LVII.—The Reaction Between Calcium Hydroxide and Sulphur in Aqueous Solution.

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OWING to the present circumstances the immediate continuation of this work is impossible, and the results obtained are therefore placed on record, although they are less complete in some particulars than is desirable.

The lime-sulphur wash, which is used extensively as a fungicide, is prepared by boiling together one part of quicklime, two or more parts of sulphur, and ten parts of water. The concentrated com-

mercial product generally contains the polysulphides, thiosulphate, sulphite, and sulphate of calcium; the polysulphides and the thiosulphate preponderate. It is usually stated that the polysulphides present are CaS_4 and CaS_5 , and van Slyke, Hedges, and Bosworth (N.Y. Agric. Expt. Stat., 1910, 329, 433) claim to have obtained these compounds as crystals from the concentrated lime-sulphur wash. When exposed to the air the solution gradually becomes colourless, and deposits sulphur and calcium sulphite, and the content of calcium thiosulphate increases. For this reason the course of the original reaction cannot be followed by examining the solution prepared by boiling, or which has been stored, in contact with air.

Of the polysulphides of calcium which may exist in solution little is known. The disulphide, CaS₂, is stated to exist (Roscoe and Schorlemner, 5th edition, Vol. II., 551, and other English textbooks), but the author can find no reference to this compound in the literature, nor is it mentioned in the modern handbooks of Gmelin-Kraut, Abegg, Moissan, or Dammer. The existence of the tetrasulphide, CaS₄, also, is apparently only assumed from the original work of Schöne (Jahresbericht, 1861, 122), who states that the compound 4CaO,CaS₄,18H₂O is formed when sulphur is boiled with calcium monosulphide in insufficient quantity to produce CaS₄. The latter has not itself been separated, and according to Divers and Shimidzu (T., 1884, 45, 282) does not exist, calcium pentasulphide only being formed when sulphur is dissolved in a solution of calcium hydrosulphide. The pentasulphide has been well characterised by the latter investigators. Disregarding the statements of van Slyke (loc. cit.), which cannot be confirmed, it may be taken that the only polysulphide of calcium at all definitely known is CaS₅. Assumptions of the existence of CaS_4 in solution when the ratio of Ca : S lies between 1 : 4 and 1:5 are not well founded, and the ratios may equally well be explained by the presence of other polysulphides, and particularly of those lower than CaS₄, since the bulk of the evidence points to the existence in solution of the pentasulphide.

There is no doubt that much of the sulphur in the lime-sulphur solution is in a very loosely combined condition, and Tartar and Bradley (J. Ind. Eng. Chem., 1910, 5, 271) have already attempted to characterise the polysulphides by extraction with sulphur solvents. They obtained indications of the existence of a lower, stable calcium polysulphide which may have been the disulphide. The preliminary experiments of the present investigation, carried out five years ago, had already tended to show the looseness of combination of much of the sulphur is the higher polysulphides of

calcium present in the lime-sulphur wash, but objection arose to these and to the results of Tartar and Bradley on account of the non-exclusion of oxygen and carbon dioxide, both during the preparation of the wash and its subsequent examination. In order to eliminate the complications due to the secondary liberation of free sulphur, the reaction has now been carried out in an atmosphere of inert gas in an apparatus so devised that the resultant liquid can be collected and examined without coming in contact with oxygen or carbon dioxide.

Extraction of the fluid with sulphur solvents causes a continuous removal of free sulphur. Tartar and Bradley (*loc. cit.*) assumed that the continuous removal of sulphur was caused by oxidation of the polysulphides, but the most rigorous exclusion of air during the exhaustion of the lime-sulphur fluid does not give any more definite end-point. The continuous formation of sulphur is due, rather, to the hydrolytic dissociation of the polysulphides, which accounts also for the strongly alkaline nature of the wash. Since, also, hydrogen sulphide is readily liberated in quantity when the liquid is heated, the formation of the sulphur is likely to be due to the following equilibria:

$$\begin{array}{l} \operatorname{CaS}_{x} + 2\operatorname{H}_{2}\operatorname{O} \end{array} \rightleftharpoons \operatorname{Ca}(\operatorname{OH})_{2} + \operatorname{H}_{2}\operatorname{S}_{x} \\ \operatorname{H}_{2}\operatorname{S}_{x} \end{array} \rightleftharpoons \operatorname{H}_{2}\operatorname{S} + (x-1)\operatorname{S}. \end{array}$$

Attempts have been made to detect the existence of a more stable polysulphide in solution by measuring the sulphur removed from the wash at stated intervals, and although, by themselves, the results cannot be regarded as conclusive owing to the experimental difficulties, yet it is significant that a lower rate of extraction sets in when the ratio between the polysulphide sulphur (S_P) plus monosulphide sulphur (S_M) and the monosulphide sulphur alone is between 1.6 and 2.3.

Extraction experiments were also repeated on the dry residue obtained by evaporating the liquor in a manner somewhat similar to that adopted by Tartar and Bradley, but the dried wash was kept under the surface of the extracting liquid during the whole time. By passing purified nitrogen through the apparatus any possible secondary decomposition was avoided. The residual material, from which sulphur is only very slowly removed, represents a more stable polysulphide than those composing the main bulk of the lime-sulphur solution. It was impossible, however, to ascribe any definite formula to the residue, the composition of which varied each time the extraction was carried out. The ratio

$(S_{\mathbf{P}}+S_{\mathbf{M}})/S_{\mathbf{M}}$

was generally less than 2, although in one instance it approached this figure. From these experiments alone it is impossible to suggest a definite formula for the lower stable polysulphide of calcium, but it is significant that the "whole-number" polysulphide nearest in composition is CaS_2 .

Attempts were made to prepare calcium disulphide by boiling together lime and sulphur in the calculated proportions (compare Roscoe and Schorlemmer, loc. cit.), but in every case Herschell's crystals were obtained. The composition of Herschell's crystals was first seriously examined by Schöne (loc. cit.), who assigned them the formula 3CaO,CaS₄,12H₂O, but this work was later traversed by Geuther (Annalen, 1884, 224, 178), who recorded the formula 2CaO,CaS₃,10H₂O. Elementary analysis shows very little difference between the empirical formulæ as given by Schöne and by Geuther and the formula CaO,CaS₂,7H₂O, except in the content of water of crystallisation. This figure is the most difficult to determine. Preparations of the crystalline substance were analysed, and the ratio of polysulphide- to monosulphide-sulphur determined. The results show that the main product corresponds with the formula CaO, CaS₂, 7H₂O, but indications were obtained of the existence of similar, probably isomorphous substances of different composition.

The existence of the complex CaS_2 throws light on the formation and the constitution of the higher calcium polysulphides, for in the circumstances it is justifiable to draw the conclusion that the CaS_2 complex, probably in attachment to CaO, is first formed whenever sulphur and lime are boiled together, and that the subsequently formed higher polysulphides still contain the complex. In this connexion it is noteworthy that Schenk and Falcke (*Ber.*, 1908, **41**, 2600) indicate hydrogen disulphide, H_2S_2 , to be the most stable hydrogen polysulphide, especially in the presence of alkali.

Tartar (J. Amer. Chem. Soc., 1914, **36**, 495) is of opinion that the first-formed polysulphide is the tetrasulphide, CaS_4 , his reasons being (1) when an excess of sulphur is boiled with lime the ratio of polysulphide to monosulphide lies between 4 and 5, this being reduced to 4 by treatment with an excess of lime; (2) when the proportions of sulphur and lime are those calculated for CaS_4 , the ratio becomes actually 4. The latter, the more cogent, contention is incorrect, as will be seen later (compare also van Slyke, Bosworth, and Hedges, *loc. cit.*, 1910, p. 417), but if it is correct it does not preclude the initial formation of calcium disulphide, and the subsequent building up of either $CaS_2,xCaO$ or CaS_2,yS , according as lime or sulphur is in excess. Tartar's conclusion is the more surprising in view of Tartar and Bradley's work, quoted above, on the probable existence of a stable lower polysulphide.

It appears, therefore, that the course of the reaction between calcium hydroxide and sulphur in aqueous solution is probably primarily:

$$6Ca(OH)_2 + 6S = 2(CaS_2, CaO) + CaS_2O_3 + 5H_2O_3$$

the other polysulphides being formed with an excess of sulphur as follows:

$$\operatorname{CaS}_2$$
, $\operatorname{CaO} + xS + H_2O = \operatorname{CaS}_{x+2} + \operatorname{Ca}(OH)_2$.

Constitution of the Polysulphides.

The constitution of the polysulphides has been frequently discussed. Apart from their popular formulation as R_2 ·S·S·S·S·· (compare Blanksma, *Rec. trav. chim.*, 1900, **20**, 146), the most important suggestions have been made by Geuther (*loc. cit.*) and by Küster and Heberlein (*Zeitsch. anorg. Chem.*, 1905, **43**, 53). Geuther's formula is cumbersome, and depends on the variable valency of the metallic radicle. For the polysulphides of sodium Küster and Heberlein offer a constitution which regards them as salts of the complex thio-acids, thus: H_2S ·S, H_2S ·S₂, H_2S ·S₃, etc.

From the present work it appears that the calcium polysulphides may be best formulated as CaS_2,S_2 , or, more fully, as:

$$C_a < S_S > S:S:S: \dots$$

On the simplest assumptions possible this allows the existence of all the "whole-number" calcium polysulphides from the disulphide upwards. Many of these possibly do exist in the solution obtained by boiling lime with excess of sulphur and water, there being great difficulty, however, in their actual isolation or even their detection. The constitution suggested agrees with observed facts, as, for example, that all polysulphides with ethyl bromide or ethyl iodide give only ethyl disulphide, and explains the looseness of attachment of most of the polysulphide sulphur. It implies that as the chain lengthens the sulphur atoms or complexes last added are so loosely combined as to behave practically as sulphur in solution. The question arises, however, as to the possible length of the chain, and whether, as is generally assumed, the pentasulphide is the highest existent. It has already been pointed out that, in the boiling liquid, prepared in the absence of air, more sulphur is dissolved than remains in solution on cooling. In the hot liquid the ratio $(S_{\rm P} + S_{\rm M})/S_{\rm M}$ frequently exceeds 5, implying the existence, at least, of the hexasulphide, CaS₆. The addition of mineral acids, also, does not cause a permanent precipitation of sulphur from the polysulphide liquor until an appreciable quantity of acid has been added. This effect is not due to the formation

of hydrogen polysulphides, but to the re-dissolving or retaining in solution of the sulphur primarily set free. At the highest temperatures the polysulphidic sulphur retained in solution may have raised the $S_{\rm P}.S_{\rm M}$ ratio so high (the monosulphide being correspondingly reduced) as to correspond with the existence of CaS₈ or CaS₉. Although such high polysulphides may not necessarily be present to any extent in the normal lime-sulphur liquid, yet their possible existence and behaviour offers an explanation of the varying composition and of the properties of the liquid, and would imply the presence of a mixture, probably in equilibrium, of a wider range of polysulphides than has hitherto been assumed.

EXPERIMENTAL.

The materials used in these experiments were of a high standard of purity. The sulphur employed was the pure large crystals of commerce, recrystallised from carbon disulphide, and ground to a fine powder. The quicklime was calcium oxide prepared from marble; it was stored in a dry atmosphere free from carbon dioxide.

A pparatus.

The apparatus used is shown in Fig. 1. The flasks A and B, in which the boiling takes place, are each of 1 litre capacity, and specially made with extra-wide necks, 63 mm. in diameter. Flask A is connected (1) with the supply of inert gas, (2) with the flask B, and (3) through the graduated dropping funnel D with the supply of lime-water or milk of lime. Both boiling flasks are fitted with double-surface reflux condensers, the upper ends of which are fitted with tubes leading to the bottle E, which contains bromine and sodium hydroxide.

In carrying out an experiment the major portion of the weighed quantity of sulphur is introduced into A and the remainder into B, and the whole apparatus fitted tightly together. Previous to this a stock of milk of lime is prepared by slaking the quicklime in a known amount of boiled distilled water in flask C, through which inert gas is continually passed; the flask is then connected as explained. The inert gas is now passed through the whole apparatus until all oxygen and carbon dioxide are expelled, each successive section being cleared out separately by manipulating the various screw clips. The gas originally used was hydrogen, but this suffers from many disadvantages, and it was replaced by nitrogen, which was purified by bubbling through sulphuric acid, strong aqueous sodium hydroxide, and pyrogallic acid and sodium hydroxide. When all air has been displaced from the apparatus,

the flask C is well shaken, and the calcium hydroxide run into D, and from thence to the boiling flask.

The sulphur and lime are boiled together for the desired time (generally one and a-half hours), during which the tube a is closed and b open. The siphon-tube a is now lowered through the seal. The seal is constructed of a close-fitting, short glass tube surmounted by "pressure" rubber-tubing; when slightly lubricated



with petroleum jelly this gives very tight-fitting yet adjustable junctures. By continuing to boil the liquid in A, the siphon is set and the liquid passes over into B after having been filtered through a small plug of cotton-wool surrounded by glass-wool and held in position with muslin.

The boiling process is similarly repeated in B with the remainder of the sulphur, possible contamination with free lime from A

being thus avoided. Eventually the filtered liquid is drawn off through the siphon c, either into the large burette for analysis or into vessels contained in a desiccator for evaporation or other examination.

By the use of this apparatus it is possible to examine the liquid thoroughly without its coming into even passing contact with the atmosphere. If necessary, the amount of hydrogen sulphide liberated during boiling can be measured by an examination of the oxidising liquid in E.

Calcium Hydroxide and Excess of Sulphur.

The following typical experiments were carried out as described above, using a 30 per cent. milk of lime. The resulting liquids were drawn off either while boiling or after allowing to cool in B to room temperature. In each experiment the proportion of sulphur to lime was not less than 100 to 30. The percentages shown are grams per 100 c.c. of liquid.

	Sulphur in solution.								
Expt No. 1 2 3	Temp. of draw- t. ing off. b.p. 18° 18°	Sulphur de- posited per cent. 0.194 	Total per cent. 7·40 1·61 1·89	Mono- sul- phide per cent. 1.01 0.26 0.32	Poly- sul- phide per cent. 3.54 0.86 1.06	Thio- sul- phate per cent. 2.85 0.43 0.51	Total CaO per cent. (\$ 3.30 0.68 0.69	$\begin{array}{c} \text{Ratio} \\ \mathbf{S}_{\mathbf{x}} + \mathbf{S}_{\mathbf{F}})/\mathbf{S}_{\mathbf{x}} \\ 4 \cdot 50 \\ 4 \cdot 30 \\ 4 \cdot 31 \end{array}$	Ratio 5. S/CaO. 2.24 2.36 2.70
*4	18°	—	8.08	1.24	5.08	2.08		5.10	
5	b.p.	appre- ciable	13.17	2.08	8.13	3.06	6.02	4 ·90	$2 \cdot 20$

TABLE I.

* This solution deposited sulphur after a few hours.

The analyses do not allow of the existence of sulphur compounds other than calcium polysulphides and calcium thiosulphate, nor is there any free lime present. This is confirmed by qualitative examination. The absence of calcium hydrosulphide is proved by the fact that no hydrogen sulphide is formed on the addition of manganous sulphate.* The composition of the liquid is largely a

^{*} It is true that Ramsay (J. Agric. Sci., 1914, 6, 194), assuming that the "monosulphide sulphur" should be present as actual CaS, explains certain properties of the liquid by the existence of the equilibrium $CaH_2S_2 + CaH_2O_2 = 2Ca(HS)(OH)$. The hydroxyhydrosulphide, however, is immediately decomposed by water with the formation of the hydrosulphide, which alone is stable in solution (Divers and Schimidzu, *loc. cit.*) and therefore determines the reaction with manganous sulphate.

function of the time of boiling, since the thiosulphate tends to increase with the continued removal of hydrogen sulphide, and consequently reduces the S/CaO ratio. Since this ratio is thus entirely dependent on the hydrolysis of the polysulphides during the boiling process, it affords no indication either of the course of the reaction or the fungicidal value of the liquid.

The second boiling of the liquid with sulphur in flask *B* not only entirely prevents the presence of free lime in the final solution, but it tends to raise the $(S_{\rm M} + S_{\rm P})/S_{\rm M}$ ratio, although not in a very marked degree. In the following pairs of experiments the compositions are calculated back to the same CaO contents from the dilutions used for actual analysis.

TABLE II.

Sulphur in solution.

		Total	Mono- sul- phide	Poly- sul- phide	Thio- sul- phate	Total CaO		
Expt.		\mathbf{per}	\overline{per}	\overline{per}	\mathbf{per}	\mathbf{per}	\mathbf{Ratio}	\mathbf{Ratio}
No.	Series.	cent.	cent.	cent.	cent.	cent.	$(S_M + S_P)/S_M$.	S/CaO.
a.	lst flask	6.31	1.10	3.99	1.22	3.00	4.63	2.10
6, b.	Both flasks	6.71	1.08	4.34	1.28	3.00	5.02	$2 \cdot 24$
7, a.	lst flask	4.05	0.54	$2 \cdot 01$	1.50	1.88	4.72	2.15
b.	Both flasks	$4 \cdot 30$	0.61	$2 \cdot 46$	1.21	1.88	5.03	$2 \cdot 30$

Removal of Hydrogen Sulphide from the Polysulphide Solution.

The continued passage of purified hydrogen or nitrogen through the polysulphide liquid removes appreciable quantities of hydrogen sulphide even at the ordinary temperature. At higher temperatures the evolution of hydrogen sulphide increases, and by boiling the liquid it is possible completely to destroy the polysulphides. This effect is in no way due to oxidation or decomposition by carbon dioxide, since it occurs in an atmosphere of inert gas, and after all dissolved gases have been removed from the solution. Since the decomposition is, then, solely indicative of the hydrolysis of the polysulphides, attempts have been made to measure the rate of evolution of hydrogen sulphide, in order, if possible, to detect the existence of more stable complexes. These attempts failed, and a description of the experimental methods need not be given. It may be noted, however, that after the polysulphides had been decomposed the residual liquid (which had been maintained at its original volume) contained only small quantities of free sulphur, a large quantity of thiosulphate, and but mere traces of calcium

sulphate. These points have, of course, bearing on the practical preparation of the lime-sulphur wash.

When, conversely, excess of hydrogen sulphide is passed into the lime-sulphur liquid, decolorisation again takes place, with the liberation of free sulphur and forma-

tion of calcium hydrosulphide (compare Divers and Shimidzu, *loc. cit.*, p. 282).

Extraction of Sulphur from the Polysulphide Solution.

experiments showed Preliminary that, even in the total absence of air or oxygen, sulphur is continually removed from the polysulphide solution by agitation with sulphur solvents. Attention was given, therefore, to the rate of removal of the sulphur, in order to detect, if possible, the existence of more stable calcium polysulphides. The extraction apparatus used is shown in Fig. 2, which sufficiently explains its action. The apparatus worked satisfactorily with benzene. Apart from the fact that a special apparatus was required for solvents heavier than the solution, it was found that chloroform was a very unsatisfactory agent, whilst carbon disulphide could not be used owing to the formation of thiocarbonates.

During the course of an experiment the polysulphide liquid and the purified benzene came in contact only with

pure nitrogen. The sulphur removed was estimated, after evaporating the benzene, by oxidising it in solution in 20 per cent. sodium hydroxide with sodium peroxide.

The following results (Expt. 8) are typical of a series. The lime-sulphur solution used was that of Expt. 7b (table II).



		TABLE 111.		
Time of	Grams of	~ •	Sulphur	Sulphur
extraction	polysulphide	Grams of	removed	removed
in	sulphur	sulphur	(total)	(fraction)
hours.	present.	removed.	per cent.	per cent.
Nil	0.2524			•
7.0	0.1893	0.0631	25.0	25.0
13.0	0.1326	0.1198	47.5	29.9
21.0	0.0841	0.1683	66.7	36.5
27.0	0.0565	0.1959	77.7	32.8
32.7	0.0398	0.2126	84.3	29.5
41.2	0.0231	0.2293	90.9	41.9
47.2	0.0110	0.2414	95.7	52.3

Column 5 represents the sulphur removed calculated as percentages of the amount left in solution at any one time. The figures in italics indicate a distinctly slower rate of removal of sulphur, and correspond with ratios of $(S_{\rm M} + S_{\rm P})/S_{\rm M}$ between 1.63 and 2.31. This is significant, although, as already stated, too much weight cannot be attached to these experiments by themselves. It is not clear, indeed, why the fractions removed should subsequently increase to the extent indicated by the curve.

Extraction of Sulphur from the Dried Product.

The lime-sulphur liquid in these experiments was evaporated to dryness in the absence of air. This was accomplished in a desiccator (calcium chloride) originally filled with nitrogen, and into which the liquid was run through siphon c (Fig. 1). The desiccator was then rendered vacuous, and arrangements made whereby any leakage allowed only purified nitrogen to enter the vessel.

The yellow solid left on drying contained quantities of needleshaped crystals (probably calcium thiosulphate), but the major portion was amorphous. The whole mass was broken up to facilitate desiccation, and the semi-crystalline material subsequently reduced to a powder, which was then spread out thinly in a glass dish and again subjected to the drying process. The powder was completely soluble in water. In the first extraction experiments pure carbon disulphide was poured over the powder, which was macerated with a light pestle under the surface of the liquid. The latter was then poured off, and the operation repeated. This extraction process was carried out at intervals over three months, and small but distinct quantities of sulphur were still being The solid residue was then dried in a vacuum, and a removed. yellow mixture of crystalline and indeterminate-shaped material again obtained. This solid was completely soluble in water, and the yellow solution precipitable by acids, so that it still contained polysulphide material. The solution was analysed (Expt. 9), and the $(S_{\rm M} + S_{\rm r})/S_{\rm M}$ ratio calculated. This was 1.40. That of the original liquid (Expt. 2) was 4.30.

In all subsequent experiments the dried polysulphide material was mixed with extracted silver sand, and extracted with carbon disulphide in a thimble in the special apparatus already described (Fig. 2). This reduced the possibility of hydrolysis or other secondary decomposition to a minimum, both by reducing the time of extraction and by preventing any possible access of air. By the construction of the apparatus the solid was always covered with a deep layer of pure carbon disulphide. In these experiments it was necessary to cool the extraction tube with a stream of water. One typical experiment will be quoted in detail (Expt. 10).

TABLE IV.

Weight of dried substance=3 grams.

Time of extraction.	Weight of sulphur removed.
Hours.	Gram.
3.0	0.0321
3.8	0.0933
2.0	
3.5	0.0460
4.0	0.0140
4.0	0.0008

The solid was removed from the cartridge, dried, and dissolved in water, and made up to 500 c.c. The solution was deep yellow, and contained polysulphide. On adding N/10-hydrochloric acid no precipitation was caused at first (compare Expt. 18), the acid thus taken up being much greater than with the ordinary polysulphide solution. Three grams of the original dry material were also dissolved in water and made up to 500 c.c. The results of the examination of both materials were as follows:

TABLE	v.
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		Sulphur i	n solution.			
Material.	Total per cent.	Mono- sulphide per cent.	Poly- sulphide per cent.	Thio- sulphate per cent.	Total CaO per cent. (Ratio $S_{M} + S_{P} / S_{M}$.
Dry non- extracted	51 ·0	6-9	27.1	14.5	25.1	4.93
Dry extracted (calculated on original amount) Original Liquid	26.3	6·3 See Expt	3·16* . 5.	5· 4 †	26.2	1·51 4·90

• For the estimation of these small quantities of polysulphides the liquid is titrated with iodine solution to apparent disappearance of the colour. The reaction $CaSx + I_2 = CaI_2xS$ is completed before the thiosulphate is attacked (compare Harris, *Expt. Stat. Mich. Tech. Bull.*, Jan. 1911).

+ This reduction in the amount of thiosulphate sulphur is due to the formation of calcium sulphate, etc.

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Attempted Preparation of Calcium Disulphide.

The compound $CaS_2, 3H_2O$ is stated (see above) to be produced in the form of yellow crusts when lime and sulphur are boiled together and the mixture is filtered hot. It is certainly not obtainable when excess of sulphur is employed, so attempts have been made with the quantities calculated from the equation:

 $3Ca(OH)_2 + 6S = CaS_2O_3 + 2CaS_2 + 3H_2O_3$

namely, 56 grams of quicklime and 64 grams of sulphur, and also with slightly larger and with slightly smaller amounts of sulphur. In two cases where the above quantities of sulphur and lime were boiled with 1 litre of water for two hours and filtered hot, the operations being conducted in the absence of air, the liquids obtained gave the following analytical results:

TABLE VI.

TABLE VIII.

			Normality	Expt 18. C.c. required for permanent
	Expt. 11.	Expt. 12.	HCI.	turbidity.
$S_{M} + S_{P}$	1.55%	1.80%	0.002	152.0
S _P	$1.24^{'}$	1.50	0.005	48.7
S	0.31	0.39	0.01	21.5
S as thiosulphate	0.50	0.62	0.02	4.8
$(S_{w} + S_{p})/S_{w}$	5.0	4.8	0.05	1.9

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After a day or two the liquids deposited yellow, prismatic crystals with sharp ends. These proved to be oxysulphides. They were, in fact, identical with Herschell's crystals. Similar results were obtained in other experiments. In no case was a crystalline polysulphide obtained by this method.

Composition of Herschell's Crystals.

Herschell's crystals were prepared by a method similar to Geuther's except that all operations were carried out under rigid exclusion of air.

As already pointed out, elementary analysis alone shows very little difference between the formulæ assigned by Schöne, by Geuther, and in the present communication, as will be seen from the following:

	3CaO,CaS ₄ ,12H ₂ O.	2CaO,CaS ₃ ,10H ₂ O.	CaS2,CaO,7H2O.
Са	. 28.98	28.03	27.97 per cent.
S	23.18	$22 \cdot 43$	22.37 ,,
H ₂ O	. 39.13	42.05	44.05 ,,

Schöne's analyses must be regarded with a certain amount of suspicion, as he washed his product with water. Geuther, on the

other hand, does not state his method of estimating the water of crystallisation, the most important of the elementary figures.

In the following analyses, which are less complete than desirable (owing to the present suspension of the work), the water was estimated by ignition in a combustion tube packed with fused lead chromate. The analyses represent four different preparations; all of these are first crops of crystals, as later crops appeared to differ somewhat in composition.

TABLE VII

		-	mong (
				Sulphur.		
	Ca.	H_2O	Total	Poly- sulphide	Mono- sulphide	
Expt.	\mathbf{per}	\mathbf{per}	\mathbf{per}	\mathbf{per}	\mathbf{per}	Ratio.
No.	cent.	cent.	cent.	cent.	cent.	$(S_M + S_P)/S_M$
13	27.88	43.85				
14	28.10		$22 \cdot 13$			
15		44.14	21.49	10.56	10.93	1.97
16			21.76	10.85	10.91	1.99
17			23.92*	10.82	10.81	$2 \cdot 00$
* ***						

* This preparation contained 2.29 per cent. of sulphur in the form of thiosulphate, probably owing to the concentration having been carried too far.

Action of Dilute Acids on the Polysulphide Solution.

When very dilute hydrochloric acid, for example, N/500, is run into the lime-sulphur solution, there is a lengthy period of non-precipitation of sulphur, and a considerable volume of acid can be added without any apparent effect being produced. With N/100- and N/10-hydrochloric acid, added drop by drop, it can be seen that sulphur is at once precipitated and at first re-dissolves; only when an excess of acid has been added is the opalescence, due to the separation of sulphur, quite permanent. Warming hastens the re-dissolving of the originally precipitated sulphur. The more dilute the acid employed, the greater the total amount of acid Thus, to quantities of 50 c.c. of the limewhich can be added. sulphur solution from Expt. 5 diluted to ten times its volume, the amounts of hydrochloric acid shown in table VIII were added at 18° to produce permanent turbidity.

This effect may be caused (1) by the formation of high polysulphides of hydrogen which take time to decompose and are more stable in the strongly alkaline solutions (compare Schenk and Falcke, *loc. cit.*):

 $CaS_5 + 2HCl = H_2S_5 + CaCl_2$ and $H_2S_5 = H_2S + 4S$,

or (2) by the re-attachment of the sulphur first liberated (probably as colloid) thus:

$$\begin{aligned} &\operatorname{CaS}_5 + 2\operatorname{HCl} = \operatorname{H}_2 S + \operatorname{CaCl}_2 + 4S, \\ & x\operatorname{CaS}_5 + 4S = x\operatorname{CaS}_{5+4/x} \end{aligned}$$

кк 2

and, since no hydrogen sulphide appears to be liberated, $CaS_5 + H_2S = Ca(SH)_2 + 4S$,

the sulphur re-dissolving as before. It is possible, of course, that the sulphur actually re-dissolves in the polysulphide solution, either wholly or in part, in non-chemical form. Indeed, the partly acidified solutions deposit sulphur more rapidly on the addition of an electrolyte, for example, sodium chloride; ordinary precipitation may therefore be deferred until an electrolyte (calcium chloride) is accumulated in sufficient concentration.

At the higher concentrations of hydrochloric acid there is produced an almost immediate turbidity which, however, clears after a few seconds if the reaction is not complete, or increases in intensity if the maximum amount of acid has been added.

If the effect is due to the formation of hydrogen polysulphides, it should be more marked at lower temperatures, at which these compounds are more stable. The reverse is the case, and much more acid may be added at the higher temperatures than at the lower.

In the experiments quoted in the following table the acid was run in drop by drop, and the solution, which was stirred continuously, was illuminated by a strong beam of light. The titrations at 0° and 1° are approximate, since at these temperatures the amount of acid added largely depends on the rate of addition. The more rapid the addition the more acid can be run in. In this case the sulphur separates suddenly as in the addition of acid to thiosulphate solutions. All results quoted are the mean of several observations. The materials and quantities used were those stated above (table VIII).

TABLE IX.

Expt. 19.

Tempera-	Normality	C.c. of	Equivalent of acid.
ture.	of HCl.	acid used.	× 10 ⁻⁵ .
1	0.002	58.0	29.0
9	0.002	27.8	13.9
18	0.002	48.7	24-3
0	0.01	18-0	18.0
9	0.01	11.6	11.6
18	0.01	21.4	21.4
32	0.01	27.4	27.4
60	0.01	35.8	35.8
75	0.01	46.4	46.4
86	0.01	55.0	55.0
93	0.01	59.9	59-9
0	0.02		
9	0.02	2.5	5.0
18	0.02	4.8	9.6
35	0.02	7.5	15.0
60	0.02	14.5	29.0
75	0.02	21.5	43.0
87	0.02	26.0	52.0
93	0.02	29.2	58 · 4
18	0.02	1.9	9.5

The figures in italics (column 4) probably represent the formation, to a certain extent, of hydrogen polysulphides.

Assuming that the equations quoted above for the action of the dilute acid are correct, then taking the figures for 0.01N-hydro-chloric acid at 93° , we get:

0.01N/HCl = 0.00197 gram CaS_{4.9} per c.c.

=0.00125 gram polysulphide sulphur per c.c.

The original content of 100 c.c. of the solution = 1.281 grams $CaS_{4.9}$. After addition of acid, content of 100 c.c. = 1.053 grams $CaS_{4.9} + 0.146$ gram S, that is, the final solution contains 0.214 gram Ca + 0.985 gram S. The ratio of calcium to sulphur present as polysulphide is therefore:

$$\frac{0.985}{32} / \frac{0.214}{40} = 6.1.$$

This implies the presence in solution of at least CaS₇.

Summary.

In the absence of air, lime and sulphur react in aqueous solution with the formation only of calcium polysulphides (or oxysulphides) and calcium thiosulphate.

When an excess of sulphur is used the ratio of $(S_{\rm M} + S_{\rm P})/S_{\rm M}$ usually lies between 4.5 and 5.0, but may exceed the latter figure under certain conditions.

Much of the sulphur of the higher polysulphides is loosely combined, and may be extracted both from solution and from the solid. Evidence is thus obtained of the probable existence of a stable CaS_2 complex. Calcium disulphide is probably not formed as such by the interaction of lime and sulphur.

The formula CaS_2 , CaO, $7H_2O$ is suggested for Herschell's crystals.

The formation of the polysulphides from lime and sulphur may probably be expressed by the equations:

 $5Ca(OH)_2 + 6S = 2CaS_2, CaO + CaS_2O_3 + 5H_2O_3$

 $CaS_{2},CaO + xS + H_2O = CaS_{x+2} + Ca(OH)_2.$

By obtaining the re-dissolution of precipitated sulphur in the polysulphide solution, evidence can be obtained indicating the possible existence of polysulphides at least as high as CaS_7 .

It is suggested that the polysulphides of calcium possess the constitution Ca < S > S:S:S ..., the atoms of sulphur in the chain becoming progressively more loosely attached.

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