LXV.—*Hydrosulphides, Sulphides, and Polysulphides of Potassium and Sodium.**

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IN a paper entitled "The Sulphides and Polysulphides of Ammonium" (Trans., 1895, **67**, 277), the author has given a statement of the results of his work in this field. The study of these compounds was continued after publication of this paper, but, owing to experimental difficulties, it was subsequently decided to abandon the further investi-

* An abstract of a paper communicated to the Chemical Society on June 1, 1899.

gation of ammonium polysulphides, and to attempt the preparation of those of potassium and sodium.

The method adopted for the preparation of ammonium polysulphides (*loc. cit.*, p. 300, *et seq.*) was applied to polysulphides of potassium and sodium, as it avoided the previous preparation of the monosulphides, K_2S or Na_2S. It was found, however, that passage of hydrogen sulphide through a solution of caustic potash or soda in contact with excess of finely powdered sulphur yielded a solution containing both polysulphide and thiosulphate. Moreover, at no observed degree of concentration or of temperature could the formation of thiosulphate be avoided. It was found that, excluding the current of hydrogen sulphide, when finely divided sulphur was digested with solutions of caustic potash and soda respectively, the products were in each case polysulphide and thiosulphate. The difference in the behaviour of sulphur on heating with solutions of caustic potash or soda, on the one hand, and ammonia on the other, seems to demonstrate that the concentrated solution of ammonia (*a*) at the ordinary pressure and at temperatures up to its boiling point, reacts with regard to sulphur as one of NH_3,Aq, whilst (*b*) under pressure it reacts as one of $NH_4 \cdot OH$, and yields polysulphide and thiosulphate.

Solutions of the normal sulphides of potassium and sodium were therefore prepared. Quantitative and qualitative experiments proved the solutions to be free from excess of hydrogen sulphide, hydrosulphide, or hydroxide. Solutions of each sulphide were warmed with excess of finely powdered sulphur, and deep red polysulphide solutions were obtained. In both cases, however, an evolution of hydrogen sulphide was observed, and as this could not result from the action of sulphur on the monosulphides, K_2S or Na_2S, a qualitative analysis (compare *Chem. News*, 1895, **72**, 63) was made, and both solutions proved to contain polysulphide and thiosulphate. It follows, therefore, that free caustic alkali is present in aqueous solutions of the monosulphides of potassium and sodium. Neither the analytical results nor the use of cupric sulphate solution (Trans., 1895, **67**, 289) gives any indication of the presence of free alkali or of hydrosulphide.

The normal sulphides having failed as sources of polysulphides, attention was now paid to the hydrosulphides. A solution of potassium hydrosulphide was prepared, and it was found that, on digestion with sulphur, hydrogen sulphide was evolved, and a red polysulphide solution obtained entirely free from oxidised sulphur. It is not a matter of indifference, therefore, as has been assumed by all previous workers on this subject, whether the normal sulphide or the hydrosulphide is employed in the preparation of polysulphides. Only when the hydrosulphide is employed is the product free from oxidised sulphur.

The complete paper contains a list of previous authors and the titles

of their papers, the list being arranged in chronological sequence.   The following is a brief general criticism of this earlier work :

(a) *Cases where solution of the theoretical amount of sulphur was effected in aqueous solutions of the monosulphides,* K_2S *or* Na_2S :

(i) The authors could in no case have obtained the definite polysulphide desired, for the sulphur added was too small in quantity, no allowance being made for the undetected, but simultaneous, formation of thiosulphate.

(ii) From the mixture of polysulphide and thiosulphate so obtained, they could not have separated pure polysulphide ; for although separately the thiosulphates of potassium and sodium may be described as insoluble in alcohol (Comey, " Dictionary of Chemical Solubilities," Inorganic, 475, 476), this is far from being the case when they are mixed with polysulphide.   The author has been unable to find any solvent capable of effecting the separation of thiosulphate from polysulphide.

(iii) It is significant that in no single case does an author give details of the yield of polysulphide obtained.   If crystalline products were obtained, they must have been mixtures of polysulphides with thiosulphate, from which separation of one component in the pure state is not at present possible.   Previous observers, however, do not make mention of any difficulty in obtaining crystals, or of obtaining crystals of doubtful purity.   An added element of doubt is the absence of description of the properties of the polysulphides.

(b) *Cases where dry methods of preparation were adopted.* The dry methods employed were still less favourable to success.   The final product must always have been a mixture, and invariably have contained oxidised sulphur, in some cases also carbonate, from which separation of the polysulphide is not at present possible.

The critical consideration of the work of authors who claim to have obtained the whole range of polysulphides, and the repetition in many instances of their experiments with negative results, justified the conclusion that up to the date of commencing the present work no single polysulphide of potassium or sodium had been obtained in the pure state. It was clear also that before any attempt could reasonably be made to prepare pure polysulphides, it was absolutely necessary to obtain the various sulphides and hydrosulphides of potassium and sodium, and to investigate their properties both in the solid state and in aqueous solution.

Sulphides and Hydrosulphides of Potassium.

Preparation of Potassium Monosulphide.

A concentrated aqueous solution of caustic potash was divided into two equal portions, one of which was saturated completely with hydrogen sulphide, and the second portion added to it.   On concentration in a vacuum over calcium chloride, small, white, glass-like, tabular crystals were deposited.   These did not correspond in appearance with the description of the crystals of $K_2S,5H_2O$ given by Schöne (*Pogg. Ann.*, 1867, **131**, 380), and on analysis yielded the following results :

$K = 23\cdot34$; $S = 9\cdot85$; H_2O (diff.) $= 66\cdot81$.
$K_2S,12H_2O$ requires $K = 23\cdot92$; $S = 9\cdot82$; $H_2O = 66\cdot26$ per cent.

This hydrate, however, has not been obtained again during the series of experiments.   The mother liquor yielded, on further concentration, a large crop of crystals of a different form which, drained free from the red mother liquor, were colourless, brilliant, four-sided, flat rhombs, and very deliquescent in air.   On analysis, the following results were obtained :

$K = 38\cdot42$; $S = 15\cdot96$; $H_2O = 45\cdot62$.
$K_2S,5H_2O$ requires $K = 39\cdot00$; $S = 16\cdot00$; $H_2O = 45\cdot00$ per cent.

Production of Dihydrated Potassium Monosulphide, $K_2S,2H_2O$.

The clear, glass-like crystals of $K_2S,5H_2O$, when exposed in a vacuum over sulphuric acid, rapidly effloresced, and when powdered repeatedly and exposed over the acid in a vacuum, eventually yielded a product giving concordant analytical results :

$K = 53\cdot20$; $S = 21\cdot52$; H_2O (diff.) $= 25\cdot28$.
$K_2S,2H_2O$ requires $K = 53\cdot42$; $S = 21\cdot91$; $H_2O = 24\cdot67$ per cent.

In appearance, dihydrated potassium monosulphide closely resembles granulated calcium chloride.

Stability of Potassium Monosulphide towards Heat.

Crystals of pentahydrated potassium monosulphide, $K_2S,5H_2O$, were placed in a small fractional distillation flask and subjected to the action of heat.   The salt melted at about 60°, and heating was continued until tranquil fusion was attained.   The final temperature reached was beyond the range of the nitrogen mercury thermometer employed (560°).   Only a trace of hydrogen sulphide was evolved

throughout the process.   On cooling, the fused mass was red and deliquesced freely.   It proved to be free from both polysulphide and oxidised sulphur ; it also reacted with cupric sulphate solution as the monosulphide.   Potassium monosulphide, therefore, is stable at a low red heat.

This degree of resistance to decomposition on heating, together with the observed action that sulphur, when gently warmed with the crystals, forms polysulphide and thiosulphate, suggested that the crystals might be tetrahydrated potassium hydroxyhydrosulphide, $KHS,KOH,4H_2O$.*   Such a compound would reasonably be expected to be stable at a high temperature, and its observed behaviour with sulphur would also be intelligible.   Distinction between the compounds $K_2S,5H_2O$ and $KSH,KOH,4H_2O$ could not be effected by the use of reagents, but could be drawn by determining the quantity of water expelled from the salt on heating.

The crystals heated in a current of dried hydrogen lost 45·10 per cent. of water, as against 45·0 per cent. required for $K_2S,5H_2O$.   They consisted, therefore, of pentahydrated potassium monosulphide.

Attempts to Prepare Potassium Hydrosulphide in the Dry Way.

Unsuccessful attempts have been made by Baur (*J. pr. Chem.*, 1858, 75, 246) and Sabatier (*Ann. Chim. Phys.*, 1881, [v], 22, 1) by the action of dry hydrogen sulphide on heated potassium carbonate.   The present author failed to obtain it by passing hydrogen sulphide through molten potassium carbonate.   The product had the composition $4KHS,K_2S$, and, notwithstanding the prolonged passage of the gas through the molten material, 3·8 per cent. of potassium carbonate was still left undecomposed.   Attempts to prepare potassium hydrosulphide, KHS, by the action of hydrogen sulphide on fused potassium hydroxide do not seem to have been made previously.   Retorts of special Jena glass were obtained, provided with a tube ground in at a right angle to serve as inlet for the gas, and proved sufficiently resistant to the action of alkali.   As a result, admixtures of sulphide and hydrosulphide were obtained—for example, K_2S,KHS and $3K_2S,KHS$, but the author failed to obtain potassium hydrosulphide.   The preparation of anhydrous potassium hydrosulphide therefore does not seem to be practicable in the dry way.

Preparation of Hemihydrated Potassium Hydrosulphide.

Two hundred grams of caustic potash were covered with 100 grams of water, and the temperature raised to 90°.   Saturation with hydrogen sulphide was effected at this temperature, the gas being rapidly

* Compare $Ca(SH)OH$, described by Divers and Shimidzu (Trans., 1884, 45, 270).

absorbed and the hydroxide passed completely into solution. On cooling, a few cubic centimetres of a strong solution of potassium hydroxide were added to the solution placed in a wide-mouth stoppered bottle, the stopper replaced, and the bottle and its contents shaken. In this way, any free hydrogen sulphide was removed. Precipitation of iron sulphide, &c., was observed, and, on filtration through a cotton-wool plug, a perfectly bright, brownish-yellow solution was obtained. On concentration in a vacuum over sulphuric acid, a crop of fine, dust-like crystals separated, which resembled those of ammonium chloride rapidly deposited from a concentrated solution. The salt is very deliquescent, rendering it most difficult to isolate a satisfactory product for analysis. The following results were obtained on analysis:

$K = 49 \cdot 78$; $S = 39 \cdot 29$; $H_2O + H$ (diff.) $= 10 \cdot 93$.
$KHS, \frac{1}{2}H_2O$ requires $K = 48 \cdot 15$; $S = 39 \cdot 51$; $H_2O + H = 12 \cdot 34$ per cent.

Preparation of Anhydrous Potassium Hydrosulphide.

The method of preparation here employed was suggested to me by Dr. Scott, who had prepared anhydrous sodium hydrosulphide in a similar fashion. In outline, it consists in passing hydrogen sulphide through rectified ether,* in which is placed metallic potassium. Hydrogen is rapidly evolved from the surface of the metal, which remains quite bright throughout the operation, and potassium hydrosulphide separates as a snow-white powder. The product is washed with rectified ether, and on drying in a vacuum over sulphuric acid, is obtained as a very slightly yellow, dust-like, crystalline powder, deliquescing with extreme rapidity on exposure to air. As the result of several analyses:

K (mean value) $= 53 \cdot 49$. KHS requires $K = 54 \cdot 17$ per cent.

This method of preparation of potassium hydrosulphide is much more rapid and convenient than that employed by Sabatier (loc. cit)., who dehydrated the crystalline hydrosulphide by heating the crystals in a current of dry hydrogen sulphide.

Stability of Potassium Hydrosulphide towards Heat.

The method employed was similar to that used in the case of potassium monosulphide (p. 756), with the exceptions that the fractional distillation flask was heated in a bath of melted solder, and that the bulb of the nitrogen mercury thermometer was placed in a protective tube of Jena glass immersed in the melted solder. At

* If ether containing alcohol be employed, the product will be contaminated with oxidation products of potassium ethoxide.

450°, fusion was observed at the edges of the crystals, and at 510° was complete and tranquil. Heating was continued to the upper limit of the thermometer, 560°, but no evolution of gas was observed. Thus the change expressed by the equation $2KHS = K_2S + H_2S$ is not effected at temperatures below 560°. Potassium hydrosulphide is therefore stable on exposure to heat, and, in this respect, will bear comparison with its oxygen analogue KOH. The melting point of the hydrosulphide was next determined, employing a nitrogen mercury thermometer, previously standardised in the vapour of boiling sulphur, and as a mean of three determinations was found to be 455°.

Stability of $K_2S,5H_2O$ and $KHS,\frac{1}{2}H_2O$ on Exposure to Air.

Previous observers unite in regarding these salts as unstable, and therefore to be preserved from contact with the air. In the progress of the present work, the following facts were established. Both salts are, it is true, exceedingly deliquescent, but if exposed to air, free from carbon dioxide, they do not evolve hydrogen sulphide. Carbon dioxide acts rapidly on the salts or their aqueous solutions, with evolution of hydrogen sulphide and formation of the corresponding carbonates. Experiments were also made to determine whether these salts were affected by moist oxygen free from carbon dioxide. As a result, very slight absorption of oxygen was observed with each. In both cases, the salts remained quite white, no polysulphide being formed.

In the case of the pentahydrate, $K_2S,5H_2O$, the main product of oxidation was sulphite; no thiosulphate could be detected, and a trace only of sulphate. In the case of the hemihydrate, $KHS,\frac{1}{2}H_2O$, however, the main product of oxidation was found to be thiosulphate; no sulphate could be detected, and a trace only of sulphite. Similar results were obtained by slowly passing a stream of oxygen, free from carbon dioxide, through aqueous solutions of each salt. These results are in opposition to the current statements that, on exposure of these salts, or their solutions, to air, polysulphides are formed and hydrogen sulphide is evolved : statements which are true only if the air contains carbon dioxide.

Change effected on boiling Aqueous Solutions of Potassium Sulphide and Hydrosulphide.

Several conflicting statements are to be found on this subject. Of earlier observers, Gay Lussac and Berzelius (*Ann. Chim. Phys.*, 1821, 20, 34) believe that solutions of potassium hydrosulphide do not decompose on boiling. Berzelius, in fact, recommends boiling, to free the solution of hydrosulphide from excess of hydrogen sulphide, and according to him, solution of potassium hydrosulphide can be evapor-

ated without decomposition. Thenard, on the other hand, asserts (*Ann. de Chimie*, 1812, **83**, 133) that the hydrosulphide decomposes on boiling. Schöne states (*loc. cit.*) that after boiling a solution of potassium hydrosulphide for $1\frac{1}{2}$ hours, it is for the most part decomposed into monosulphide, and regards it as possible that in this way, not only is monosulphide formed, but that the decomposition goes further. Solutions of the so-called monosulphide lose hydrogen sulphide continually on boiling, although only very slowly and with difficulty, so that, according to Schöne, the conclusion may be drawn that on continuing the boiling long enough, all hydrosulphide, monosulphide, or hydroxyhydrosulphide would be transformed into hydroxide.

To test these various and conflicting statements, aqueous solutions of the sulphide and hydrosulphide, of 20 per cent. concentration, were boiled, in the first instance, in air, but later, in a current of hydrogen, to eliminate the influence of the action of the air. Twenty per cent. solutions were employed in order that the results might be compared with those previously obtained by Walker (*Proc. Roy. Soc. Edin.*, 1894, **20**, 255).

On boiling a 20 per cent. solution of the pentahydrate, $K_2S,5H_2O$, for $2\frac{1}{2}$ hours in contact with air, the evolution of hydrogen sulphide was negligible, and the solution contained only traces of polysulphide and sulphite and very little more thiosulphate. A similar solution, boiled for $1\frac{1}{2}$ hours, while hydrogen was led through it, evolved only a trace of hydrogen sulphide. Thus Schöne's statement is incorrect, and the stability, on boiling, of a 20 per cent. aqueous solution of this hydrate is established.

In similar fashion, a 20 per cent. solution of $KHS,\frac{1}{2}H_2O$ was boiled. The solution contained 18·1236 grams of crystals dissolved in 72·49 grams of water, and was boiled vigorously for $1\frac{1}{2}$ hours in a current of hydrogen, the escaping gas being led through copper sulphate solution. The amount of sulphuric acid liberated was 0·231 gram, equivalent to 0·080 gram of hydrogen sulphide, and corresponds to a destruction of 0·191 gram of $KHS,\frac{1}{2}H_2O$, or of 1·05 per cent. of the total salt present. The result of this experiment is opposed to the experience of Schöne, who found that a solution of potassium hydrosulphide (of which the concentration is not stated), after boiling for $1\frac{1}{2}$ hours, is for the most part decomposed into monosulphide.

It follows, then, that although a solution of potassium hydrosulphide is not so stable on boiling as one of potassium sulphide of the same concentration, the rate of change on boiling is very slow, and that neither of the equations

$$2KHS = K_2S + H_2S ; \ 2KHS + 2H_2O = 2KOH + 2H_2S$$

put forward as expressing its mode of decomposition under these conditions can be accepted.

SULPHIDES AND HYDROSULPHIDES OF SODIUM.

A considerable amount of work has been published on these compounds by Berthier (*Ann. Chim. Phys.*, 1822, **22**, 225), Kircher (*Annalen*, 1839, **31**, 339), Finger (*Pogg. Ann.*, 1866, **128**, 635). Sabatier (*loc. cit.*) and others, but from the present summary a criticism of the results obtained by these authors is excluded for the sake of brevity.

Preparation of Sodium Monosulphide, $Na_2S,9H_2O$.

This preparation was effected, on the lines recommended by Finger and by Sabatier, by saturating a concentrated solution of caustic soda with hydrogen sulphide. One hundred grams of caustic soda (prepared from sodium) were dissolved in 100 grams of water. On passing hydrogen sulphide into the solution, needle-like crystals were deposited in considerable quantity (compare Finger and Sabatier). These could not be hydrosulphide, as the quantity of gas which had passed into the solution was altogether insufficient. Further, if the crystals were those of hydrosulphide, it would be necessary to assume :—(*a*) that it is the first product of the reaction, (*b*) that it is practically insoluble in solution of caustic soda. The crystals might be those of hydrated sodium monosulphide (compare Finger and Sabatier) or might have the composition $Na_2S,xNaOH$. On continuing the current of gas, the crystals dissolved before saturation was complete ; thus it seems probable that they are of the latter type, and it is noteworthy that subsequently (p. 764) crystalline substances of this character were isolated. The flask and its contents were left undisturbed for three days, when large, colourless, octahedral crystals were deposited. Some of these were examined and found to consist of the enneahydrate $Na_2S,9H_2O$ (compare Finger and Sabatier). Solution of the main portion of the crystals was now attempted by addition of hot water and application of heat. Two kinds of crystals were observed to be present during the progress of solution (compare Finger and Sabatier). Through the hot liquid still containing crystals, hydrogen sulphide was passed, until solution was complete and the gas ceased to be absorbed. To the solution, which was now presumably one of sodium hydrosulphide, was added 100 grams of powdered caustic soda, which dissolved with considerable evolution of heat, and when cold the whole was concentrated over sulphuric acid under 15 mm. pressure. Crystallisation, from a supersaturated solution, occurred during the night, particles being projected on to the glass bell jar. Solution was again effected by addition of small quantities of

hot water. On further concentration over sulphuric acid under 15 mm. pressure, no crystals were obtained during 24 hours. Air was therefore admitted to the receiver and some of the solution withdrawn in a pipette. On transference to a test tube, crystallisation took place and some of the crystals were used as nuclei for the main solution. Rapid crystallisation followed, in radiate masses of prismatic forms, altogether unlike the octahedra previously obtained. Analysis of these crystals gave the following results:

$Na = 18\cdot89$; $S = 12\cdot99$; H_2O (diff.) $= 68\cdot12$.
$Na_2S,9H_2O$ requires $Na = 19\cdot16$; $S = 13\cdot33$; $H_2O = 67\cdot51$ per cent.

The crystals were accepted as another form of the enneahydrate, and on keeping them under the mother liquor they changed into the ordinary form of octahedra. Finger and Sabatier obtained crystals, under similar experimental conditions, undergoing transformation into the stable octahedra. To these, the following formulæ were given : $Na_2S,5H_2O$ (Sabatier), and $Na_2S,6H_2O$ (Finger). It is possible that a series of unstable lower hydrates of sodium monosulphide may exist, all passing into the stable octahedral form by further hydration. The author has not obtained either of these hydrates, and, but for the analytical data, given by Sabatier and Finger, would be of opinion that the unstable salt had, in all cases, the composition $Na_2S,9H_2O$.

Stability of $Na_2S,9H_2O$ and its Aqueous Solutions.

The author finds himself in agreement with Walker (*loc. cit.*), who states that the crystals of $Na_2S,9H_2O$ do not evolve hydrogen sulphide in air free from acid, and that, at the ordinary temperature, a solution of sodium monosulphide does not smell of this gas. The account of Walker's experiments with a 20 per cent. solution of this hydrate, boiled in a current of hydrogen, is not accompanied by figures to show the loss of hydrogen sulphide.

The following are the figures obtained by the author. $17\cdot459$ grams of $Na_2S,9H_2O$ were dissolved in $69\cdot84$ grams of water. In the cold, a current of hydrogen did not carry off hydrogen sulphide from the solution, and on boiling for 25 minutes only a trace of copper sulphide was deposited. The acid so liberated from copper sulphate solution amounted to $0\cdot0318$ gram $H_2SO_4 = 0\cdot011$ gram H_2S, indicating that $0\cdot435$ per cent. of $Na_2S,9H_2O$ had been decomposed. The salt is then slightly less stable than one of $K_2S,5H_2O$, under the same conditions (p. 756).

From the observed rate of decomposition of a 20 per cent. solution of $Na_2S,9H_2O$, it would be necessary to boil it for an infinitely long

period in a current of hydrogen to completely decompose it in the sense : $Na_2S + 2H_2O = 2NaOH + H_2S$.

Attempts to prepare Sodium Hydrosulphide.

Sabatier (*loc. cit.*) claimed to have prepared the hydrosulphide NaHS by acting on crystals of $Na_2S,9H_2O$ with hydrogen sulphide, but the author, following his process, has failed to obtain it. The crystals of $Na_2S,9H_2O$ do not absorb hydrogen sulphide at all rapidly, even when finely powdered and agitated with the gas, and progressive dilution with small quantities of water does not ensure its absorption. The behaviour of the crystals is comparable with that of the compound $(NH_4)_2S,2NH_4HS$ in similar circumstances (Trans., 1895, **67**, 284).

When about four volumes of solution were present for one volume of the original crystals of $Na_2S,9H_2O$ the gas current was maintained for 4 hours and an examination made of the product obtained. On concentration over sulphuric acid in a vacuum, plate-like crystals were deposited, which resembled in general appearance the crystals of $(NH_4)_2S,2NH_4HS$, previously referred to. On analysis, the following results were obtained :

$Na = 26·20$; $S = 19·17$.   NaHS ($Na = 26·20$ per cent.) requires $S = 36·41$. Na_2S ($Na = 26·20$ per cent.) requires $S = 18·23$.

The salt has approximately the composition Na_2S, but, by its action on cupric sulphate solution, is found to contain some hydrosulphide, $2·32$ per cent. of the total sulphur being present in this form. The proportions correspond to those required for a compound $7Na_2S,NaHS,40H_2O$, which requires $Na = 26·09$; $S = 19·36$; $H = 0·07$; $H_2O = 54·48$ per cent. The failure of crystals of $Na_2S,9H_2O$ to take up hydrogen sulphide to form 2NaHS, and the similar failure, even in the case of aqueous solutions of sodium monosulphide, Na_2S, taken together with the formation of intermediate products observed during saturation of aqueous solutions of caustic soda with hydrogen sulphide, bear a considerable resemblance to the phenomena observed when ammonia solution is saturated with hydrogen sulphide. This observation is the more remarkable, for nothing of the kind was noticed during the saturation of solutions of caustic potash with the gas.

As the system $Na_2S,9H_2O$, in the solid state, and at the temperature of the air, is proof against attack by hydrogen sulphide, and as only a very small proportion of NaHS was formed at the ordinary temperature on increasing the amount of water very considerably, experiments were now made to test the effect of increase of temperature on the absorption of the gas. The crystals of $Na_2S,9H_2O$ commenced to melt when heated to 53° and were completely fused at 80°. The substance so melted was kept at 85° and saturated with hydrogen sulphide. The

relation Na/S, determined in the solution, was found to be that required by NaHS, the figures showing only a slight deficiency of 0·19 per cent. of sulphur.

Action of Hydrogen Sulphide on a Solution of approximately the Composition $2NaOH,7H_2O$, kept at $0°$.

The strength of the solution of caustic soda was suggested by the consideration that a solution of the concentration $Na_2S,9H_2O$, maintained at 85°, takes up hydrogen sulphide in accordance with the equation $Na_2S,9H_2O + H_2O = 2NaHS + 9H_2O$.   Proceeding from a solution of caustic soda to one of sodium hydrosulphide, we have the following relation :

$$2NaOH + 7H_2O + 2H_2S = 2NaHS + 9H_2O.$$

A solution of the composition $2NaOH + 7H_2O$ would contain 38·83 per cent. of caustic soda ; that employed contained 36·91 per cent. From the first, on passing the gas, plate-like crystals were deposited, and their formation continued until a semi-solid mass was obtained. The current of gas was continued until saturation was effected, but the crystals did not dissolve. After separation from the mother liquor, they dissolved readily in water, did not smell of H_2S, and, on testing with solution of cupric sulphate gave a filtrate which was free from acid, whilst the precipitate contained cupric hydrate, $Cu(OH)_2$. The crystals therefore contain free NaOH, and must be of the type $NaOH,NaHS,xNaOH$ or $Na_2S,xNaOH$. The main portion of crystals was dissolved in water, and the solution, on analysis, gave numbers which showed :

(i) That there was not sufficient sulphur present for the formation of sodium monosulphide, Na_2S.

(ii) That of the total sodium, 79·60 per cent. was present as sodium monosulphide, and 20·40 per cent. as caustic soda.

From these figures are obtained the empirical numbers 1·730/0·887, or, in whole numbers, 2/1.   The constitution of the crystals is then $(Na_2S)_{2x}(NaOH)_x$, of which the simplest expression is $2Na_2S,NaOH$.

As the result of the foregoing experiments, it follows that, if sodium hydrosulphide could be obtained at all by direct saturation of solutions of caustic soda with hydrogen sulphide, the solution must be dilute and saturation effected in a hot solution.

Preparation of Sodium Hydrosulphide by Saturation of Solution of Sodium Hydroxide containing 27·82 per cent. of NaOH with Hydrogen Sulphide at 100°.

This strength of solution was selected as being within the limits of $2NaOH,9H_2O$, which would contain 33·04 per cent. of NaOH, The

gas was rapidly and completely absorbed, and no deposition of crystals was observed. Analysis of the saturated product showed it to be one of sodium hydrosulphide.

$Na = 12\cdot91$; $S = 17\cdot84$ per cent.
    NaHS requires $S = 17\cdot94$ for $Na = 12\cdot91$ per cent.

From this solution, on concentration in a vacuum over sulphuric acid, brilliant, prismatic crystals were obtained, which, on analysis, gave the following results :

$Na = 24\cdot88$; $S = 34\cdot01$; $H = 1\cdot07$; $H_2O = 40\cdot04$.
$NaHS,2H_2O$ requires $Na = 25\cdot00$; $S = 34\cdot78$; $H = 1\cdot09$; $H_2O = 39\cdot13$
                    per cent.

Dihydrated sodium hydrosulphide is stated to have been obtained previously by Sabatier (*loc. cit.*). On keeping the prismatic crystals under their mother liquor, they are transformed into large, colourless, lustrous rhombs. The results of analysis showed that the crystals were those of a trihydrate.

$Na = 20\cdot59$; $S = 29\cdot15$; $H = 0\cdot89$; $H_2O = 49\cdot37$.
$NaHS,3H_2O$ requires $Na = 20\cdot90$; $S = 29\cdot09$; $H = 0\cdot92$; $H_2O = 49\cdot09$
                    per cent.

Of the two crystalline hydrosulphides, the trihydrated salt is to be regarded as the more stable form.

Experiments were made on the stability of crystals of $NaHS,3H_2O$ with regard to heat and on the stability of aqueous solutions of sodium hydrosulphide, with results which may be briefly described. Trihydrated sodium hydrosulphide melts at $22°$, and when heated at $360°$ loses $20\cdot53$ per cent. of its sulphur. Experiments were made with 20 per cent. aqueous solutions in the manner described for potassium hydrosulphide (p. 760), and it was found that the sodium compound is the less stable, although it is not true, as has been repeatedly stated, that a solution of sodium hydrosulphide, on boiling, becomes converted into one of the monosulphide, Na_2S.

CONSTITUTION OF AQUEOUS SOLUTIONS OF THE SULPHIDES AND HYDROSULPHIDES OF POTASSIUM AND SODIUM.

It has been already stated (p. 754) that, as a source of polysulphides it is not a matter of indifference whether a solution of normal sulphide or of a hydrosulphide be used as a solvent for sulphur. Sulphur by its action reveals a vital distinction existing between the two solutions, as in the first case polysulphide and thiosulphate are formed, in the second case polysulphide only. This fact had not been recognised by any previous workers on polysulphides, and in consequence their procedure

was faulty (p. 755). It is sufficient to say that the action of sulphur on aqueous solutions of sulphides and hydrosulphides of potassium and sodium is due to the fact that, whilst the normal sulphide becomes, as a result of hydrolysis, a mixed solution of hydrosulphide and hydroxide, the hydrosulphide exists in solution unaltered (Walker, *loc. cit.*). From these considerations, it follows that, as sources of polysulphides, aqueous solutions of normal sulphides of potassium or sodium are altogether unsuitable, and that the only source of polysulphide available at present is the solid hydrosulphide or its solution.

Attempted Preparation of Polysulphides of Sodium.

Attempts were made to obtain the various disodium polysulphides reputed to exist, namely, Na_2S_2 ; Na_2S_3 ; Na_2S_4 ; Na_2S_5. In no case, however, was any product obtained corresponding to these salts, when the calculated amounts of sulphur were dissolved in solutions of sodium hydrosulphide, under the influence of heat and during the passage of a current of hydrogen sulphide. In one case only was a positive result obtained and under the following experimental conditions,* the object being to prepare disodium pentasulphide.

One hundred grams of a solution of sodium hydrosulphide (containing 20·6 per cent. of sulphur) were treated with 41·2 grams of sulphur, being the theoretical amount necessary for the reaction : $2NaHS + S_4 = Na_2S_5 + H_2S$. On heating, nearly all the sulphur was dissolved, but on cooling a large quantity separated. This was removed by filtration from the viscous liquid, which, on standing, did not yield crystals. On analysis of the solution, the following results were obtained, indicating that it is one of tetrasodium enneasulphide, Na_4S_9.

$Na = 11·82$; S (total) $= 36·48$; S (polysulphide) $= 27·65$ per cent.

Taking the total sulphur found, 36·48 per cent. as the basis of calculation,

Na_4S_9 requires $Na = 11·65$; S (polysulphide) $= 28·35$ per cent.

The solution, when cooled to $-22°$ by immersion of the flask in a freezing mixture, gave no crystals. It was therefore further concentrated by heating in a current of hydrogen sulphide, and on cooling, crystals were obtained which, on analysis, yielded the following results :

$Na = 14·64$; S (total) $= 45·18$; S (polysulphide) $= 34·71$; $H_2O = 40·18$ per cent.

$Na_4S_9,14H_2O$ requires $Na = 14·55$; S (total) $= 45·56$; S (polysulphide) $= 35·44$; $H_2O = 39·89$ per cent.

* The paper by Locke and Austell (*Amer. Chem. J.*, 1898, **20**, 592) appeared subsequently to the completion of this portion of the work.

This compound for the present stands alone, the author having failed to obtain any other polysulphides of sodium, a result which is remarkable, as the method employed in the case of potassium hydrosulphide yielded a series of polysulphides.

It is to be noted that the salt obtained is analogous to the ammonium polysulphide, $(NH_4)_4S_9$, obtained previously. Also that the formula cannot correctly be written on the type of a disodium polysulphide, for the sulphur relations existing in the salt are expressed by $Na_4S_2 \cdot S_7$.

Preparation of Potassium Polysulphides.

These preparations were made by acting on solutions of potassium hydrosulphide with sulphur. Two distinct series of experiments were conducted.

Series I, in which sulphur, in calculated quantity, was digested with solution of potassium hydrosulphide, and hydrogen sulphide passed through the hot solution, concentration being effected by boiling in a current of the gas.

Series II, in which sulphur, in calculated quantity, was digested with solution of potassium hydrosulphide, concentration being effected in a vacuum over sulphuric acid.

The results of both series of experiments are given in the table (p. 768). In the left hand column are found the formulæ of the products obtained,* arranged in order of their sulphur values, commencing with K_4S_{10} and ending with K_4S_6.

Reference to the middle column will reveal the object with which the experiment was made, and furthermore, whether the experiment belongs to Series I or II.

The following remarks are made on the results of experiments grouped together in the table.

(1) The highest product obtained by direct solution of sulphur in potassium hydrosulphide is K_4S_9, and of this both a solution and crystals are obtained (see β and γ). Sufficient sulphur is taken up on heating to form K_4S_{10}, but some is deposited on cooling, leaving a stable solution of K_4S_9 (see β).

(2) If, however, concentration of a hot solution of K_4S_9 is effected

* The old conception of diammonium, disodium, and dipotassium polysulphides is abandoned, and all the polysulphides are held to be of the same character, namely, tetrammonium, tetrasodium, or tetrapotassium compounds. This step is, in the author's opinion, rendered necessary by the existence of certain definite polysulphides, whose composition cannot be expressed by formulæ written on the type M'_2S_x. Thus, we have representatives of this class in the case of all three metals : $(NH_4)_4S_7$ and $(NH_4)_4S_9$·, Na_4S_9, and K_4S_5 and K_4S_9.

Expt.	Sulphides obtained.	Object and method of experiment.	Remarks.
(α).....	K_4S_{10}, xH_2O	KHS + S (excess). I. Concentration in current of H_2S.	A solution of K_4S_{10} obtained, and from it crystals of K_4S_{10}, xH_2O.
(β).....	K_4S_9, xH_2O	KHS + S (for K_4S_{10}). II. No current of H_2S.	All sulphur dissolved on heating, but deposition of sulphur on cooling. Solution of K_4S_9, and crystals of K_4S_9, xH_2O, from it.
(γ).....	K_4S_9, xH_2O	KHS + S (excess over requirements of K_4S_{10}). II. No current of H_2S.	Crystals of K_4S_9, xH_2O, admixed with sulphur. On exhaustion with carbon disulphide K_4C_9, xH_2O, yielded $K_4S_5, 10H_2O$.
(δ).....	$K_4S_8, 6H_2O$	KHS + S (for K_4S_5). II. No current of H_2S.	Only 50 per cent. of KHS active. K_4S_8, yields K_4S_5 on treatment with CS_2.
(ϵ)....	$K_4S_8, 6H_2O$ $K_4S_8, 19H_2O$	KHS + S (for K_4S_6). I. Concentration in current of H_2S.	$K_4S_8, 6H_2O$, yields, on recrystallisation from alcohol, $K_4S_8, 19H_2O$.
(ζ).....	K_4S_7 (approx.)	KHS + S (for K_4S_6). I. Concentration in current of H_2S.	Product obtained higher than that for which sulphur added was sufficient.
(η)....	K_4S_6 (approx.)	KHS + S (for K_4S_4). I. Concentration in current of H_2S.	Product obtained higher than that for which sulphur added was sufficient.

by passage of hydrogen sulphide, then a solution of K_4S_{10} is obtained, and from it crystals of K_4S_{10}, xH_2O, (see α).

Here some explanation seems to be required to account for the formation of a higher polysulphide than can be obtained by direct solution of sulphur in potassium hydrosulphide. It has been repeatedly observed that hydrogen sulphide rapidly decomposes polysulphides, if passed through a *cold* solution, sulphur being copiously deposited and potassium hydrosulphide formed. If, however, hydrogen sulphide is passed through a *hot* solution of a polysulphide, no deposition of sulphur is observed, but the depth of colour is increased. The necessary explanation may be found in these facts, and it is suggested that, in the experiments α under consideration, some

potassium hydrosulphide is formed on passage of hydrogen sulphide through a *hot* solution of K_4S_9, and that the liberated sulphur, at the moment of its separation, is taken up by unaltered K_4S_9, forming the higher compound K_4S_{10}.

(3) It is to be noted that in all cases the polysulphide obtained is *richer* in sulphur than that for which the sulphur added was sufficient. This requires elucidation and two suggestions are made :

(*a*) All the sulphur added unites selectively with a *portion* only of the potassium hydrosulphide, forming a higher polysulphide than was designed in the experiment, and leaving potassium hydrosulphide in solution unaltered.

(*b*) That the formation of the higher polysulphide is due to the action of the current of hydrogen sulphide on the polysulphide first formed (see paragraph 2).

(4) It is evident on considering the results of experiments a, ϵ, ξ, η (Series I), that it is not possible to discriminate between (*a*) the first product obtained on dissolving sulphur in potassium hydrosulphide, and (*b*) the condensing effect of the current of hydrogen sulphide on the polysulphide first formed.

(5) Attention may now be directed to the experiments of Series II, (see β, γ, δ), in which no current of hydrogen sulphide was employed. Turning to the experiment marked δ in the Table, the intention was to produce K_4S_5, for which the sulphur added was sufficient. As a matter of fact, *the product obtained* was K_4S_8, and 50 *per cent. of the hydrosulphide was found unaltered* after solution of the sulphur had been effected. The following equations represent (i) the action expected, (ii) the change which actually took place.

$$\text{(i) } 4KHS + S_2 = K_4S_5 + H_2S$$
$$\text{(ii) } 8KHS + S_6 = K_4S_8 + 4KHS + 2H_2S.$$
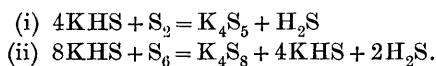
The validity of the latter equation seems to be established, for the proportion KHS/S on the left hand side was that existing in the experiment δ (see Table) ; and, of the three items on the right hand side, two were definitely established, the existence of K_4S_8, and the survival unaltered of 50 per cent. of the original hydrosulphide. It would follow then, from the fact that this proportion remains unaltered, that, by natural selection, under the given experimental conditions, the relation of the reacting materials is not that of the latter equation, but the simpler one : $4KHS + S_6 = K_4S_8 + 2H_2S.$
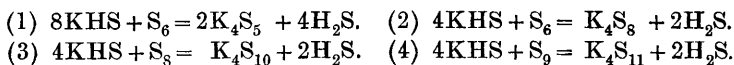
(6) As the result of treatment of crystals of K_4S_9 and K_4S_8, with carbon disulphide, a lower polysulphide, $K_4S_5,10H_2O$, has been obtained, which resists further removal of sulphur by this solvent.

Furthermore, K_4S_5 is a stable polysulphide, mustard-yellow in colour, easily and completely soluble in water, and in it the following relation

exists, $K_4S_2 \cdot S_3$, that is, of the five sulphur atoms, three are in the polysulphide position. There seems, then, good reason for suggesting that the *prime product*, in the case of potassium polysulphides, is *tetrapotassium pentasulphide*, K_4S_5, and that the other crystalline polysulphides obtained are solid solutions of sulphur in this substance.

(7) Regard must also be paid to the fact that the polysulphides of ammonium and sodium are of the same degree of complexity, which seems to indicate that the source of this complexity is *in the sulphur molecule itself*.   Now, it has long been held as a fact that sulphur, at temperatures above its boiling point, possesses a vapour density corresponding to a molecular formula of S_6, and that only as the temperature rises to 860—1040°, does it conform to the type S_2.*   During the past few years also, certain papers have appeared dealing with the molecular weight of sulphur in solution (compare Paternò and Nasini, *Ber.*, 1888, **21**, 2153 ; Beckmann, *Zeit. physikal. Chem.*, 1890, **5**, 76 ; Hertz, *ibid.*, 1890, **6**, 358 ; Guglielmo, *Real. Accad. Linc.*, 1892, ii, 210 ; Orndorff and Terrasse, *Amer. Chem. J.*, 1895, **18**, 173), and as a result of this work, the molecule of sulphur is stated to exist in solution as S_6, S_8, or S_9.

Now the simplest expressions that can be written involving the action of such molecular groupings, and limited by the observed experimental behaviour of potassium hydrosulphide, are as follows :

(1) $8KHS + S_6 = 2K_4S_5 + 4H_2S.$ (2) $4KHS + S_6 = K_4S_8 + 2H_2S.$
(3) $4KHS + S_8 = K_4S_{10} + 2H_2S.$ (4) $4KHS + S_9 = K_4S_{11} + 2H_2S.$

Of these reactions, (2) and (3) have been already obtained, but for (1) and (4) the experimental conditions are not yet known.

* Biltz (*Ber.*, 1888, **21**, 2013) does not, however, consider that the existence of gaseous molecules S_6 can be established. He finds the vapour density varies *gradually* with the temperature.