^{aq}$ Gibbs free energy and pK_1 . Thus, the $1/n$ -extrapolations for 50 and 70°C were based on two points only, namely, $pK_1(H_2S_2)$ and $pK_1(H_2S_\infty)$. These extrapolations give

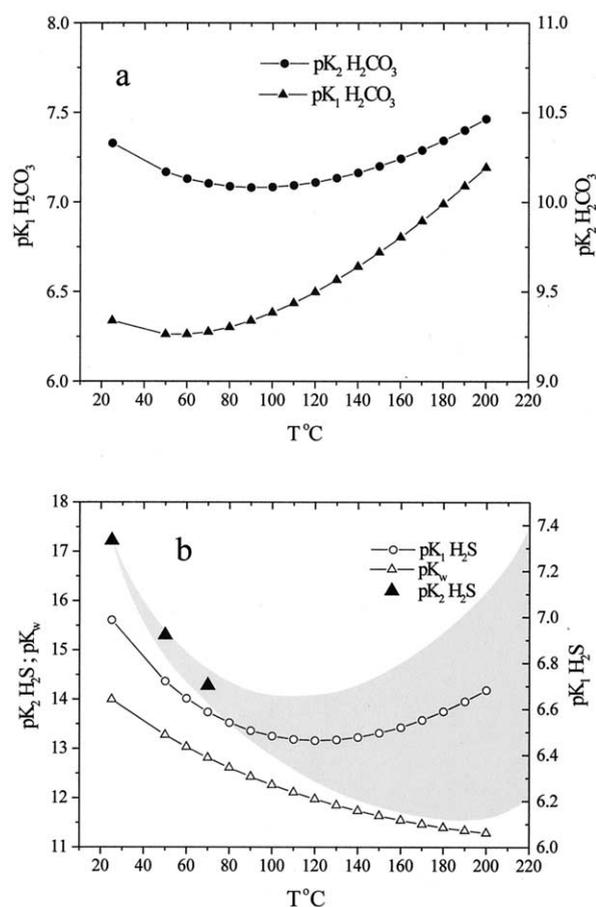


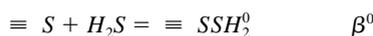
Fig. 6. (a) Calculated values for the first and second dissociation constant (pK_1 and pK_2) for H_2CO_3 vs. temperature. The data were derived from the standard thermodynamic properties of H_2CO_3 and HCO_3^- recommended by Johnson et al. (1992). (b) Values of pK_1 for H_2S vs. temperature calculated from Johnson et al. (1992). Also shown are values for the ionization constant of water (pK_w) from Kestin et al. (1984) and the values of pK_2 for H_2S derived in this study. The shaded field indicates the possible range of pK_2 values for H_2S .

values of $pK_2(H_2S)$ of 15.7 and 14.5 at 50 and 70°C, respectively (Table 6), but because of the limitations of two-point extrapolations, these values may be accurate to no better than one log unit. Unfortunately, quantitative information on pK_2 for hydrogen sulfide could not be obtained at elevated temperatures because of the lack of information on pK_1 and pK_2 for polysulfanes at temperatures $> 70^\circ C$. However, some rough extrapolations can be made to estimate the behaviour of S^{2-} ion at elevated temperatures. For example, by extrapolating the experimentally obtained pK_2 values from 20 to 25°C and noting that the temperature dependence of the dissociation constant of most weak acids is very similar, Schoonen and Barnes (1988) suggested to a first approximation that the temperature dependence of pK_2 is the same as that of the first dissociation step. Although valid for short-range extrapolations, this assumption cannot be used for long-range extrapolations, e.g., from 70 to 200°C, because the error is likely to be on the order of several log units, judging by the data for H_2CO_3 (Fig. 6a). Thus, while we cannot quantitatively extrapolate our data to higher temperatures, we can assume that as the temper-

ature dependence of pK_1 and pK_2 for H_2S are likely to be similar and pK_1 has a minimum at 125°C, pK_2 will have a minimum at temperatures between 100 and 200°C. This assumption permits us to roughly compare the values of pK_2 for hydrogen sulfide with the ionisation constant of water (pK_w) and conclude with a relatively high level of confidence that at temperatures up to 200°C, pK_2 values are above those of pK_w (Fig. 6b). This, in turn, supports the hypothesis that the S^{2-} complex is never dominant over the range of pH values found in nature.

4. CONCLUSIONS

Our experimental data indicate that in H_2S -bearing solutions, the adsorption of hydrogen sulfide on the surface of crystalline sulfur occurs via sulfidation, a process similar to that of hydroxylation on oxide surfaces (Schindler and Gamsjaeger, 1972; Schindler and Stumm, 1987), i.e.,



The process of deprotonation of the SSH_2^0 complex can be described by the reaction:



for which the value of the dissociation constant ($\log \beta^-$) is estimated to be -2.8 ± 0.23 and is independent of temperature over the interval 25 to 70°C.

The value of the second dissociation constant for hydrogen sulfide is estimated to be 17.4 ± 0.3 at 25°C and is indistinguishable from the values determined experimentally by Giggenbach (1971) at 17 ± 0.1 , Meyer et al. (1983) at 17 ± 1 , Licht and Manassen (1987) at 17.6 ± 0.3 , and Licht et al. (1990) at 17.1 ± 0.3 . This proves not only the effectiveness of the method proposed by Schoonen and Barnes (1988) but also the similar physico-chemical nature of aqueous polysulfanes and sulfur surface complexes.

Values of pK_2 estimated for 50 and 70°C (15.7 and 14.5, respectively), suggest that the S^{2-} species is never dominant over the range of pH values found in nature.

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