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Article *in* Geochimica et Cosmochimica Acta · August 1998

DOI: 10.1016/S0016-7037(98)00188-4

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Geochimica et Cosmochimica Acta, Vol. 62, No. 15, pp. 2627–2635, 1998
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0016-7037/98 $19.00 + .00

PII S0016-7037(98)00188-4

Experimental study of polysulfane stability in gaseous hydrogen sulfide

ART. A. MIGDISOV,*,[1] O. M. SULEIMENOV,[2] and YU V. ALEKHIN[3]

[1]Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec H3A 2A7, Canada
[2]Institut für Mineralogie und Petrographie, ETH-Zentrum, CH-8092 Zürich, Switzerland
[3]Moscow State University, Geological Faculty, Department of Geochemistry, Vorobievi Gori, 119899 Moscow, Russia

(*Received October* 23, 1997; *accepted in revised form May* 11, 1998)

Abstract—The solubility of sulfur in gaseous hydrogen sulfide has been studied in the H_2S-S system. Experiments were carried out at temperatures between 50 and 290°C and pressures up to 200 bars. The experimentally determined concentrations of sulfur in the gas phase are 6–7 orders of magnitude higher than the corresponding concentrations calculated for a system free of hydrogen sulfide. The results of experiments show significant interaction between S and H_2S. These interactions can be of two kind: solvation by hydrogen sulfide (solubility), as with formation of new stable gaseous chemical compounds, like polysulfanes (chemical reaction). The data obtained can be reasonably well described by the formation of a $H_2S \cdot S$ compound. Thermodynamic parameters for polysulfanes and equilibrium compositions of the S-H_2S system have been calculated ab initio for the experimental conditions. At temperatures above 170°C, results (of calculations) are in good agreement with experimental data, although the difference between the calculated and experimental mole fraction of the sulfur in the gas phase reaches 2 orders of magnitude at 125–170°C. It is theorized that sulfur solubility in gaseous H_2S is related to two main chemical reactions, dominated in the different temperature ranges: sulfur solvation by H_2S (125–170°C) and polysulfane formation (200–290°C). *Copyright © 1998 Elsevier Science Ltd*

1. INTRODUCTION

The formation of ore deposits is a complicated process which involves complex interactions among all aggregate states of matter: gas, liquid, and solid. Recently collected data indicates that the transport in the gas phase can play an important role in understanding physicochemical processes responsible for ore formation (Nieva et al., 1997; Fein and Williams-Jones, 1997; Heinrich et al., 1996; Puddephatt et al., 1989). Typical examples of such systems include fumarole exhalation and sublimation at active volcanoes and geothermal fields. Chemical analysis of precipitated sublimates at Besymyannyi volcano (Kamchatka, eruptions 1955–1963) reveals the gas transport of S, Na, K, and Mg at temperatures of 90–380°C. It is of interest to note that maximum precipitation from fumaroles took place at 200°C (Gorshkov and Bogoyavlenskaya, 1966). Fumaroles of Kudryavyi Volcano (Kuril Islands) show active transport of the chalcophile metals in the gas phase at temperatures of 100–900°C and precipitation of metals in the form of sulfides and chlorides (Taran et al., 1995). Also, it has been determined that the gas phase of the Uzon caldera hydrothermal system contains up to 1 vol% of zero-valence sulfur (S°) at 100°C (Bychkov et al., 1995). In all of the above cases, the transport media was a water vapor and a gas phase with a CO_2 content of up to 90% and H_2S content of up to 6% (calculated for dry gas). The contribution of vapor and gas transport to the shallow mineralization of As, Sb, and Hg has been suggested by numerous authors (White et al., 1971; White, 1981; Smith et al., 1987; Spycher and Reed, 1989). These studies modelled gas phase transport in hydrothermal systems by using component fugacities or solubility in water vapor. However, we assume that hydrogen sulfide in the gas phase can also be an important transport medium for sulfur and chalcophile components of hydrothermal fluids.

It is well known that sulfur compounds, as well as elemental sulfur, form long chain molecules. All these substances can be regarded as derivatives of hydrogen polysulfides (polysulfanes) H_2S_n. The presence of both native sulfur and hydrogen sulfide is a feature common to geothermal systems (Sverjensky, 1989; Brand et al., 1989; Bedell and Hammond, 1988; Hannington and Scott, 1988; Boulegue and Michard, 1973; Cloke, 1963). Recent investigations of such systems show significant concentrations of sulfur species in intermediate valence states (e.g., thiosulfate, sulfite, and polysulfanes) in fluids (Keller et al., 1995; Eberhard et al., 1995; Veldeman et al., 1991; Bedell and Hammond, 1988; Boulegue and Michard, 1973; Cloke, 1963). One of the most plausible explanations for this could be the rather slow rate of the redox reactions between the sulfur species at temperatures below 250°C. (Benning and Seward, 1996; Adema and Heeres, 1995; Botha et al., 1994; Rafalskii et al., 1983; Malinin and Khitarov, 1969). The types of intermediate sulfur species are dependent on the overall oxidation state of the system with thiosulfate, sulfite, and polythionates being found in weakly reducing conditions and polysulfanes and polysulfides in more reducing environments. The possible importance of polysulfanes for sulfur mass balance has been noted in several publications. For example, in seawater systems (Neretin et al., 1996; Lei et al., 1995; Boulegue and Michard, 1973) and in hydrothermal environments (Migdisov and Bychkov, 1998; Cloke, 1963). In a number of studies, the thermodynamic description of polysulfane behavior was proposed (Migdisov and Bychkov, 1998; Boulegue and Michard, 1973; Cloke, 1963). However, the thermodynamic data used in these papers were obtained on the basis of various kinds of extrapolations and were only partly confirmed by direct experimental mea-

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*Author to whom correspondence should be addressed (artas@geosci.lan.mcgill.ca).

surements. Experimental studies have examined polysulfane liquids, and in several cases, aqueous solution species. In the gas phase, only standard enthalpies of formation and heat capacities (25°C) for gaseous low polysulfane homologes (up to H_2S_5) have been measured (Féher and Winkhaus, 1957; Féher and Schulze-Rettmer, 1958).

There is an absence of experimental information is available on the temperature dependence of the heat capacities of polysulfanes, which precludes calculating the thermodynamic properties of those compounds at high temperatures. The necessary thermodynamic information could be obtained using the data calculated from solubility measurements of native sulfur in gaseous hydrogen sulfide. Published data on this subject are sparse and consist only of solubility measurements of sulfur in a variety of natural gases. Solubility in the CH_4-CO_2-H_2S-S system at pressures of up to 400 bar and temperatures of up to 121°C were reported by Kennedy and Wieland (1960). Roof (1971) investigated the solubility of sulfur in hydrogen sulfide at pressures up to 300 bar and temperatures up to 110°C, but the results differ considerably from those of Kennedy and Wieland (1960). The data, obtained by Brunner and Woll (1980) are in good agreement with those of Swift (1976) and Roof (1971) and differ from the results of Kennedy and Wieland (1960) by up to 1 log unit at 100–200 bar. All other studies were done at high pressure (up to 600–1400 bar), and it is not possible to extrapolate the values of sulfur solubility in the gas phase to hydrothermal conditions because of the lack of reliable experimental information.

In view of the fact that hydrogen sulfide is the important volatile component of hydrothermal fluids, it is logical to expect polysulfanes to be potentially significant constituents of a coexisting gas phase. However, up to the present it is not possible to formulate a quantitative description of such systems with reduced sulfur species. The aim of the present work was to obtain thermodynamic information on the polysulfane gases required for geochemical modeling at temperatures up to 300°C and pressures up to 200 bars.

2. EXPERIMENTAL METHOD

Experiments were carried out at temperatures between 50 and 290°C (Table 1). An electric oven equipped with a large steel box (for reducing temperature gradients) was used. Before the runs, the temperature gradient in the experimental setup was measured by three thermocouples. Thermocouples were located on the top, bottom, and in the center of the box. It was determined that the vertical temperature gradients were less than 1–2°C. For solubility runs, thin-walled titanium alloy VT-8 autoclaves (Fig. 1) were placed inside of the steel box, and a built-in thermal regulator was used to control temperature to an accuracy of approximately 1°C. During the run, temperature was measured with a chromel-alumel thermocouple and a mercury thermometer. The internal surface of each autoclave was initially conditioned with nitric acid. The autoclave was then charged with H_2S at 90–100 bar and placed in the oven for 1 week at 200°C to allow a protective layer of sulfides to form. The volume of the autoclave was determined from the difference between the weight of the autoclave filled with distilled water at 25°C and its empty weight. A typical volume was in the range 45–50 cm^3; a typical weight of sealed autoclave was 120–150 g.

The autoclave was loaded with a gold ampoule containing native rhombic sulfur (REAKHIM, O. S. Ch. grade, corresponding to 99. 998% purity). The ampoule was kinked at several points along its length to prevent uncontrolled sulfur transport during heating and cooling. Before each run, the autoclave was flushed with Ar for 50–80 min to remove atmospheric gases and then flushed with H_2S for 30 min. The H_2S gas was generated by one of the following reactions:

$$Al_2S_3 + 6 \cdot H_2O = 2 \cdot Al(OH)_3 + 3 \cdot H_2S$$

$$FeS + 2 \cdot HCl = FeCl_2 + H_2S$$

The hydrogen sulfide was purified by passing it through two gas-washing bottles with distilled water. The final H_2S purity was 99. 8% (measured by GC GasoChrom 3101). The purified hydrogen sulfide was then frozen out (1–4 g) in the autoclave at temperatures of between −68 and −74°C (mixture of dry ice and hexane). The amount of H_2S frozen in the autoclave was controlled in such a way that the formation of liquid H_2S was prevented at 50º C. The gas-phase volume was calculated taking into account the sulfur and gold volumes.

The amount of hydrogen sulfide in the autoclave was determined by weighing. Due to the extremely low vapor pressure of crystal (at 50°C) or liquid sulfur compared to the hydrogen sulfide pressure, the total pressure was assumed to be equal to the pressure of hydrogen sulfide. The total pressure in the system was calculated from the volume of the gas phase, the amount of hydrogen sulfide and the P-V-T properties of the hydrogen sulfide (Goodwin, 1983; Rau and Mathia, 1982). The low solubility of hydrogen sulfide in liquid sulfur at temperatures below 200°C (Fanelli, 1949), makes it unnecessary to correct for hydrogen sulfide dissolved in the liquid sulfur in the calculation of the total pressure.

After the run, the autoclave was cooled down to room temperature with compressed air. It was then weighed again to check for possible leaks. The autoclave was opened and the sulfur condensed on the walls was dissolved by introducing a large quantity of hexane. The dissolved sulfur was determined spectrophotometrically (Dadze and Sorokin, 1993) on a Hitachi-124 instrument using a 1-cm quartz cuvette. The absorbency was determined at a wavelength of 264 nm. Eight standard solutions with concentrations ranging between 20 mg/L and 0. 05 mg/L were used for the calibration. For some experiments the mass of sulfur dissolved into the gas phase was measured by weighing the gold ampoule before and after heating (analytical balance Mettler M3). The spectrophotometric data was reproduced within a 10–15% error. Due to hydrogen sulfide solubility in the sulfur melt such error was interpreted as a rather good agreement between two methods. The concentration of sulfur remaining in the gas after cooling was also checked in some of the runs using the method of cyanide titration of sulfur (Szekeres, 1974). The gas was dissolved in an aqueous solution of 0.01M KCN. The spectrophotometric data was reproduced within a 5% error. This technique permitted the total quantities of the dissolved native sulfur S° and that of the $H_2S \cdot S_n$ type compounds to be determined:

$$CN^- + S^o_{aq} = CNS^-$$

$$CN^- + H_2S \cdot S_n = n \cdot CNS^- + H_2S$$

3. RESULTS

An initial set of experiments was used to determine the time required to attain equilibrium at each temperature. The longest time required for equilibrium was twenty days (see Fig. 2). It was found that the amount of the sulfur transported out of the ampoule during one day was less than 10% of the equilibrium concentration of sulfur in the gas phase. As long as autoclave cooling and heating took less than 40 min, the concentration of the bulk-dissolved sulfur remained at the equilibrium value at the temperature of the experiment. The amount of sulfur in the gas phase is shown in Fig. 3 and summarized in Table 1. From Fig. 3 it can be seen that the amount of sulfur in the gas phase increases with increasing of H_2S amount in the system and

Table 1 Experimental results, where S is the amount of sulfur in the gas phase (mol), H_2S is moles of hydrogen sulfide in the runs, P_{H_2S} is the hydrogen sulfide pressure, $\log(X_S)^{gas}$ - dissolved sulfur mole fraction for gas phase, $\log(X_S)^{melt}$ is the sulfur mole fraction in the melt, $\log(X_{H_2S_2})^{gas}$ and $\log(X_{H_2S_3})^{gas}$ -is polysulfane mole fractions in the gas phase, calculated from low pressure experimental data for different sulfur mole fraction in the melt.

S, mol, $x10^{-4}$	H_2S, mol	P_{H_2S}, bar	Gas density kg m^{-3}	$\log(X_S)^{gas}$	$\log(X_{H_2S_2})^{gas}$	$\log(X_{H_2S_3})^{gas}$	$\log(X_S)^{melt}$
				290°C			
3.8	0.0409	47.80	34.202	-2.032			
1	0.0159	18.39	13.232	-2.201			
6	0.0662	77.56	56.264	-2.042			
				250°C			
4.93	0.0782	91.74	66.373	-2.200			
0.45	0.0109	12.51	9.138	-2.383			
2.02	0.0285	33.27	24.053	-2.150			
				200°C			
5.62	0.118	121.26	98.666	-2.324	-2.327	-2.415	-0.0877
5.91	0.115	118.18	97.648	-2.291	-2.325	-2.410	-0.0851
8.26	0.158	162.37	132.834	-2.284	-2.362	-2.483	-0.1218
1.01	0.0195	20.04	16.504	-2.288	-2.253	-2.267	-0.0133
8.45	0.172	176.75	143.900	-2.311	-2.374	-2.509	-0.1344
3.85	0.07	71.93	58.407	-2.262	-2.290	-2.340	-0.0498
3.64	0.0754	77.48	62.653	-2.318	-2.294	-2.348	-0.0539
				170°C			
16.91	0.2003	195.38	168.433	-2.077	-2.128	-2.256	-0.1282
13.63	0.161	154.96	135.869	-2.076	-2.098	-2.197	-0.0984
7.51	0.0779	74.98	64.843	-2.020	-2.045	-2.090	-0.0448
4.54	0.0489	47.06	40.756	-2.036	-2.027	-2.055	-0.0276
4.05	0.0472	45.43	39.567	-2.070	-2.027	-2.053	-0.0266
12.5	0.136	130.89	112.967	-2.040	-2.081	-2.163	-0.0816
8.31	0.0942	90.66	78.550	-2.057	-2.055	-2.110	-0.0548
				151°C			
1.92	0.014	12.89	11.705	-1.869	-1.844	-1.849	-0.0045
4.15	0.03	27.62	24.950	-1.865	-1.850	-1.860	-0.0098
0.773	0.0054	5	4.520	-1.850	-1.842	-1.843	-0.0017
2.49	0.0168	15.47	14.196	-1.835	-1.845	-1.851	-0.0055
11.41	0.0798	73.48	67.742	-1.851	-1.867	-1.893	-0.0266
18.2	0.132	121.55	112.077	-1.866	-1.885	-1.930	-0.0450
				125°C			
9.29	0.0521	45.07	43.534	-1.756	-1.751	-1.761	-0.0106
4.22	0.0231	19.98	19.267	-1.746	-1.745	-1.749	-0.0047
4.85	0.0268	23.18	22.429	-1.750	-1.745	-1.751	-0.0054
13.1	0.0714	61.76	60.466	-1.744	-1.755	-1.769	-0.0146
25.4	0.142	122.84	120.088	-1.755	-1.769	-1.799	-0.0296
				50°C			
0.0081	0.009118	7.88	7.731	-4.051			
0.0012	0.014706	12.71	12.288	-4.088			

decreases with increasing of temperature at temperatures above 115°C (above melting point of S; Fig. 4). The experimental results show a close-linear dependence between the amount of dissolved sulfur and the amount of hydrogen sulfide.

The intercept of each isotherm with the ordinates in Fig. 3 corresponds to the amount of sulfur that could be transported in a system free of hydrogen sulfide. This value was calculated using the gas-phase volume and partial pressures of sulfur polymers (S_1–S_8) from Glushko (1982) and Lenain et al. (1988). It was found to be less than 10^{-8} mol for all isotherms. In a set of blank experiments involving an atmosphere free of hydrogen sulfide (argon atmosphere), the amount of sulfur in the vapor phase was less than the detection limit of the analytical technique used. Consequently, it is evident that the experimentally determined amount of dissolved sulfur in H_2S is up to 5–6 orders of magnitude higher than the amount of sulfur calculated for a system free of hydrogen sulfide.

Due to absolute dominance of H_2S in the gas phase and the low partial pressure of sulfur vapor, the total pressure in the autoclave depended mainly on the amount of hydrogen sulfide. That means that the mole fraction of sulfur in the gas phase

$$\left(X_S = \frac{M_s}{M_{H_2S} + M_S} \cong \frac{M_S}{M_{H_2S}} \right)$$

where M is number of moles of the corresponding compound) is independent of the total pressure in the system. Comparison of our results for the solubility of sulfur in hydrogen sulfide, plotted vs. gas density, with measurements made by other authors at similar pressures shows good agreement with the values reported by Brunner and Woll (1980; Fig. 5a) and show similar trends at lower gas density. It is interesting to note that the trends in the data, plotted vs. hydrogen sulfide pressure (Fig. 5b), are vastly different. This dichotomy will be discussed later.

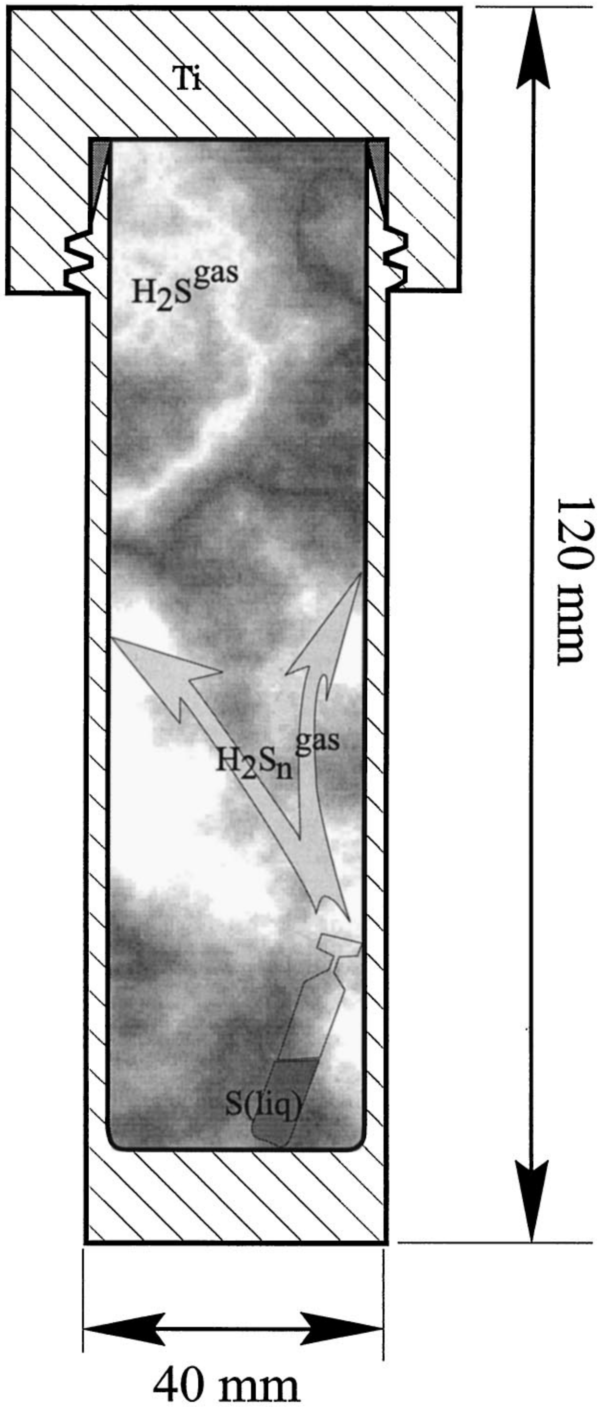

Fig. 1. A section through an autoclave made of a thin-walled titanium alloy VT-8.

4. DISCUSSION

The set of experimental points, obtained for each isotherm, can be described to a first approximation as an isochoric system at constant temperature. The fact that the sulfur mole fraction remains constant as H_2S increase can only be explained by the chemical interaction between S and H_2S in the gas phase.

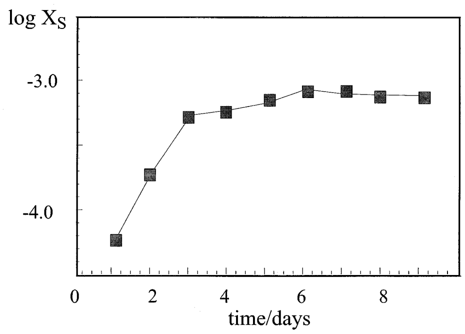

Fig. 2. Determination of the time required to attain equilibrium at 200°C. (the longest time required for equilibrium was twenty days for 50°C).

Possible interactions could be, initially, the sulfur solvation by hydrogen sulfide (solubility), and second, the formation of new stable gaseous chemical compounds, like polysulfanes (chemical reaction). However, the solvated complex can be described to a first approximation as a normal gaseous particle, characterized by the stoichiometry $(H_2S)_m \cdot S_n$ and standard properties of gaseous compounds, like partial pressure and fugacity. For the both cases (solubility and chemical reaction) this process can be expressed in the following form:

$$m \cdot H_2S^{gas} + n \cdot S^{liquid,crystal} = (H_2S)_m S_n^{gas} \quad (1)$$

The equilibrium constant of reaction 1 can be expressed as

$$\ln K = \ln f_{(H_2S)_m S_n} - n \cdot \ln a_S - m \cdot \ln f_{H_2S} \quad (2)$$

where $f_{(H_2S)_m S_n}$ is the polysulfane (or solvated complex) fugacity, a_S the activity of the sulfur in the melt, and f_{H_2S}, the hydrogen sulfide fugacity.

Hydrogen sulfide can be dissolved in the sulfur melt, and, therefore, in the range of sulfur-melt stability, the activity of the sulfur in the melt is not a constant value but is dependent on the hydrogen sulfide pressure. The data of Fanelli (1949) can be used to calculate the hydrogen sulfide solubility in the sulfur melt. However, some difficulties occur in the calculation of the sulfur mole fraction (or activity) in the melt due to the unknown

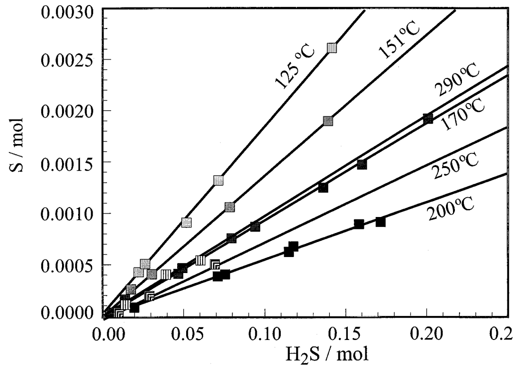

Fig. 3. The amounts of sulfur transported by H_2S in autoclave volume. The intercept of each isotherm with the ordinates corresponds to the amount of sulfur that could be transported in a system free of hydrogen sulfide.

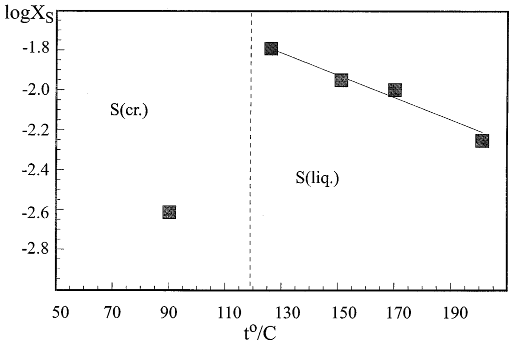

Fig. 4. Sulfur mole fraction in H_2S^{gas} plotted against temperature with stability fields of liquid and solid sulfur.

stoichiometry of the dissolved forms of hydrogen sulfide. Thus, the activity of sulfur in the melt can be calculated only as a first approximation, proceeding from the assumption that interaction between hydrogen sulfide and sulfur does not significantly change the mole fraction of sulfur in the melt. Therefore, the activity of native sulfur is assumed to be equal its mole fraction.

Also, in real gas systems, the sulfur solubility will be complicated by the nonideal behavior of the components and the gas solution. To a first approximation it can be assumed that the fugacity coefficients of the components in a gas solution do not differ greatly from unity.

Using Eqn. 2 and assuming ideality,

$$\ln K = \ln (P_{H_2S} \cdot X_{(H_2S)_mS_n}) - n \cdot \ln X_S^{melt} - m \cdot \ln P_{H_2S} \quad (3)$$

where P_{H_2S} is the hydrogen sulfide pressure, $X_{(H_2S)_mS_n}$ is the polysulfane (or solvated complex) mole fraction, and X_S^{melt} is the sulfur mole fraction in the melt. It is then possible to determine the conditions at which the sulfur mole fraction in a gas phase is virtually constant and does not depend on the pressure:

$$\frac{d \ln X_{(H_2S)_mS_n}}{d \ln P_{H_2S}} = m - 1 + n \cdot \frac{d \ln X_S^{melt}}{d \ln P_{H_2S}} \quad (4)$$

The sulfur mole fraction in a melt was calculated from the data of Fanelli (1949) and found to be in the range from 0. 98 to 0. 74 (Table 1). The slope in coordinates $\log X_{(H_2S)_mS_n} - \log P_{H_2S}$ is defined by the number m, and the term containing n defines the nonlinearity of the dependence. As the slope is rather close to 0 for all the temperatures investigated, it is assumed that the polysulfanes (or solvated complex) are present in a gas phase in the form H_2S_{n+1}(m = 1).

The equilibrium constant of reaction 1 can be calculated from the experimental data at the lowest hydrogen sulfide pressure and then can be used for predicting sulfur mole fraction in the gas phase as a function of hydrogen sulfide pressure and stoichiometry of polysulfane (solvate complex) gases. Such plots are presented in Fig. 6 . It was noted that the stoichiometry changing from disulfide to trisulfide must result in significant curvature increasing of solubility dependence from P_{H_2S}. The experimental data can be reasonably well described by stoichiometry $H_2S \cdot S$ within experimental error (n = 1).

In order to check the polysulfane formation version, an attempt was made to calculate thermodynamic functions of the polysulfanes and equilibrium compositions of the S-H_2S system at the experimental conditions. The standard enthalpy of formation of polysulfane gases was taken from the NBS tables of chemical thermodynamic properties (Wagman et al., 1982) based on experimental data of Féher and Winkhaus (1956, 1957). Heat capacities and entropies for the polysulfanes were calculated using statistical thermodynamics (rigid rotator-harmonic oscillator approximation). The heat capacity and entropy were obtained as a sum of translational, rotational, and vibrational contributions. Required thermodynamic relations are given in Mayer and Mayer (1957) and Lewis and Randal

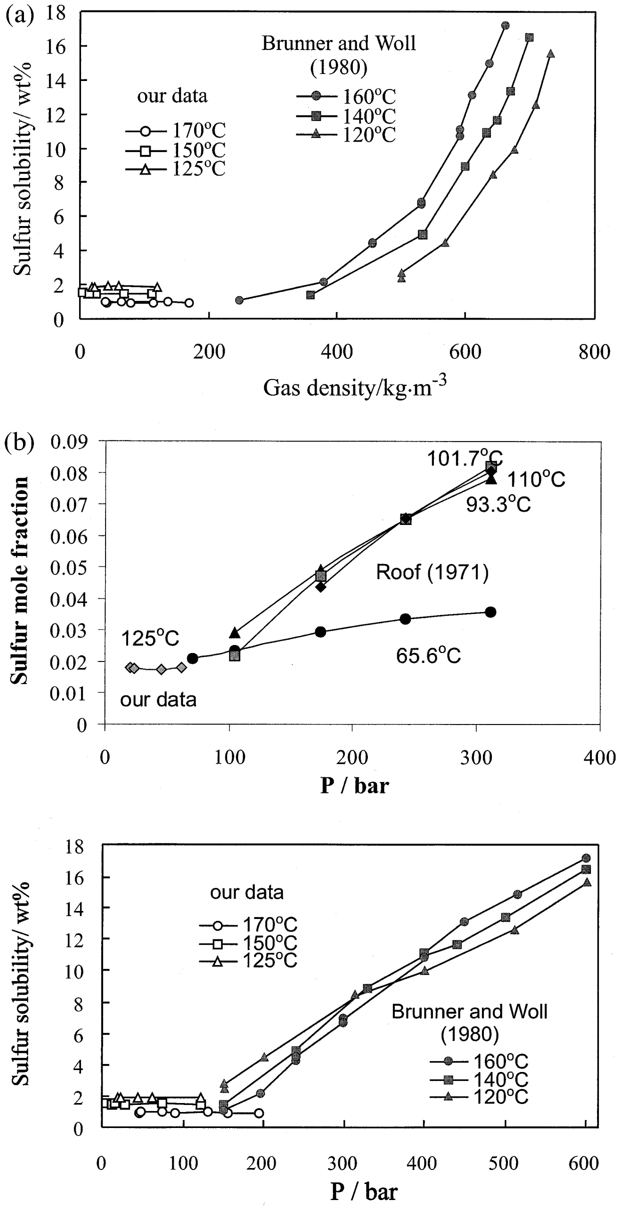

Fig. 5. Comparison of obtained values of sulfur solubility in hydrogen sulfide with literature data. (a) Sulfur solubility plotted as a function of the hydrogen sulfide pressure. (b) Sulfur solubility plotted as a function of the gas density.

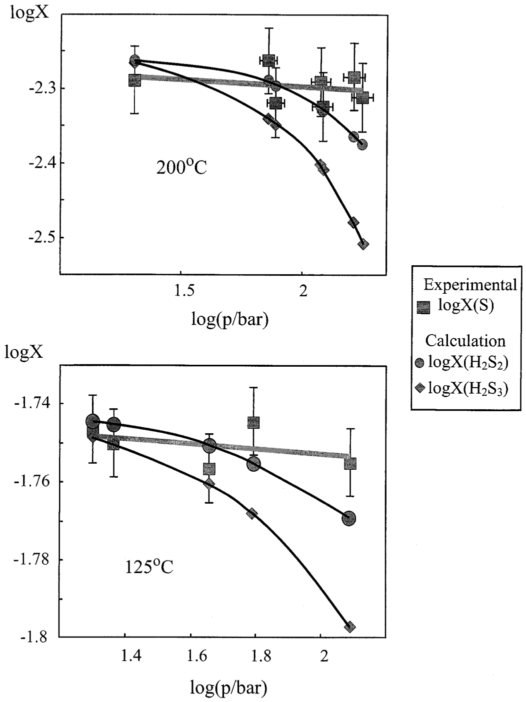

Fig. 6. The polysulfane mole fractions in the gas phase, calculated from low pressure experimental data and experimental polysulfane mole fractions (125–200°C).

Table 2. Entropy and coefficients for the heat capacity equiation (Eq. 5) temperature dependence of gaseous polysulfanes

	S J mol^{-1}K^{-1}	a	b	c	d	e
H_2S_2	258.24	134.152	-4.601×10^{-2}	5.483×10^{5}	2.613×10^{-5}	-1390.13
H_2S_3	300.71	162.515	-4.835×10^{-2}	2.613×10^{5}	2.758×10^{-5}	-1440.93
H_2S_4	342.77	200.578	-5.866×10^{-2}	1.959×10^{5}	3.181×10^{-5}	-1666.69
H_2S_5	390.73	236.215	-7.010×10^{-2}	1.179×10^{5}	3.686×10^{-5}	-1813.31

Table 3 . Calculated compositions and the experimentally determined components, where $X(H_2S_2^{gas})$, $X(H_2S_3^{gas})$, $X(H_2S_4^{gas})$, $X(H_2S_5^{gas})$ are the calculated mole fractions of polysulfanes in the system H_2S-S, X_S^{total} is the calculated total mole fraction of the dissolved sulfur in the gas phase in the system H_2S-S and X_S is the experimentally determined total mole fraction of the dissolved sulfur in the gas phase

t/°C	$X(H_2S_2^{gas})$, $\times 10^{-4}$	$X(H_2S_3^{gas})$, $\times 10^{-4}$	$X(H_2S_4^{gas})$, $\times 10^{-5}$	$X(H_2S_5^{gas})$, $\times 10^{-5}$	X_S^{total}, $\times 10^{-4}$	X_S, $\times 10^{-4}$
50	0. 284	0. 0255	0. 0441	0. 0136	0. 354	0. 852
125	3. 09	0. 54	1. 59	0. 861	4. 99	175. 31
151	5. 55	1. 11	3. 62	2. 20	9. 74	135. 46
170	8. 09	1. 77	6. 11	3. 96	15. 05	84. 64
200	13. 6	3. 33	12. 4	8. 76	27. 52	47. 57
250	27. 9	7. 85	31. 9	25. 1	63. 21	56. 97
290	44. 6	13. 7	58. 2	48. 8	108. 92	80. 97

(1961). Molecular constants are taken from the results of ab initio geometry optimization performed at MP2/6-311G**++ level of theory. The calculations were done using GAUSSIAN 94 (Gaussian 94, 1995) on a DEC 8400 5/300 computer. The vibrational contributions to the heat capacity and entropy were calculated using experimental vibrational frequencies taken from Wieser et al. (1969), Féher and Winkhaus (1956), Winnewisser (1970), and Winnewisser and Winnewisser (1968). Temperature dependence of the heat capacity of the gaseous polysulfanes was fitted to the following equation:

$$Cp = a + bT + \frac{c}{T^2} + dT^2 + \frac{e}{\sqrt{T}}, \tag{5}$$

where T is Kelvin and heat capacity is in J mol^{-1}K^{-1}. Results of calculations are summarized in Table 2. The obtained standard thermodynamic properties of the gaseous polysulfanes were used to calculate equilibrium compositions in the system H_2S-S at experimental pressures and temperatures. Equilibrium composition calculations were performed using very robust algorithm based on Gibbs free energy minimization from the HCH package (Shvarov, 1976; Shvarov, 1978). Results of the calculations together with the experimental data are summarized in Table 3. As shown in Table 3, the equilibrium concentration of each polysulfanes in the system decreases with increasing sulfur chain length and gradually increases with the temperature.

In order to compare our experimental data with the results of the calculations, the total mole fraction of the dissolved sulfur in the gas phase (X_S^{total}) was calculated. The conversion of the mole fraction of the polysulfanes in the gas phase to mole fraction of the total dissolved sulfur was made keeping in mind that decomposition of 1 mole of H_2S_2 will produce 1 mole of sulfur and 1 mole of H_2S, decomposition of 1 mole of H_2S_3 will produce 2 mole of sulfur and 1 mole of H_2S and so on.

It is interesting to note that at 50°C and at temperatures above 170°C results of calculations are in rather good agreement with experimental data (Fig. 7) however the difference between calculated and experimental mole fraction of the sulfur in the gas phase reaches 2 orders of magnitude in the temperature range 125–170°C (Table 3, Fig. 7).

The existence of the solubility maximum in this temperature interval is difficult to explain based only on the formation of polysulfane gases. One possible explanation for the solubility maximum could be formation of the liquid polysulfanes according to the following reactions:

$$H_2S^{gas} + (n - 1) \cdot S^{liq} = H_2S_n^{liq} \tag{6}$$

$$(n - 2) \cdot H_2S + H_2S_n^{liq} = (n - 1) \cdot H_2S_2^{gas}, \tag{7}$$

As shown by Steudel and Mausle (1978) and Steudel et al. (1985), a high degree of polymerization of the sulfur melt corresponds to the temperature range 120–160°C. At this temperature almost all physical properties like viscosity, specific heat, density, electric conductivity, and velocity of sound show discontinuities. This is caused by the equilibrium polymerization of sulfur, which is initiated by the ring scission (Tobolsky and MacKnight, 1965):

$$\text{cyclo-S}_8 \leftrightharpoons \text{catena-S}_8 \tag{8}$$

A change in the melt properties due to polymerization can cause a changed equilibrium composition in the gas phase. Unfortunately, due to the lack of complete thermodynamic information, such processes cannot be addressed here.

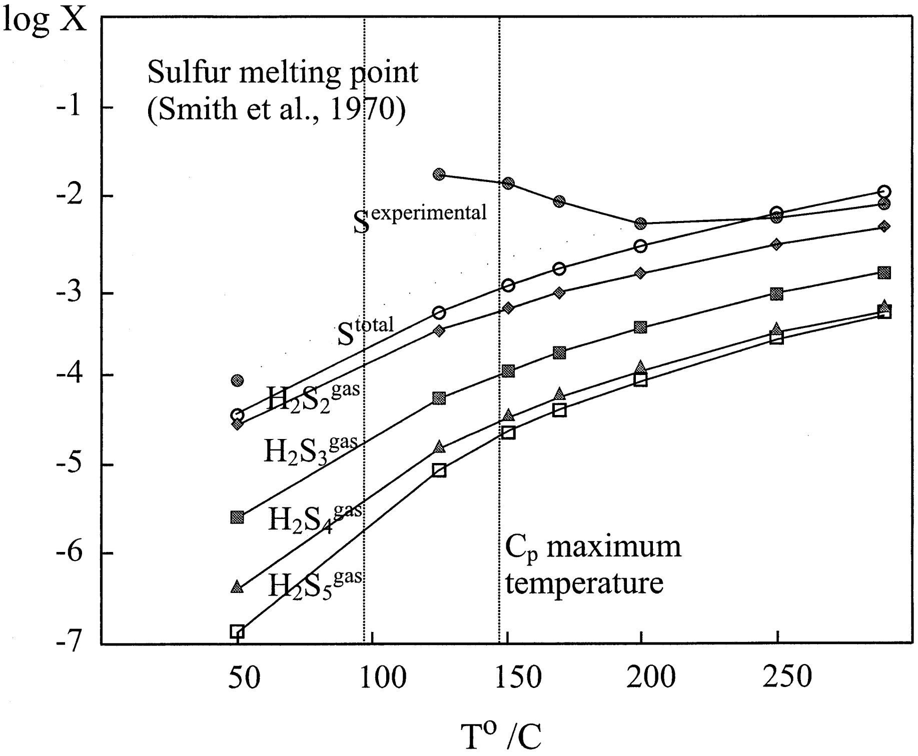

Fig. 7. Calculation of the equilibrium mole fractions of the polysulfanes $X(H_2S_2^{gas})$, $X(H_2S_3^{gas})$, $X(H_2S_4^{gas})$, $X(H_2S_5^{gas})$ in the system H_2S-S, together with experimental data on the sulfur mole fraction in the gas phase.

It is interesting to note that as shown by Brunner and Woll (1980), the sulfur solubility depends on the H_2S pressure at pressures higher than 150 bar (Fig. 5b). This dependence was obtained for the temperature range 120–160°C, characterized by anomalous sulfur behavior, and, in accordance with Eqn. 4, can be related with changing of gaseous particle stoichiometry from $H_2S \cdot S$ to $(H_2S)_2 \cdot S_n$. The fact of its presence in the gaseous phase can be accepted as indirect demonstration of solvation process domination (solubility) under polysulfane formation at H_2S pressures higher than 150 bar. It was supposed that sulfur solubility in gaseous H_2S is related with two main chemical reactions, dominated in the different temperature ranges: sulfur solvation by H_2S ((50),125–170°C) and polysulfane formation (200–290°C; Table 4).

For natural hydrothermal systems, the dominant case of sulfur precipitation is described as oxidation of H_2S, both aqueous and gas, and the proposed mechanism for sulfur transportation in the gas phase can not be responsible for formation of native sulfur deposits. Nevertheless, such a process can play an important role in some specific cases of reduced environments, and in cases of freezing of redox equilibrium. The phenomenon of freezing of compositions is often described in the number of geothermal system studies (Arnold and Gonzalez-Partida, 1987; Hannington and Scott, 1988). The absence of equilibrium in gaseous phase, with the presence of H_2S and O_2 in the most exotic cases (Migdisov and Bychkov, 1998), is characteristic for heterophase systems. It can be explained by the rather slow rate of the redox reactions between the sulfur species at temperatures below 250°C (Malinin and Khitarov, 1969; Rafalskii et al., 1983; Benning and Seward, 1996). In the cases where redox processes are suppressed or there is no oxidizer (Oppenheimer, 1996; Hentz and Henry, 1989), the sulfur retransportation in the H_2S could participate significantly in the mass balance of native sulfur.

Table 4. The values of log K, calculated from the experimental data for the reactions studied.

$H_2S^{gas} + S^{liquid} = H_2S \cdot S^{gas}$ solubility (solvation)		$H_2S^{gas} + S^{liquid,solid} = H_2S_2^{gas}$ polysulfane formation	
t/°C	log K	t/°C	log K
125	-1.76	50	-4.07
151	-1.87	200	-2.32
170	-2.07	250	-2.24
		290	-2.09

It should be noted that real hydrothermal systems include not only cases of decreasing activity of native sulfur, but also cases where formal activity increases reaching values greater than one (where $aS_{cr} = 1$). In such a case, the formation of colloidal sulfur is the characteristic processes in crater lakes and low-temperature hydrothermal systems rich in H_2S (Hannington and Scott, 1988; Zhu and Tong, 1987; Celenk et al., 1987). It is well known that decreasing of the sulfur grain size leads to change in equilibrium composition of the coexisting solution. Therefore, according to Eqn. 1, the stability of gaseous polysulfanes should increase.

An example of this special case can be found in the hydrothermal system of the Uzon caldera (Kamchatka) where gaseous polysulfanes and solvated complexes of sulfur are important components of the near-surface hydrothermal fluid (Migdisov and Bychkov, 1998). Native sulfur is present throughout the mineralization and redox state of the system is controlled by equilibrium between H_2S and H_2S_n in the gas phase and can be expressed by the S(aq) activity:

$$H_2S_n^{gas} = H_2S^{gas} + (n - 1) \cdot S_{aq}$$

A decrease in temperature causes the solution to become saturated with respect to colloidal sulfur because of continued H_2S_n dissolution:

$$H_2S_n^{gas} = H_2S_{aq} + (n - 1) \cdot S^{colloidal}$$

Colloidal sulfur with a high surface free energy is formed during this process and the concentrations of other sulfur species ($S_2O_3^{2-}$, H_2SO_3, H_2S_n, S(aq)) are in equilibrium with the colloidal sulfur (Migdissov and Bychkov, 1998).

At present, we are unable to discuss further the geochemical significance of volatile polysulfanes in active geothermal systems because of the lack of suitable analytical data. However, the polysulfanes will occur in all sulfur-containing hydrothermal environments but have not been previously identified.

5. CONCLUSIONS

The experimental results allow us to postulate that the sulfur dissolution in H_2S gas is not simply a mixture of inert gases. Concentrations of sulfur in the gas phase are 6–7 orders of magnitude higher than the concentrations calculated for a system free of hydrogen sulfide. Anomalous sulfur solubility must be related to $H_2S \cdot S$ particle formation. It was proposed that this particle formation could be related first to sulfur solvation by hydrogen sulfide (solubility; (50), 125–170°C), and, secondly, to the formation of new stable gaseous chemical compounds such as polysulfanes (chemical reaction; 200–290°C), dominated in the different temperature ranges.

Acknowledgements—The authors are grateful to B. W. Mountain, A. E. Williams-Jones, and S. Archibald who assisted in the preparation of the manuscript.

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