THE CONSTITUTION
OF SOME HEAVY METALLIC SULFIDES
(AN X-RAY AND ADSORPTION STUDY)

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CONTENTS

I. PRECIPITATED ROSE MANGANOUS SULFIDE

Mickwitz and Landesen (2), in attempting to explain the presence of extra sulfur in precipitates of rose manganous sulfide, suggested the formation of compounds of the type $H_2Mn_3S_4$, precipitated with NH_4HS in the absence of free ammonia, and $NH_4HMn_3S_4$, precipitated in the presence of free ammonia.

Feigl (1) assumed the existence of what he called iso- and hetero-polymers of the type M-S-S-M, M-S-S-Ma, M-S-S , and M-S-S-H$_2$, where M and Ma are metals.

Weiser and Milligan (4) made x-ray and analytical examinations of the rose sulfides obtained by the method of Mickwitz and Landesen in the presence and absence of free ammonia. The x-ray patterns showed the two sulfides to be the same, and no evidence could be found for the existence of such compounds as assumed above.

While the possibility of the existence of more than one form of the rose sulfide of manganese had been recognized, H. Schnaese (3) was the first person to demonstrate the actual existence of at least two crystalline modifications. He prepared the rose sulfide in a number of ways, and found that the crystal structure of the preparation varies with the method of formation. The sulfide prepared by precipitation with H_2S from manganese

acetate of high concentration was found to be mostly of the
cubic form, while the sulfide prepared in the same way from
a dilute solution of manganese acetate contained a larger
amount of the hexagonal form. Schnaase found that the
nearly pure hexagonal form could be prepared by precipita-
tion from dilute manganous chloride solution, containing a
small amount of ammonia, with H_2S and subsequent heating
of the precipitate for two days in the presence of ten
per cent NH_4Cl. He also found that the cubic modification
is formed when manganous sulfide is precipitated from
strongly alkaline solutions, i. e. with sodium sulfide,
and that the hexagonal results from precipitation from
weaker alkaline solutions, i. e. with ammonium sulfide.
The analysis of the rose precipitates showed them to con-
tain approximately theoretical amounts of manganese and
sulfur, with the sulfur in excess over the theoretical
amount.

The following experiments were made in order to
test further the possible formation of compounds of the
type suggested by Mickwitz and Landesen and Feigl, and to
determine the conditions of formation of the two crystal-
line forms of the rose manganous sulfide.

EXPERIMENTAL

In order to study the composition of precipitated
manganous sulfide, a constant amount of standard manganous

chloride was mixed with increasing amounts of standard
sodium sulfide. The final volume was a hundred c.c. in
each mixture. A rapid mixer was devised which consisted
of a 250 c.c. wide-mouth bottle containing a 30 c.c. beaker
and fitted with a rubber stopper through which a piece of
glass rodding was run to hold the beaker secure against
the bottom of the bottle. Ten c.c. of standard manganous
chloride was pipetted into the beaker, and the sodium sul-
fide, properly diluted, was placed in the bottle outside
the beaker. The solutions were mixed rapidly, and were
shaken vigorously for fifteen seconds. The precipitate
and the supernatant liquid were then transferred to a 125
c.c. Erlenmeyer flask containing methane, and this was
placed in a thermostat at $25°C$ and kept there for one hour
with occasional shaking. At the end of an hour the sus-
pensions were centrifuged, and samples of the supernatant
liquid were taken for analysis of the remaining sodium
sulfide. From a knowledge of the amounts of reagents
added and the amount of sodium sulfide left in the super-
natant liquid, the ratio of mols of S to mols of Mn in
the precipitate could be calculated.

The sodium sulfide was determined and standard-
ized by adding samples of the stock solution and the
supernatant liquid from the precipitates to a known
amount of standard iodine containing HCl. The excess
iodine was titrated with standard sodium thiosulfate.

A series of determinations was made in the same

way using cobalt chloride in place of manganous chloride.
The results of these experiments are given in Tables A and B.

In order to study the conditions of formation of
the two forms of rose manganous sulfide, samples were pre-
cipitated from saturated and dilute solutions of manganous
chloride and manganous sulfate. Also, the sulfide was pre-
pared by precipitation with dilute and concentrated sodium sul-
fide.

Manganous chloride solution was made up saturated
0.05 molar by dissolving the "c. p." grade reagent in dis-
tilled water (boiled). Manganous sulfate was made by dis-
solving the washed carbonate in enough sulfuric acid to cause
complete solution, and then was concentrated by evaporation
until crystallisation took place. The ammonium sulfide solu-
tion was prepared by saturating one molar ammonium hydroxide
with hydrogen sulfide and subsequent addition of an equal
amount of ammonium hydroxide to the ammonium hydrosulfide.

100 c.c. of the ammonium sulfide solution was added
slowly and with vigorous stirring to 10 c.c. of the saturated
manganous chloride solution. The precipitate was washed free
of chloride ion with the aid of the centrifuge, using water
containing hydrogen sulfide as a washing medium to prevent
oxidation. The precipitate was washed then with carbon di-
sulfide several times and dried in an atmosphere of hydrogen
sulfide at approximately 60 degrees Centigrade. Then the
dried sample was sealed in a tube containing hydrogen sul-
fide for keeping.

In the manner just described manganous sulfide was prepared also from the saturated manganous sulfate.

The sulfide was prepared from the 0.05 molar solutions by addition of 50 c.c. of 1 molar ammonium sulfide to 400 c.c. of the manganous solutions as described above. The precipitates were washed, dried, and sealed as above also.

The samples prepared were finely ground, and were x-rayed in the General Electric X-Ray Apparatus by the powder method. Values of the intensities and spacings are given in Tables I, II, III, IV, V, VI, IIIa, IVa, Va, VIa.

From the analytical data curves of mols of S/mols of Mn and mols of S/mols of Co were plotted against the final concentration of sodium sulfide in the supernatant liquid. However, only representative tables of data from each will be shown here. The curves were extremely difficult or impossible to duplicate. This fact may have been caused by slight variations in the mixing of the samples, or by inherent errors in the method. The values of the ratio found at the different concentrations demonstrate a point which will be brought out later.

The x-ray patterns were diagramed as shown below. The interplanar distances in Angstrom units are indicated by the position of the vertical lines, and the height of the lines indicates the visually estimated relative intensities.

Table A

Adsorption of Na_2S by MnS

Mols $MnCl_2$ added in 100 c.c.	Mols Na_2S added in 100 c.c.	Mols Na_2S found in 100 c.c.	Mols Na_2S adsorbed in 100 c.c.	$\dfrac{\text{Mols S}}{\text{Mols Mn}}$	Na_2S left mol x 10^2 per liter
0.008095	0.01189	0.002900	0.000893	1.110	2.900
0.008095	0.01785	0.008671	0.001066	1.130	6.671
0.008095	0.02378	0.01457	0.001111	1.138	14.57
0.008095	0.02970	0.02031	0.001315	1.162	20.31

Table B

Adsorption of Na_2S by CoS

Mols $CoCl_2$ added in 100 c.c.	Mols Na_2S added in 100 c.c.	Mols Na_2S found in 100 c.c.	Mols Na_2S adsorbed in 100 c.c.	$\dfrac{\text{Mols S}}{\text{Mols Co}}$	Na_2S left mols x 10^2 per liter
0.007699	0.01037	0.001590	0.001081	1.140	1.590
0.007699	0.01556	0.006651	0.001205	1.156	6.651
0.007699	0.02593	0.01681	0.001416	1.184	16.81
0.007699	0.03630	0.02702	0.001576	1.205	27.02

Table I	
Indices	Interplanar spacings in Angstroms
10$\bar{1}$0	3.44
00$\bar{0}$2	3.22
10$\bar{1}$1	3.04
10$\bar{1}$2	2.55
11$\bar{2}$0	1.985
10$\bar{1}$3	1.820
20$\bar{2}$0	1.720
11$\bar{2}$2	1.691
20$\bar{2}$1	1.662
20$\bar{2}$2	1.519
20$\bar{2}$3	1.340
21$\bar{3}$0	1.300
21$\bar{3}$1	1.273
21$\bar{3}$2	1.209
10$\bar{1}$5	1.209
30$\bar{3}$0	1.150
21$\bar{3}$3	1.110
30$\bar{3}$2	1.080
20$\bar{2}$5	1.030
22$\bar{4}$0	0.994

Schnaase's hexagonal

ZnS values

Table II	
Indices	Interplanar spacings in Angstroms
111	3.23
220	1.980
311	1.689
400	1.400
331	1.284
422	1.143
511	1.078
333	
440	0.990

Schnaase's cubic

ZnS values

Table III	
Relative intensity	Interplanar spacings in Angstroms
2	3.43
9	3.22
2.5	3.04
10	1.978
1	1.820
8	1.684
2	1.400
4	1.280
5	1.140
1	1.075
-	0.990
-	0.944

Values for MnS

from saturated

MnCl$_2$

Table IV	
Relative intensity	Interplanar spacings in Angstroms
8	3.44
7	3.22
6	3.03
1	2.70
10	2.48
9	1.980
3	1.817
8	1.668

Values for MnS from

0.05 molar MnCl$_2$

The blank spaces under the intensity heading indicate lines of such low intensity that the estimated value of the intensity would be less than one on a scale of ten.
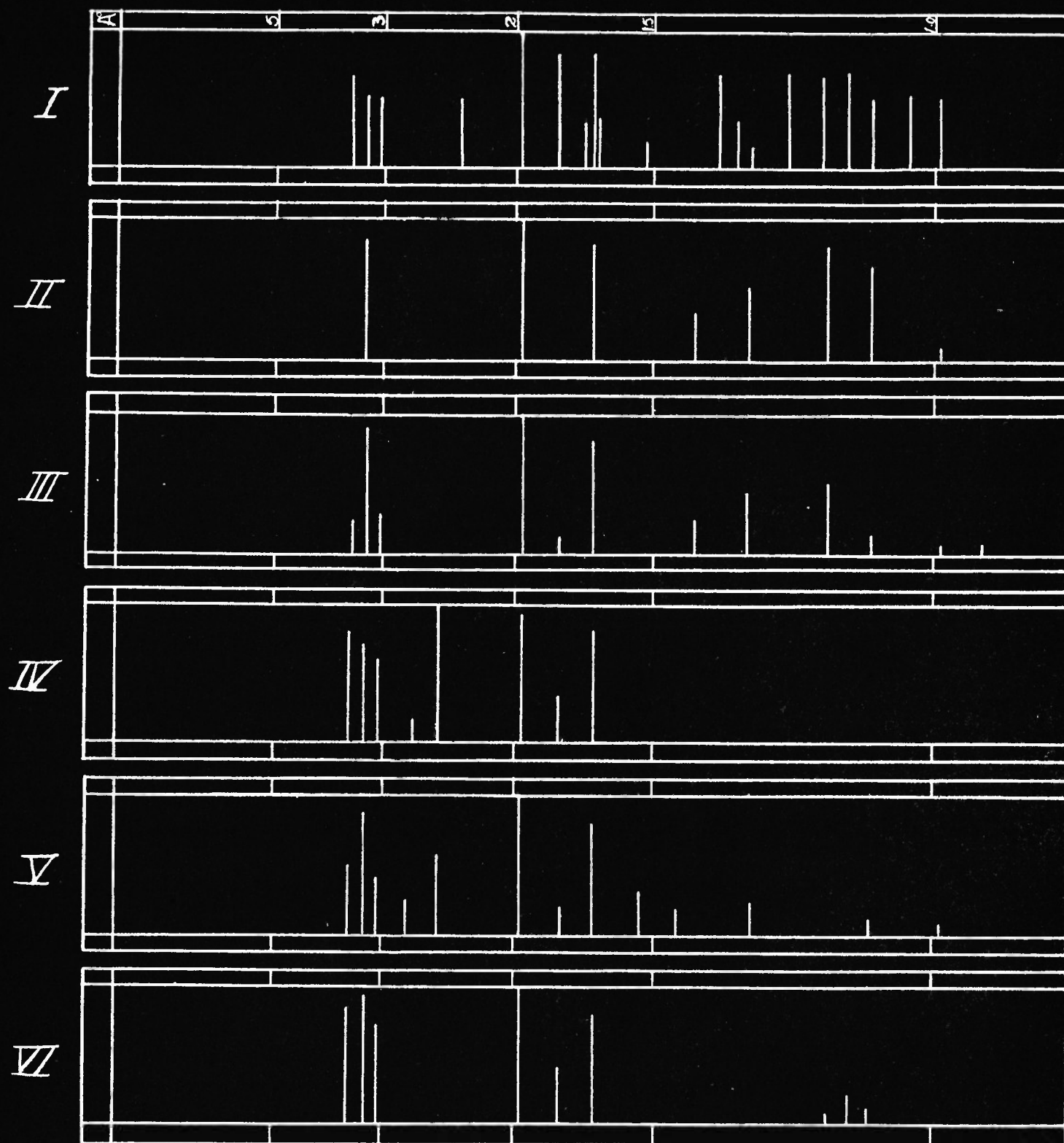
Table V	
Relative intensity	Interplanar spacings in Angstroms
5	3.44
9	3.20
4	3.05
3	2.73
6	2.49
10	1.978
2	1.802
8	1.685
3	1.533
2	1.440
2	1.278
1	1.078
1	0.990
1	0.943

Values for MnS from saturated MnSO$_4$

Table VI	
Relative intensity	Interplanar spacings in Angstroms
8	3.44
9	3.22
7	3.04
10	1.982
4	1.820
8	1.690
1	1.144
2	1.112
1	1.080

Values for MnS from 0.05 molar MnSO$_4$

X-Ray Diagrams

I Schnaase's Hexagonal MnS   IV MnS from 0.05 Molar MnCl₂

II Schnaase's Cubic MnS   V MnS from Saturated MnSO₄

III MnS from Saturated MnCl₂   VI MnS from 0.05 Molar MnSO₄

Table IIIa		Table IVa	
Relative intensity	Interplanar spacings in Angstroms	Relative intensity	Interplanar spacings in Angstroms
4	3.44	5	3.42
9	3.22	10	3.22
2	3.04	2	3.03
10	1.975	9	1.975
1	1.816	1	1.814
8	1.682	9	1.684
-	1.397	1	1.394
-	1.346	1	1.340
-	1.280	2	1.280
2	1.140	-	1.202
-	1.109	3	1.140
-	1.075	1	1.109
-	1.990	1	1.074
-	1.943	1	0.990
		2	0.943

Values for MnS from $MnCl_2$ and a small excess of Na_2S-Fresh precipitate

Values for MnS from $MnCl_2$ and a large excess of Na_2S-Fresh precipitate

Table Va		Table VIa	
Relative intensity	Interplanar spacings in Angstroms	Relative intensity	Interplanar spacings in Angstroms
4	3.46	6	3.46
10	3.22	7	3.22
3	3.03	5	3.04
9	1.982	10	1.990
2	1.820	9	1.819
8	1.689	8	1.690
-	1.400	1	1.344
1	1.344	-	1.280
3	1.280	2	1.145
1	1.203	2	1.113
4	1.144	2	1.079
2	1.112	2	0.994
3	1.077	-	0.946
-	0.990	-	
1	0.945		

Values for MnS from MnCl₂ and a small excess of Na₂S-Precipitate allowed to stand one month in the supernatant liquid

Values for MnS from MnCl₂ and a large excess of Na₂S-Precipitate allowed to stand in the supernatant liquid for one month

X Ray Diagrams

I — Schnaase's Hexagonal MnS

II — Schnaase's Cubic MnS

IIIa — MnS from MnCl₂ and slight excess Na₂S - Fresh ppt

IVa — MnS from MnCl₂ and large excess Na₂S - Fresh ppt

Va — MnS from MnCl₂ and slight excess Na₂S - Ppt aged 1 mo.

VIa — MnS from MnCl₂ and large excess Na₂S - Ppt aged 1 mo.

From a consideration of the data in Tables A
and B, it appears that the ratio of mols of S to mols of
Mn and Co increases steadily with increasing concentration
of the Na_2S. There is no indication of a constant ratio
which would imply the existence of a compound in which the
ratio of S to metal is greater than one.

X-ray diagram III indicates the presence of a
small amount of the hexagonal form of MnS. However, the
hexagonal lines are very few in number and the relative
intensity is very low. This sample seems to be almost
pure cubic.

In diagram IV the hexagonal lines are more in
evidence, and the pattern seems to indicate that this
sample is a mixture of both cubic and hexagonal in which
neither form predominates greatly over the other. The
extra lines shown are probably caused by the presence of
some of the oxidation product of the MnS.

In diagram V the cubic pattern is more pronounced
than the hexagonal. It is evident that the cubic form is
in greater abundance here than the hexagonal, but there
seems to be more of the hexagonal form present than there
is in the sample for diagram III.

Again in diagram VI the hexagonal form shows in
greater abundance than it did in V. Indeed, this sample
could well contain more hexagonal MnS than cubic, although
it is obviously a mixture. The cubic lines here are
stronger than they are in diagram IV.

Diagram IIIe shows both the cubic and hexagonal forms of the MnS to be present in large amount. From the relative intensities of the lines though, it appears that the cubic outweighs the hexagonal to some extent.

Diagram IVa does not differ greatly from IIIa. Here again the cubic lines appear to be more pronounced than the hexagonal.

Diagram Va also does not differ greatly from IIIa. However, certain of the hexagonal lines seem to be more pronounced.

On the other hand diagram VIa shows a much larger effect of the hexagonal form than any of the others of this series. Some of the cubic lines have become less pronounced and the hexagonal lines have become more prominent.

To summarize these observations on the x-ray patterns, it seems that from the saturated solutions the MnS is mostly cubic, although from the saturated $MnSO_4$ slightly more of the hexagonal form is obtained than from the saturated $MnCl_2$. From the dilute solutions mixtures of both forms are obtained in which the presence of the hexagonal form is much more pronounced than in the precipitates from the saturated solutions.

In the samples obtained by precipitation of $MnCl_2$ with Na_2S, mixtures of both forms are obtained. In the precipitates which were not allowed to stand in the mother liquor both forms are present in large amount with the cubic somewhat in excess. The precipitate allowed to stand

for one month in the mother liquor did not differ greatly
from the fresh precipitates if the H_2S concentration was
low. In the sample in which the H_2S concentration was rela-
tively high the presence of the hexagonal form is much more
pronounced. It is of interest to note that the precipitates
which were allowed to stand for a month in the mother liquor
gave much sharper patterns than those which were washed and
dried immediately after precipitation.

DISCUSSION

The variation of the ratio of S to Mn and Co with
the final concentration of H_2S seems to follow a typical ad-
sorption process. If any such compounds as the ones suggested
by Feigl, Mickwitz and Landesen actually existed, there would
have been a concentration range with respect to H_2S over
which the value of the above ratio would have remained con-
stant. No such thing was observed in these experiments, hence
it seems that the excess S found in the precipitated sulfides
is present by adsorption of some of the excess H_2S present by
the precipitate. The x-ray diagrams indicate that the precip-
itate is the same in all instances, since the patterns for the
precipitates from different solutions and using different
precipitants are shown to be invariably of the same two
crystalline forms.

The rose manganous sulfide seems to be dimorphous,
exhibiting a cubic form and a hexagonal form depending on
the mode of formation. Of the two forms the hexagonal seems

to be the most stable. Schnaase demonstrated this by his
method of preparation of the hexagonal sample for the de-
termination of the cell constants for this form. He pre-
cipitated the sulfide in the presence of a small amount of
ammonia, and later heated the precipitate for two days in
ten per cent ammonium chloride solution. Thus, one would
expect the most stable modification to be the one most in
abundance after such treatment. The hexagonal form appeared
almost pure in this preparation. Also, the precipitate pre-
pared by precipitation of manganous acetate with hydrogen
sulfide would be expected to contain at least a small amount
of an instable form, if one were formed, along with some of
the stable form. In this preparation of Schnaase's is found
both the cubic and the hexagonal modifications with the cubic
in much the greater abundance. These observations were borne
out in the present work. In the precipitates prepared with
Na_2S, the aged samples showed more of the hexagonal form than
the cubic. All this follows too from analogy with zinc and
cadmium sulfides in which the cubic modifications are trans-
formed into the hexagonal.

The conditions for formation of the two modifications
would seem to be as follows: The cubic form will be precipi-
tated in much greater amount from saturated or very concen-
trated solutions than the hexagonal. The cubic form is pre-
cipitated first and then goes over to the hexagonal, the rate
and amount of transformation depending on the properties and
treatment of the solution from which precipitation was

carried out. The hexagonal modification will be precipitated in greater abundance from dilute solutions, and will be formed in larger amount in the precipitate which is allowed to age before purification. In any preparation, however, it seems that both may be found, and the relative amounts will depend on the conditions just named.

The effect of the concentration of the solution in determining which modification will be present in greater amount is interesting. The following explanation of this fact is suggested: In the highly concentrated solutions the manganous ion will be present in very large excess on addition of an amount of ammonium sulfide, for example, which is much less than the manganous ion content present. Therefore, the precipitate would be most likely to adsorb a relatively large amount of the manganous ion. This adsorbed material would be expected to have a protective or inhibitive effect on the change from the first precipitated cubic form to the hexagonal. This explanation applies very well since it is seen that in the saturated solution the precipitated MnS is mostly cubic, and that in the dilute solution, in which the relative amount of manganous ion is exceedingly small, the hexagonal form is present in greater amount. The MnS from the saturated $MnSO_4$ seems to have slightly more of the hexagonal form present than that from the saturated $MnCl_2$. This is probably caused by the difference in the anions present. The tendency of the sulfate ion to neutralize the effect of the adsorbed manganous ion would be greater than that of the

chloride ion.

In the precipitates prepared with Na_2S the presence
of a quite appreciable amount of adsorbed Na_2S has been demon-
strated. Therefore, one would expect such precipitates to
show an appreciable representation of the cubic modification.
This has been shown to hold even in the precipitate which
was aged in a slight excess of sodium sulfide. However, in
the precipitate allowed to age in a large excess of sodium
sulfide the hexagonal form is represented very strongly. In
fact, it is possible that the hexagonal form outweighs the
cubic in this sample. The presence of a large amount of the
hexagonal in this precipitate may be accounted for on the basis
of a suggestion of Weiser and Milligan (4) to the effect that
a factor in the transformation of the rose manganous sulfide
to the green is the solubility of the rose form in sodium
sulfide. Thus, it would seem that in the instance above
even the protected cubic form would be soluble in the large
excess of sodium sulfide, and thereby the transformation to
the hexagonal form would be more easily brought about.

SUMMARY

(1). The presence of excess sulfur in the pre-
cipitated rose manganous sulfide has been shown to be caused
by the adsorption of the sodium sulfide by the precipitate.

(2). Sohnaase's x-ray patterns of two crystalline
modifications of rose manganous sulfide were checked, and the
conditions for formation of the two modifications were

pointed out.

(3). An explanation of why one modification will be formed in greater quantity than the other under different conditions of formation has been proposed.

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II. PRECIPITATED COPPER SULFIDE

The composition of the products from the reaction of copper ion and a soluble sulfide has long been a matter of controversy. Precipitates from cupric solution and hydrogen sulfide have been found to contain free sulfur. Thomsen (13), Brauner (2), Posnjak, Allen, and Merwin (10), Kolthoff (9), and Sauer and Steiner (12) and others have obtained free sulfur by extraction of precipitated copper sulfide with carbon disulfide.

This has led to the belief that the sulfide from cupric solution is not cupric sulfide, but is some lower sulfide of copper mixed with free sulfur. Fischbeck (7) believed the precipitated sulfide to be cuprous sulfide, and observed that the latter could take up sulfur. He concluded that copper and sulfur produce cuprous sulfide and that this substance can then take up sulfur at high or low temperature to give cupric sulfide.

Feigl (5) stated that copper sulfide precipitates in acid solution probably consisted of cupric sulfide or cuprous sulfide and free sulfur, and that in alkaline solution a mixture of cuprous and cupric sulfides results. He concluded that there was no feasible way to determine the exact composition of the precipitate. However, Feigl (6) later decided that cupric sulfide was first precipitated and later changed partially to cuprous sulfide in the following manner: $2 CuS = \begin{matrix} Cu \\ Cu \end{matrix} S = S = Cu_2S + S$, the intermediate compound being
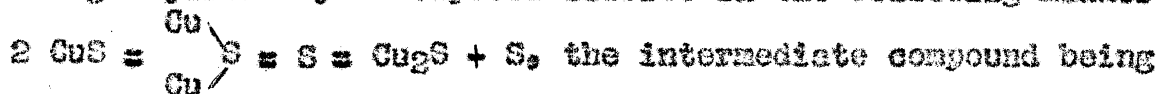
cuprous disulfide. He stated that freshly precipitated copper
sulfide contains a small amount of the cuprous sulfide and
that this increases on aging.

Kolthoff (9) and Jordis and Schweitzer (8) also
observed that the aged sulfide and that precipitated from
hot solutions contains more cuprous sulfide and free sulfur
than the fresh, cold precipitate.

Brauner (2), Ditte (4), Coppock(3), and Antony and
Luchesi (1) concluded that the sulfide from cupric solution
was cupric sulfide.

Most of the conclusions as to the composition of
the precipitated sulfide were based on analytical methods.
Such a procedure would not differentiate between cupric sul-
fide and cuprous sulfide and sulfur. In order to remedy
this Rossing (11) extracted the sulfide with silver nitrate
and attempted to determine the composition according to the
following reactions:

$$Cu_2S + 4AgNO_3 = Ag_2S + 2Ag + 2Cu(NO_3)_2 \quad and$$

$$CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2.$$

but again the possible presence of free sulfur in cuprous
sulfide and sulfur mixture would mask the true composition
by reacting according to the second equation.

Posnjak, Allen, and Merwin (10) modified the above
procedure by making use of the reaction of ferric nitrate
with the silver formed in the above reaction. Kolthoff (9)
improved this method, and from the results of his experiments
concluded that the precipitate is practically pure cupric

Sulfide with the cuprous sulfide content increasing with the temperature and the age of the precipitate. He studied the precipitates from cupric sulfate in the hot and in the cold and found them both to consist of cupric sulfide mixed with a negligible amount of cuprous sulfide. He also stated that the x-ray patterns of the hot and cold precipitates were the same.

Sauer and Steiner (12) objected to Kolthoff's method and studied the precipitates from cupric and cuprous solutions with sulfur and hydrogen sulfide. Also, these investigators studied the products of the interaction of copper and sulfur sols by a colorimetric method. Their observations of the color changes attending the interaction of copper and sulfur sols led them to believe that the composition of precipitates could be found in a like manner. They studied the color changes of the products obtained from the interaction of copper and sulfur sols, copper ion and colloidal sulfur, and copper ion and hydrogen sulfide. Sols in which the copper to sulfur ratio was two to one are golden brown and remain unchanged on heating. However, in some instances the golden brown sol turned green on heating. They assumed the color change to be caused by the formation of cupric sulfide from cuprous sulfide and sulfur originally present. In both sols and precipitates formed in the cold the copper sulfide present is assumed to be cuprous sulfide. In instances where the ratio of copper to sulfur is one, it is assumed that there is present equivalent amounts of cuprous sulfide and

sulfur. Hence, it follows that on heating the latter the color caused by the cuprous sulfide and sulfur changes to the color of cupric sulfide. Their results and observations are interesting, but drawing conclusions from the color changes of sols and precipitates of varying particle size and heat treatment seems hardly sound.

In passing, it was observed by Kolthoff (9) that the cold precipitate of copper sulfide was brown black and quite easy to filter, while the precipitate obtained in the hot (as well as the aged precipitate) has a greenish appearance, and that the hot precipitate was slimy and hard to filter. This was also observed in the work presented here and will be considered in a later section of the paper.

The following experiments were undertaken to show whether the precipitated copper sulfide is mostly cupric sulfide as believed by Kolthoff, or consists of cuprous sulfide in accordance with the views of Sauer and Steiner.

EXPERIMENTAL

Copper sulfide was prepared by the method used by Kolthoff (9). Hydrogen sulfide was bubbled through 125 c.c. of 0.05 molar cupric sulfate solution at room temperature and at 100 degrees Centigrade. The precipitates were washed free of sulfate ion with distilled water, washed several times with carbon disulfide, and dried at room temperature in the air. The cold precipitate is marked number 1, and the hot precipitate is marked 2 on the diagrams following.

The second series of copper sulfide samples was made after the method used by Sauer and Steiner (12). 250 c.c. of hydrogen sulfide water, made by saturating distilled water with washed hydrogen sulfide at room temperature, was added to 50 c.c. of 0.05 molar cupric chloride solution. The resulting precipitate was separated into two portions. One of the portions was boiled and the other was not. The precipitates then were washed free of chloride ion, and were washed also several times with carbon disulfide. They were dried at room temperature in the air. The boiled precipitate is marked 4, and the unboiled precipitate is marked 3 on the following diagrams.

The samples thus prepared were finely ground and x-rayed by the powder method in the Phillips-Metallix x-ray apparatus. The mineral covellite (CuS) was also x-rayed and is marked number 5 on the following diagrams.

The x-ray patterns of the precipitated sulfides turned out to be the same as that for the covellite with the exception of three lines near the center of the patterns. Hence, the crystal structure for only one of the samples was calculated, since it would be characteristic of all the precipitated samples. The Kolthoff hot precipitated sample (number 2) was chosen for the calculations. In the following table are given the results of the measurements and calculations on the pattern.

X-Ray Data on Copper Sulfide--Diagram Number 2

2l mm.	degrees	dhkl Angstroms	hkl	dhkl calculated
20.9	10.39	4.26		
22.9	11.39	3.89		
24.9	12.38	3.59		
27.9	13.87	3.21	100	3.21
29.8	14.82	3.00	012	2.98
32.5	16.16	2.76	013	2.74
36.0	17.90	2.50	014	2.50
39.5	19.64	2.29	007	2.28
44.6	22.18	2.04	008 016	2.04
48.7	24.22	1.87	017 110	1.87
53.5	26.60	1.72	018	1.70
58.2	28.87	1.59	020 0010	1.60
60.1	29.88	1.54	023	1.54
64.4	32.02	1.45	0011	1.45
68.4	34.01	1.37	026	1.37
70.8	35.20	1.33	0012	1.33
74.9	37.24	1.27	119	1.28
79.8	39.68	1.20	210 120	1.21
84.7	42.12	1.15	0113 0014	1.15
90.3	44.90	1.09	300	1.08
94.6	47.04	1.05	032	1.06

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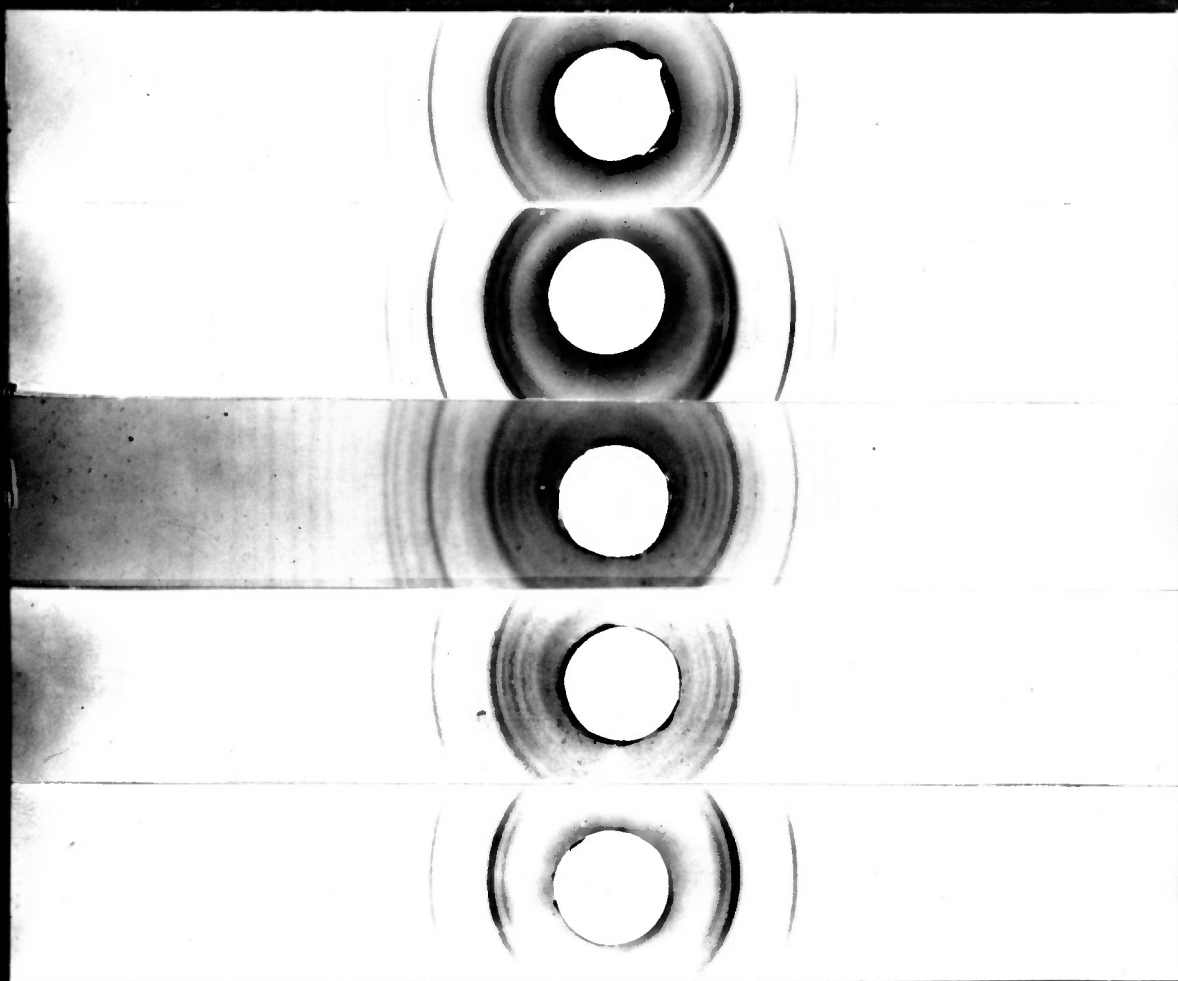
X-Ray Diagrams

of

Precipitated and Natural Copper Sulfide

The sample was exposed to copper radiation for 45 minutes in the Phillip-MetalliX apparatus using an aperture of one mm. The d_{hkl} values were obtained by the usual method from the film measurements, and the d_{hkl} calculated values were obtained from the equation for the hexagonal system:

$$\frac{d_{hkl}}{n} = a_0 \bigg/ \sqrt{\frac{4}{3}(h^2 + hk + k^2) + \frac{l^2}{c^2}}$$

where n is the order of reflection, hkl are the indices, and c is the axial ratio. a_0 is the side of the unit cell. From this equation a_0 is found to be 3.70 and c_0 is 16.1. These values agree reasonably well with those calculated for covellite by Oftedal (14). The density of substance in the hexagonal system is given by the equation:

$$D = \frac{m \times M \times 1.65}{a^2 \times c_0 \times \sin 60°}$$

where m is the number of chemical molecules in the unit, M is the molecular weight, D is the density, and a_0 and c_0 are defined above. Substituting in this equation gives m to be 5.7, which means that there are six molecules of copper sulfide in the unit cell. This agrees with the value of Oftedal and others.

The first three values of d_{hkl} do not have indices that can be calculated from the above equation. This can be shown in the following way: On substitution of the anomalous values of d_{hkl} in the above equation, the following are given:

$$\left[\frac{4}{3}(h^2 + hk + k^2) + \frac{l^2}{c^2}\right]^{\frac{1}{2}} = 3.7/4.26$$
$$'' = 3.7/3.89$$
$$'' = 3.7/3.59$$

Simplification of these equations gives:

$$\frac{4}{3}(h^2 + hk + k^2) + \frac{l^2}{c^2} = 0.755$$
$$'' \qquad = 0.906$$
$$'' \qquad = 1.06$$

Thus, it can be seen that h and k can only be zero in these equations. If they are any other values, then l will be imaginary. For h and k equal to zero, l has the values: 3.74, 4.10, 4.50, and thus these values of d_{hkl} do not belong to this system.

It was thought that these extra lines might be caused by the presence of cuprous sulfide in the samples, or by the presence of sulfur. In order to check this, x-ray patterns were taken of the mineral chalcocite (Cu_2S) and of sulfur prepared in the following manner. Distilled water was saturated with hydrogen sulfide, and air was bubbled through this solution to oxidize the hydrogen sulfide to sulfur. The resulting suspension was boiled for 45 minutes, and then was washed with the aid of the centrifuge, air dried, and x-rayed. These patterns showed that there was no cuprous sulfide or sulfur in the precipitate, since no agreement between the corresponding values of d_{hkl} could be obtained. These extra values may have been caused by some impurity in the sample, by the presence of some oxidation product of the copper sulfide, or by another crystalline modification of the sulfide. However, the last named possibility is very doubtful.

DISCUSSION

The data indicates rather conclusively that the samples of precipitated copper sulfide, whether precipitated from hot or cold solution, are practically pure cupric sulfide. This follows from the good agreement between the calculated crystal structure of the samples prepared here and the values obtained by Oftedal for the mineral covellite. The reason for the appearance of the extra lines in the precipitated sulfide patterns will have to be investigated further. They have some significance since they are present in all the patterns.

It seems from the above results that the theory of Sauer and Steiner, assuming precipitation of cuprous sulfide in the cold and subsequent change to cupric sulfide on heating, is untenable. Kolthoff's data showing the precipitated sulfide to be cupric sulfide seems to show the true nature of the material.

The observation that the hot precipitated sulfide is slimy and more gelatinous than the one precipitated in the cold seems contrary to experience. However, the x-ray patterns of the hot and cold precipitated material shows the primary particle size to be about the same in both samples. Therefore, the difference in physical character of the precipitate must be attributed to a difference in size of the secondary particles.

SUMMARY

(1). Copper sulfide was precipitated hot and cold, and x-rayed.

(2). The values of a_0 and c_0 were calculated to be 3.70 and 16.1 Angstrom units respectively, and the crystal structure seems to be hexagonal, with six molecules of copper sulfide in the unit cell. These values agree well with those of Oftedal.

(3). It has been shown that precipitated copper sulfide (whether from hot or cold solutions of cupric ion) consists of nearly pure cupric sulfide.

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III. REACTION BETWEEN SODIUM SULFIDE AND FERRIC OXIDE

J. C. Witt (J. Am. Chem. Soc. 43, 734 (1921)) studied
the products of the reaction between sodium sulfide and ferric
oxide. He heated ferric oxide with a large excess of sodium
sulfide until the mixture was liquid. Then he poured the
liquid into a beaker of distilled water; and he found that
a black amorphous substance was precipitated, and that the
precipitate, after separation from the mother liquor, would
give a green solution when placed in water. He concluded
that the green solution was a sol, and analyzed this and
the filtrate obtained after removal of the precipitate above.
He found Fe, Na, and S in the sol, and only Na and S in the
filtrate. The sol changed to a brown color on dialysis for
36 hours, and a precipitate similar in appearance to ferric
oxide settled out in a few days. All of the S had diffused,
and was present in the diffusate mostly as sulfate ion.
He concluded that the green liquid or sol mentioned above
was colloidal with no combined sodium or sulfur present.

An attempt was made to identify the products
formed by comparison of their x-ray patterns with those
from precipitated ferric sulfide, ferrous sulfide, and
ferric oxide. However, this turned out to be impossible
because the x-ray patterns of the products of the reaction
and those of the ferric sulfide used for comparison showed
no definite lines. In some cases a few very broad bands were
barely discernible.

IV. PRECIPITATED ZINC SULFIDE

An attempt was made to study the conditions of formation of the cubic and hexagonal forms of zinc sulfide. Zinc sulfide was precipitated, as a test of concentration effect, from saturated zinc chloride solution and from the saturated solution diluted three times, with sodium sulfide. The samples were washed and dried and x-rayed in the General Electric X-Ray Apparatus. The patterns showed no lines, indicating that the samples were too amorphous to give much of a diffraction pattern.