

ACTION OF CARBON TETRACHLORIDE VAPOUR ON SULPHIDES

Part II.—CuS and ZnS

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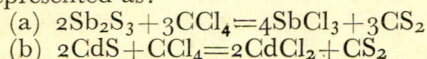
Carbon tetrachloride vapour reacted directly with cupric sulphide according to $2\text{CuS} + \text{CCl}_4 = 2\text{CuCl}_2 + \text{CS}_2$. Some elementary sulphur was formed due to the decomposition of cupric to cuprous sulphide. At the optimum temperature of 500°C , yield of CS_2 was 80%, together with about 20% of elementary sulphur. No side reactions were noted.

With zinc sulphide, the reaction followed the course $2\text{ZnS} + \text{CCl}_4 = 2\text{ZnCl}_2 + \text{CS}_2$; but this was accompanied by the (unexpected) decomposition of carbon tetrachloride itself. This produced unsatisfactory results up to 400°C mainly due to the formation of sulphur chlorides, which apparently decomposed by 500°C . At this temperature (optimum), yield of CS_2 was 85-90%. The remaining sulphur was believed to be adsorbed in the carbon formed by decomposition of the tetrachloride.

Until recently preparation of anhydrous metal chlorides, either from the corresponding oxides or the sulphides have been made by high temperature chlorination with gaseous chlorine or when necessary with its admixture with reducing gases like carbon monoxide, sulphur dioxide or even by incorporation of carbon in the solid reactant. The recent trend has been to use carbon tetrachloride as chlorinating agent for the refractory oxides; thus neptunium and niobium oxides have been effectively chlorinated^{1,2} by carbon tetrachloride. In other studies oxides such as TiO_2 , BeO , ZrO_2 and ThO_2 have been converted to their anhydrous chlorides in a similar manner.³

The possibility of chlorinating metal sulphides with carbon tetrachloride has been little explored. An old observation⁴ claims that at moderate temperatures a number of sulphide minerals showed considerable reaction with CCl_4 -air mixtures. The observation was of a qualitative nature and without any attempt to elucidate the reaction mechanism. Iron pyrites was reported⁵ to react with CCl_4 at 300 - 400°C giving chlorides of iron, FeS , S , C , and CSCl_2 (thiocarbonyl chloride); but with Sb_2S_3 at 300 - 320°C , the products were claimed to be SbCl_3 and CS_2 .

Formation of CS_2 in a simple reaction between metal sulphides and carbon tetrachloride is indeed an interesting reaction not only from the theoretical point of view but also from its practical significance. Considering the very low temperature claimed for the reaction, Khundkar *et al.*⁶ restudied the reaction for Sb_2S_3 and also included that for CdS . It was noted that the reactions with these sulphides produced sulphur chlorides at low temperatures but above 450°C the reactions could be represented as:



with some side reactions that indicated the formation of a small percentage of free sulphur.

In the present investigation, a study of the action of CCl_4 vapour on CuS and ZnS was undertaken because no reference is available on these reactions; and earlier work^{7,8} in this laboratory on the action of gaseous chlorine on Cu_2S and ZnS showed similar behaviour of these sulphides as that for Sb_2S_3 and CdS .

Thermodynamic considerations represented in the next section indicated favourable free energy values for the reaction leading to the formation of respective metal chlorides and carbon disulphide.

Thermodynamics

The thermodynamic feasibility of the respective reactions were estimated from the ΔG_T values for the formation of the different compounds calculated from the simple equation: $\Delta GT = \Delta H_{298} - T\Delta S_{298}$. The values for ΔH_{298}° and entropies for the different entities were collected from standard sources^{9,10} and their mean values were taken where they differed.

For the reaction, $2\text{CuS}(\text{s}) + \text{CCl}_4(\text{g}) = 2\text{CuCl}_2(\text{s}) + \text{CS}_2(\text{g})$ the following data were used:

Entities:	CuS(s)	CCl ₄ (g)	CuCl ₂ (s)	CS ₂ (g)
$\Delta H_{298}^\circ(\text{cal/mole})$	-12,100	-25,500	-49,000	27,550
$S_{298}^\circ(\text{cal}^\circ\text{K mole}^{-1})$	15.9	74.0	27.0	56.8

The ΔH_{298}° for $\text{S}_2(\text{g})$ was taken as 31,000 cal/mole. The S° for C (graphite), $\text{S}_2(\text{g})$, Cl_2 and $\text{Cu}(\text{s})$ were taken to be 1.36, 54.4, 53.3 and 7.97 cal^o/K mole⁻¹ respectively.

Using the above data the ΔG_T for the reaction: $2\text{CuS}(\text{s}) + \text{CCl}_4(\text{g}) = 2\text{CuCl}_2(\text{s}) + \text{CS}_2(\text{g})$ can be found to be equal to $(-21,150 - 5.04T)$

For the reaction, $2\text{ZnS}(s) + \text{CCl}_4(g) = 2\text{ZnCl}_2(s) + \text{CS}_2(g)$ the following data were used:

Entities ZnS(s)	ZnS(s)	CCl ₄ (g)	ZnCl ₂ (s)	CS ₂ (g)
$\Delta^\circ H^\circ_{298}(\text{cal/mole})$	-48,200	-25,500	-99,500	27,550
$S^\circ_{298}(\text{cal/}^\circ\text{K mole}^{-1})$	13.8	74.0	25.9	56.8

The S° for Zn(s) was taken as 9.95 cal/°K mole⁻¹. The other data were the same as in the previous calculation.

Using the above data the ΔG_T for the reaction: $2\text{ZnS}(s) + \text{CCl}_4(g) = 2\text{ZnCl}_2(s) + \text{CS}_2(g)$ was found to be equal to $(-49,550 - 7.04 T)$.

Experimental

Materials Used.—Hopkin's and William's black copper sulphide (99% pure), BDH grade white zinc sulphide (98.6% pure) and E. Merck grade sulphur-free carbon tetrachloride were used.

Apparatus and Procedure.—The experimental set up and procedure were the same as in the earlier investigation.⁶ The only difference was in the analysis of the metal chlorides formed.

A weighed amount of the chosen sulphide was taken on a porcelain boat and introduced into the reaction tube placed inside an electrically heated tube furnace. CCl₄ vapour was introduced into the reaction zone in a similar manner as in the previous experiment. The nonvolatile reaction products were analysed from the boat while the CS₂ was absorbed in alcoholic KOH solution. Soluble ZnCl₂ was determined as zinc pyrophosphate (gravimetrically). In the case of CuS the mixture after the reaction was treated with 10% CaCl₂·2H₂O to dissolve out the mixture of CuCl₂ and Cu₂Cl₂; cuprous and cupric copper were subsequently determined.¹¹ The unreacted CuS left over was analysed for copper and sulphur using standard procedure. CS₂ formed was

determined as xanthate from the alcoholic KOH, by the method of Khundkar and Eusuf.¹² This involved treatment of the alcoholic KOH with glacial acetic acid and sodium acetate to obtain a buffered solution of pH 5 to 6, followed by titration with standard iodine solution.

Results and Discussion

The highest temperature used for the reaction with CuS was 500°C, and that for ZnS, 550°C. Therefore the reactions must have taken place through the direct interaction with CCl₄ vapour, and not through its decomposition. Although the mechanism of chlorination of inorganic compounds by CCl₄ at such low temperature does not seem to be very clear, formation of metal chlorides and carbon disulphide does take place (in case of CuS, together with elementary sulphur). As the two reactions reported here appear to be somewhat different, these will be discussed separately.

Reaction with CuS

Effect of Temperature.—The first set of experiments were carried out at different temperatures (100–500°C) keeping other entities the same (Table 1). CuS taken for each experiment was relatively higher than could be consumed by the CCl₄; this resulted in an advantage that at no temperature, sulphur chlorides were formed. There was no reaction up to 200°C, and from the curve in Fig. 1, it will be seen that the reaction starts in the neighbourhood of 300°C, but thereafter proceeds steadily up to 500° (the highest temperature of study). The product in the boat after reaction was treated with 10% CaCl₂·2H₂O to dissolve the chlorides in which cuprous and cupric copper was determined according to a method earlier developed in the laboratory.¹¹ The amount of sulphide reacted was taken for the basis of sulphur (or

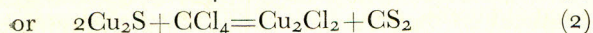
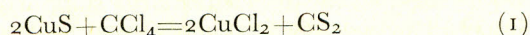
TABLE I.—REACTION BETWEEN CCl₄ VAPOUR and CuS AT DIFFERENT TEMPERATURES.

CuS taken = 4.0 ± 0.1 g; CCl₄ used = 3.19 g; flow rate of CCl₄ = 1.60 g/hr (10.4 m-moles/hr); duration of experiment = 2 hr ± 5 min.

Temp °C	CuS reacted		Soluble Cu recovered				Total S recovered				Remarks	
			Cu (II) (g)	Cu (I) (g)	Total Cu		S as CS ₂		Free S (g)	Total S S + CS ₂		
	g	as % input			(g)	% through- put	(g)	% through- put		(g)		% through- put
100	Nil	—	—	—	—	—	—	—	—	—	—	No reaction
200	Nil	—	—	—	—	—	—	—	—	—	—	" "
300	0.52	13.0	0.336	—	0.336	97.6	0.108	60.0	0.040	0.148	80.0	Only CS ₂
400	1.82	45.5	1.157	0.018	1.175	98.8	0.430	69.5	0.099	0.521	84.8	and sulphur
450	2.44	61.0	1.560	0.020	1.580	98.0	0.582	71.0	0.127	0.709	85.3	obtained.
500	2.90	72.5	1.872	0.038	1.910	98.1	0.690	71.5	0.221	0.911	93.4	

sulphide) throughput. It was noted that the copper component of the reacting sulphide was converted virtually quantitatively to chlorides, mainly to the cupric chloride with only about 2% of cuprous chloride.

The sulphur component of the reactant (CuS), finds itself mainly as carbon disulphide but about 15–20% as elementary sulphur. The total sulphur accounted for was only 80% at 300°C, but went steady to 93% at 500°C. Considering the very small amount of sulphur handled in the product which however, increases sharply, this gap is understandable. Formation of the above mentioned proportion (15–20%) of elementary sulphur must have been due to the decomposition of CuS ($2\text{CuS} = \text{Cu}_2\text{S} + \frac{1}{2}\text{S}_2$). Observing the various aspects, it appears that the main reaction should be fairly simple and as follows:



But, as the product contained mainly CuCl_2 and less than 2% of Cu_2Cl_2 , the latter must be further chlorinated through some mechanism with CCl_4 . It should also be noted that by complete decomposition of 4.0 g CuS, 1.34 g elementary sulphur should be formed; but actually only 16–20% of this was obtained at the highest temperature of 500°C. Thus with CuS, the direct reaction with CCl_4 should be considered predominant. Another point should be noted from the curve for CuS in Fig. 1. The rate of feeding of CCl_4 was 1.60 g/hr i.e. 20.8 m-mole in 2 hr. This should have been able to react with 41.6 m-mole of CuS. While in a flow system like this some allowance must be made for escape of the vapour, the reactivity was very low at 300°C, while it sharply increased to about 50% at 400°C (i.e. consumption of 20 m-mole), afterwards increasing to about 75% (30 m-mole) at 500°C. Therefore 500°C was considered quite suitable for study of time effect. As 93.4% of the sulphur throughput was accountable, a higher temperature of 550°C was not studied. As no side reaction involving formation of undesirable sulphur chloro-compounds was observed, the reaction must follow the simple mechanism as postulated earlier.

Progress of Reaction at 500°C.—Choosing the optimum temperature for the reaction, it was necessary to study the progress of reaction with time. The relevant data are presented in Table 2 and also compared in Fig. 2 with that for ZnS.

At 500°C, the reaction (amount of the sulphide reacting) follows nearly a straight line till by about 3.5 hr, nearly all the CuS has been exhausted. The proportion of CS_2 formed should have, in a sense, remained more or less the same. But the variation is understood; although attempts were

made to maintain a steady feeding rate, it would be on the average more uniform over a longer range of time; this explains some increase in the increase of yield of CS_2 . As for elementary

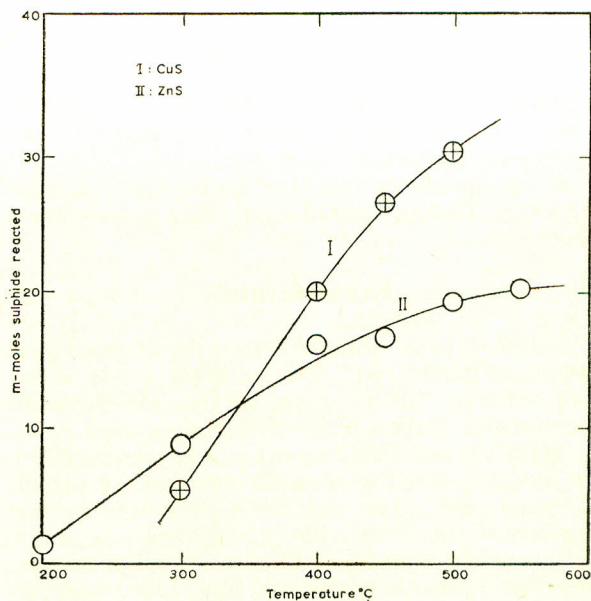


Fig. 1.—Reaction between CCl_4 vapours and CuS and ZnS respectively at different temperature.

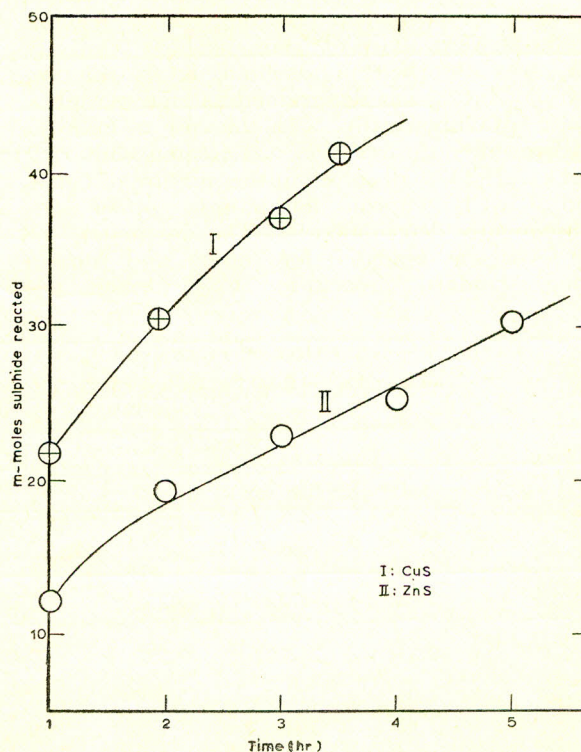


Fig. 2.—Progress of reaction between CCl_4 vapour and CuS and ZnS respectively at 500°C.

sulphur, it seems that the decomposition of CuS mainly takes place during the first hour after which it is only slow. These two effects taken together have given rather impressive results. With CuS at 500°C, action of CCl₄ vapour produces rapidly carbon disulphide (80%) and elementary sulphur (20%) nearly quantitatively.

Reaction with ZnS

Effect of Temperature.—Reactions with ZnS were carried out in the range of temperature of 100–550°C. The amount of ZnS taken (4.0 g) was somewhat in excess of that required by CCl₄ in 2 hr) for the reaction $2\text{ZnS} + \text{CCl}_4 = 2\text{ZnCl}_2 + \text{CS}_2$. Results presented in Table 3 will show that the reaction was inappreciable up to 200°C after which it became active. The percentage of ZnS reacting (throughput) was relatively low and did not reach 50% even at 550°C; but the zinc component was quantitatively converted to its chloride.

With the sulphur component of the reactant, some unexpected results were obtained. At lower temperatures much sulphur chloride and some elementary sulphur were formed. This continued up to 400°C, after which neither S₂Cl₂ nor sulphur was found but only carbon disulphide. Carbon was found deposited on the boat and around at

temperatures of 300°C and above. This must have been possible through the decomposition of CCl₄, apparently catalysed by the presence of ZnS. Such behaviour of CCl₄ offers scope for further study.

There are then two simultaneous reactions in which the CCl₄ is taking part; the direct reaction with the zinc sulphide giving carbon disulphide (and of course ZnCl₂); and the other simple decomposition of CCl₄ giving carbon and chlorine, which will also attack the sulphide. Obviously the latter reaction is responsible for the formation of sulphur chloride, some sulphur and possibly small amounts of other complex sulphur compounds. This, therefore, decreases the formation of CS₂ up to 400°C. Although some decomposition of CCl₄ is believed to take place at higher temperatures also, the direct reaction ($2\text{ZnS} + \text{CCl}_4 = 2\text{ZnCl}_2 + 2\text{CS}_2$) becomes predominant, forming only CS₂; at 500°C, 85% of the sulphur is converted to CS₂. The remaining amount of sulphur remains unaccounted. It is, however, believed that in view of the formation of S₂Cl₂ at lower temperature, some elementary sulphur may be formed at 500°C. An amount of about 0.055 g of elementary sulphur would have accounted for another 10% of sulphur throughput; and it is possible that this sulphur

TABLE 2.—PROGRESS OF REACTION BETWEEN CCl₄ VAPOUR AND CuS WITH TIME AT 500°C
CuS taken=4.0±0.01; temp of experiment=500°C; flow rate of CCl₄=1.600 g/hr (10.4 m-moles/hr).

Time in hrs	CCl ₄ input g	CuS reacted		Soluble copper recovered				Total sulphur recovered				
		g	% throughput	as Cu(I)		Total Cu		S as CS ₂		Free sulphur g	Total sulphur S+CS ₂	
				g	g	g	% throughput	g	% throughput		g	% throughput
1	1.595	2.08	52.1	0.048	1.300	1.348	97.8	0.462	66.0	0.175	0.637	91.0
2	3.190	2.90	72.5	0.038	1.872	1.910	98.1	0.690	71.5	0.221	0.911	93.4
3	4.785	3.54	88.5	0.020	2.280	2.300	98.0	0.900	75.6	0.248	1.148	96.5
3.5	5.582	3.95	98.8	0.010	2.550	2.560	98.0	1.030	77.5	0.260	1.290	97.0

TABLE 3.—REACTION BETWEEN CCl₄ VAPOUR AND ZnS AT DIFFERENT TEMPERATURES.
ZnS taken (input)=4.00±0.01 g; CCl₄ passed=3.19 g (2 ml); duration of CCl₄ feeding=2 hr±5 min;
rate of CCl₄ vapour flow=1.6 g (10.4 m-moles)/hr.

Temp of reaction (°C)	ZnS reacted		ZnCl ₂ formed		CS ₂ formed		Remarks
	(g)	% of input	as Zn (g)	as % of Zn reacted	as S (g)	as % of S reacted	
100	Nil	—	—	—	—	—	No reaction
200	0.12	3.00	0.078	97.9	0.018	45.00	Much S ₂ Cl ₂ formed; detn. of CS ₂ difficult.
300	0.85	21.10	0.557	98.0	0.145	52.00	Traces of S ₂ Cl ₂ and S; carbon deposited.
400	1.56	37.50	1.010	97.8	0.286	56.00	No S ₂ Cl ₂ only C deposited
450	1.60	40.00	1.035	97.8	0.350	66.10	C deposited
500	1.87	46.75	1.220	98.0	0.530	85.40	
550	1.97	48.60	1.290	98.1	0.480	73.70	

TABLE 4.—PROGRESS OF REACTION BETWEEN CCl_4 VAPOUR AND ZnS WITH TIME AT 500°C

ZnS (input) = 4.00 ± 0.01 g; CCl_4 passed = 1.6 g (1.0 ml) per hr.

Duration of expt. (hr)	ZnS reacted		ZnCl ₂ formed		CS ₂ formed	
	(g)	% of input	as Zn (g)	as % of Zn reacted	as S (g)	as % of S reacted
1	1.18	29.50	0.77	97.20	0.32	82.00
2	1.87	46.75	1.22	98.00	0.53	85.40
3	2.21	55.25	1.44	98.10	0.62	85.20
4	2.44	61.00	1.57	98.30	0.70	86.900
5	2.94	73.50	1.92	98.00	0.88	90.0

remains adsorbed (chemisorbed) in the carbon.¹³ The latter phenomena may also explain the slightly lower yield of CS_2 at 550°C . Considering all aspects, a temperature of 500°C was taken as optimum, and a further set of experiments was carried out at 500°C .

Progress of Reactions at 500°C with Time.—The detailed results obtained with progress of time are given in Table 4 (see also Fig. 2; comparison with CuS). The chlorination of the ZnS is somewhat slow in the first hour, after which it steadily increases with time. The reactivity is less (compared to CuS) and in 5 hr only about 75% of the sulphide was converted into its chloride.

As had already been mentioned in the reaction with ZnS , at higher temperature CS_2 was the only sulphur compound formed, and it was suggested that some elementary sulphur might have remained chemisorbed on the carbon formed. The CS_2 yield was 85.40% of the throughput in 2 hr. This remained more or less the same up to 4 hr of the reaction. In 5 hr, however, the yield increased to 90%. This may be due to some chemisorbed sulphur reacting with the carbon giving CS_2 .

The reaction thus follows the simple way as $2\text{ZnS} + \text{CCl}_4 = 2\text{ZnCl}_2 + \text{CS}_2$. The only peculiarities are that some CCl_4 decomposes at low temperatures, thus affecting the overall rate of formation and some 10% of sulphur formed remains in the carbon. Under the best conditions 90% of reacting sulphide was converted to CS_2 .

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