REDUCTION OF STIBNITE BY METHANE

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Reduction of stibnite by methane gives metallic antimony and chiefly hydrogen sulphide. The overall reaction takes place as follows: $2Sb_2S_3 + 3 CH_4 = 4 Sb + 6 H_2S + 3C$. A small portion of hydrogen sulphide reacts with carbon yielding carbon disulphide. Reduction is slow in the range of 480 - 580°C., but can be accelerated by the use of incorporates. Best results are obtained in the presence of active carbon, when virtually complete desulphurization was achieved at 530 - 580°C., in three hours. The reaction is considered suitable for large scale production of antimony.

Although stibnite contains a high percentage of sulphur (28.3% for pure Sb_2S_3), during the extraction of antimony seldom is the sulphur utilized. In the usual iron reduction process, the sulphur is lost as iron sulphide. Simultaneous utilization of both the metal and sulphur contents of a mineral would not only put the metallurgy on a better economic footing, but also ease the general shortage of sulphur in the world.

A series of investigations was carried out in this laboratory on the chlorination of metal sulphides.[1-6] A general reaction was noted, which under optimum conditions produced elementary sulphur and the respective metal chloride.

Metal sulphide $+ Cl_2 =$ Metal chloride $+$ Sulphur (or sulphur chlorides).

In many cases the metal may be recovered from the chloride through the intermediate formation of oxide (simultaneously regenerating the chlorine) or by direct reduction of the chloride by hydrogen.

From a consideration of the relative free energy changes with temperature, the possibility of reduction of sulphides by hydrogen was first suggested by Ellingham.[7] Clark and Spittle[8] studied the reaction between hydrogen and iron pyrites and found that only the labile sulphur atom in the FeS_2 can be removed by hydrogen; thus although the reaction was unsatisfactory for direct production of iron, it was considered a good method for manufacture of hydrogen sulphide.

Recently it was observed by Khundkar[9] that stibnite could be completely desulphurized by hydrogen. Optimum temperature was 500-525°C. and the reaction showed promise for large scale production of antimony. In view of our resources of natural gas, reducibility of stibnite by methane was next studied and the results are summarized in the present paper.

No information is available in the literature regarding the action of methane on antimony trisulphide. But with the oxides, reduction by methane usually takes place at temperatures somewhat higher than that by hydrogen. On the basis of this it was expected that stibnite also may be reduced by methane. According to the free energy of formation data,[10] methane should be thermodynamically unstable above 500°C. Although the pyrolysis of methane is complex, it is known[11] to take place mainly as $CH_4 \rightarrow C + 2H_2$. In conformity with this, it has been found in the present investigation that stibnite is reduced by methane giving metallic antimony and hydrogen sulphide.
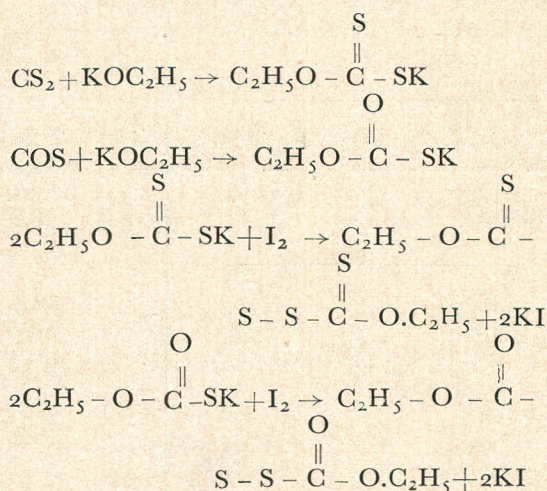
Experimental

The stibnite used in the investigation was a sample of well-liquated ore that contained about 99% of Sb_2S_3 (sulphur content 27.0%).

Methane was prepared by heating a mixture of sodium acetate and soda lime and was purified by passing the gas successively through alkaline pyrogallate, ammoniacal Cu_2Cl_2, conc. H_2SO_4 and CuO contained in a tube heated to about 260-280°C. and finally through caustic soda beads kept in a U-tube. The purified gas was then passed through a silica tube heated in an electric tube furnace to a desired temperature (measured by a Cambridge Pt/Pt-Rh thermocouple together with a temperature indicator, and controlled by a rheostat). Stibnite (with or without incorporate) was taken in a porcelain boat and placed inside the silica tube at the central zone of the furnace.

For each experiment, a weighed quantity of stibnite was placed inside the silica tube in the furnace, and heated to the desired temperature. A steady flow of the dry methane gas was then passed for a definite period. The volatile products from the exit end of the silica reaction tube were collected in absorbers and analyzed. At the end of the experiment, the residual solid in the boat was analyzed for sulphur content to determine what proportion of the stibnite was desulphurized (and converted to the metal).

Qualitative tests detected the formation of hydrogen sulphide and carbon disulphide as the chief volatile products. These were determined quantitatively from their mixture. The method essentially consists of absorbing the mixture under careful conditions in alcoholic KOH. The sulphide or hydrosulphide (formed from H_2S) is then selectively precipitated by ammoniacal zinc chloride solution and determined by evolution method; the xanthate in the solution was then determined iodimetrically.[12]

In some of the experiments, a small proportion of air was admixed with methane as the throughput gas. This introduced a possibility of formation of COS, which also would form xanthate[13] like carbon disulphide.

$$CS_2 + KOC_2H_5 \rightarrow C_2H_5O - \overset{\overset{S}{\|}}{C} - SK$$

$$COS + KOC_2H_5 \rightarrow C_2H_5O - \overset{\overset{O}{\|}}{C} - SK$$

$$2C_2H_5O - \overset{\overset{S}{\|}}{C} - SK + I_2 \rightarrow C_2H_5 - O - \overset{\overset{S}{\|}}{C} - S - S - \overset{\overset{S}{\|}}{C} - O.C_2H_5 + 2KI$$

$$2C_2H_5 - O - \overset{\overset{O}{\|}}{C} - SK + I_2 \rightarrow C_2H_5 - O - \overset{\overset{O}{\|}}{C} - S - S - \overset{\overset{O}{\|}}{C} - O.C_2H_5 + 2KI$$

Therefore, for some such experiments the issuing gas from the reaction was successively bubbled through iodine solution (to absorb H_2S), KI solution (to absorb iodine), ammoniacal $CaCl_2$ (to absorb COS), 50% H_2SO_4, and finally through alcoholic KOH (to absorb CS_2). The COS absorbed in ammoniacal $CaCl_2$ solution was oxidized and determined as $BaSO_4$. It was, however, observed that under our conditions of experiment, the proportion of COS formed was really insignificant, never exceeding 2% of the total sulphur products.

Results and Discussion

Exploratory work revealed that the desulphurization of stibnite by methane was indeed slow below 480°C. and for complete desulphurization at a reasonable rate, higher temperatures were required. On the basis of this, a range of temperature between 480°C. and 580°C. was chosen for further study.

The first set of experiments was carried out at three different temperatures, with stibnite only, and without any incorporate. Results (Table 1) show that hydrogen sulphide is the main product, with a very small proportion of carbon disulphide. As hydrogen sulphide and carbon disulphide, together with the residual sulphur (remaining unreacted in the stibnite) could account for 97-99.9% of sulphur input, it was taken that the reduction did not yield any other sulphur compound in any significant amount.

The reduction is slow at 480°C., nearly 85% of the sulphide remaining unreacted. It increases steadily with the increase of temperature and at 580°C. nearly 70% of the sulphide (31.5% unreacted residue) is reduced in three hours — 58.0% forming H_2S and 7.5% CS_2. For complete desulphurization, therefore, a higher temperature was warranted. But due to considerable volatility of stibnite itself use of higher temperatures was found unsatisfactory in a flow system. Possibility of finding suitable incorporates that would accelerate the desulphurization was explored and the results obtained with some of them are presented in Table 2.

With MgO as incorporate, (Table 2, also Fig. 1) at 480°C., yields of both hydrogen sulphide and carbon disulphide are slightly higher. But that does not appear very useful, because at higher temperatures it has not much effect; in fact it actually slows desulphurization.

With alumina (Table 2, Fig. 1) the rate of desulphurization is more rapid, particularly at 580 C., at which temperature the reduction is nearly complete. With this catalyst, a maximum of 78.5% of the sulphide was converted to hydrogen sulphide. The formation of carbon disulphide also takes place; in fact the proportion of carbon disulphide is a little more (than without any incorporate).

Most effective desulphurization takes place with active carbon as incorporate. With active carbon, the desulphurization is virtually complete (residual sulphide 1.6%) at 530°C. and 95.0% of the sulphide is converted to hydrogen sulphide (Table 2). In the presence of active carbon, formation of carbon disulphide is relatively less (1.7% at 530°C., as compared to 4.3% without any incorporate). The lower figures for hydrogen sulphide at 580°C. is due to the higher proportions of carbon disulphide.

It can thus be concluded that reduction of stibnite by methane takes place at higher temperatures than by hydrogen.[9] The product of reduc-

Table 1.—Reduction of Stibnite by Methane. Effect of Temperature on Reduction. Stibnite taken = 0.50 g. (corresopnding to 0.135 g. Sulphur). Period of Reduction = 3 hours. Rate of CH$_4$ Flow = 5 – 6 c. c./min.

Temp. °C.	Total H$_2$S formed		Total CS$_2$ formed		Residual Sulphide		Total sulphur accounted for, %
	as g. sulphur	% input	as g. sulphur	% input	as g. sulphur	% input	
480 ..	0.0186	13.8	0.0023	1.7	0.1140	84.4	99.9
530 ..	0.0481	35.6	0.0058	4.3	0.0787	58.3	98.2
580 ..	0.0783	58.0	0.0101	7.5	0.0425	31.5	97.0

Table 2.—Reduction of Stibnite by Methane in the presence of Different Incorporates. Stibnite Taken = 0.50 g. (correspoding to 0.135 g Sulphur). Period of Reducton = 3 Hours. Rate of CH$_4$ Flow = 5–6 cc./min.

Incorporate added	Reduct-tion Temp. °C.	Total H$_2$S formed		Total CS$_2$ formed		Residual Sulphide		Total sulphur accounted for, %
		as g. sulphur	% Input	as g. sulphur	% Input	as g. sulphur	% Input	
0. 5 g. MgO ..	480	0.0272	20.2	0.0049	3.6	0.1014	75.1	98.9
	530	0.0317	23.5	0.0058	4.3	0.0952	70.5	98.3
	580	0.0525	38.9	0.0096	7.1	0.0695	51.5	97.5
0.5 g. alumina ..	480	0.0301	22.3	0.0056	4.2	0.0968	71.7	98.2
	530	0.0613	45.4	0.0122	9.1	0.0587	43.5	98.0
	580	0.1060	78.5	0.0222	16.1	0.0043	3.2	97.8
0.3 g. active carbon ..	480	0.0944	69.9	0.0022	1.6	0.0367	27.2	98.7
	530	0.1283	95.0	0.0023	1.7	0.0022	1.6	98.3
	580	0.1210	89.6	0.0087	6.5	0.0014	1.0	97.1

Table 3.—Reduction of Stibnite by Methane. Effect of Incorporating Traces of Air in the Presence of Different Incorporates. Temperature of Reduction = 580°C. Peroid of Reduction = 3 Hrs. Stibnite taken = 0.5 g. Rate of CH$_4$ Flow = 5 – 6 c.c./min.

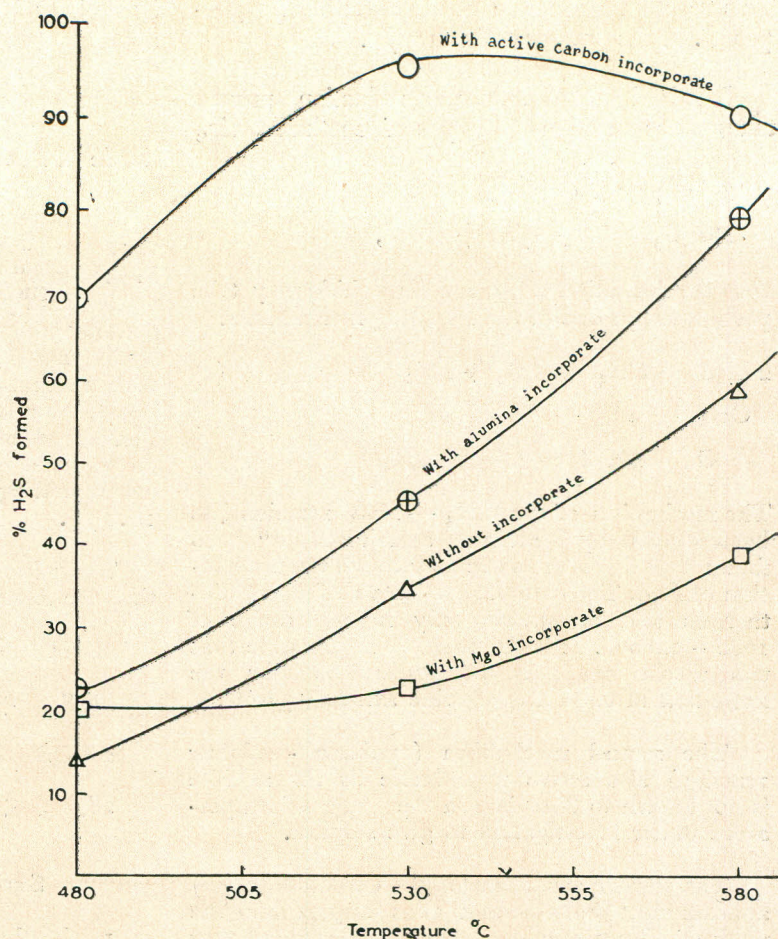| Incorporate added	Total H$_2$S formed		Total CS$_2$ formed		Residual Sulphide		Total S accounted for, %
	as g. sulphur	% Input	as g. sulphur	% Input	as g. sulphur	% Input	
None	0.0783	58.0	0.0101	7.5	0.0425	31.5	97.0
0.3 g. active carbon + trace of air.	0.0961	71.2	0.0337	25.0	0.0015	1.1	97.3
0.5 g. alumina + trace of air ..	0.1013	75.0	0.0264	19.6	0.0039	2.9	97.5

Fig. 1.—Reduction of stibnite by methane,

tion with methane is mainly hydrogen sulphide, but some carbon disulphide is also formed. Desulphurization is slow (and incomplete) without any incorporate. Both alumina and active carbon accelerate desulphurization. Of these, from the point of view of complete desulphurization and higher yields of hydrogen sulphide, active carbon is more effective.

Mechanism of Reduction and Formation of CS_2

The formation of hydrogen sulphide by reduction of stibnite by methane is not difficult to understand. In all probability, the reduction takes place through the prior decompositon of methane into carbon and hydrogen and subsequent reduction of the sulphide by hydrogen. The slow rate of desulphurization in the absence of incorporates believed to be due to the slowness of the decompositon of methane itself. The effect of the incorporates is also believed to be indirect, i.e., by accelerating the decomposition of methane into

hydrogen. Reduction of stibnite by hydrogen had been found to be rapid at 525°C.

Another aspect of the reduction is, however, the simultaneous formation of a small amount of CS_2. No information is available in the literature on the direct formation of CS_2 from stibnite or any other metal sulphide. A reaction may be suggested as follows:

$$8\ CH_4 + 6\ Sb_2S_3 \rightarrow 12\ Sb + 16\ H_2S + CS_2 + 7C$$
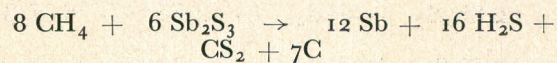
but it appears rather improbable on the basis of our knowledge of reactions that yield carbon disulphide. The simplest reaction that gives carbon disulphide is that between charcoal and sulphur vapour. This is widely used commercially at a temperature of about 900°C. An alternative reaction that has been developed commercially in the U.S.A. and Europe is the substitution of carbon by methane,[14-15] viz.,
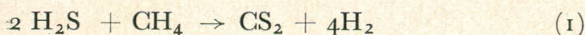
$$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$$

This reaction is effective at tempeatures of 500-700°C. in the presence of a catalyst.

If it is believed that the reduction process takes placc through pyrolysis of methane, viz.,

$$3\ CH_4 \rightarrow 3C + 6H_2$$
$$2Sb_2S_3 + 6H_2 — 4Sb + 6H_2S,$$
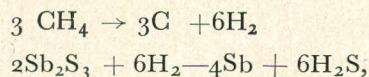
then the formation of carbon dipulphide may take place through one of the following mechanisms:

$$2\ H_2S + CH_4 \rightarrow CS_2 + 4H_2 \tag{1}$$
$$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S \tag{2}$$
$$C + 2H_2S \rightarrow CS_2 + 2H_2 \tag{3}$$

The mechanism of the $CH_4 — H_2S$ reaction has been studied by Waterman and Vlodrop[16] who found that the process occurs through the dissociation of H_2S. The overall reaction was found endothermic and favourable only in the range of 1080 – 1280°C. It looks therefore improbable that this mechanism may be responsible for the formation of carbon disulphide at 480 – 580°C.

The second mechanism (methane - sulphur reaction) also seems improbable as the stibnite is not known to dissociate in the range of temperature under investigation to give sulphur.

The third mechanism (H_2S - carbon reaction) appears most probable and gains support from the work of Owen and co-workers[17] who found that equilibrium conversion of H_2S to CS_2 according to this reaction was about 15% at temperatures around 700°C. During the present study, lustrous carbon particles were found in the boat after reaction. This gives definite support on the decomposition of methane. Thus, tentatively the reduction mechanism is postulated as follows:

$$3\ CH_4 \rightarrow 3\ C + 6\ H_2$$
$$2\ Sb_2S_3 + 6\ H_2 \rightarrow 4\ Sb + 6\ H_2S$$
$$2\ H_2S + C \rightarrow CS_2 + 2\ H_2$$
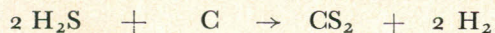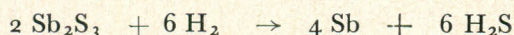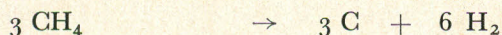
The larger extent of formation of hydrogen sulphide in the presence of active carbon may be due to its catalytic effect on the pyrolysis of methane. Apparently active carbon has no influence on the C - H_2S reaction and as such carbon disulphide formation does not increase in its presence.
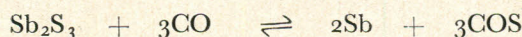
Similarly, it can be suggested that alumina also catsalyses the decomposition of methane, although its activity is less than that of active carbon. It appears that alumina catalyses to some extent the C - H_2S reaction, thereby yielding more carbon disulphide.

Role of Traces of Air: Increased Yield of CS_2

If carbon disulphide formation does take place through C - H_2S reaction, its yield should increase in the presence of air as was found in another investigation by Owen & co-workers.[18] That this is actually true will be seen from results in Table 3. By the use of 3-5 % by volume of air in admixture with methane, in case of active carbon incorporate the carbon disulphide yield was 25.0% (compared to only 6.5% with active carbon alone). In the case of alumina incorporate however, the corresponding increase was less (19.6% from 16.1%).

The role of oxygen can be explained by postulating the following mechanism:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$
$$Sb_2S_3 + 3CO \rightleftharpoons 2Sb + 3COS$$
$$2\ COS \rightleftharpoons 2CO + S_2$$
$$2S_2 + CH_4 \rightarrow CS_2 + 2H_2S$$

Summary and Conclusions

1. Methane has been found to be an effective reducing agent for stibnite, producing metallic antimony and primarily hydrogen sulphide.

2. The reaction mechanism is believed to follow the course

$$3\ CH_4 \rightarrow 3C + 6H_2$$
$$2\ Sb_2S_3 + 6\ H_2 \rightarrow 4\ Sb + 6\ H_2S.$$
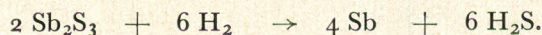
3. In the absence of any incorporate, the reaction is incomplete in the range of temperature 480-580°C. Alumina and active carbon are suitable incorporates to accelerate the desulphurization.

4. Best results are obtained with active carbon, in the presence of which virtually complete desulphurization can be effected in the range 530-580°C. Ninety-five per cent of the sulphur in the stibnite is converted to hydrogen sulphide that can be further utilized.

5. The trace of residual sulphur (ca. 1%) remaining in the pure metal can be removed by

further increase of temperature for a short while towards the end of reaction.

6. Carbon disulphide is formed as a side reaction, probably through the following mechanism: $C + 2H_2S \rightarrow CS_2 + 2H_2$. The formation of carbon disulphide, in the presence of active carbon, is small (between 1.7 and 6.5% in the range 530-580°C.). In the presence of a little air admixture (with methane) the yield may be increased to 25%.

7. The reaction is considered feasible for exploitation on a commercial basis for simultaneous extraction of antimony and recovery of sulphur.

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