# Stibnite ($Sb_2S_3$) Solubility in Sodium Sulfide Solutions

Abstract. *The solubility of stibnite* ($Sb_2S_3$) *was measured at 25°C and 1 atmosphere in solutions ranging from 0.45 to 7.16 percent* $Na_2S$ *by weight.* $Sb_2S_3$*:* $Na_2S$ *mole ratios of saturated solutions range from 0.238 to 0.403. Stibnite solubility increases at an increasing rate with rising* $Na_2S$ *concentration. The reaction that best fits the experimental data is* $2Sb_2S_3 + HS^- + OH^- = Sb_4S_7^{2-} + H_2O$*, for which an equilibrium constant was estimated to be about 5.0.*

Interest by geologists has long been centered on the nature of solutions capable of transporting the components of sulfide-ore minerals. Sulfide ion forms soluble complexes with some substances, such as HgS, $Sb_2S_3$, and $As_2S_3$. For this reason, alkaline aqueous sulfide solutions have been postulated to be a possible ore-forming solution implicated in the formation of some epithermal deposits of cinnabar (HgS), stibnite ($Sb_2S_3$), and orpiment ($As_2S_3$).

With regard to the origin of epithermal ore deposits, we have determined at 25°C the saturation curve of stibnite ($Sb_2S_3$) in $Na_2S$–$H_2O$ solutions ranging in concentration from 0.45 to 7.16 percent $Na_2S$ by weight. Fiala and Konopik (*1*) demonstrated that the solubility of stibnite at 20°C increased markedly with increasing $Na_2S$ concentration; however, in addition to stibnite they encountered some solid phases that we did not find.

Artificial stibnite was prepared by heating to 800°C finely ground antimony and sulfur in evacuated silica-glass tubes and allowing the mixture to cool slowly for 24 hours. The interplanar spacings of the resultant solid phase were identical with the spacings of natural stibnite, and microscopic examination revealed homogeneous stibnite only.

Clear, colorless $Na_2S \cdot 9H_2O$ and boiled distilled $H_2O$ were used to make up the $Na_2S$ solutions. Stibnite and $Na_2S$ solutions were agitated in rotating Teflon bottles at 25.00°C for periods ranging from 3 weeks to longer than 2 months. The $Sb_2S_3$ and $Na_2S$ contents of solutions after 3 weeks did not differ significantly from the contents of solutions allowed to react for 2 months.

The saturated solutions were filtered through a fritted-glass crucible and were divided into two portions; one for the antimony analysis and the other for the total-sulfur analysis. Antimony was determined electrolytically by a modification of Treadwell and Hall's procedure (*2*). Total sulfur was determined by oxidizing the sulfur of dissolved $Sb_2S_3$ and $Na_2S$ to sulfate and precipitating the sulfate as barium sulfate (*3*). The percentage of $Na_2S$ was calculated from the determined concentrations of $Sb_2S_3$ and total sulfur. Water percentage was obtained by difference. Table 1 presents these and other data.

Figure 1 shows the 25°C saturation curve of stibnite. The convexity of the saturation curve toward the unsaturated solution field indicates that the ratio of dissolved $Sb_2S_3$ to total $Na_2S$ increases with increasing concentration of $Na_2S$; dilution of saturated solutions would therefore cause supersaturation.

Table 1. Solutions saturated with stibnite ($Sb_2S_3$) at 25° ± 0.02°C and 1 atm : compositions, mole ratios, and calculated constants.

| Composition | | | | | $Sb_2S_3$ : $Na_2S$ | *K* |
|---|---|---|---|---|---|---|
| Percentage by weight | | | Mole per kilogram | | | |
| $Na_2S$ | $Sb_2S_3$ | $H_2O$ | $Na_2S$ | $Sb_2S_3$ | | |
| 0.45 | 0.47 | 99.08 | 0.058 | 0.0138 | 0.238 | 7.7 |
| .73 | .85 | 98.42 | .094 | .0250 | .266 | 6.4 |
| 1.21 | 1.45 | 97.34 | .155 | .0426 | .275 | 3.4 |
| 0.88 | 2.32 | 95.80 | .241 | .0683 | .283 | 3.1 |
| 1.95 | 2.42 | 95.63 | .250 | .0712 | .285 | 3.0 |
| 2.46 | 3.67 | 93.87 | .315 | .1080 | .343 | 5.5 |
| 3.62 | 5.66 | 90.72 | .464 | .1667 | .360 | 4.9 |
| 3.87 | 6.00 | 90.13 | .496 | .1766 | .356 | 4.4 |
| 4.91 | 7.90 | 87.19 | .629 | .2325 | .371 | 4.4 |
| 5.25 | 8.75 | 86.00 | .672 | .2576 | .383 | 5.3 |
| 5.68 | 9.11 | 85.21 | .728 | .2682 | .368 | 3.6 |
| 6.48 | 11.16 | 82.36 | .830 | .3285 | .397 | 5.5 |
| 7.16 | 12.55 | 80.29 | .917 | .3694 | .403 | 5.8 |

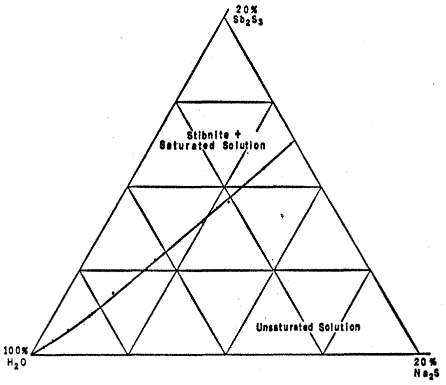

Fig. 1. Saturation curve of stibnite ($Sb_2S_3$) in a portion of the system $Sb_2S_3$–$Na_2S$–$H_2O$ at 25° ±0.02°C. Points represent the compositions of the analyzed saturated solutions.

The reaction between $Sb_2S_3$ and $Na_2S$ solution is usually written (*4*)

$$Sb_2S_3 + 3\,Na_2S = 2\,Na_3SbS_3 \tag{1}$$

which suggests the possibility that a complex anion with the general formula $Sb_nS_{3n}{}^{3n-}$ exists in solution. If such a complex predominated, the saturated solutions should show no more than a 1 : 3 mole ratio of $Sb_2S_3$ to $Na_2S$, and the closest approach to the 1:3 ratio would be expected in the most concentrated solutions. The mole ratios of the saturated solutions (Table 1) range from 0.238 for the most dilute $Na_2S$ solutions to 0.403 for the most concentrated. The reaction of stibnite and solution cannot be wholly as in Eq. 1.

The ratio of $Sb_2S_3$ to $Na_2S$ of the complex anion may correspond to the composition of one or more of the known solid compounds of $Sb_2S_3$ and $Na_2S$; they are: $Sb_2S_3 \cdot 3Na_2S$, $Sb_2S_3 \cdot 2Na_2S$, $2Sb_2S_3 \cdot 3Na_2S$, $Sb_2S_3 \cdot Na_2S$, and $2Sb_2S_3 \cdot Na_2S$. Reaction between stibnite and sulfide ion can be written

$$m\,Sb_2S_3 + n\,S^{2-} = (Sb_2S_3)_m(S)_n{}^{2n-}$$

If one complex predominates in the solution, the equilibrium constant for the reaction is

$$K = [(Sb_2S_3)_m(S)_n{}^{2n-}]/[S^{2-}]^n$$

in which expression formulas in brackets indicate activities. The solubility of stibnite would therefore be a function of the sulfide-ion concentration. However, the sulfide-ion concentration is low in $Na_2S$–$H_2O$ solutions because of the extensive hydrolysis reactions $S^{2-} + H_2O = HS^- + OH^-$, and $HS^- + H_2O = H_2S + OH^-$. The hydrolysis of sulfide becomes relatively less with increase in $Na_2S$ concentration, and the sulfide-ion concentration increases as a consequence. The ratio $Sb_2S_3:Na_2S$ in the saturated solutions should increase with increasing $Na_2S$ if the hydrolysis reaction plays a significant role. The ratio does increase with increasing $Na_2S$ concentration (Table 1). However, even in the most concentrated $Na_2S$ solution, 0.917 mole/kg, hydrolysis is strong, and 0.4 is probably considerably less than the true value of $m:n$.

The strong hydrolysis of sulfide ion in water solution largely converts the sulfide ion to $HS^-$. Hydroxide ions are produced in quantity equivalent to $HS^-$. A reaction between stibnite and $Na_2S$ solutions can therefore be written

$$mSb_2S_3 + n\,HS^- + n\,OH^- = (Sb_2S_3)_m(S)_n^{2-} + n\,H_2O,$$

and the equilibrium constant is

$$K=[(Sb_2S_3)_m(S)_n^{2-})]/[(HS^-)^n(OH^-)^n]$$

If the $S^{2-}$ concentration is small enough to be neglected, values for $K$ may be calculated from the experimental data for various assumed reactions by making the approximation that concentrations can be substituted for activities. Of the reactions considered, only calculations based on

$$2Sb_2S_3 + HS^- + OH^- = Sb_4S_7^{2-} + H_2O$$

yielded reasonably constant values for $K$. The calculations were made as follows: If $A$ is total $Na_2S$ in moles per kilogram and $B$ is total $Sb_2S_2$ in moles per kilogram, $A - 2B = (HS^-) = (OH^-)$. The $K$ for the reaction can be written

$$K = B/2/(A - 2B)^2$$

The values of $K$ calculated in this way (Table 1) range from 3.0 to 7.7, with a mean of 5.0; no particular trend of the value of $K$ with increase in concentration of $Na_2S$ was noted.

The following reaction is therefore tentatively proposed as being compatible with the data:

$$2Sb_2S_3 + S^{2-} = Sb_4S_7^{2-}$$

Adding to the plausibility of the postulated reaction is the existence of a solid compound having formula $2Sb_2S_3 \cdot Na_2S$, in which the mole ratio $Sb_2S_3:Na_2S$ is 2 : 1.

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### References and Notes

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## Retrograde Melting in the System Mg-Fe-Si-O

With regard to possible retrograde melting in the system Mg-Fe-Si-O (*1*), two comments are in order.

First, the lines (*1*, figs. 1 and 2) representing equilibrium conditions for the assemblages ol+py+I+liq and py+sil+I+liq must both have positive slopes steeper than that of the line for ol+sil+I+liq and flatter than that for ol+py+sil+I. This is seen from the chemographic relations of the phases in the projected compositional triangle Fe-Mg-Si (projected from the O corner of the tetrahedron Fe-Mg-Si-O) by the methods elaborated by Schreinemakers (*2*).

When the figures are thus corrected, it becomes evident that the possibilities for "retrograde melting" are in fact significantly greater than recognized by Speidel and Nafziger. Pyroxene-iron-silica assemblages cooled at constant or increasing $f_{O_2}$ from temperatures above 1305°C and oxygen fugacities above $10^{-11.3}$ atm (or lower, if $f_{O_2}$ increases on cooling) will react to form melt on crossing the line py+sil+I+liq, as will pyroxene-olivine-iron assemblages in the same $T$-$f_{O_2}$ region on cooling across the line ol+py+I+liq.

Second, the so-called "heat" of reaction derived by Speidel and Nafziger from the slope of the line for ol+sil+I+liq is in fact only an intermediate result in what could be a calculation of the standard heat of the reaction

$$2Fe + O_2 + SiO_2 = Fe_2SiO_4$$

if the activity coefficients of $Fe_2SiO_4$ in olivine and melt were accurately known as a function of temperature and composition. In the absence of such knowledge, slopes of lines on diagrams of log $f$ plotted against $1/T$ cannot be interpreted in terms of physical heat. In any event, comparison with Darken and Gurry's (*2*) value for the standard enthalpy of formation of wustite (not the enthalpy of oxidation of metallic iron to the divalent ion, as stated) provides at best only a crude qualitative indication of the energy balance in the process under consideration.

An additional comment relates to the use of the term "retrograde melting" to describe a reaction between a gas and one or more solids to produce a liquid different in composition from either. The reaction considered here is entirely analogous to what takes place on cooling a system consisting of NaCl crystals and steam at 1 atm from 200°C to a temperature below 100°C; if there is enough $H_2O$, the salt crystals disappear and a liquid appears; but one would not normally call the process "retrograde melting."

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Toulmin's first comment to our report is correct if the four-phase assemblages considered could be projected onto the Mg-Fe-Si plane. However, vapor is present in equilibrium with all the phase assemblages presented (*1*, figs. 1 and 2). Oxygen must also be considered and Schreinemakers' relations for quaternary (*2*) rather than ternary systems (*2*, p. 531) must be used. The relations (*1*, figs. 1 and 2) are therefore correct and have been verified experimentally (*3*). The vapor-absent curve lies between (ol+py+sil+liq) and the metastable extension of py+sil+I+liq. Toulmin's comments on the heat of reaction are well taken. All we intended was a qualitative indication of energy relations.

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