

XCV.—*The Polysulphides of Barium and Calcium.*

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THE polysulphides of the alkaline-earth metals have already been partially investigated. Schöne (*Annalen*, 1861, **112**, 194) examined the products obtained from an aqueous solution of barium trisulphide prepared in the dry way, and also those from solutions of calcium and strontium polysulphide obtained by adding sulphur to the monosulphide in water, whilst Divers and Schimidzu (*J.*, 1884, **45**, 271) and also Veley (*J.*, 1886, **49**, 378) described the formation of calcium and barium hydrosulphides and related compounds.

The present paper deals with a reinvestigation of these compounds by other methods, *viz.*, (i) the thermal investigation of a portion of the system barium-sulphur, (ii) the examination of material crystallised from a solution of sulphur in barium hydro-

sulphide, and (iii) the preparation of calcium polysulphides in alcoholic media.

#### EXPERIMENTAL.

*Materials.*—Calcium turnings were kept in a desiccator throughout the work (Found : Ca, 97.80; Fe, 0.55; total 98.35%).

The alcohols were dried by refluxing over freshly burnt quicklime for at least 6 hours, followed by distillation from fresh quicklime. Further distillation from metallic calcium had no retarding effect on the action of such alcohol on calcium.

The sulphur was finely ground roll; when required anhydrous, it was dried for several hours at 80° immediately before use.

#### *Barium Polysulphides.*

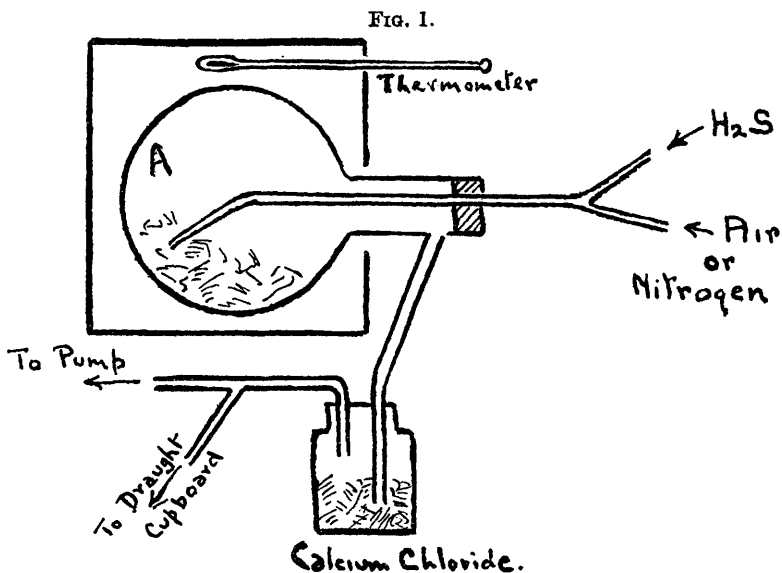
Schöne (*loc. cit.*) melted barium monosulphide with half its weight of sulphur, distilled off excess of the latter below 360°, and obtained a yellowish-green substance, described as barium trisulphide, melting at 400° with loss of sulphur. An aqueous solution of this, when evaporated in a vacuum, gave crystals to which the following formulæ were ascribed,  $\text{BaS}\cdot 6\text{H}_2\text{O}$ ,  $\text{Ba}_4\text{S}_7\cdot 25\text{H}_2\text{O}$ , and  $\text{BaS}_4\cdot \text{H}_2\text{O}$  (or  $2\text{H}_2\text{O}$ ). The formation of the tetrasulphide from aqueous solutions of monosulphide and sulphur was also reported. By treating aqueous hydrosulphide with sulphur and cooling the hot saturated solution, Veley (*loc. cit.*) obtained crystals which analysed as  $4\text{BaS}_4\cdot 7\text{H}_2\text{O}$  but were believed to be  $\text{BaS}_4\cdot 2\text{H}_2\text{O}$ . Schöne's attempts to prepare a trisulphide were fruitless; neither disulphide nor pentasulphide has been isolated, and the system barium-sulphur has not hitherto been studied.

*The System Barium-Sulphur (in part).*—The system in question can only be investigated over a limited range at the atmospheric pressure, since rapid dissociation occurs with material of sulphur content below 32% or above 44% at temperatures lower than the respective melting points. This practically restricts the inquiry to the trisulphide region, although attempts were made by rapid heating and cooling to extend the investigation beyond these compositions.

*Preparation of Materials.*—The price of metallic barium prohibited its use, and consequently the monosulphide was employed as the source of the element. Veley's method for one-gram portions was adapted to the preparation of batches of 150 g. Barium hydroxide, recrystallised out of contact with carbon dioxide, was dehydrated by passing a current of air over the material in the flask A, Fig. 1, fusion being avoided. This vessel fitted into a closed, electrically heated air-bath, and was provided with a tube through which could be led, at will, dry carbon dioxide-free air, or

nitrogen, or hydrogen sulphide. When a flaky, loose mass of monohydrate had been obtained, hydrogen sulphide was substituted for air, and the temperature gradually raised in stages of roughly  $50^\circ$  per day, to  $350^\circ$ ; the product was then washed with nitrogen, and contained 2% of free sulphur (from dissociated hydrogen sulphide), but no oxygen. The conditions specified were necessary to ensure the decomposition of the last traces of hydrosulphide.

The monosulphide was intimately mixed with the required amount of sulphur, and the whole ground to a fine powder. For melts below  $600^\circ$ , Pyrex-glass test-tubes were used, provided with a side-



limb to prevent sulphur evaporating from the melt returning thereto. After the observation of the upper arrests, but whilst the temperature was still above the boiling point of sulphur, the furnace was tilted in order that the sulphur condensed on the sides of the tube should not contaminate the product. The quantity of polysulphide used (40 g.) allowed a 6-cm. immersion for the thermocouple.

The instrument and couples used were similar to those employed by Pearson and Robinson (J., 1930, 1490), but as higher temperatures were involved, additional lagging was added to the furnace, giving cooling rates at  $950^\circ$  of approximately  $1^\circ$  in 6 secs., and at  $800^\circ$  of  $1^\circ$  in 8 secs.

The results are in Table I. The periods of arrests in cols. 5, 6, and 7 were obtained by plotting cooling curves in the manner

described by Tammann (*Z. anorg. Chem.*, 1905, **47**, 289), but the values are only approximate since their smallness makes them difficult of estimation. Rapid loss of sulphur made it impossible to prepare melts of given sulphur content other than trisulphide. Analyses of various parts of the melt were made after solidification, and the divergence between the top and bottom of the material amounted in extreme cases to 5% of sulphur. This variation produced an untoward result in the region between mono- and di-sulphide, since one part would be reduced to monosulphide, solidify, and thus prevent stirring. The analyses used in the diagram are invariably those on material from the bottom of the tube and adjacent to the thermocouple junction.

TABLE I.

No.	1. S, %.	2. Upper arrest.	3. Lower arrest.	4. Third arrest.	5. Time, upper (secs.).	6. Time, lower (secs.).	7. Time, third (secs.).
1	45.60	543°	508°	—	380	120	—
2	44.40	551.5	513	—	460	107	—
3	44.39	549	501	—	434	198	—
4	43.87	548	515	—	447	146	—
5	43.61	551	501	—	385	146	—
6	41.81	553.5	—	—	424	—	—
7	41.53	553	508	—	—	—	—
8	41.27	555	—	—	405	—	—
9	39.69	553	—	—	242	—	—
10	38.00	775	670	551°	—	15	441
11	36.84	*	—	551	—	—	163
12	34.93	904	664	544	—	153	158
13	33.43	*	665	520	—	192	130
14	33.08	†924	—	—	—	—	—
15	29.17	974	922	660	—	140	159
16	27.53	—	927	664	—	125	165
17	24.69	—	930	663	—	45	55
18	24.35	—	930	663	—	50	82
19	22.51	—	—	663	—	—	142
20	19.36	—	928	658	—	10	5
21	19.00	—	—	—	—	—	—

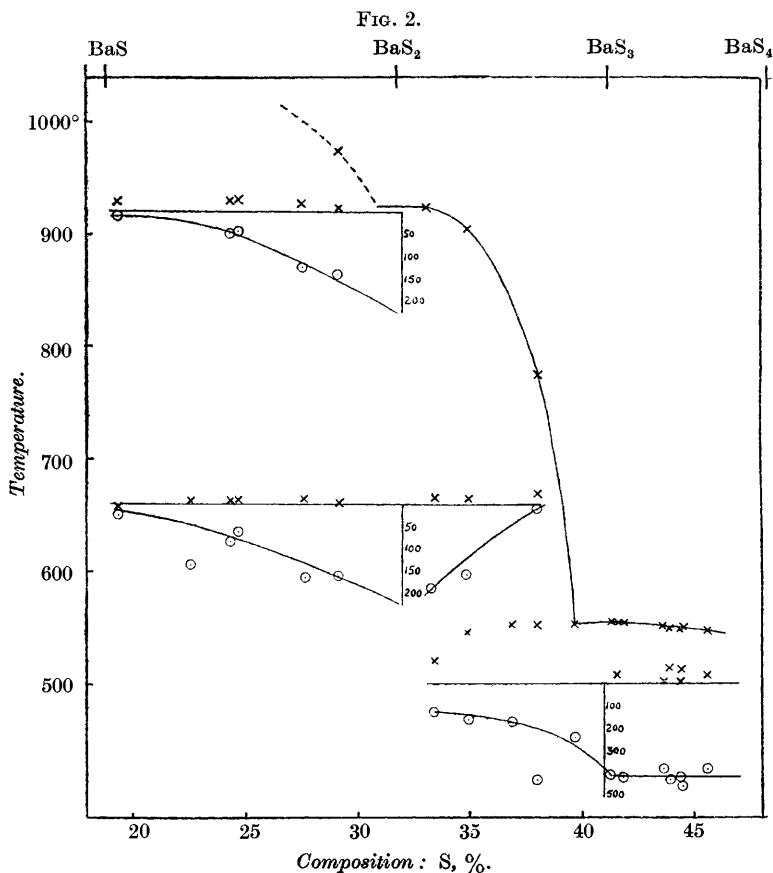
\* Cooled from below the liquidus point.

† From heating curve.

From these data the temperature-composition diagram of the system barium sulphide-sulphur is plotted (Fig. 2). The highest temperature attainable with the furnace, *viz.*, 1150°, was below the m. p. of the monosulphide. Many attempts have been made to establish the liquidus between mono- and di-sulphide, but only one point has been obtained. The curve probably descends to the disulphide, a compound dissociated at its m. p. (925°). From this point its fall is extremely rapid, dropping 350° for 4% alteration in composition, to the trisulphide (554°), a region where the flattened maximum typical of a compound dissociated at its m. p.

is found. The small arrest at  $664^{\circ}$  is apparently due to a transition of the disulphide, the halt periods reaching a maximum in material of this composition. The inflexion in the cooling curve at about  $505^{\circ}$  is so small and irregular that it is not further discussed.

*Micro-examination.*—Though hydrolysed by atmospheric moisture sufficiently to give a perceptible odour of hydrogen sulphide, these



materials are more stable than the alkali-metal polysulphides, and the difficulty experienced in preparing specimens for examination was due to the friable character shown at some compositions. A few sections suitable for examination were obtained by mounting on glass slides with hot Canada balsam in xylene and rubbing down on various grades of emery cloth. These were thin enough to be examined by transmitted light. With S, 44.40%, m. p.  $551.5^{\circ}$ , an almost pure yellowish-brown compound was found with a small

quantity of bright yellow material, which could not, owing to its thickness, be sufficiently resolved to reveal a definitely eutectic structure. In fact, no trustworthy evidence of such a structure was obtained from any of the sections. Material with a sulphur content of 41.27%, m. p. 555°, had obviously all the characteristics of a pure compound, the crystals of which had straight extinction. Nearer the disulphide region, a section from material with composition S, 38.00%, m. p. 775°, showed a definitely crystalline constituent with straight extinction, of a light yellow colour in a matrix of paler material, consisting of interfering crystals which are obviously different from the first constituent. With S, 29.17%, m. p. 974°, a section typical of this region was obtained and had a finer structure, believed to be due to disulphide. This material was so friable that sections were extremely difficult to prepare, and the dark lines which appeared between crystals were caused by emery powder embedded in the softer ground mass. Limitations imposed by the thickness of the sections prevented a rigorous optical examination of the molecular species present, but the results of the observations possible accord well with the conclusions reached from a consideration of the thermal diagram.

*Preparation of Barium Polysulphides from Solution.*—(1) *The action of sulphur on aqueous barium monosulphide.* The slight solubility of the monosulphide, its ready hydrolysis, and the slow dissolution of sulphur in dilute solutions rendered working with mixed solids necessary. Known quantities of intimately mixed monosulphide and sulphur were added to carbon dioxide-free water and the mixture was boiled (15 mins.) under oxygen-free nitrogen, and filtered from undissolved sulphur and products of hydrolysis. The solution was analysed, evaporated in a vacuum over calcium chloride until crystals separated, and the atomic ratio S/Ba determined in the mother-liquor and in the crystals, the latter giving Ba, 48.03; (S)\*, 33.00; S, 45.60 [Calc. for  $\text{BaS}_4 \cdot \text{H}_2\text{O}$ : Ba, 48.49; (S), 33.88; S, 45.16%]. It was soon seen that this method was unsatisfactory for obtaining lower sulphides owing to the small quantity of the monosulphide reacting, whilst solutions containing sulphur in excess of that required for pentasulphide precipitated this extra sulphur on cooling (compare Schöne, *loc. cit.*).

(2) *The action of sulphur on aqueous barium hydrosulphide.* Aqueous hydrosulphide solutions were prepared by passing hydrogen sulphide into roughly dried recrystallised barium hydroxide, complete solution being obtained in about 4 days. Three such preparations gave on analysis S/Ba = 2.006, 2.083, 1.977. During the passage of the gas a hard crystalline material (Found: Ba, 47.27;

\* (S) = Polysulphide sulphur.

S, 11.35. Calc. for  $\text{BaO}, \text{H}_2\text{S}, 5\text{H}_2\text{O}$ : Ba, 49.53; S, 11.54%) was readily formed, but its transformation into soluble hydrosulphide was a much longer process. Veley did not record this phenomenon, possibly owing to his having made periodic additions of oxide in the preparation. Crystallisation of hydrosulphide solutions by evaporation over calcium chloride in a vacuum yielded colourless plates [Found: Ba, 52.68; S, 24.57; S/Ba = 2.003. Calc. for  $\text{Ba}(\text{SH})_2, 3\text{H}_2\text{O}$ : Ba, 53.40; S, 24.86%]. Veley's analysis (Ba, 49.42; S, 22.78) led him to conclude that the material was the tetrahydrate (Calc.: Ba, 49.90; S, 23.27%). In view of the difficulty of drying the material, our analyses would indicate rather the trihydrate.

The hydrogen sulphide evolved when concentrated standardised barium hydrosulphide solutions were treated with finely powdered sulphur, was estimated by washing the gas with a stream of nitrogen into iodine solution and titrating the latter (compare Rule and Thomas, J., 1914, 105, 177). The reaction was considered to be complete after an hour, because the slow rate of evolution suggested that it was then due solely to hydrolysis. There is an uncertainty of  $\pm 5\%$  in the figures on account of this hydrolysis (which fell with increased sulphur concentrations), but two sets of results (Table II) from independent preparations obviously lie on the

TABLE II.

	Preparation I (Fig. 3, x).						Preparation II (Fig. 3, o).			
(S)/Ba .....	3.79	3.15	2.23	2.06	1.06	0.00	3.75	3.00	1.00	0.00
$\text{H}_2\text{S}$ evolved, % of theoretical .....	96.4	88.8	68.0	68.7	40.5	4.5	93.1	84.8	38.6	2.1

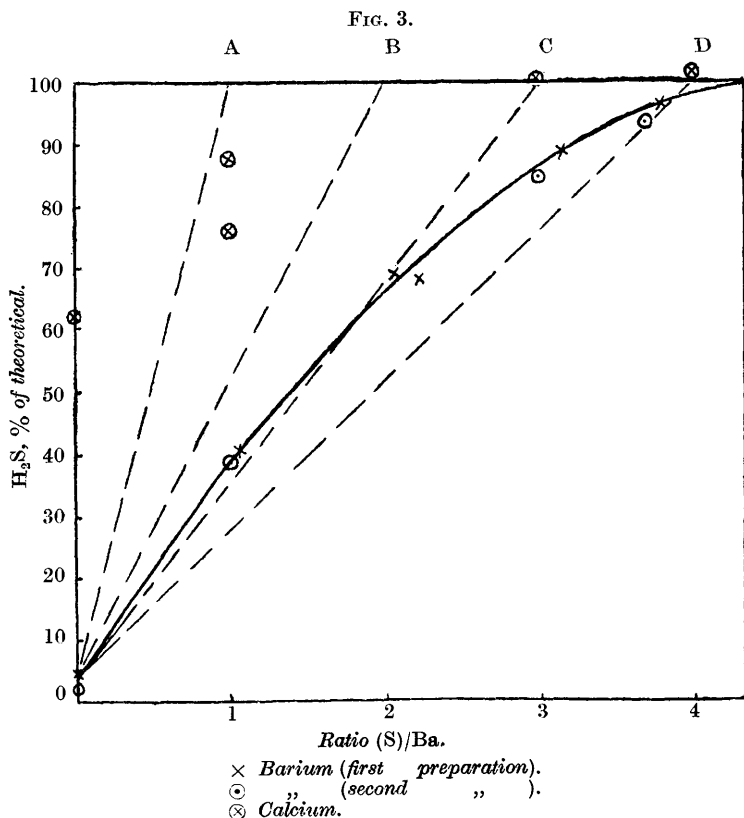
same curve (Fig. 3). In all cases the atomic ratio (S)/Ba was determined after dissolution was complete. The broken lines from the origin to points A, B, C, and D show the theoretical evolution of hydrogen sulphide if di-, tri-, tetra-, or penta-sulphide respectively were the only sulphide formed. The curve indicates that with sulphur below tetrasulphide proportion a small quantity of a sulphide lower than this is formed, and, furthermore, since the theoretical yield of hydrogen sulphide is not reached with this proportion, some penta- or higher polysulphide is probably produced: clearly, however, the main product is tetrasulphide.

Preparations of polysulphides were made by boiling together in a stream of nitrogen appropriate quantities of hydrosulphide solution and sulphur for 10 minutes after the latter had dissolved. The solution was cooled, filtered, and, after analysis, partially crystallised in a vacuum over calcium chloride at laboratory temperature. Crystallisation usually took a few days, and the crystals were of considerable size and characteristic appearance. The mother-

liquor was filtered and analysed. The results obtained are given in Table III, and the plot of the atomic ratio (S)/Ba of the crystals against that of the mother-liquor is shown in Fig. 4.

Consideration of these results leads to the following conclusions.

(1) Crystallisation of solutions of higher proportions of sulphur than tetrasulphide yields a mixture of this sulphide and free sulphur.



(2) Monohydrated barium tetrasulphide separates from solutions with ratios (S)/Ba from 4.0 to about 0.6. Freshly crystallised tetrasulphide is deep orange-red, becoming paler on exposure to air, although the decomposition is less than with the other sulphides. Crystals well dried between filter paper gave Ba, 48.50; (S), 33.43; S, 45.71 [Calc. for  $\text{BaS}_4 \cdot \text{H}_2\text{O}$  : Ba, 48.49; (S), 33.88; S, 45.16%].

(3) Between (S)/Ba = 0.2 and 0.6, pale yellow acicular crystals separate [Found (mean of four preparations, dried between filter paper) : Ba, 48.43; (S), 21.33; S, 36.90; (S)/Ba = 1.891; S/Ba =



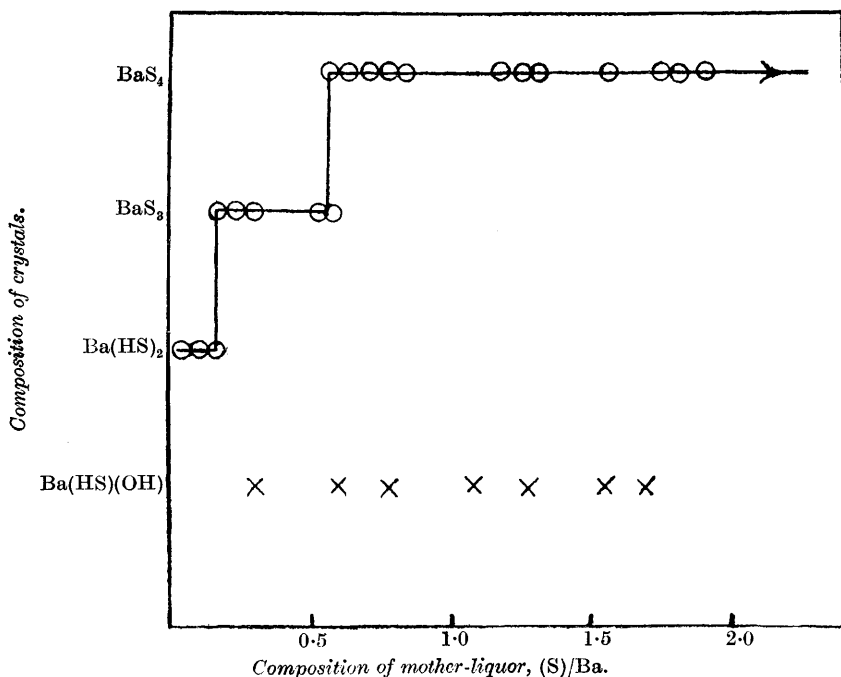
TABLE III.

No.	Original solution. (S)/Ba. S/Ba.	Relative cont.	Ba, %.	(S), %.	Crystals. (S), %.	S, %.	(S)/Ba. S/Ba.	S/Ba.	Composition.	(S)/Ba. S/Ba.	Mother-liquor. (S)/Ba. S/Ba.
1	3 +	—	{ 43.95	39.56	51.22	3.865	5.005	BaS <sub>4</sub> .H <sub>2</sub> O ÷ 8.70% S.	3.374	—	
2	3 +	—	{ 47.75	33.48	45.50	2.908†	4.100	BaS <sub>4</sub> .H <sub>2</sub> O	3.862	—	
3	1.005	—	{ (i) 48.02	27.69	41.65	2.476	3.725	Mixture (i) = BaS <sub>4</sub> .H <sub>2</sub> O;	0.775	—	
4	{ (a)	—	{ (ii) 40.31	none	13.30	—	1.158	(ii) = Ba(OH)(SH).5H <sub>2</sub> O	—	—	
											0.972
5	{ (b)	—	{ (i) 48.10	32.28	29.34	2.882	2.369	(i) = Ba(SH) <sub>2</sub> .3H <sub>2</sub> O;	—	—	
											0.693
6	{ (c)	—	48.50	33.43	45.71	2.960	4.047	BaS <sub>4</sub> .H <sub>2</sub> O	—	—	
											0.985
7	{ (d)	—	—	—	—	—	—	Mainly BaS <sub>4</sub> .H <sub>2</sub> O; BaS <sub>3</sub> .3H <sub>2</sub> O	—	—	
											0.811
8	{ (e)	—	47.58	21.51	37.26	1.942	3.363	Just commencing	—	—	
											0.760
9	{ (f)	—	48.30	20.81	34.76	1.849	3.163	BaS <sub>3</sub> .3H <sub>2</sub> O	—	—	
											0.567
10	{ (g)	—	—	—	—	—	—	Mixture BaS <sub>3</sub> .3H <sub>2</sub> O and	—	—	
											0.687
11	{ (h)	—	53.92	none	28.96	—	2.307	Ba(SH) <sub>2</sub> .3H <sub>2</sub> O	—	—	
											0.716
12	{ (i)	—	50.38	22.89	38.11	1.951	3.246	Mixture BaS <sub>3</sub> .3H <sub>2</sub> O and	—	—	
											0.152
13	{ (j)	—	49.51	none	11.65	—	1.000	Ba(SH)(OH).5H <sub>2</sub> O	—	—	
											0.287
14	{ (k)	—	47.36	24.65	—	2.235	—	Mainly Ba(SH)(OH).5H <sub>2</sub> O;	—	—	
											—
15	{ (l)	—	—	—	—	—	—	BaS <sub>4</sub> .H <sub>2</sub> O just commencing	—	—	
											1.568
16	{ (m)	—	—	—	—	—	—	Mixture BaS <sub>4</sub> .H <sub>2</sub> O with	—	—	
											1.568
17	{ (n)	—	—	—	—	—	—	BaS <sub>4</sub> .H <sub>2</sub> O	—	—	
											1.786
18	{ (o)	—	—	—	—	—	—	BaS <sub>4</sub> .H <sub>2</sub> O	—	—	
											1.786
19	{ (p)	—	—	—	—	—	—	BaS <sub>4</sub> .H <sub>2</sub> O	—	—	
											1.775
20	{ (q)	—	—	—	—	—	—	Mixture BaS <sub>4</sub> .H <sub>2</sub> O and	—	—	
											1.687
21	{ (r)	—	—	—	—	—	—	BaS <sub>3</sub> .3H <sub>2</sub> O	—	—	
											1.170
22	{ (s)	—	47.46	20.13	36.57	1.821	3.309	BaS <sub>3</sub> .3H <sub>2</sub> O	—	—	
											0.567
23	{ (t)	—	—	—	12.62	—	—	Mainly Ba(SH)(OH).5H <sub>2</sub> O;	—	—	
											0.549
24	{ (u)	—	48.35	18.06	34.28	1.605	3.045	BaS <sub>3</sub> .3H <sub>2</sub> O	—	—	
											0.610
25	{ (v)	—	—	—	25.54	—	—	Ba(SH) <sub>2</sub> .3H <sub>2</sub> O	—	—	
											0.193

† This ratio was obtained on a solution of the crystals from which free sulphur had been removed by filtration

3.271. Calc. for  $\text{BaS}_3 \cdot 3\text{H}_2\text{O}$ : Ba, 47.81; (S), 22.27; S, 33.41%. The crystals from another preparation were centrifuged [Found: Ba, 48.35; (S), 18.06; S, 34.28%; (S)/Ba = 1.605; S/Ba = 3.045. (From the nature of the analytical method, (S) is always low.)]. These crystals lose their lustre more rapidly in air than the tetrasulphide, and this, together with their distinctive colour and analysis, leaves little doubt that they are  $\text{BaS}_3 \cdot 3\text{H}_2\text{O}$ . This trihydrate is always formed in small yield compared with that of crystals from solutions of higher sulphur content. In the isolated experiment

FIG. 4.



4b (Table III), tetrasulphide was obtained from solutions lying within this region of composition.

(4) Concentration of solutions still weaker in polysulphide sulphur yields the hydrosulphide.

In certain preparations, colourless, positive, uniaxial, probably hexagonal crystals appeared (Found: Ba, 49.51; S, 11.65. Calc. for  $\text{BaO} \cdot \text{H}_2\text{S}_5 \cdot 5\text{H}_2\text{O}$ : Ba, 49.53; S, 11.54%). Schöne described a compound of this composition as the first fraction obtained from solutions of barium trisulphide, but actually we have found that it may occur throughout the range indicated in Fig. 4, and its appear-

ance is apparently independent of the (S)/Ba ratio of the solution. Its ubiquitous occurrence would seem to account for crystals of the type  $Ba_4S_7 \cdot 25H_2O$  reported by Schöne, which must have been mixtures of this compound and the tetrasulphide. That this compound is formed by hydrolysis of the unchanged hydrosulphide in polysulphide solutions was shown by allowing a dilute solution of the hydrosulphide to evaporate over calcium chloride in an evacuated desiccator at  $35^\circ$ , whereupon crystals of this compound were obtained after 4 days; from analysis, it may be either  $BaS \cdot 6H_2O$  or  $Ba(SH)(OH) \cdot 5H_2O$ , but both its methods of formation (p. 698) would suggest the latter constitution.

Further experiments with various concentrations of polysulphide showed that this compound is formed from solutions in which the concentration of barium and sulphur is originally low, and a consideration of relative concentrations in Table III affords an explanation of its apparently abnormal occurrence. Solutions of density up to 1.32 g./c.c. yielded hydroxyhydrosulphide first or in large bulk; those giving both this compound and the tetrasulphide in about equal amount had a mean density of 1.36, whilst above this concentration tetrasulphide was the only product. Incidentally, the average concentration used throughout this work, *viz.*, 1.35 g./c.c., was that from which it was just possible for hydroxyhydrosulphide to be formed.

*Analytical Methods.*—The total sulphur was determined by adding a weighed amount of the polysulphide to 40 c.c. of 10% sodium hydroxide, to which were added 10 c.c. of bromine. The solution was gently heated until almost colourless, 30 c.c. of concentrated hydrochloric acid were then added, and the whole was boiled until colourless; the sulphate was then estimated gravimetrically. Polysulphide sulphur and barium were determined together on the same weighed sample: (1) a slight excess of dilute hydrochloric acid was added, and the solution boiled to coagulate the precipitated sulphur, which was filtered off, thoroughly washed, and dried in an electric oven at  $70-80^\circ$ ; (2) to the filtrate was added a slight excess of dilute sulphuric acid, and the barium estimated as sulphate. For solutions, 2.5 c.c. were weighed and then analysed as above.

#### *Calcium Polysulphides.*

All previous attempts to prepare these compounds have been made in an aqueous medium, and have produced oxysulphides, such as  $4CaO \cdot CaS_4 \cdot 18H_2O$  (Schöne, *Annalen*, 1862, **117**, 58, 224), and other products of hydrolysis. This has been avoided in the present investigation by using alcoholic media for solution (compare Rule and Thomas, *J.*, 1911, **99**, 558; 1914, **105**, 177).

*Calcium Ethoxide and Methoxide.*—Perkin and Pratt (J., 1909, 95, 159) investigated the interaction of calcium with the alcohols. Contrary to their statement, we find an immediate reaction at the laboratory temperature with methyl alcohol: after removal of the alcohol at 160—170° in dry hydrogen, we found Ca, 39.31, 39.25 [Calc. for  $\text{Ca}(\text{CH}_3\text{O})_2$ : Ca, 39.22%]; hence the reaction was complete. The ethoxide is much the more soluble at the boiling point of the parent alcohol, and yields crystals of  $\text{Ca}(\text{C}_2\text{H}_5\text{O})_2 \cdot 2\text{C}_2\text{H}_5 \cdot \text{OH}$  on cooling, whilst the amorphous methoxide remains suspended in the boiling liquid.

*Calcium Hydrosulphide.*—The alkoxides were formed from a weighed quantity of calcium in a measured volume of alcohol, the reaction vessel being fitted with condenser and drying tube. After the vigour of the reaction had ceased, the flask was heated at 100° for a further 15 mins. in the case of the methoxide and 60 mins. in that of the ethoxide. Dry hydrogen sulphide was passed through the suspended alkoxide at laboratory temperature for about 6 hours, whereupon dissolution was complete, the reaction vessel being protected meanwhile with a calcium chloride tube; the liquid was then filtered from traces of impurities. As with barium, the solutions are pale yellow from traces of polysulphide. Analysis of a solution, after removal of excess hydrogen sulphide with nitrogen, gave  $\text{S}/\text{Ca} = 2.018$ . Using a method analogous to that employed by Divers and Schimidzu (*loc. cit.*) for aqueous solutions, and by repeatedly adding alkoxide and maintaining a stream of hydrogen sulphide to saturate the solution, we obtained crystals from a concentration of 0.12 g. of calcium per c.c. After being washed with alcohol, these gave hydrogen sulphide copiously with hydrochloric acid, and a clear solution after boiling, whereas when warmed with water they yielded hydrogen sulphide and a calcium hydroxide suspension. When heated dry, they gave monosulphide, hydrogen sulphide, and alcohol, and they could be preserved at 0° in hydrogen sulphide but were readily decomposed at the ordinary temperature on exposure to air.

Separation of the crystals for analysis was difficult, but cold weather enabled washing with alcohol, drying on a porous plate, and weighing to be carried out below 0°. Owing to rapid loss of hydrogen sulphide, the initial weighing may be in error by  $\pm 0.004$  g. A typical analysis gave Ca, 12.34; S, 19.14;  $\text{S}/\text{Ca} = 1.944$  [Calc. for  $\text{Ca}(\text{HS})_2 \cdot 7\text{CH}_3 \cdot \text{OH}$ : Ca, 12.12; S, 19.40%].

*Calcium Monosulphide.*—This has been previously prepared pyrophorically and by heating  $\text{Ca}(\text{HS})_2 \cdot 6\text{H}_2\text{O}$  in hydrogen sulphide (Divers and Schimidzu, *loc. cit.*). Sample 1 (Table IV) was obtained by passage of hydrogen sulphide over the ethoxide suspended in

boiling alcohol, washing the product with alcohol and ether, and drying it in a vacuum desiccator. Sample 2 was prepared by passing the gas during the formation of the ethoxide and drying the product at 100° in hydrogen.

TABLE IV.

No.	Ca, %.	(S), %.	S, %.	Total, %.	S/Ca.
1	49.80	Trace	37.23	87.03	0.935
2	48.11	Trace	37.06	85.17	0.963
3	—	None	—	—	0.986
4	—	None	—	—	0.985
5	49.88	1.49	38.70	88.58	0.933
6	50.80	Trace	37.72	88.52	0.928

Monosulphide was prepared from solutions of the hydrosulphide in ethyl alcohol by boiling the solution in a current of dried hydrogen: the white precipitate was formed within 2 mins. Moist material gave Sample 3, from which hydrochloric acid did not precipitate sulphur. The substitution of hydrogen sulphide for hydrogen gave the same moist product (Sample 4). Sample 5 was material dried over calcium chloride in a vacuum for 48 hours, and Sample 6 was dried at 130° (30 hours) and at 360° (36 hours) in nitrogen. These results show that the action of hydrogen sulphide on the ethoxide in boiling alcohol is  $\text{Ca}(\text{OC}_2\text{H}_5)_2 + \text{H}_2\text{S} \longrightarrow \text{CaS} + 2\text{C}_2\text{H}_5\cdot\text{OH}$ , and is quite distinct from the reaction leading to the formation of the hydrosulphide, which occurs at the laboratory temperature. In drying the material by distilling off the alcohol, some alcoholysis takes place [ $\text{Ca}(\text{HS})_2 + 2\text{C}_2\text{H}_5\cdot\text{OH} \longrightarrow \text{Ca}(\text{C}_2\text{H}_5\text{O})_2 + 2\text{H}_2\text{S}$ ], whereby one-tenth of the calcium in the final product occurs as ethoxide. Thus, in Sample 6,  $(\text{C}_2\text{H}_5\text{O})_2 = 11.48\%$  (by difference from 100%), and is equivalent to 5.10% of calcium. The S/Ca ratio becomes 1.032 when allowance is made for this fact.

*Preparation of Calcium Polysulphides from Alcoholic Hydrosulphide Solutions.*—Schöne (*Annalen*, 1862, **117**, 58) and Berzelius prepared tetra- and penta-sulphide solutions by prolonged boiling of an aqueous suspension of monosulphide and sulphur, whilst Divers and Schimidzu (*loc. cit.*) obtained a solution of the penta-sulphide by dissolving sulphur in aqueous hydrosulphide. No true polysulphide has, however, been crystallised. Work in aqueous-alcoholic solutions has confirmed that oxysulphides only are found when water is present: analysis of six different preparations, though varying considerably, gave as a mean: Ca, 29.33; (S), 11.24; S, 20.99 [Calc. for  $\text{CaS}_3, 3\text{Ca}(\text{OH})_2, 10\text{H}_2\text{O}$  (Büchner's crystals): Ca, 29.74; (S), 11.90; S, 17.84%].

Attempts to prepare polysulphide solutions in ethyl alcohol were very unsatisfactory, owing to the rapid precipitation of the mono-

sulphide by the boiling necessary for completing the dissolution of the sulphur. Although some polysulphide is formed, precipitation of the monosulphide takes place in less than 2 mins. and long before the sulphur has dissolved; furthermore, there is apparently no reaction between the monosulphide and sulphur suspended in alcohol. On the other hand, monosulphide separates more slowly from methyl-alcoholic solution, and a perfectly clear liquid is obtainable provided special precautions be taken with polysulphides of lower S/Ca ratios.

Estimation of the hydrogen sulphide evolved on the addition of sulphur to the hydrosulphide in methyl alcohol (compare p. 699) gave very indefinite results owing to the formation of monosulphide [compare points  $\otimes$  in Fig. 3].

For the preparation, weighed quantities of calcium were converted to hydrosulphide, sulphur was added in amount appropriate for the polysulphide required, and the mixture was heated at 100° under reflux until the sulphur was completely dissolved (about 10 mins. were required with a concentration of 5 g. of calcium in 80 c.c. of alcohol). Sulphur up to about that required for  $\text{CaS}_{5.5}$  can be dissolved in the hydrosulphide, the excess beyond pentasulphide proportion being precipitated on cooling, as with the barium compounds in aqueous solution.

Dark red solutions were thus obtained with S/Ca ratios from 2 to 5, but disulphide proportions never gave clear solutions at 100°, whilst in the case of the trisulphide the clear solution first formed rapidly became clouded. This precipitate was increased by boiling or by dilution, and analyses, though divergent, indicated that the material consisted essentially of calcium methoxide formed by alcoholysis [ $\text{CaS}_2 + 2\text{CH}_3\cdot\text{OH} \longrightarrow \text{Ca}(\text{OCH}_3)_2 + \text{H}_2\text{S} + \text{S}$ ] and of monosulphide formed by the reaction  $\text{Ca}(\text{SH})_2 \longrightarrow \text{CaS} + \text{H}_2\text{S}$ , already described. The mean analysis was: Ca, 41.82; (S), 1.71; S, 3.08; loss on ignition, 35.88 [Calc. for a mixture of 4 parts of methoxide to 1 part of sulphide: Ca, 41.67; (S), nil; S, 6.67; loss, 38.33%]. Schöne obtained a similar material from aqueous-alcoholic solutions of barium polysulphides, but did not identify it.

Solutions of di- and tri-sulphide ratios, free from this precipitate, could be obtained by heating the mixture at a temperature not exceeding 70° until solution of the sulphur was complete.

Crystals were obtained from the polysulphide solutions with great difficulty and only from critical concentrations. For instance, a solution of pentasulphide ratio gave no crystals on cooling to - 10° until a concentration of 1 g. of calcium in 9 c.c. of solution was reached. The best method of obtaining such concentrations, and at the same time avoiding decomposition, was by evaporation in

a vacuum over calcium chloride at the laboratory temperature. The solutions were then transferred to a tightly stoppered glass tube, and cooled in an ice-salt mixture.

The treacle-like nature of the solutions rendered separation of any crystals formed almost impossible. Attempts to filter them off under reduced pressure were fruitless, as was also washing by decantation owing to the immiscibility of the viscous solution with alcohol. Even a centrifuge at 4,000 r.p.m. surrounded with an ice-salt mixture proved ineffective. In all cases, therefore, the crystals were contaminated with mother-liquor to the extent of at least 50%. The analyses of crystals and mother-liquors obtained from solutions of various ratios of (S)/Ca are given in Table V. From comparison of atomic ratios (S)/Ca of crystals and mother-liquor, it is evident that there is no perceptible difference between their compositions, and it has not been shown whether a number of polysulphides exist or whether the materials are solid solutions of sulphur in one sulphide.

TABLE V.

No.	Original solution.	Crystals.						Mother-liquor.	
		Ca, %.	(S), %.	S, %.	(S)/Ca.	S/Ca.	%.	(S)/Ca.	
1	(4)*	9.71	32.79	41.86	4.232	5.402	48.43	—	
2	(4)	8.66	29.36	36.52	4.249	5.285	54.82	—	
3	4.105	8.41	28.28	35.88	4.213	5.347	55.71	4.010	
4	(a) (3.5)	9.69	30.92	38.40	3.999	4.966	51.91	3.954	
	(b) 3.954	9.40	30.26	38.34	4.035	5.112	52.26	4.006	
5	(3)	9.67	24.04	31.96	3.116	4.142	58.37	—	
7	(2.5)	10.90	26.55	—	3.052	—	—	2.943	
8	(3)	10.92	25.39	34.31	2.914	3.937	54.77	—	
9	(2)	19.48	32.45	—	2.087	—	—	—	
10	(2+)	12.73	23.20	34.30	2.283	3.377	52.97	—	
11	(2)	13.51	24.82	35.86	2.302	3.327	50.63	—	
12	(1.5+)	11.40	17.12	30.00	1.882	3.297	58.60	1.755	
13	(2+)	11.93	22.06	33.43	2.318	3.512	54.64	2.397	
14	2.316	11.30	20.78	32.10	2.305	3.560	56.60	2.278	
15	(1)	11.82	10.98	18.96	1.164	2.010	69.22	1.159	
16	(1)	13.22	10.89	27.84	1.017	2.638	58.94	—	
17	(1)	12.31	11.27	25.45	1.147	2.591	62.24	1.183	
18	0.996	12.93	10.24	24.62	0.992	2.386	64.45	0.981	
19	1.145	—	—	—	1.066	—	—	1.126	

\* Figures in parentheses indicate deductions from quantities used in preparations, and not analytical estimations.

The analytical data, however, give positive evidence of true polysulphides, and not the oxysulphides found previously. In the case of the lower sulphides their preparation involves the retention of hydrogen sulphide, hence the high total sulphur contents (Table V, Nos. 12, 16, 17, 18).

*Analytical Methods.*—The method was analogous to that used for the barium compounds except in the estimation of the metal, where oxalate was substituted for sulphate.

Two properties of solutions of pentasulphide ratio are noteworthy. The reversibility of the reaction  $\text{Ca}(\text{HS})_2 + 4\text{S} \longrightarrow \text{CaS}_5 + \text{H}_2\text{S}$ , observed by Divers and Schimidzu (*loc. cit.*), occurs in alcoholic solution; thus, after passage of dry hydrogen sulphide into a clear solution of the pentasulphide, a crystalline precipitate of sulphur began to form round the jet. The precipitation is more rapid when water is present. Divers and Schimidzu found that a colourless solution of the hydrosulphide is eventually formed; but in the anhydrous condition, after passage of the gas for 6 hours at  $0^\circ$  to assist the reaction in this direction, the solution was still dark red.

Whilst solutions and crystals of lower sulphur content gave clear solutions in water, those containing sulphur above tetrasulphide ratio precipitated this extra sulphur on the addition of water, and on being filtered, yielded a clear solution of tetrasulphide ratio. The amount of water required to precipitate the sulphur depends on the concentration of alcohol, and the precipitate redissolves on the addition of alcohol.

This fact seems inimical to the view of Divers and Schimidzu that the reaction takes the course  $\text{CaOH}(\text{HS}_5) + \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{H}_2\text{S}_5 (= 4\text{S} + \text{H}_2\text{S})$ , since the amount of polysulphide sulphur should be much larger; rather does it indicate that the fifth atom is in solution in the tetrasulphide and is precipitated with water, and as with barium pentasulphide, tetrasulphide and free sulphur are formed on crystallisation.

Attempts to prepare the polysulphides thermally by the vigorous reaction between calcium metal and sulphur at a temperature near the boiling point of the latter resulted in the formation of the monosulphide only [Found (after distillation of excess sulphur in a vacuum): Ca, 54.30; S, 44.63; (S), 1.00%].

#### *Summary.*

(1) A thermal study of the system barium sulphide-sulphur indicates that the disulphide is extremely unstable at its m. p.,  $925^\circ$ , as is also the trisulphide, m. p.  $554^\circ$ . Higher sulphur compounds could not be obtained at atmospheric pressure.

(2) On dissolution of various proportions of sulphur exceeding  $(\text{S})/\text{Ba} = 0.6$  in aqueous solutions of barium hydrosulphide, the product is  $\text{BaS}_4 \cdot \text{H}_2\text{O}$ ; with less sulphur,  $\text{BaS}_3 \cdot 3\text{H}_2\text{O}$  and hydrosulphide are produced. From dilute solutions the compound  $\text{Ba}(\text{SH})(\text{OH}) \cdot 5\text{H}_2\text{O}$  crystallises. Solutions with pentasulphide proportion yield a mixture of tetrasulphide and sulphur.

(3) The stability of the polysulphides of the alkaline-earth metals is greatest, as would be expected, in the case of barium. Calcium



polysulphides are so hydrolysed by water that they could not be prepared in this medium. Moreover, they could not be prepared thermally from the elements.

(4) Crystalline polysulphides of calcium have been prepared for the first time by using anhydrous alcohol as a solvent. The nature of these compounds and of the solutions from which they are crystallised makes it impossible to obtain material suitable for analysis; consequently, individual polysulphides have not been isolated. From the peculiar stability of barium tetrasulphide, it is probably justifiable to infer that at least the tetrasulphide is formed.

Acknowledgment is made to the Research Committee of this College for a grant towards the cost of the centrifuge employed in this and other researches.

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[*Received, November 4th, 1930.*]

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