CLXXXIX.—*The Polysulphides of the Alkali Metals. Part I. Sodium* (i).

By Thomas Gibson Pearson and Percy Lucock Robinson.

In spite of much research, little is definitely known of the polysulphides of the alkali metals, for none of the earlier work has escaped criticism, and, indeed, only the latest work, that of Rule and Thomas (J., 1914, **105**, 177, 2819; 1917, **111**, 1063), has remained unchallenged. Two anomalies, typical of many, are that one published equilibrium diagram shows *eight* and another *four* compounds; also, that the existence of a series of disodium compounds, described either by Schöne or by Böttger, was contradicted by Bloxam, whose tetrasodium enneasulphide, in turn, Rule and Thomas were unable to prepare. Moreover, certain standard treatises in English appear to have been misled by several mistranslations in abstracts. In view of the great diversity of opinion, and as we were interested in the individual polysulphides as a possible source of pure persulphides of hydrogen (compare Mills and Robinson, J., 1928, 2326), we decided that an extensive re-examination of this field was essential.

The present paper describes a careful reinvestigation of all the previous work on the polysulphides of sodium, with the exception of that of Hugot (*Compt. rend.*, 1899, **129**, 388) in liquid ammonia, of Küster and Heberlein on the electrochemistry of aqueous polysulphide solutions, and of Sabatier (*Ann. Chim. Phys.*, 1881, **22**, 15) on thermochemical aspects. An endeavour to account for previous discrepancies has in great measure been successful. Moreover, certain other methods of attack have been applied to these problems for the first time, particularly (1) the amplification of thermal analysis of the system sodium monosulphide–sulphur by microscopic methods; (2) the confirmation of the existence of di-, tetra-, and penta-sulphides in melts by measurement of the loss of sulphur at various temperatures; and (3) the partial study of the system sodium monosulphide–sulphur–water–alcohol.

The conclusions reached are summarised on p. 1496. The peculiar stability of sodium tetrasulphide is significant. It appears to be readily obtained from solution in both anhydrous and hydrated forms and, furthermore, to be the only polysulphide obtainable from the hydrosulphide. Trisulphide, on the other hand, appears to be formed at 120° but to be completely decomposed into a mixture of di- and tetra-sulphides at temperatures far below its melting point. It would seem, however, that this stability is an inherent property of the molecular type Na_2X_4, rather than of the tetrasulphide itself, since dehydration of the highest hydrates at 100° produces $Na_2S,3H_2O$, $Na_2S_2,2H_2O$, Na_2S_3,H_2O, and Na_2S_4, and leads to the hydrolysis of pentasulphide.

Further work, designed to elucidate the structure of these polysulphides, is in progress.

EXPERIMENTAL.

Preparation of Materials Used.—The sodium from Imperial Chemical Industries, Ltd., was kept under dry liquid paraffin containing 1% of amyl alcohol, which is known to preserve a fresh metallic surface. Experience enabled the metal to be cut to within 0·1 g. of the desired weight, thereby reducing oxidation to a minimum.

The sulphur was twice recrystallised from carbon disulphide and dried for several hours at 100°.

Absolute alcohol was dried by being twice refluxed for 3 hours over freshly burnt quick-lime and then distilled from the same material, with rejection of small head and tail fractions.

Toluene was dried by refluxing over metallic sodium, then over a polysulphide, and distillation from metallic sodium, small head and tail fractions being rejected.

Analytical Methods.—The total sulphur content was determined by adding a weighed amount of the polysulphide in aqueous solution to 50 c.c. of 10% sodium hydroxide containing 7 c.c. of bromine. The solution was gently heated until of a light straw colour, whereupon 30 c.c. of hydrochloric acid were added and the whole was boiled until colourless. The sulphate was then estimated in the usual way with barium chloride.

The polysulphide sulphur and the sodium were determined together on the same weighed sample: (1) a slight excess of 10% sulphuric acid was added, and the solution boiled to coagulate the precipitated sulphur, which was filtered, thoroughly washed, and dried in an electric oven at 70—80°; (2) the filtrate was concentrated to a suitable volume, transferred to a platinum dish, evaporated to dryness, fused to the sulphate, and weighed.

Blanks were done on all the reagents used.

Experimental details are described under the relevant sections.

I. *The Preparation of Polysulphides from Solution.*

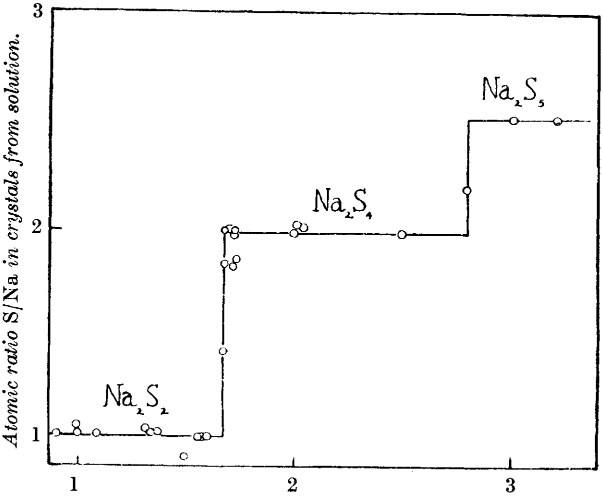
(i) *The Action of Sulphur on Sodium Monosulphide in Aqueous Alcohol.*—Schöne (*Pogg. Ann.*, 1867, **131**, 380) dissolved excess of sulphur in aqueous sodium monosulphide, evaporated the solution to crystallisation in a vacuum, triturated it with alcohol, and cooled it in a freezing mixture, obtaining pale yellow plates of hydrated sodium tetrasulphide, $Na_2S_4,6H_2O$. The mother-liquor on being chilled after further concentration gave orange-yellow crystalline pentasulphide, $Na_2S_5,6H_2O$. Later, Filhol (*Ann. Chim. Phys.*, 1873, **28**, 529) failed to obtain any polysulphides from sulphur and aqueous monosulphide in sealed tubes, but Böttger (*Annalen*, 1884, **226**, 335) described the formation of four polysulphides, $Na_2S_2,5H_2O$, $Na_2S_3,3H_2O$, $Na_2S_4,8H_2O$, and $Na_2S_5,8H_2O$, by solution of the calculated amounts of sulphur in aqueous-alcoholic sodium monosulphide. These results were criticised by Bloxam (J., 1900, **77**, 753) on the grounds that the alleged polysulphides could not have been formed since the sulphur added did not allow for the simultaneously formed thiosulphate (compare *Chem. News*, 1895, **72**, 63), or, alternatively, if formed, the polysulphides would have been contaminated with this thiosulphate, which becomes soluble in alcohol in their presence; further, he criticised the absence of data as to yield or description of the product, and doubted whether any pure polysulphide had been obtained. In consequence, Bloxam attempted to prepare them by the action of sulphur on aqueous hydrosulphide in a stream of hydrogen sulphide, but obtained only an alleged tetrasodium enneasulphide, $Na_4S_9,14H_2O$ (compare p. 1483).

Küster and Heberlein (*Z. anorg. Chem.*, 1905, **43**, 53, 431) found that the solubility of sulphur in solutions of the monosulphide diminished only slightly with rise in temperature between 0° and 50° and depended mainly on the concentration of the monosulphide, being at a maximum at 0·063*N*; the elements were then present in the atomic ratio Na : S = 2 : 5·24. They advanced evidence that a complex equilibrium rather than definite compounds existed in the solutions. They also noted the unique stability of solutions of tetrasulphide composition and showed that the polysulphides undergo hydrolysis to an extent which diminishes regularly with increasing sulphur content.

It is evident that the formation of a number of polysulphides by Böttger's method was possible, and that the problem could be best solved by a phase-rule study of the system monosulphide–sulphur–water–alcohol. As a complete investigation was impracticable, however, we examined the solid phases separating from a series of solutions having a wide range of S : Na ratios at one temperature, *viz.*, $-18° \pm 2°$ (compare Lash Miller and Kenrick, *J. Physical Chem.*, 1903, **7**, 259). These ratios for corresponding solid and liquid phases are plotted in Figs. 1*a* and 1*b*, and indicate unquestionably the formation of hydrated forms of di-, tri-, tetra-, and penta-sulphide, excluding the possibility of solid solutions. The work of Böttger and Schöne is therefore confirmed, although in several cases our hydrates differed from theirs; the new *hydrates* are : $Na_2S_2,6H_2O$; $Na_2S_3,8H_2O$; $Na_2S_4,9H_2O$; and $Na_2S_4,11H_2O$; $Na_2S_5,6H_2O$. To these must be added a tetrasulphide which may be either a hepta- or a mixture of octa- and hexa-hydrates. Dehydration of these materials at 100° led to the formation of $Na_2S_2,2H_2O$ and Na_2S_3,H_2O. A more extensive study of these hydrates is being undertaken by means of vapour-pressure measurements.

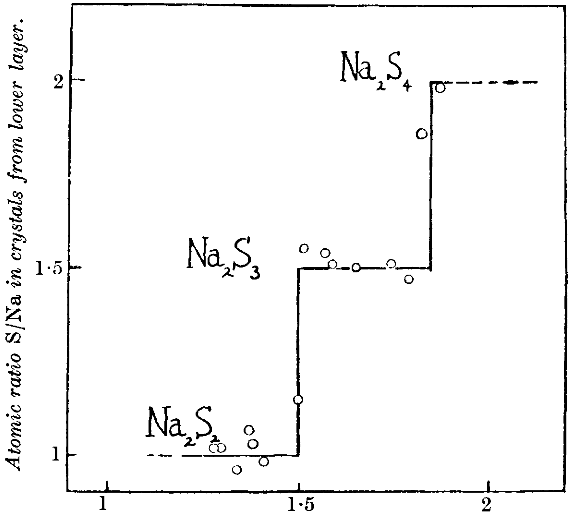
We therefore dissent from Bloxam (*loc. cit.*), not only as to the formation of these compounds, but also as to their alleged serious contamination with thiosulphate and alcohol: with suitable precautions only traces of these substances are present. Further, it is significant that Biltz and Wilke-Dörfurt (*Ber.*, 1905, **38**, 123; *Z. anorg. Chem.*, 1906, **48**, 297) prepared rubidium and cæsium polysulphides by a similar method without observing the formation of thiosulphates.

FIG. 1*a*.



Atomic ratio S/Na *in solution.*

FIG. 1*b*.



Atomic ratio S/Na *in liquor from lower layer.*

Experimental. Solutions of the hydroxide for conversion to monosulphide were prepared by the action of clean metallic sodium on aqueous alcohol (Küster, *Z. anorg. Chem.*, 1904, **41**, 474) of known composition. One-half of the solution was treated with hydrogen sulphide, giving pearly crystals which redissolved as saturation proceeded. The addition of the second half of the caustic soda immediately produced a nacreous crystalline precipitate which disappeared on warming. In this solution the requisite weight of sulphur was then dissolved by gentle heating on the water-bath for the minimum time. The resulting solutions varied in colour from light yellow at the disulphide composition to deep red at the pentasulphide. Within a specific range of composition, between di- and tetra-sulphide, a dark-coloured oil separated as a lower layer from the bulk of the solution on standing (see below).

The solutions—separated from the oils where necessary—were sampled for analysis and then crystallised in standard freezing mixtures of salt and ice (*i.e.*, at $-18° \pm 2°$) except in runs 27 and 28, in which cooling was effected in ether and solid carbon dioxide at about $-60°$. In the preliminary experiments, the solutions were crystallised completely in one cooling period of several hours, but the products generally had complex S : Na ratios and, as shown by subsequent fractional crystallisation, were mixtures formed by the successive crystallisation of individual polysulphides. In those exceptional cases, however, where large fractions of definite stoicheiometric composition were obtained, the first solid phase had obviously continued to be formed although metastable to the changed liquid, *e.g.*, runs 15, 16, 17. In general, therefore, fractions of crystals small enough to effect but little alteration in the composition of the solution were removed by filtration, washed first with ice-cold absolute alcohol and then with dry ether, exposed to phosphoric oxide and paraffin chips in a vacuum desiccator for 20 minutes, and analysed. Where large fractions were taken the resultant liquors were analysed (see footnote to runs 5, 15, 16, 17, 19, Table I). The results are shown in Table I and Fig. 1*a*, the S/Na ratios being, as elsewhere, atomic ratios. The "polysulphide" sulphur is denoted throughout by (S).

The red oily liquid separating when the ratio S : Na in the solution was between 1·09 and 1·94 proved to be an aqueous polysulphide of such high concentration as to suggest that it consisted of molten hydrates; moreover, it invariably approximated to the trisulphide in composition, *e.g.*, when the upper layer had S : Na = 1·879 : 1, the lower had the ratio 1·650 : 1. The oils were sampled for analysis, cooled to $-7°$, and the smallest possible fraction of crystals was separated and dried as above. This was extremely difficult, for, once started, crystallisation tended to spread rapidly through the system. The mother-liquors after filtration were therefore frequently analysed to check changes due to the crystallisation

TABLE I.

	Solution.				Crystals.			
No.	Na, g.	Water, c.c.	Alcohol, c.c.	S/Na.	Na, %.	(S), %.	S, %.	S/Na.
1	6	65	25	0·974	20·33	13·83	28·94	1·023
2	6	65	25	1·007	20·33	14·20	30·00	1·061
3	6	80	6	1·007	21·68	14·53	30·10	1·021
4	6	80	6	1·007	24·36	17·39	35·00	1·033
†5	6	80	25	1·087	21·25	13·83	29·50	1·021
6	6	80	12	1·322	20·51	17·10	29·75	1·042
7	6	85	25	1·348	19·63	13·26	27·27	1·033
8	6	65	25	1·383	20·56	16·63	29·36	1·027
9	3·7	80	7·5	1·503	21·20	14·31	28·62	0·970
10	6	80	10	1·561	21·11	14·75	29·62	1·009
11	6	65	25	1·564	21·09	—	29·92	1·016
12	5·6	84	6	1·618	21·23	13·37	29·37	0·994
13	6	80	7·5	1·602	21·22	13·55	33·53	1·136
14	6	65	25	1·685	16·10	20·33	—	1·408
†15	6	80	25	1·689	16·44	31·17	42·67	1·839
†16	6	85	20	1·680	16·02	32·24	44·16	1·982
†17	6	65	25	1·706	19·58	38·97	53·65	1·970
18	6	80	10	1·718	15·85	24·77	39·41	1·787
†19	6	80	25	1·744	16·02	30·82	41·24	1·854
20	6	65	25	1·744*	15·75	31·65	43·12	1·967
21	6	65	25	1·744*	15·76	31·58	42·90	1·957
22	6	65	25	1·744*	15·72	31·54	43·31	1·980
23	6	80	12	1·946	15·73	36·08	46·22	2·112
24	6	65	25	1·999	14·75	29·51	42·43	2·068
25	6	65	35	1·999*	14·14	29·73	39·14	1·989
26	6	65	25	1·999*	15·43	31·32	43·36	2·020
27	6	65	40	1·999*	13·59	28·75	38·06	2·013
28	6	65	40	1·999*	12·49	25·64	34·10	1·962
29	6	70	25	2·500	15·61	32·01	42·92	1·976
30	4	60	15	2·814	15·33	37·59	48·25	2·262
31	6	65	15	3·011	14·70	40·45	51·15	2·502
32	6	65	15	3·219	14·68	40·62	51·20	2·506

* Computed from weight of sulphur added, not by analysis of solution.

† The S/Na ratio in solution after crystallisation in these runs was as follows :

Run	5	15	16	17	19
Ratio	1·216	1·228	1·144	1·276	1·721

of too large a fraction. The results are given in Table II and Fig. 1*b*.

The products were tested for the presence of alcohol by distilling 5 g. samples in nitrogen until all volatile matter had been evolved, the water condenser finally being thoroughly rinsed into the ice-cooled receiver. The distillate was then submitted to Dupré's modification of Thresh's test [*Pharm. J.*, (3), **9**, 408], and the quantity of alcohol shown to be less than 0·02% of the original crystals. Comparative experiments using the iodoform reaction indicated a quantity of the order of 0·01%. Thiosulphate, produced partly by aerial oxidation and partly by solution of sulphur in the hydrolysed monosulphide, was invariably present in small quantities in the crystals; that due to oxidation could be minimised by

TABLE II.

Oil.					Crystals.			
No.	Na, g.	H_2O, c.c.	Alcohol, c.c.	S/Na.	Na, %.	(S), %.	S, %.	S/Na.
*33	6	80	25	1·279	21·40	14·33	30·29	1·018
34	6	85	25	1·292	21·08	14·15	29·85	1·018
35	6	80	25	1·344	22·05	13·80	29·57	0·964
36	6	80	25	1·374	20·03	14·77	29·99	1·076
37	6	85	25	1·383	20·55	16·00	29·40	1·029
*38	6	80	25	1·409	22·13	15·05	30·28	0·983
39	6	80	25	1·499	21·97	19·00	35·21	1·152
40	6	65	25	1·512	16·19	23·88	34·95	1·548
*41	6	60	25	1·574	16·25	22·55	34·73	1·536
42	6	80	25	1·585	16·35	23·20	34·42	1·514
*43	5·15	60	25	1·650	16·11	22·76	33·74	1·501
44	6	60	35	1·743	16·02	22·56	33·72	1·513
45	6	80	25	1·790	17·45	23·34	35·85	1·477
*46	6	80	25	1·826	16·51	32·25	42·85	1·864
47	6	65	25	1·870	15·85	31·32	43·85	1·988

* The S/Na ratio in solution after crystallisation in these runs was :

Run	33	38	41	43	46
Ratio	1·512	1·790	1·620	1·790	1·905

avoiding access of air to the polysulphides or their solutions, and the remainder by dissolving the sulphur as quickly as possible in the monosulphide at the lowest convenient temperature, *viz.*, 60°. If the first precaution was not observed, 20 minutes' boiling gave in octahydrated tetrasulphide crystals a thiosulphate content of 2·6—3·0%; by careful exclusion of air, this was reduced to 1·6%, and the second precaution reduced this still further to 0·5—1%.

Properties of the hydrated polysulphides. The disulphide *hexahydrate* is a cream-coloured, acicularly crystalline compound; like the other hydrated sulphides, it is very soluble in water and less so in alcohol, giving clear, light yellow solutions. The mean of the analyses of twelve different samples gave: Na, 21·11 ± 0·23; (S), 14·51 ± 0·33; S, 29·79 ± 0·23 [$Na_2S_2,6H_2O$ requires Na, 21·10; (S), 14·68; S, 29·36%]. Two samples when heated at 100° in a stream of pure hydrogen lost 34·20 and 34·80% of water, giving the *dihydrate* ($Na_2S_2,6H_2O$ requires $4H_2O$, 33·02%). The hexahydrate on heating to 200° could be almost completely dehydrated (Loss: 47·80, 48·50, 48·82. Calc.: 49·54%), but the removal of the last trace of water involved loss of hydrogen sulphide.

The hydrated trisulphide obtained from the oily layer consisted of dark yellow lamellæ melting at about 25° to a thick, oily, reddish-brown liquid. It appeared to be an *octahydrate* [Found (mean of 17 analyses on independent preparations): Na, 16·21 ± 0·14; (S), 23·08 ± 0·40; S, 34·03 ± 0·20. $Na_2S_3,8H_2O$ requires Na, 16·08; (S), 22·38; S, 33·57%]. On dehydration at 100° in a stream of hydrogen, three samples lost 43·96, 44·92, and 44·49% of water, giving a *monohydrate* ($Na_2S_3,8H_2O$ requires $7H_2O$, 44·05%). The remaining water cannot be completely removed without considerable hydrolysis; *e.g.*, at 200° three samples lost 47·94, 48·51, 49·20% (Calc. for $8H_2O$: 50·35%).

The hydrated tetrasulphides formed golden-yellow, glistening plates. The degree of hydration depended upon temperature and water concentration of the liquid from which they were crystallised. With high water content at low temperatures, two higher *hydrates* were obtained [Found in *A* : Na, 13·59; (S), 28·75; S, 38·05. $Na_2S_4,9H_2O$ requires Na, 13·69; (S), 28·58; S, 38·10%. Found in *B* : Na, 12·49; (S), 25·64; S, 34·10. $Na_2S_4,11H_2O$ requires Na, 12·37; (S), 25·81; S, 34·41%]. When the water content was reduced, an octahydrate separated [Found (mean of 8 analyses on 8 different samples): Na, 14·45 ± 0·14; (S), 29·62 ± 0·40; S, 40·78 ± 0·32. Calc.: Na, 14·47; (S), 30·19; S, 40·26%]. By reducing the proportion of water or raising the temperature, a product which might be either a hepta- or mixture of hexa- and octa-hydrates was obtained [Found: Na, 15·76; (S), 31·58; S, 43·24. Calc. for heptahydrate: Na, 15·33; (S), 32·00; S, 42·66%].

Dehydration of any of these preparations at 100° gave no evidence of lower hydrates, and the whole of the water could be removed at 140°: thus three separate samples of octahydrate lost 46·35, 44·92, and 45·67% (Calc.: 45·27%).

The pentasulphide is an orange-coloured hexahydrate, crystallising in minute plates [Found: Na, 14·67; (S), 40·54; S, 51·18. Calc.: Na, 14·65; (S), 40·77; S, 50·96%]. This material obviously suffered decomposition by hydrolysis on dehydration even at 100°.

(ii) *The Action of Sulphur on Anhydrous Alcoholic Solutions of Sodium Monosulphide.*—Solutions of polysulphides have been prepared by dissolving sulphur in alcoholic solutions of sodium monosulphide. Through an examination of the solids crystallising from solutions varying considerably in the ratio S:Na, it has been established that, although unsuitable for preparation of pure polysulphides, the method yields di-, tri, tetra-, and probably penta-sulphide. There is also some evidence of the existence of alcoholates, and this is being investigated by means of vapour-pressure measurements.

Experimental. A solution of sodium (4 g.) in anhydrous alcohol was converted to the monosulphide by dividing it into two equal portions, saturating one with hydrogen sulphide, gently boiling it in a stream of nitrogen to remove excess of gas, and adding it to the other. The requisite weight of sulphur was dissolved by boiling for the minimum time. The resulting liquids were, after analysis, partly crystallised by evaporation in a vacuum at 15°.

The small fraction of crystals deposited was quickly collected on a Buchner funnel, well pressed, washed with several small quantities of anhydrous alcohol, dried by exposure to calcium chloride in a vacuum desiccator, and analysed. The results are in Table III.

The solubility of the polysulphides increased with their sulphur content, so that with solutions above the tetrasulphide composition the separation of a primary fraction was prevented by crystallisation taking place in one stage with the removal of all but the last trace of alcohol. These products obviously had the composition of the mother-liquor and were therefore examined under the microscope without analysis. About the composition $Na_2S_{4\cdot5}$, a large proportion of yellow crystals, typical of tetrasulphide, appeared, together with some brownish-yellow crystals, characteristic of pentasulphide. The light yellow constituent was largely replaced by the darker constituent at about the pentasulphide stage, whilst in the hexasulphide region this replacement was complete, but light yellow crystals of sulphur appeared. The products were in every case homogeneous microcrystalline polysulphides, uncontaminated by thiosulphate, but containing alcohol in such quantities as to indicate the presence of alcoholates (compare Rule and Thomas, J., 1914, **105**, 177). The disulphide was golden-yellow, acicular, and microcrystalline; the trisulphide formed dull yellow, tabular crystals; the tetrasulphide, dull yellow cubes with an olive-green tinge; and the pentasulphide, deep, orange, tabular crystals.

TABLE III.

Solution.	Crystals.				Solution.	Crystals.			
S/Na.	Na, %.	(S), %.	S, %.	S/Na.	S/Na.	Na, %.	(S), %.	S, %.	S/Na.
1·100	40·73	27·69	56·41	0·996	1·675	25·46	45·01	62·80	1·773
1·250	25·88	37·31	52·91	1·471	1·751	22·04	45·63	61·14	1·994
1·501	27·41	38·15	57·36	1·505	2·001	26·41	54·00	72·00	1·960
1·600	27·11	37·36	56·22	1·490	2·150	25·33	53·22	71·87	2·040

(iii) *The Action of Sulphur on Sodium Hydrosulphide.*—Rule and Thomas (*ibid.*) dissolved various proportions of sulphur in a solution of sodium hydrosulphide in anhydrous alcohol and found pure tetrasulphide to be formed only with the elements present in the calculated ratio. With less sulphur the products were considered to be mixtures of tetrasulphide and unchanged hydrosulphide, with pentasulphide proportions a mixture of tetrasulphide and sulphur resulted, but with more sulphur still there was some indication of higher polysulphides in the mixture. These authors confirmed their conclusions by estimating the hydrogen sulphide evolved during the dissolution of the sulphur.

We have repeated and confirmed these results, and have extended the experiments to aqueous-alcoholic solutions. This was done because the nearly equal solubility of hydrosulphide and tetrasulphide in anhydrous alcohol makes it impossible fractionally to separate them from this medium. In aqueous alcohol, however, the former appears to be definitely less soluble than the latter, and thus it has been possible to crystallise tetrasulphide as a late fraction even from solutions initially containing only sufficient sulphur to form trisulphide. Consequently, it would seem that sodium tetrasulphide is the only product from hydrosulphide over an extended range of sulphur concentration.

Bloxam (*loc. cit.*) stated that only one definite compound, *viz.*, $Na_4S_9,14H_2O$, could be obtained from solutions of sulphur in aqueous hydrosulphide. In an endeavour to obtain such tetrasodium salts, we passed hydrogen sulphide through aqueous-alcoholic solutions of the hydrosulphide whilst the sulphur was dissolving. Products of extremely variable composition were obtained, and only a fortuitous choice would have given compounds apparently of the type described by Bloxam. If such compounds were actually produced, they would have to contain at least 14 molecules of water. This high state of hydration is unusual, and the cumulative evidence suggests that the materials were *mixtures* of disodium compounds.

Experimental. 6-G. portions of sodium, dissolved in 150-c.c. lots of pure dry alcohol, were converted to hydrosulphide by the usual process (p. 1478); in the gently boiling solutions the required weights of sulphur were dissolved, and the solutions were evaporated to crystallisation or precipitated with dry ether. In appearance, composition, and properties, the products so obtained were identical with those described by Rule and Thomas (*loc. cit.*, pp. 179—183), tetrasulphide being the only definite polysulphide. The formation of disulphide by the action of sodium on the tetrasulphide was also confirmed (*idem, ibid.*, pp. 187—188), and, by a modification of these authors' method, we obtained further support for our results by measuring the hydrogen sulphide evolved during the dissolution of the sulphur.

For work in aqueous alcohol, lots of 10·3 g. of sodium were converted to hydrosulphide in an alcohol–water mixture (120 and 65 c.c. respectively), and sufficient sulphur was subsequently added to give the trisulphide composition. In the first case, the solution. after being kept at $-22°$ for 7 hours, deposited a large mass of plate-like crystals [Found: Na, 15·51; (S), 26·59; S, 36·75%; Na : S = 1 : 1·703]. In a second preparation, the material was fractionally crystallised; the first fraction, produced by cooling to $-15°$ for one hour, was presumably a mixture of tetra- and hydro-sulphides

[Found: Na, 15·44; S, 41·82%; Na : S = 1 : 1·947], whilst a second fraction, obtained by cooling to − 22° for 2 hours, and a third, by evaporating the mother-liquor to half bulk in a vacuum at room temperature followed by cooling to − 30°, were pure tetrasulphide [Found: for (ii), Na, 15·62; S, 43·64; for (iii), Na, 14·68; S, 41·00%; Na : S = 1 : 2·009, 1 : 2·007].

These experiments were modified by passing hydrogen sulphide through the liquid during the dissolution of the sulphur, but the solids produced on cooling were of indefinite and variable composition.

II. *Preparation of Polysulphides by Dry Methods.*

(i) *Reaction between Sulphur and Sodium Carbonate or Hydroxide.*—Polysulphides have been prepared by the action of sulphur on heated metallic oxides, hydroxides, or carbonates. Berthollet (*Ann. Chim.*, 1798, **25**, 233) believed them to be pure, and ascribed the occurrence of sulphate in their solutions to a reaction with water, but Gay-Lussac (*ibid.*, 1811, **78**, 87) and Vauquelin (*Ann. Chim. Phys.*, 1817, **6**, 5) contended that it was a primary product, and this was confirmed by numerous subsequent workers. Fordos and Gelis (*Ann. Chim. Phys.*, 1846, **18**, 86) found that a similar reaction took place in solution, producing thiosulphate and polysulphide, and Rose (*Annalen*, 1829, **17**, 324; 1842, **45**, 415, 533) confirmed this for potassium carbonate.

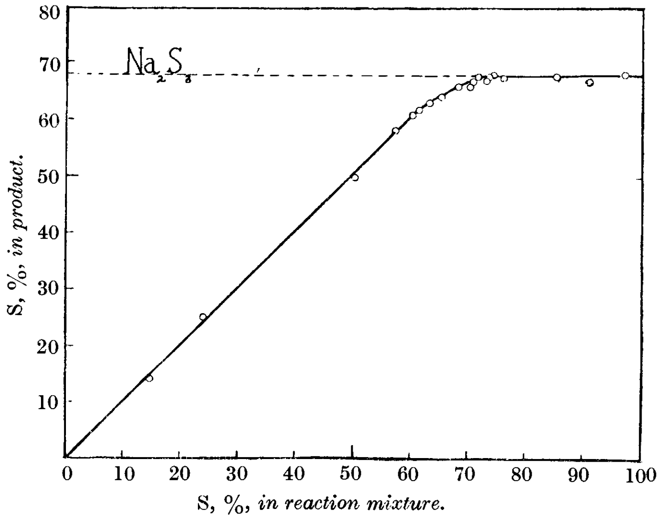
These results assume importance through Friederich's claim (*Met. Erz.*, 1914, **11**, 80) to have obtained pure polysulphides by the reaction between sulphur and sodium carbonate in carbon dioxide, and through his having used them in the investigation of the sodium sulphide–sulphur equilibrium (see p. 1489).

Experimental. 8·21 G. of sulphur and 6·79 g. of anhydrous sodium carbonate were heated under nitrogen. Reaction commenced slowly at about 200°, giving thiosulphate and polysulphide. At 350° the product contained 11·25% of thiosulphate, less than 0·05% of sulphate, and some unchanged material; whilst at 640° a loss of 2·85 g., corresponding to the whole of the carbon dioxide in the carbonate, was found, and the residue contained 17·70% of sodium sulphate and 4·22% of sodium sulphite, but no thiosulphate.

Analogous reactions were observed with sodium hydroxide, but similar experiments in boiling aqueous solutions led only to thiosulphate and polysulphide.

(ii) *The Action of Sodium on Sulphur.*—The preparation of polysulphides by the action of metallic sodium on molten sulphur has been attempted by Jones (J., 1880, **37**, 1461), Rosenfeld (*Ber.*, 1891, **24**, 1658), and others. The method is unsatisfactory owing to the violence of the combination and to contamination of the product either by silicates from the container or by oxidation. A more convenient process, due to Locke and Austell (*Amer. J. Sci.*, 1898, **20**, 592), is to allow the elements to react under toluene. From purely qualitative observations of the presence of free sulphur in the toluene or of metallic sodium in the product according as the added sulphur sufficed for the formation of trisulphide or not, these authors concluded that no material is obtainable with less sulphur than a mixture of tri- with some tetra-sulphide. As these results have been generally held by subsequent writers to indicate that only trisulphide is produced under these conditions, we have repeated this work quantitatively. Our findings (see Fig. 2) indicate that no compound higher than the trisulphide is produced. Free sodium in diminishing quantities is invariably present until this composition is reached, but not afterwards, provided that the reactants have been brought into intimate contact by crushing. The reaction is unique in that a polysulphide appears to be the first product, for even with a trace of sulphur no white film appears on the sodium surface such as might indicate monosulphide—under these conditions the metallic surface is partially coated with distinctly yellow patches, as though a polysulphide must be formed even at the cost of leaving available surface unattacked.

FIG. 2.



Experimental. The required weight of clean metallic sodium was melted under 250 c.c. of carefully dried toluene in a 500-c.c. flask fitted with a reflux condenser through which was added a weighed quantity of sulphur in 0·5 g. portions. The sodium was immediately coated with a yellow coherent film, but the reaction did not become vigorous until 1·5 atomic proportions of sulphur had been added, whereupon the film burst. The escaping sodium reacted vigorously with the dissolved sulphur, and it became necessary to cool the flask in water. After each subsequent addition of sulphur, we ground the spongy, friable masses with a long glass pestle to free the imprisoned sodium. Finally, the toluene was boiled for 20 minutes to complete the operation.

The sulphide was quickly collected on a Buchner funnel, well pressed, washed with cold toluene, and heated at 100° for 2 hours under a good vacuum applied through a drying train. With material below trisulphide composition, free sulphur was always present at this stage. When, however, sulphur equivalent to pentasulphide was used, there was a tendency for this element to crystallise on the cold filter pad; this was avoided by heating the funnel and washing with boiling toluene. The remainder of the toluene was removed by cautiously melting the sulphide. The products were homogeneous masses of pure sodium sulphides which gave clear solutions in water. If, however, insufficient care was taken to moderate the reaction in toluene by cooling, carbon to the extent of 0·05% might be present. Table IV compares the proportion of sulphur originally used with that found in the final product after melting.

Fig. 3.

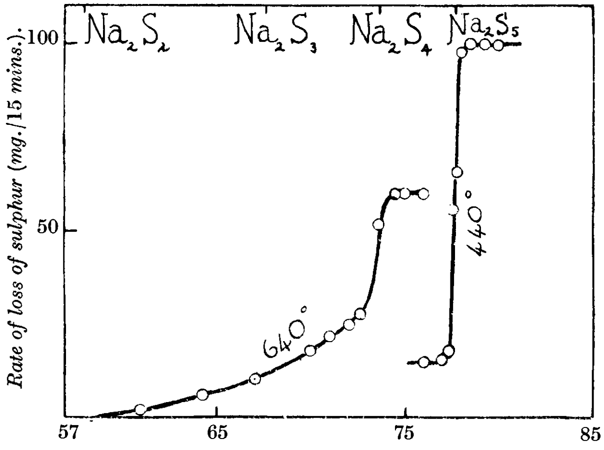


TABLE IV.

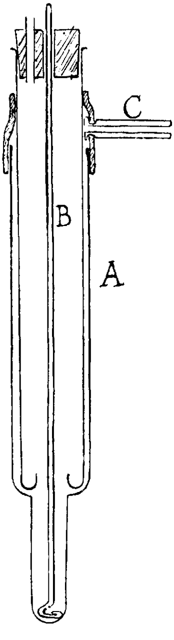
S, %, in reactants	14·7	24·2	50·0	57·2	60·0	61·3	63·3	64·7	67·8	69·7
,, in products	14·0	25·0	50·1	58·4	60·9	62·0	63·4	63·8	65·7	66·0
S, %, in reactants	70·6	71·4	73·1	73·7	74·1	74·6	76·2	85·0	91·2	96·8
,, in products	67·2	68·3	66·8	67·8	68·6	68·6	67·6	67·8	67·0	68·1

(Calc. for Na_2S_3 : S, 67·6%.)

(iii) *Desulphurisation of the Polysulphides.*—Rule and Thomas (J., 1917, **111**, 1063) measured the loss in weight of sodium tetrasulphide when heated in a stream of hydrogen for consecutive ½-hour periods, the temperature being raised by 50° between each period. The results, when plotted as time against composition, indicated that the disulphide is the most stable polysulphide at high temperatures. Their experiment was not designed to demonstrate the possible existence of lower polysulphides, and indeed, could not have done so, for the period of heating at each temperature was quite insufficient for equilibrium to be reached. In the experiments outlined below, rate of loss of sulphur with changing composition has been determined by weighing the sulphur evolved on heating a known quantity of polysulphide at various fixed temperatures in a stream of nitrogen of constant velocity. The results, shown graphically in Fig. 3, indicate the presence of di-, tetra-, and penta-sulphides by well-defined changes in the rate of loss of sulphur. The exceptional stability of the disulphide is here confirmed by the very low gradient.

Experimental. The apparatus (Fig. 4) consisted of an outer vessel, *A*, 28 cm. long and 32 mm. wide, fitted with a lining *B* provided with a gutter at the bottom which served for condensing and collecting the sulphur liberated. The annular space between the tubes was closed at the top by rubber through which the tube *C* delivered nitrogen in order to prevent sulphur vapour passing between the tubes. A little sulphur condensed on the thin glass stirrer (which could not be removed during the runs), but this was inappreciable compared with that deposited on *B*.

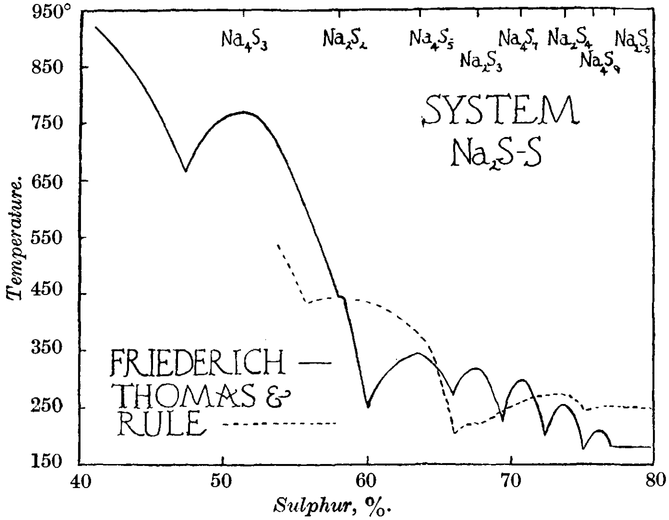
FIG. 4.



10 G. of the polysulphide were weighed into the tube and melted by heating the latter to a depth of 14 cm. in a suitable electric furnace, the temperature of which could be maintained to within 10° of a desired temperature. A weighed condensation tube was then pushed into position, and its upper portion cooled by a blast of

air. After 15 minutes, it was quickly removed, and replaced by a similar weighed tube. The process of weighing and replacing the tubes gave the information required. To observe the changes in rate of sulphur evolution, however, it was essential for the heating to be carefully adjusted. If the temperature was too high, the rapid decomposition prevented observation of the change in rate in materials of higher sulphur content, and if too low, the rate of evolution was impracticably slow. The results, being entirely dependent upon the size and form of the apparatus, are only relative, but a few are given below as specimens (see Fig. 3).

Fig. 5.



At 640°.

Rate of loss of S (mg. per 15 mins.)...	3	7	10	17	22	25	28	52	60	60	60
S, %, in material ...	61·0	64·4	67·0	70·0	71·0	72·0	72·6	73·6	74·2	75·0	76·0

At 440°.

Rate of loss of S (mg. per 15 mins.)	15	15	15	19	58	65	98	100	100	99
S, %, in material ...	76·0	76·5	76·9	77·2	77·6	77·8	78·0	78·4	79·0	80·0

III. *The System Sodium Monosulphide–Sulphur.*

This system has been studied by Friederich (*loc. cit.*) and by Rule and Thomas (J., 1917, **111**, 1063). Their results, shown graphically in Fig. 5, are obviously discordant : the former obtained indications of seven compounds from well-defined maxima on the temperature–composition curve, together with an eighth, Na_2S_5, from a hidden maximum, whilst the latter workers had evidence of di-, tri-, tetra-, and penta-sulphides, but not of compounds of the type Na_4S_x.

Both these researches are open to criticism. Friederich prepared the higher polysulphides by heating sodium carbonate and sulphur in carbon dioxide, but the material so obtained is invariably contaminated with both sulphite and sulphate, even to the extent of 20% (see p. 1484). Furthermore, his lower polysulphides, produced by dehydrating hydrated monosulphide, must also have contained salts of the sulphur oxy-acids. Neither he nor Rule and Thomas brought forward any other evidence in support of their deductions from arrest temperatures. The extreme depression of some of the eutectic points of the latter authors suggests, in the absence of any statement as to cooling rates, that these were far too rapid in view of the type of material involved.

We have obtained definite indication of di-, tetra-, and penta-sulphides and, apart from its trisulphide region, are in general agreement with the diagram of Rule and Thomas; our melting points, however, are higher in every case but one, and by as much as 30°.

Certain difficulties encountered in our reinvestigation call for comment. (1) There was a pronounced tendency to supercooling, particularly at certain compositions; *e.g.*, with pure sodium tetrasulphide, this sometimes reached 87°, even with vigorous stirring. Traces of moisture aggravated this difficulty, and the intensely hygroscopic nature of the material rendered seeding impracticable. The only way to overcome it was to take a cooling curve with the stirrer constantly scraping the bottom of the containing vessel, remelt the contents, allow the temperature to fall slightly below the maximum temperature reached in the previous solidification, and stir and scrape vigorously. By this means results might be repeated to within 5°. At the solidus, supercooling was somewhat reduced by causing the stirrer to vibrate rapidly, and when this failed, recourse was had to heating curves, since Tammann's more exact method (*Z. anorg. Chem.*, 1905, **45**, 24) was inadmissible.

(2) Molten polysulphides are also characterised by very slow rates of crystallisation: a melt of sodium trisulphide composition required 7 days to reach even approximate equilibrium at 50° below the liquidus temperature. The rates of cooling had, therefore, to be kept as low as practicable.

(3) Again, rapid change in melting points with composition between mono- and di-sulphide and above the eutectic Na_2S_2–Na_2S_4 renders it imperative to have precisely known compositions and

accurately determined temperatures. The runs were therefore repeated several times on each melt, and the mean temperatures of commencement and completion of solidification taken as the correct ones.

Experimental. The materials used for these measurements were prepared under hot toluene (see p. 1485); for those of higher sulphur content than the trisulphide, this element was added to the compound, and for those below this composition sodium was added, the mixtures being carefully melted with thorough mixing. Although this method was useful down to disulphide composition, material with less sulphur than this was difficult to melt in the quantities required, owing to the violence of the combination of such quantities of free metal with the polysulphide when the reaction temperature was reached. In such cases, small quantities of sodium were cautiously added to molten disulphide; this procedure proved perfectly satisfactory, and it is of interest that monosulphide prepared by the method of Rule and Thomas was found to have precisely the same melting point. The total weight of material obtained from a known amount of sodium served as a useful check on the triplicate sulphur and sodium analyses made of the substances after solidification. This precaution was particularly useful in those cases where segregation occurred.

Melting, according to the temperature required, was done in test tubes of Pyrex glass (25 cm. by 28 mm., and 2 mm. thick) or of glazed porcelain (20 cm. by 26 mm., and 3 mm. thick) closed by a cork or asbestos stopper which carried a stirrer (3 mm. diameter) and a thin-walled thermocouple sheath of glass or porcelain, together with a tube for the delivery of nitrogen. The quantity of polysulphide used (50 g.) allowed the thermocouple sheath to be immersed to a depth of 5 cm.

The couple used up to 600° was the " chromel-eureka " 30 S.W.G. wire of the Foster Instrument Co., Letchworth, giving one millivolt for about 12·5°. This was frequently standardised during the course of the work, ice and the boiling points of water, naphthalene, and sulphur being the reference temperatures; it proved to be remarkably constant in use. For higher temperatures, the usual platinum–platinum-rhodium junction was used; it was calibrated as above and also at the freezing points of antimony, sodium chloride, and silver. In all experiments the cold junction was surrounded by melting ice. The potential measurements involved were made in a thermocouple potentiometer (" Laboratory Pattern," by the Cambridge Instrument Co.), reading to 1 microvolt, in conjunction with a 500-ohm A. and M. galvanometer which gave a scale deflexion of 11 mm. per 0·01 millivolt. So far as actual temperature measurements were concerned, an accuracy of ± 0·025° and ± 0·20°, respectively, may be claimed for the base and noble-metal couples. Consideration of the concordance between successive remelts, however, indicates that the operation of other factors reduces these accuracies to ± 0·5° and ± 5° respectively. Over certain regions covering a large number of melts the actual curve certainly represents an accuracy of a much higher order than this in the arrest temperature.

To ensure suitable cooling conditions, a heavily lagged, nichrome-wound furnace was made for use over the lower temperature ranges, and for the upper ranges this was placed in a sheet-iron canister which acted as an air-jacket. The cooling rates employed were approximately as follows :

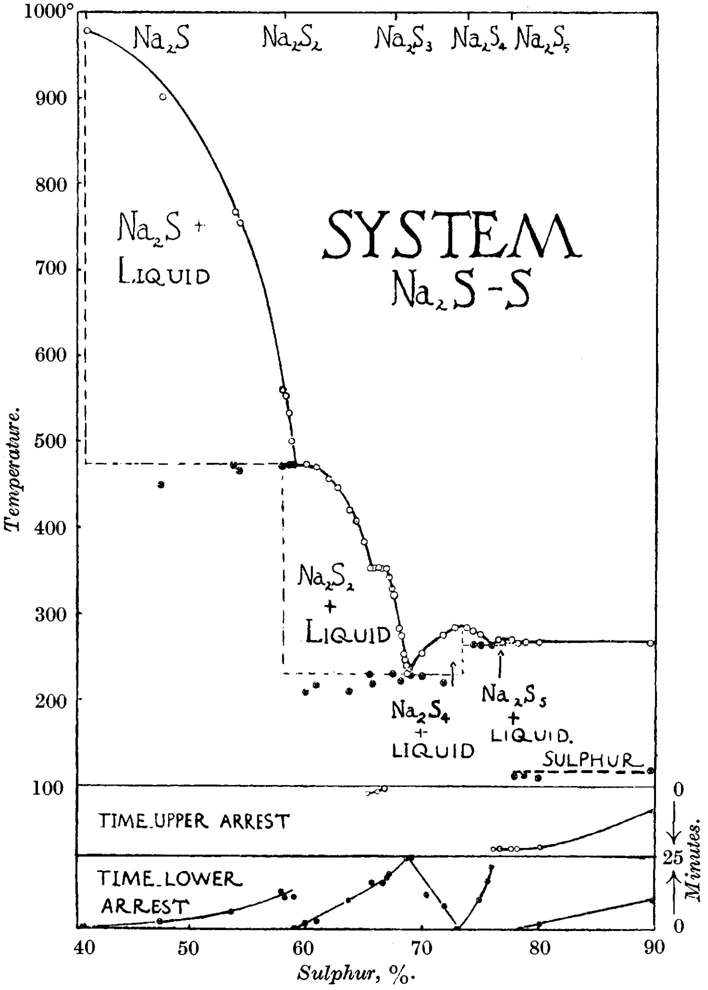
	Seconds per degree at				
	1000°.	800°.	600°.	400°.	200°.
Furnace jacketed	1·5	2	3	5	—
Furnace unjacketed	—	—	17	20	40

At the conclusion of each determination, the tube and its contents were allowed to reach room temperature in the furnace, the tube was broken, and a portion of the sulphide removed and immediately analysed, the remainder being stored in a sealed tube for microscopic examination.

The results are set out in Table V. The periods of arrest given in cols. 4 and 5 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 correction for supercooling cannot satisfactorily be applied. From these data, the temperature–composition diagram of the system sodium monosulphide–sulphur is plotted (Fig. 6).

The diagram begins at the melting point of sodium monosulphide (978°), which appears to be a stable compound under these conditions. From this point the curve descends steeply until disulphide proportions are reached, a break at 473·9° and at a composition slightly beyond that of Na_2S_2 indicating that this compound is dissociated to some extent at its melting point. The almost flat portion between 58·9 and 60·2% supports this view. The break at 66·0% of sulphur, followed immediately by the flat portion to 67·0%, indicates the existence of two immiscible liquids. This is borne out by the steep descent to the eutectic which immediately follows. The liquidus curve thus gives no suggestion of sodium trisulphide. Following the Na_2S_2–Na_2S_4 eutectic (232·1°) at 68·77% of sulphur there is a steady rise to a maximum at tetrasulphide composition (compare Rule and Thomas), followed by the Na_2S_4–Na_2S_5 eutectic (249·2°) at 76·4% of sulphur, and finally by a slight maximum at the pentasulphide composition. This is in agreement with the findings of Rule and Thomas, who suggest that the melting point of this compound is largely depressed by decomposition products. A saturated solid solution of sulphur in

Fig. 6.



pentasulphide appears at 78·5% of sulphur, as may be deduced from the constancy of the melting points (251·2°), from the gradual development of a free sulphur arrest point beyond this composition, and from the intersection of the composition–arrest period curve and the composition axis at this place. This agrees with the results

TABLE V.

S, %.	Upper arrest.	Lower arrest.	Time, upper (mins.).	Time, lower (mins.).	Solid.	Fracture.
41·00	*978°	—	—	0	Na_2S	Chocolate.
47·52	900	†450·0°	—	2		
53·80	766	472·0	—	6		
54·25	755	†465·0	—	8		Light brownish-amber.
58·00	560	473·4	—	13	Na_2S_2	Brownish-amber.
58·25	554	475·5	—	11		
58·51	534	472·0	—	11		
58·75	501	474·8	—	11		
60·18	472·7	†210	10	2		
60·90	470·6	219	—	3		
62·04	457·6	—	5	—		
62·75	445	—	—	—		Red-brown.
63·83	420	210·6	—	10		Dark yellow, with brownish tinge.
64·35	407·5	—	—	—		
64·95	385	—	—	—		
65·51	354	*232·0	—			
65·71	356·4	217·2	2·5	16		
66·18	350	—	—	—		Dark yellow.
66·33	349	222	2	—		
66·55	353	—	—	—		
66·80	353	†215	1	16		
67·17	343	219·6	—	18		
67·60	330	228·8	—	19	Na_2S_3	
67·77	321	226·0	—	17		
68·26	285	219·0	—	—		
68·39	275	223·0	—	—		Dark yellow, with faint green tinge.
68·58	250	213	—	—		
68·59	247	223	—	—		Dark yellow, with olive-green tinge.
68·77	—	232·1	0	25		
68·99	236·1	232·1	—	25		
70·40	254·0	228·1	—	12		Deep olive-green.
71·99	275·0	217	—	8		
73·00	284·8	—	19	0		
73·96	284·8	—	21	0	Na_2S_4	
74·40	283·5	—	18	—		Yellowish-green.
75·10	267·0	249·0	—	10		
75·70	262·8	249·2	—	17		
76·40	—	249·2	—	22		
76·72	252·2	—	22	—		
77·77	254·0	—	22	0	Na_2S_5	Dark yellow.
77·92	252·2	111	22	—		
78·40	251·2	112	22	—		
80·20	251·2	†107	21	2		Light yellowish-green.
89·90	251·2	117	8	10		Grey, with yellow tinge.
94·51	250·0	119	4	20		Grey.
100·00	—	119·2	0	35		Greyish-yellow.

* Temperature obtained from heating curve. † Severe supercooling.

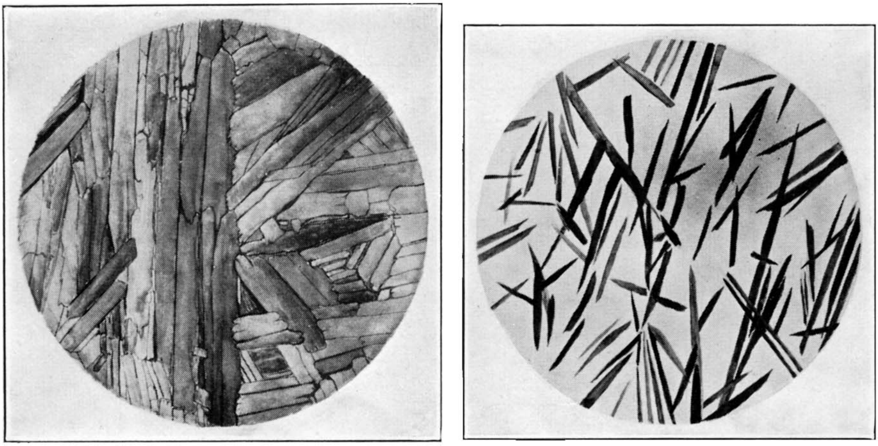
of Rule and Thomas and also with those of Küster and Heberlein (*loc. cit.*) and Jones (*loc. cit.*).

It is significant that we disagree entirely with Rule and Thomas on that portion of the curve where the upper arrest points are particularly difficult to ascertain, *viz.*, between 64 and 69% of sulphur. The step-up in the liquidus line of their diagram between their alleged Na_2S_2–Na_2S_3 eutectic and trisulphide finds ready explanation in the prevalence of eutectic supercooling at these compositions. Indeed, by neglecting suitable precautions, we have been able to repeat very approximately the points recorded by these workers. Only by many repetitions, supplemented by careful heating curves, was it possible to establish the straightness of the eutectic line in this area. Nearer the disulphide it frequently failed to appear, or suffered supercooling by as much as 45°—an extent which makes it highly improbable that the true eutectic temperature could be reached even approximately with so little of that material present. It is noteworthy that Biltz and Wilke-Dörfurt (*Z. anorg. Chem.*, 1906, **48**, 297) experienced so much difficulty in the trisulphide regions of the equilibria, CsS–S and RbS–S, that in the former case no points are given, and in the latter the curve is left discontinuous.

The appearance in certain melts in the region 65—69% sulphur of a small arrest at about 190° may have been due either to a transition or to the formation of another compound, possibly the trisulphide, only stable below about 200°. This phenomenon is being investigated.

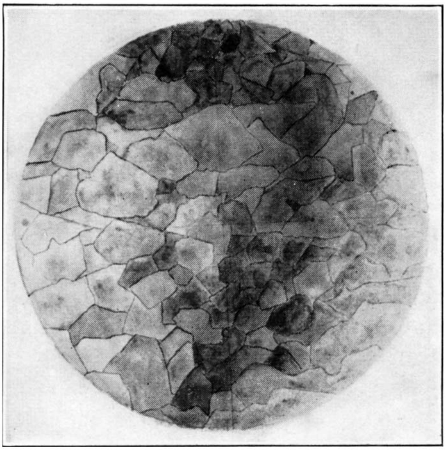
Micro-examination. The ease with which much of the material was oxidised, and also its extremely hygroscopic nature, prevented the preparation of specimens for micro-examination by the usual means. Polishing, although difficult owing to softness and friability, was effected on various grades of emery paper under toluene or medicinal paraffin, but the polish-etch resulting was insufficient to characterise the structures present. Aqueous or ethyl-alcoholic reagents destroyed the surface, but a mixture of equal parts of amyl alcohol and carbon disulphide gave excellent results on certain specimens, notably those between disulphide and the Na_2S_2—Na_2S_4 eutectic and beyond pentasulphide (Plate 1, *b*, *d*, *e*). As, however, the materials were transparent, suitable sections were made by mounting them on glass slides with hot Canada balsam and rubbing them down under paraffin. Considerable patience was required, for only a very small proportion of the attempts were successful, and even these failed to realise single-crystal thicknesses or to transmit sufficient light for sharp photographic reproduction. They were, however, capable of giving a very good idea of the nature of the material, particularly if examined with the aid of oblique in addition to the normal direct illumination. The etched specimens were examined visually with oblique illumination, but here again the colour and the nature of the surfaces made successful

PLATE 1.



(*a*)—*Sodium disulphide.*

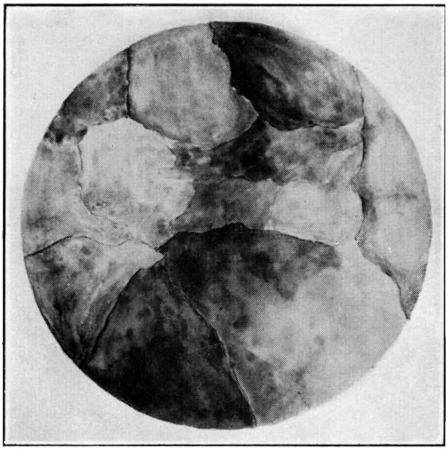
(*b*)—64·12% *Sulphur content.*



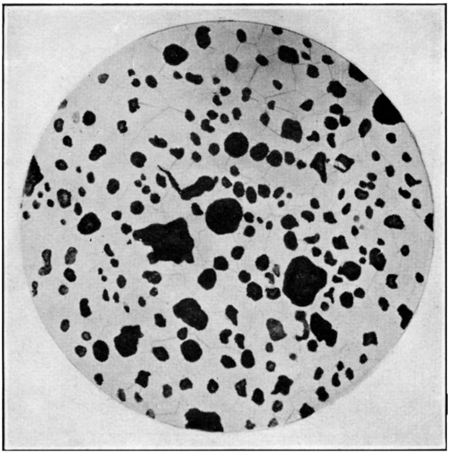
(*c*)—*Sodium tetrasulphide.*

Magnification × 80.

Plate 1 (*contd.*).



(*d*)—78·00% *Sulphur content.*



(*e*)—89·90% *Sulphur content.*

Magnification × 80.

photography particularly difficult. In both cases, permanent records were made from typical regions by a drawing and painting directly from the microscope. These faithful reproductions were photographed and appear as Plate 1 with a magnification of 80.

The monosulphide, m. p. 978° (compare m. p. 970°, Steck, Slavin, and Ralston, *J. Amer. Chem. Soc.*, 1929, **51**, 3241; m. p. 920°, Friederich, *loc. cit.*), is a reddish-chocolate substance, yellowish in section, and possesses the ordinary polygonal grained structure. Melts between mono- and di-sulphide showed no evidence of any eutectic material, and thus disagree with Friederich's diagram.

The disulphide consists of characteristic transparent, light yellow, needle-like crystals frequently twinned, with straight extinction. The dark lines at the crystal boundaries in the section (Plate 1, *a*) are due to emery powder embedded in the softer eutectic material. A similar structure in yellowish-brown appeared in etching with carbon disulphide and amyl alcohol. Materials of 64·12% sulphur content etched or in section showed needle-like crystals in a ground mass (Plate 1, *b*), which could barely be resolved under high magnification on account of the thickness of the sections, but showed evidence of pearlitic intergrowths typical of eutectic material. This structure was present in proportions increasing with the diminution of the acicular constituent in specimens up to the Na_2S_2–Na_2S_4 eutectic. Beyond this, polygonal grains began to appear until at tetrasulphide composition the structure revealed was that associated with a metal or other homogeneous crystalline substance (Plate 1, *c*).

As the pentasulphide region was approached, the material became increasingly brittle until, at the pure pentasulphide, it was so friable that it broke down to a powder of tiny crystals on the slightest mechanical shock. This rendered polishing impossible, but a surface obtained by letting the melt slowly cool in contact with a glass slide showed homogeneous polygonal grains quartered with two dark lines across the centre. One specimen of saturated solid solution containing 78·00% of sulphur was (after thirty attempts) successfully polished and etched (Plate 1, *d*), and showed the cored structure typical of such a constituent. A section (Plate 1, *e*) from more tractable material further along the diagram shows the same solid solution in the form of spherical masses embedded in a matrix of polygonal grains of sulphur.

Without exception, these results accord well with our reinvestigation of the thermal analysis, and provide further evidence invalidating previous conclusions respecting a trisulphide and polysulphides of the tetrasodium type.

Summary.

A critical reinvestigation of the formation and properties of sodium polysulphides, amplified by original work, has yielded the following results.

(1) The action of sulphur on aqueous-alcoholic solutions of sodium monosulphides gives polysulphide solutions from which may be crystallised: $Na_2S_2,6H_2O$; $Na_2S_3,8H_2O$; $Na_2S_4,8H_2O$; $Na_2S_4,9H_2O$; $Na_2S_4,11H_2O$; $Na_2S_5,6H_2O$; and a tetrasulphide which may be either $Na_2S_4,7H_2O$ or a mixture of $Na_2S_4,6H_2O$ and $Na_2S_4,8H_2O$. Dehydration of the first two affords $Na_2S_2,2H_2O$ and Na_2S_3,H_2O respectively.

(2) The action of sulphur on anhydrous alcoholic solutions of sodium monosulphide, although unsuited for the preparation of pure compounds, gives anhydrous di-, tri-, tetra-, and penta-sulphide.

(3) By dissolution of various proportions of sulphur in alcoholic solutions of sodium hydrosulphide, only one pure compound, Na_2S_4, is obtained: $2NaHS + 3S \longrightarrow Na_2S_4 + H_2S$. With less sulphur the products are mixtures of tetrasulphide and unchanged hydrosulphide, with pentasulphide proportions a mixture of tetrasulphide and sulphur, and with still more sulphur possibly a higher polysulphide.

(4) The action of metallic sodium on alcoholic solutions of sodium tetrasulphide gives only the disulphide.

(5) Sulphur reacts with sodium carbonate or hydroxide at low temperatures or in solution to produce polysulphides and thiosulphate, and at higher temperatures to give polysulphides, sulphate, and a little sulphite.

(6) Sulphur reacts with molten sodium under toluene to produce only the trisulphide.

(7) By desulphurising the polysulphides of sodium in an atmosphere of nitrogen at carefully regulated temperatures, changes in decomposition velocity indicate the existence of penta-, tetra-, and di-sulphides.

(8) A phase-rule study of the system Na_2S–S indicates that monosulphide is stable at its melting point, 978°; disulphide slightly decomposes, as indicated by a hidden maximum at 473·9°; tetrasulphide is stable at its melting point, 284·8°; a saturated solid solution of sulphur in the pentasulphide occurs with material containing 78·5% sulphur; and finally, that tetrasodium compounds are not formed.

The peculiar stability of the tetrasulphide and the marked instability of the trisulphide have been re-affirmed.

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UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.

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