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An experimental study of stibnite solubility in gaseous hydrogen sulphide from 200 to 320°C

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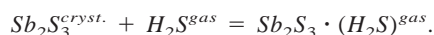
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Abstract—The solubility of stibnite in gaseous hydrogen sulphide was investigated experimentally in the systems Sb_2S_3 -S- H_2S and Sb_2S_3 - H_2S at temperatures between 200 and 320°C (pressures of up to 200 bars). The concentrations obtained are several orders of magnitude higher than those calculated for H_2S -free systems and display a prograde dependence on temperature in the range of 200 to 290°C. Concentrations of Sb_2S_3 are relatively constant at temperatures ranging from 290 to 320°C with a proposed solubility maximum at 300°C. In order to be able to describe stibnite solubility in the gas phase a simple solvation model was used, namely:



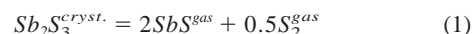
Equilibrium constant for this solvation reaction varied from $10^{-6.76}$ to $10^{-5.77}$ over the temperature range from 200 to 320°C. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Although most studies of ore genesis assume that the ore forming elements are transported by aqueous liquid solutions, relevant investigations of active volcanoes indicate that there is appreciable transport of these elements in the gas phase (Stoiber and Rose, 1970, 1974; Crowe et al., 1987; Nriagu, 1989; Shinohara, 1993; Hedenquist et al., 1994; Korzhinsky et al., 1996; Taran et al., 1995; Barnes and Seward, 1997; Wahrenberger et al., 2000). One of these elements is antimony which has been reported to occur in volcanic gases at concentrations ranging from 3 ppb at 456 to 770°C from Nicaraguan and Costa Rican volcanoes (Gemmell, 1987) and up to 1.7 ppm in high temperature (886°C) condensates from Momotombo (Nicaragua) (Quisefit et al., 1989). Antimony is also present in significant concentrations up to 108 ppm in Pb-Bi sulphide sublimates and up to 70 ppb in the volcanic gas condensates at Volcano (Italy) (Wahrenberger et al., 2000). Similar concentrations of antimony in the gas phase have also been reported from geothermal fields where temperatures are considerably lower. For example, Smith et al. (1987) report concentrations of 4 to 300 ppb of antimony in condensate traps in the Geysers Geothermal Field (~150°C) (USA).

Several thermodynamic models have been proposed to describe the transport of antimony in natural vapor-gas systems (Symonds et al., 1987; Quisefit et al., 1989; Spycher and Reed, 1989; Symonds and Reed, 1993), all based on the assumption that stibnite (Sb_2S_3), the dominant form of antimony in nature, controls the behaviour of this element in the gas phase. These models also assume that antimony is transported primarily as the species SbS^{gas} (Spycher and Reed, 1989) and that the concentrations of this species in the gas phase is determined by

its fugacity over stibnite. The models do not consider other interactions, i.e., between gas and solvent or solute, which might control metal solubility in the vapor phase. Thermodynamic data used in the calculations were obtained either at very high temperatures where complexation is suppressed, or at conditions close to vacuum. This approach successfully describes the high-temperature (800–400°C) gaseous transport of the antimony, but underestimates the capacity of the gas phase to transport metals at lower temperatures (400–100°C). The data, on which the above models were based, were obtained using the methods of Knudsen and Langmuir, as well as the results of mass spectrometric studies. Previous measurements of the vapour pressure over solid stibnite (Gospodinov et al., 1970; Piacente et al., 1992) indicated that SbS^{gas} , and S_2^{gas} are the dominant components of the vapour phase, and that Sb_2S_3 sublimates at elevated temperatures, primarily according to the reaction:



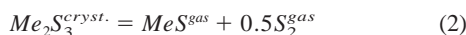
Mass spectrometric studies show, however, that in addition to the above species, also $Sb_2S_3^{gas}$ and the polymers $(SbS)_n$ ($n = 2, 3$ and 4) are present in minor amounts in the vapour phase (Sullivan et al., 1970; Faure et al., 1972). Although these above authors assumed that reaction (1) is dominant. Steblevskii et al. (1989a, 1989b) later reported a non-trivial composition for the vapor phase, describing such entities as $Sb_4S_5^{gas}$, $Sb_4S_4^{gas}$, $Sb_4S_3^{gas}$, $Sb_3S_4^{gas}$, $Sb_2S_3^{gas}$ and $Sb_2S_2^{gas}$.

Taking into account all those different gaseous species does not give adequate estimates to explain antimony transport in the gas phase. This can indicate that the transport of Sb in the gas phase is far more complex than that described by current thermodynamic models (Symonds et al., 1987; Quisefit et al., 1989; Spycher and Reed, 1989; Symonds and Reed, 1993), and that to fully represent transport, particularly at low temperature,

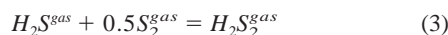
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interaction between gaseous solute and gaseous solvent should be taken into account. Because water vapor is the dominant component of hydrothermal systems and volcanic exhalations, the simplest model of antimony transport in the gas phase that can be constructed is in the system Sb-S-H-O. The gas phase of the system is composed of both water vapor and hydrogen sulphide, and its description therefore requires experimental information on the system stibnite—water vapor and stibnite—hydrogen sulphide. Unfortunately, there are no data available for the solubility of stibnite in water vapor or hydrogen sulphide. In view of the fact that hydrogen sulphide is one of the most important volatile components of natural hydrothermal fluids and also forms sulphide liquid complexes, for example with antimony sulphide (Krupp, 1988), it is logical to expect hydrogen sulphide gas complexes to be significant constituents of the gas phase.

Two mechanisms increasing the mobility of antimony sulphides in the gaseous phase are expected. One of them can be generalized for a number of relatively volatile metal sulphides, characterized by the stoichiometry Me_2S_3 , which undergo appreciable transport in the gas phase and coexist with hydrogen sulphide (Krupp and Seward, 1990). Examples of these sulphides are As_2S_3 , and Sb_2S_3 which sublime via the following generalised reaction:



Disulphane gas formation in a hydrogen sulphide atmosphere may increase the measured solubility as shown by the following equations:



Another mechanism for the formation of significant Sb concentrations in the vapor-gas phase is the process of solvation (hydration in the case of an aqueous solvent) of Sb by H_2S or H_2O molecules. This is analogous to sulphur solvation by hydrogen sulphide (Migdisov et al., 1998) or chlorargyrite and mercury hydration (Migdisov et al., 1999; Barnes and Seward, 1997). Migdisov et al. (1998) studied the solubility of sulphur in gaseous hydrogen sulphide in the H_2S -S system. The experimentally determined concentrations of sulphur in the gas phase were 6 to 7 orders of magnitude higher than the corresponding concentrations calculated for a system free of hydrogen sulphide. The data obtained has been well described by the formation of a $H_2S \cdot S$ compound. Unfortunately there are no data on the solubility of stibnite in gaseous H_2S or water vapor. The object of this study is therefore to document the thermodynamic properties of stibnite solubility in gas H_2S and to investigate forms of antimony transport in the gaseous phase.

2. EXPERIMENTAL METHOD

Experiments were carried out in titanium alloy autoclaves at temperatures of 200 to 320°C (pressures of up to 200 bar), and involved measuring the solubility of stibnite in gaseous H_2S . An electric oven equipped with a massive steel box (to reduce thermal gradients) was used to heat the autoclaves and a built-in thermal regulator allowed the temperature to be controlled to an accuracy of $\pm 1^\circ\text{C}$. The temperature was measured with a chromel-alumel thermocouple and a mercury thermometer. The autoclaves are of relatively small size (18 cm height

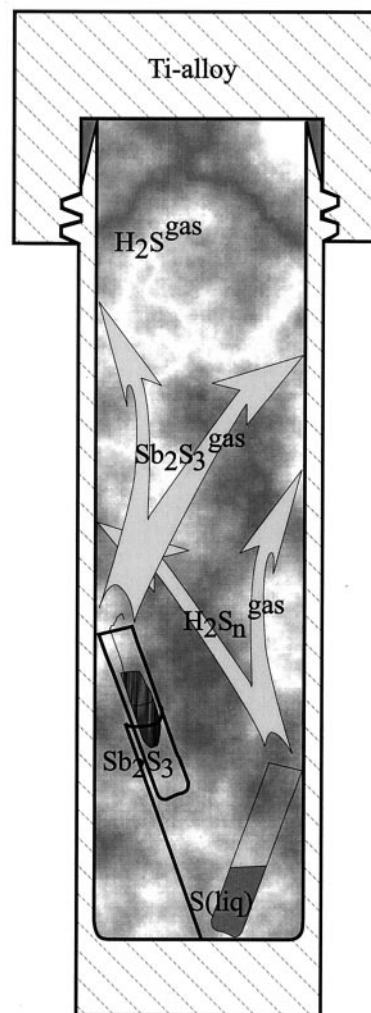
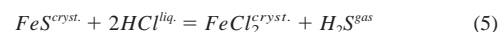


Fig. 1. Schematic drawing showing the experimental set-up with an autoclave containing a silica glass ampoule loaded with a single stibnite crystal and a second open silica glass ampoule containing natural sulphur.

with 2.5 mm thick walls) and constructed of titanium alloy VT-8 (VT-8: Ti-6Al-3Mo-0.3Si) (Fig. 1). The design construction allows determining pressure in autoclaves by weighting. Autoclaves weights ranged from 140 to 160 g and their respective interior volumes were calculated from the difference between the weight of the autoclave charged with distilled water at 25°C and its weight when empty. Typical volumes were in the range 39 to 42 cm³. The internal surface of each new autoclave was conditioned initially with nitric acid. Before each run, a strong current of H_2S was produced from the following reaction:



which was passed through the autoclave for 15 to 20 min to remove atmospheric gases.

Hydrogen sulphide was purified by passing it through two gas-washing bottles and a water trap which was kept at -10°C . The final H_2S purity was 99.8% as measured by gas chromatography by using a GasoChrom 3101 instrument. The purified hydrogen sulphide was frozen out in the autoclave using liquid nitrogen and its mass was determined to an accuracy of ± 10 mg. Owing to the relatively low vapor pressure of stibnite and sulphur (Gospodinov et al., 1970; Novoselova and Paschinkin, 1978; Glushko, 1982; Piacente et al., 1992) compared to the hydrogen sulphide pressure, the total pressure was

Table 1. The results of solubilities in the gas phase of the H₂S-S-Sb₂S₃ system.

moles H ₂ S	10 ⁸ moles Sb ₂ S ₃	10 ⁶ X _{Sb₂S₃} ^{gas}	10 ⁴ moles S	10 ³ X _S ^{gas}	p/bar
200°C					
0.014	0.29	0.21	0.80	5.79	13.59
0.039	0.59	0.15	2.30	5.97	37.88
0.050	0.88	0.18	2.97	5.94	49.16
0.060	0.59	0.10	3.50	5.83	58.99
0.095	1.76	0.19	5.23	5.49	93.69
0.096	1.76	0.18	5.77	5.98	94.84
0.099	2.06	0.21	5.63	5.70	97.16
260°C					
0.024	1.18	0.49	1.59	6.67	26.39
0.040	2.94	0.74	2.67	6.72	43.99
0.065	3.24	0.50	4.61	7.06	72.34
0.072	5.29	0.73	4.57	6.32	80.16
0.076	3.82	0.50	5.09	6.66	84.72
0.155	9.71	0.63	9.50	6.12	172.04
290°C					
0.019	5.29	2.73	1.59	8.19	22.35
0.029	2.94	1.02	2.30	7.98	33.97
0.038	5.00	1.33	2.95	7.84	44.08
0.039	3.53	0.91	3.13	8.06	45.44
0.074	10.59	1.42	5.68	7.63	87.06
0.095	14.71	1.54	7.50	7.87	111.04
0.099	14.71	1.48	7.65	7.72	116.41
0.119	18.53	1.56	8.98	7.56	139.47
320°C					
0.018	2.94	1.67	1.64	9.29	21.75
0.029	4.41	1.50	2.61	8.87	36.25
0.052	8.82	1.69	4.80	9.17	64.53
0.074	17.06	2.29	6.40	8.60	91.72
0.096	15.00	1.57	8.46	8.85	117.82
0.111	15.88	1.43	9.34	8.40	137.03

H₂S refers to the number of moles of frozen hydrogen sulphide, Sb₂S₃ is the moles of dissolved stibnite, X_{Sb₂S₃}^{gas} is the mole fraction of Sb₂S₃ in the gas phase, S is the moles of dissolved sulphur, X_S^{gas} is the mole fraction of sulphur in the gas, *p* is the pressure of hydrogen sulphide (bar) calculated from the pVT properties of hydrogen sulphide under experimental conditions.

assumed to be equal to the pressure of hydrogen sulphide. The total pressure in the system was calculated from the volume of the gas phase as well as the mass and pVT properties of hydrogen sulphide (Rau and Mathia 1982; Goodwin, 1983).

The autoclave was loaded with an open silica glass ampoule containing a natural stibnite crystal. Clean crystals of stibnite were selected with the aid of a microscope. Emission spectroscopy showed stibnite crystals, taken from the Kadamzhai (Kyrgyzstan), to be of high purity (99.98%), however, with minor amounts of trace elements (Fe, Ti, Mg, Al, Cu). After the run, the autoclave was quenched to room temperature with compressed air (quenching rate was approximately 2.5°C per minute) and was weighed again to check for possible leaks. The amount of vaporized and dissolved stibnite was determined by weighing the stibnite crystal before and after each run on a Mettler-3 balance to an accuracy of ±2 μg. The experimental uncertainty (±6 μg) was calculated from the blank runs with N₂ as the gas-solvent, and was related to physical losses during the weighting procedure and during heating and cooling of the crystal. In some runs, a powder of synthetic stibnite was used, and the results of these runs are in a good agreement with those using natural stibnite. A synthetic stibnite has been hydrothermally synthesized and characterized 99.99% purity as a product of high purity antimony and sulphur. The amount of transported stibnite was determined by weighing the silica ampoule containing a powder of synthetic stibnite. However, the accuracy of these results was lower (±30 μg), because of physical losses of the powder.

Experiments were carried out in the systems Sb₂S₃-S-H₂S and Sb₂S₃-H₂S. For the Sb₂S₃-S-H₂S system, an open silica glass ampoule containing rhombic sulphur was added to the autoclave (0.2 g). After cooling, the sulphur that had condensed on the autoclave walls and on the crystals of stibnite was dissolved in hexane, and the concentration determined spectrophotometrically at 264 nm (Dadze and Sorokin,

1993) on a Hitachi-124 instrument, by using a 1 cm path length quartz cuvette. Eight standard solutions with concentrations ranging from 20 mg/L to 0.05 mg/L were used for calibration. The uncertainty of spectrophotometric measurements was ±3%.

3. RESULTS

The mole fraction of Sb₂S₃ in the gas phase was calculated from the stibnite mass loss during each run and the initial mass of hydrogen sulphide introduced into the autoclaves (Tables 1 and 2). Owing to the low partial pressure of Sb₂S₃, the total pressure in the autoclave was effectively equal to the pressure of H₂S. Conse-

quently, the mole fraction of Sb₂S₃ ($X_{Sb_2S_3} = \frac{M_{Sb_2S_3}}{M_{H_2S} + M_{Sb_2S_3}}$) in the hydrogen sulphide could be approximated as $X_{Sb_2S_3} \cong \frac{M_{Sb_2S_3}}{M_{H_2S}}$, where *M* is number of moles of the corresponding compound. The stoichiometry of Sb₂S₃ was taken to express the amount of stibnite, transported to the gaseous phase.

Sets of experiments were carried out at each of the temperatures investigated to determine the time required to attain equilibrium in the systems studied. The duration of all runs was longer than 11 d, and unsaturated gas mixtures were never obtained (Fig. 2). As is clear from Figure 2, once equilibrium was attained, solubilities were reproducible to approximately ±5 to 10% of the absolute value. In the blank runs, which were

Table 2. Results of solubility experiments in the gas phase of the H_2S - Sb_2S_3 system.

moles H_2S	10^8 moles Sb_2S_3	$10^6 X_{\text{Sb}_2\text{S}_3}^{\text{gas}}$	p/bar
200°C			
0.015	0.29	0.19	14.75
0.034	0.59	0.17	33.54
0.069	1.76	0.26	67.95
0.075	1.47	0.20	73.73
0.101	2.06	0.20	99.76
260°C			
0.032	2.16	0.67	35.52
0.041	2.74	0.67	45.62
0.056	3.60	0.64	61.91
0.089	5.33	0.60	98.4
0.098	6.66	0.68	108.18
0.124	7.99	0.64	137.5
0.155	9.33	0.60	171.72
290°C			
0.054	8.60	1.59	62.64
0.069	8.87	1.29	80.88
0.071	9.32	1.31	83.29
0.107	16.29	1.52	124.94
0.112	14.03	1.25	131.47
0.116	20.46	1.76	135.95
0.182	28.24	1.55	213.04
320°C			
0.007	0.96	1.37	8.7
0.012	1.36	1.13	14.86
0.056	7.33	1.31	68.88
0.074	8.93	1.21	90.63

H_2S refers to the numbers of moles of frozen hydrogen sulphide, Sb_2S_3 is the moles of dissolved stibnite, p is the pressure of hydrogen sulphide (bar) calculated from the pVT properties of hydrogen sulphide at the conditions of the experiments, $X_{\text{Sb}_2\text{S}_3}^{\text{gas}}$ is the mole fraction of Sb_2S_3 in the gas phase.

carried out in a nitrogen atmosphere, the stibnite and sulphur mass losses were equal to or lower than the determined experimental uncertainty ($\pm 6 \mu\text{g}$).

The composition of the gas phase is reported in Tables 1 and 2 for the Sb_2S_3 -S- H_2S and Sb_2S_3 - H_2S systems, respectively. The absolute amounts of stibnite (in moles) transported to the gas phase versus the amounts of H_2S (in moles) are shown in Figure 3. It is evident from this figure that the amount of

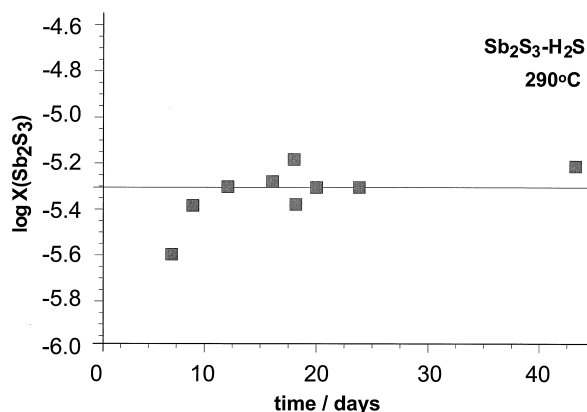


Fig. 2. Mole fractions of Sb_2S_3 in the gas phase of the system Sb_2S_3 - H_2S for a series of experiments of variable duration. At 290°C the system reaches equilibrium after 11 d.

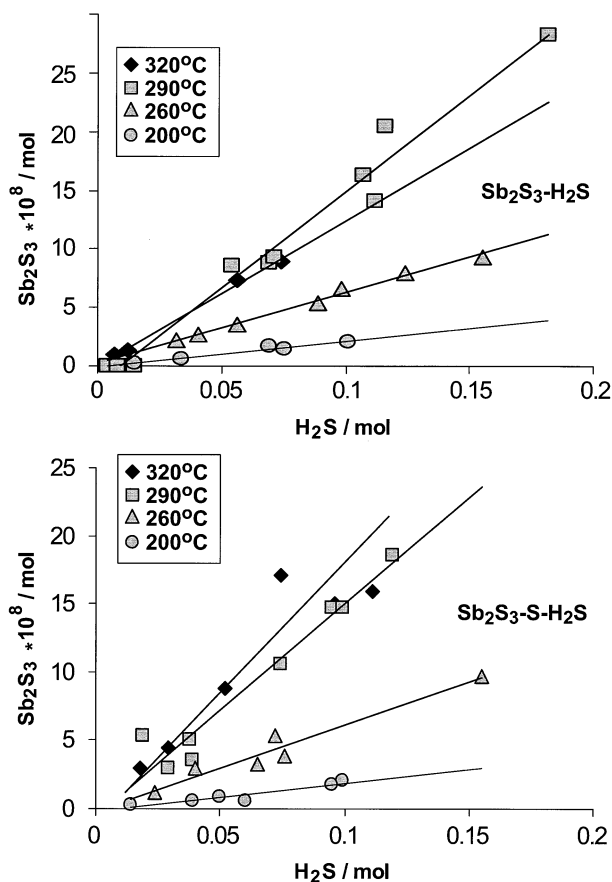


Fig. 3. Concentration of Sb_2S_3 in the gas phase of the systems Sb_2S_3 - H_2S and Sb_2S_3 -S- H_2S ranging from 200°C to 320°C versus the concentration of H_2S in the system.

transferred Sb_2S_3 is directly proportional to the amount of H_2S in the gas phase. It should be noted that the increase in H_2S is directly related to the increase in pressure because of the isochoric nature of the system. The behavior of antimony was identical in both systems investigated. The calculated mole fractions at each pressure are illustrated in Figure 4. It was found that at similar conditions the concentrations of dissolved Sb_2S_3 were nearly equal in both systems. The differences between the two systems were within the experimental error, and thus any effect that sulphur may have had on stibnite solubility was masked. Owing to the linear relationship between the amount of Sb_2S_3 transported and the amount of hydrogen sulphide, introduced into the system (see equation above for the mole fraction calculation), the calculated mole fractions of Sb_2S_3 were approximately independent of the H_2S pressure and constant at constant temperature and mass of H_2S . The temperature dependence of $X_{\text{Sb}_2\text{S}_3}$ is illustrated in Figure 5 for both the H_2S - Sb_2S_3 and H_2S -S- Sb_2S_3 systems. From this figure it can be seen that the concentration of Sb_2S_3 in gaseous hydrogen sulphide increases with increasing temperature in the range of 200 to 290°C. However, at 290 and 320°C Sb_2S_3 solubilities are essentially the same for the same mass of H_2S , suggesting a solubility maximum between 290 and 320°C.

The solubility of sulphur in the hydrogen sulphide-dominated gas phase (H_2S -S- Sb_2S_3 system) was similar to that

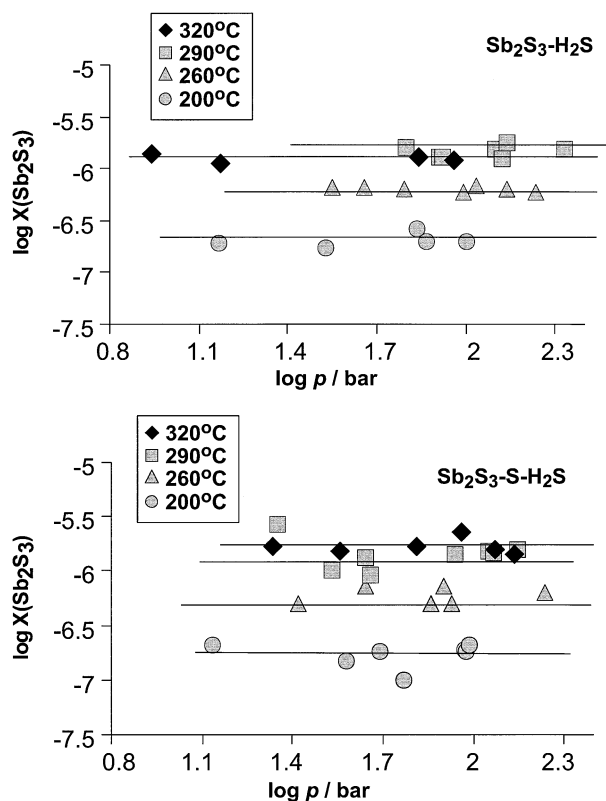


Fig. 4. Log of Sb_2S_3 concentration in the gas phase versus log of total pressure in the Sb_2S_3 - H_2S and Sb_2S_3 - S - H_2S systems.

reported by Migdisov et al. (1998) and can be explained by the formation of disulphane (H_2S_2) (Eqn. 3) and the solvated complex $H_2S \cdot S$. Detailed description of methods and approaches used in the data interpretation can be found in the publication (Migdisov et al., 1998).

4. DISCUSSION

The solubilities of Sb_2S_3 in H_2S gas determined in this study were compared with those estimated from the vapor pressure of antimony over crystalline stibnite. Because of the dominance of

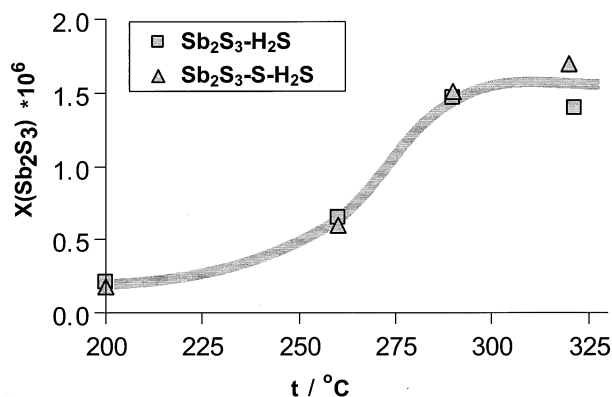
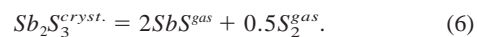


Fig. 5. The average mole fraction of Sb_2S_3 in the gas phase in the H_2S - Sb_2S_3 and H_2S - S - Sb_2S_3 systems versus temperature. The data suggest that there is a solubility maximum at approximately 300°C.

SbS in the vapor over crystalline stibnite in the single component system (Sullivan et al., 1970; Faure et al., 1972; Piacente et al., 1992), initial estimations were made assuming that the solubility of stibnite in the gas phase defined by the reaction:



Calculations were made based on the SbS^{gas} properties summarised in Table 3.

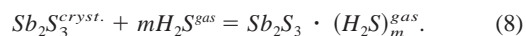
Alternatively, if the interaction between hydrogen sulphide and sulphur is taken into account, the solubility of stibnite in the gas phase is more realistically described by the following reaction:



The concentrations of SbS^{gas} were calculated by using available estimates of its thermodynamic properties (Faure et al., 1972; Gospodinov et al., 1970; Hino et al., 1986) and those for the gaseous sulphur species (Glushko, 1982; Migdisov et al., 1998). The thermodynamic properties of the above species are summarised in Table 3. The Gibbs free energies of formation and standard entropies of SbS^{gas} were derived from Faure et al. (1972) and corrected using data of Steblevskii et al. (1989a) and Hino et al. (1986); and the heat capacities were taken from Gospodinov et al. (1970). The standard enthalpy of formation of disulphane gas was taken from the NBS tables of chemical thermodynamic properties (Wagman et al., 1982), which are based on the experimental data of Feher and Winkhaus (1957). Heat capacities and entropies for H_2S_2 were calculated by Migdisov et al. (1998) by using statistical thermodynamics (rigid rotator-harmonic oscillator approximation). The standard enthalpy of formation of crystalline stibnite was taken from Mills (1974) and Sorokin et al. (1988) and standard entropy and heat capacity data from Romanovskii and Tarasov (1960).

Equilibrium composition calculations at experimental conditions were performed for the Sb - S - H system by using the HCH package (Shvarov, 1976; 1978). The system was assumed to consist of native sulphur, stibnite and a gas composed of H_2S , H_2S_2 , H_2S_3 , H_2S_4 , H_2S_5 , S_8 , and SbS . The results of the calculations are compared with the experimental data in Table 4. From this table it is evident that the experimentally determined concentrations of stibnite in the gas phase are several orders of magnitude greater than the calculated concentrations of SbS^{gas} . Furthermore, the calculated concentrations of SbS^{gas} in the Sb_2S_3 - S - H_2S system are lower by 1 to 1.5 orders of magnitude than those in the system Sb_2S_3 - H_2S . This is because the higher sulphur partial pressure of the latter system (see Eqn. 1). The independence of stibnite solubility from the sulphur partial pressure indicates that stibnite dissolves in hydrogen sulphide gas without changing its stoichiometry. This indicates that antimony is dissolved in the gas phase not as SbS , but rather as Sb_2S_3 .

A simple solvation model was used to describe these processes. For the case where both solvation and chemical reaction are taken into account this interaction can be described by the following equation:



This model is analogous to those used in a previous study of the S - H_2S gas system (Migdisov et al., 1998), and is similar to the

Table 3. Thermodynamic properties of components.

	a	b	c	d	e	S_{298}^0 , J/(mol K)	ΔG_{298}^0 , kJ/mol
Gas							
H_2S_2	134.152 ^a	$-4.60 \cdot 10^{-2a}$	$5.48 \cdot 10^{5a}$	$2.61 \cdot 10^{-5a}$	-1390.13^a	258.24 ^a	-4.826^b
H_2S_3	162.516 ^a	$-4.84 \cdot 10^{-2a}$	$2.61 \cdot 10^{5a}$	$3.00 \cdot 10^{-5a}$	-1440.93^a	300.71 ^a	1.918 ^b
H_2S_4	200.579 ^a	$-5.87 \cdot 10^{-2a}$	$1.96 \cdot 10^{5a}$	$3.00 \cdot 10^{-5a}$	-1666.69^a	342.77 ^a	6.887 ^b
H_2S_5	236.216 ^a	$-7.01 \cdot 10^{-2a}$	$1.18 \cdot 10^{5a}$	$3.69 \cdot 10^{-5a}$	-1813.31^a	390.73 ^a	10.456 ^b
H_2S_6	271.205 ^a	$-7.82 \cdot 10^{-2a}$	$3.38 \cdot 10^{5a}$	$4.02 \cdot 10^{-5a}$	-1984.02^a	435.55 ^a	12.304 ^b
H_2S	32.677 ^c	$1.24 \cdot 10^{-2c}$	$-1.92 \cdot 10^{5c}$	0	0	205.69 ^c	-33.431^c
SbS	21.89 ^d	$2.54 \cdot 10^{-2d}$	0	0	0	257.81 ^e	83.889 ^e
Solid							
S	14.979 ^f	$2.61 \cdot 10^{-2f}$	0	0	0	32.054 ^f	0
Sb_2S_3	115.045 ^g	$1.98 \cdot 10^{-2g}$	$-2.08 \cdot 10^{5g}$	$1.41 \cdot 10^{-5g}$	0	182.00 ^g	-149.30^g

ΔG_{298}^0 —standard Gibbs free energy, S_{298}^0 —standard entropy, a, b, c, d, e—coefficients of the temperature dependence of heat capacity

$$\left(C_p = a + bT + \frac{c}{T^2} + dT^2 + \frac{e}{\sqrt{T}} \right).$$

^a Migdisov et al. (1998).

^b Calculated from the data of Wagman et al. (1982) and Migdisov et al. (1998).

^c Robie et al. (1978).

^d Gospodinov et al. (1970).

^e Faure et al. (1972).

^f Naumov et al. (1971).

^g Romanovskii and Tarasov (1960), Mills (1974), and Sorokin et al. (1988).

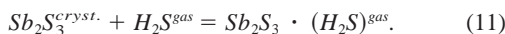
models developed for NaCl-H₂O vapor systems (Martynova, 1964; Styrikovich, 1969; Galobrades et al., 1981; Alekhin and Vakulenko, 1988; Armellini and Tester, 1993). Accepting, that the fugacity of $Sb_2S_3 \cdot (H_2S)_m^{gas}$ can be expressed to a first approximation as:

$$f_{Sb_2S_3 \cdot (H_2S)_m^{gas}} = f_{total} X_{Sb_2S_3 \cdot (H_2S)_m^{gas}} \cong f_{H_2S^{gas}} X_{Sb_2S_3 \cdot (H_2S)_m^{gas}} \quad (9)$$

where f_{total} is the sum of gas fugacities in the system, $X_{Sb_2S_3 \cdot (H_2S)_m^{gas}}$ is the mole fraction of the solvated complex and f_{H_2S} is the hydrogen sulphide fugacity, the equilibrium constant of reaction (8) can be written as:

$$\begin{aligned} \log K &= \log X_{Sb_2S_3 \cdot (H_2S)_m^{gas}} + \log f_{H_2S} - m \log f_{H_2S} \quad (10) \\ &= \log X_{Sb_2S_3 \cdot (H_2S)_m^{gas}} - (m-1) \log f_{H_2S} \end{aligned}$$

Inspection of Eqn. 10 indicates that the mole fraction of stibnite in the gas phase is only independent of the hydrogen sulphide pressure (Figs. 3 and 4) when $m = 1$. Based on our experimental data the dominant antimony-bearing gas species is $Sb_2S_3 \cdot (H_2S)^{gas}$:



Equilibrium constants for reaction (11) were calculated from the experimental data and are summarised in Table 5.

As was discussed above, two processes can produce the gaseous antimony species described above: gaseous solvation—formation of the solvated particle $Sb_2S_3 \cdot (H_2S)^{gas}$ (van der Waals bonding) and/or chemical reaction with formation of the stable gaseous chemical compound $H_2Sb_2S_4^{gas}$ (covalent bonding). To test the hypothesis that a chemical with the stoichiometry $H_2Sb_2S_4^{gas}$ could have formed, ab initio calculations were conducted to determine its thermodynamic properties. It is known that four-membered rings of the type X_2Y_2 (where X is an atom of group 15 (VA) and Y is an atom of

group 16(VIA), for example Te_2N_2 , Sb_2O_2 , As_2S_2 , or Sb_2S_2) are the main building blocks of many chemically significant compounds. (Chivrs et al., 1996; Bordner et al., 1986; France et al., 1997). The geometry determined by X-ray crystal structure analysis for the N_2S_2 compound shows that N_2S_2 is a nearly square-planar ring with equivalent S-N bonds. (Mikulski et al., 1975; Cohen et al., 1976). It is logical to expect that a covalent compound with bulk stoichiometry $H_2Sb_2S_4$ has a four membered Sb_2S_2 ring with two [SH] groups attached to the antimony atoms. To test this hypothesis, the gas phase thermodynamic properties of this compound were estimated by using ab initio calculations and the partial pressure of $H_2Sb_2S_4$ that would be present in our system at the experimental conditions. Quantum chemical calculations were performed using the Gaussian98 set of programs (Frisch et al., 1998). All of the geometrical parameters of the $H_2Sb_2S_4$ were optimized by using density functional theory (DFT) with the popular hybrid B3LYP functional (Becke 1993; Lee et al., 1988) in conjunction with a double- ζ -type valence-electron basis set as described by Godbout et al. (1992). Geometries of the two found conformers are shown in Figure 6. The *cis*-conformer has C_{2v} symmetry; the ring Sb-S bond lengths are equal and the ring is nearly square and nearly planar with an SbSSbS dihedral angle of 8.8 degrees. The *trans*-conformer has C_{2h} symmetry with a planar SbSSbS ring. Vibrational analyses show that the two determined stationary points are minima on the potential energy surface. Heats of formation (ΔH_{f298}) were calculated from atomization energies using the experimental heats of formation of atoms taken from Lias et al. (1988). Enthalpy temperature corrections were derived using scaled vibrational frequencies and standard statistical thermodynamic methods. The resulting thermodynamic data required for the further calculations are summarized in Table 6.

These calculations showed that the species $H_2Sb_2S_4$ should develop partial pressures 25 orders of magnitude lower than

Table 4. Comparison between the experimentally determined solubility of Sb_2S_3 in the gas phase for the systems H_2S - Sb_2S_3 and H_2S - Sb_2S_3 and the calculated concentrations obtained by using the data summarized in Table 3.

Sb_2S_3 - H_2S			Sb_2S_3 - S - H_2S		
p	$\log X^{\text{exp}}$	$\log X^{\text{calc}}$	p	$\log X^{\text{exp}}$	$\log X^{\text{calc}}$
200°C			200°C		
14.75	-6.721	-16.692	13.59	-6.683	-17.637
33.54	-6.769	-17.041	37.88	-6.820	-18.073
67.95	-6.585	-17.334	49.16	-6.754	-18.181
73.73	-6.698	-17.367	58.99	-7.007	-18.256
99.76	-6.698	-17.487	93.69	-6.732	-18.443
			94.84	-6.736	-18.448
			97.16	-6.681	-18.458
260°C			260°C		
35.52	-6.173	-14.272	26.39	-6.308	-15.050
45.62	-6.173	-14.377	43.99	-6.133	-15.266
61.91	-6.193	-14.504	72.34	-6.302	-15.472
98.4	-6.221	-14.692	80.16	-6.133	-15.513
108.18	-6.167	-14.730	84.72	-6.298	-15.536
137.5	-6.193	-14.823	172.04	-6.2203	-15.812
171.72	-6.221	-14.907			
290°C			290°C		
62.64	-5.798	-13.341	22.35	-5.555	-13.778
80.88	-5.889	-13.446	33.97	-5.994	-13.955
83.29	-5.882	-13.458	44.08	-5.880	-14.065
124.94	-5.818	-13.620	45.44	-6.043	-14.078
131.47	-5.903	-13.640	87.06	-5.844	-14.346
135.95	-5.754	-13.653	111.94	-5.810	-14.447
213.04	-5.809	-13.821	116.41	-5.828	-14.462
			139.47	-5.807	-14.533
320°C			320°C		
8.7	-5.863	-11.454	21.75	-5.786	-12.688
14.86	-5.946	-11.685	36.25	-5.817	-12.905
68.88	-5.882	-12.334	64.53	-5.770	-13.147
90.63	-5.917	-12.446	91.72	-5.637	-13.291
			117.82	-5.806	-13.391
			137.03	-5.844	-13.450

p is the pressure (bar), $\log X^{\text{exp}}$ is the log of the mole fraction of Sb_2S_3 obtained in the runs, $\log X^{\text{calc}}$ is the calculated log of the mole fraction of Sb_2S_3 .

those determined in our experiments. Despite the high error associated with ab initio estimations (orders of magnitude in some cases) we can therefore confidently conclude that solvation dominates in the system investigated, and that $H_2Sb_2S_4$ formation is negligible. All the experimental data obtained can be satisfactorily explained by Sb_2S_3 solvation (solubility) in gaseous H_2S (Reaction 11), and the congruent dissolution of the solid phase.

The data obtained on the solubility of stibnite in H_2S gas indicate that potentially significant concentrations of antimony

can be transported in the gas phase of hydrothermal systems. In the case of boiling systems, the antimony transport capacity is determined by the relative fluxes of gaseous and liquid phases. Given that the viscosity of the gas phase is commonly several orders of magnitude lower than that of the liquid, it is quite likely that the lower solubility of antimony in the gas phase will be compensated by the much higher mobility of the gas phase.

Proposed mechanism of the transport of antimony by the gas phase can cause significant concentration of antimony in natural systems (Krupp and Seward 1990; Barnes and Seward, 1997) and also, for example, explains the bothersome, often nearly complete separation of stibnite and cinnabar even between adjacent hot springs, such as in Tuscan in Bagnoli Petrolio and at the Tafone Sb mine (Klemm and Neumann, 1984). The importance of gaseous transport and processes of solvation and hydration (low-energy hydrogen-bonding interactions) in ore formation processes was also shown by Henley and McNabb (Henley and McNabb, 1978), whereby, 1) intrusions associated with porphyry Cu-Mo deposits would be typ-

Table 5. Values of $\log K$, calculated from the experimental data for the reaction $Sb_2S_3^{\text{cryst.}} + H_2S^{\text{gas}} = Sb_2S_3 \cdot (H_2S)^{\text{gas}}$.

$t/^\circ\text{C}$	$\log K$
200	-6.76
260	-6.22
290	-5.82
320	-5.77

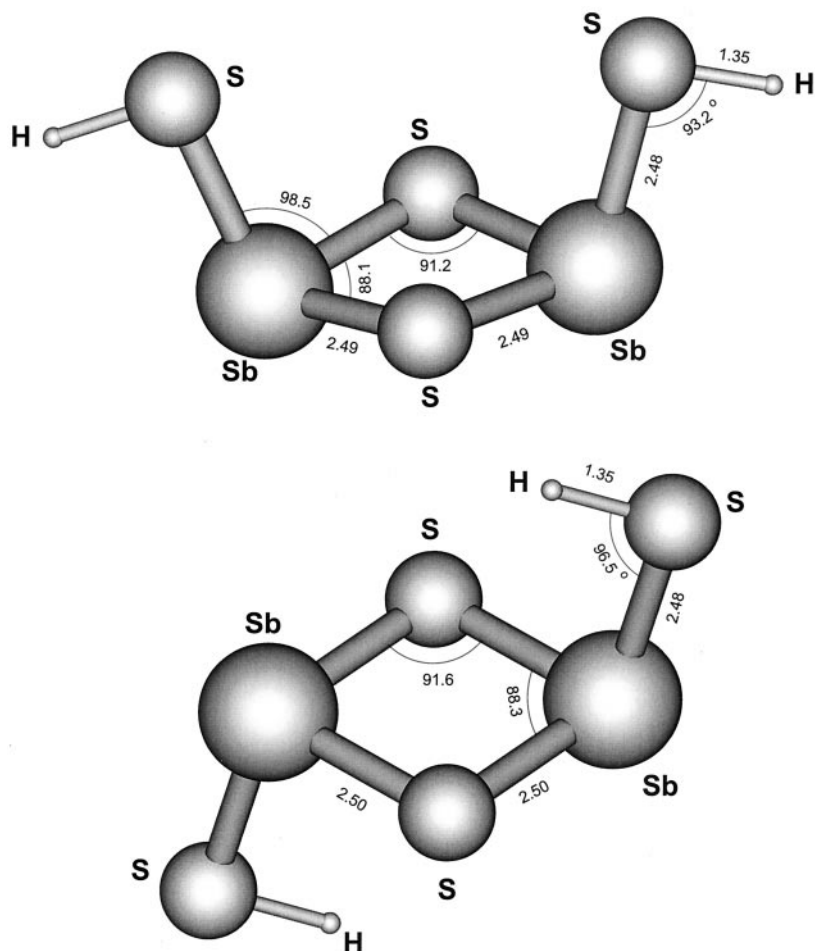


Fig. 6. Optimized structure of two conformers of the $H_2Sb_2S_4$ at B3LYP level of theory.

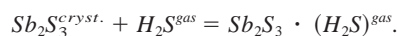
ically emplaced at sufficiently shallow levels for the aqueous fluid to exsolve in the two-phase region, 2) the mass of vapor would exceed that of liquid, and 3) the two fluids would be stratified by density.

CONCLUSIONS

Based on experimental data presented in this study we conclude that the presence of hydrogen sulphide substantially increases the stability of antimony sulphides in the gas phase. The concentrations measured were several orders of magnitude higher than those calculated for H_2S -free systems and demon-

strate a prograde dependence on temperature in the range of 200 to 290°C. Similar concentrations at 290 and 320°C suggest a solubility maximum at approximately 300°C.

Stibnite solubility in gaseous hydrogen sulphide is attributed to the solvated complex $Sb_2S_3 \cdot (H_2S)^{gas}$, which can be produced by the reaction:



The stability constant of this reaction was experimentally estimated for each of the temperatures investigated.

Table 6. Thermodynamic properties of *cis*- $H_2Sb_2S_4$ and *trans*- $H_2Sb_2S_4$, calculated from quantum chemical calculations.

	ΔH_{298}^0 kJ/mol	ΔS_{298}^0 J/(molK)	ΔG_{298}^0 kJ/mol	<i>a</i>	<i>b</i>	<i>c</i>
<i>cis</i> - $H_2Sb_2S_4$	124.1393	-10.0416	127.1518	36.83834	0.0042	-284437.8074
<i>trans</i> - $H_2Sb_2S_4$	125.9384	-3.9748	127.1099	37.10691	0.00392	-283464.5596

ΔH_{298}^0 – standard enthalpy of formation, ΔG_{298}^0 – standard Gibbs free energy of formation, S_{298}^0 – standard entropy of formation, a, b, c – coefficients of the temperature dependence of heat capacity $\left(C_p = a + bT + \frac{c}{T^2} \right)$.

We conclude that the gas phase can be an important agent in the transport of antimony in natural hydrothermal systems and the next step to a complete understanding of nature of antimony gas transport will be to study stibnite solubility in water vapor.

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