CLXXIII.—*The Polysulphides of the Alkali Metals. Part III. Potassium.*

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THE present work aims at bringing our knowledge of the polysulphides of potassium into line with that of the corresponding compounds of sodium (J., 1930, 1473) and lithium (this vol., p. 413), for the chemistry of these compounds has been much obscured by contradictory experimental data (see Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1922, Vol. II, pp. 629 *et seq.*).

The results (see *Summary*), although showing a great similarity to those recorded for the sodium and lithium compounds, uniformly indicate a greater tendency on the part of potassium to form polysulphides.

EXPERIMENTAL.

Potassium, from Imperial Chemical Industries Ltd., was kept under dry liquid paraffin, and scraped clean before use. The preparation of the other materials and the analytical methods employed were essentially similar to those previously described (J., 1930, 1474).

The Preparation of Polysulphides from Solution.—(i) *The action of sulphur on potassium monosulphide in aqueous-alcoholic and aqueous solution.* Schöne (*Pogg. Ann.*, 1867, **131**, 380) dissolved sulphur in aqueous solutions of potassium monosulphide, and crystallised therefrom the di- and tri-hydrates of the tetrasulphide, and the latter on exposure to sulphuric acid in a vacuum gave the semihydrate. Bloxam (J., 1900, **77**, 753), by crystallising a pentasulphide solution, obtained hydrated pentasulphides.

By dissolution of various proportions of sulphur in aqueous or aqueous-alcoholic monosulphide solutions, we have found that within definite limits of the ratio S : K in the solutions (Fig. 1) the following sulphides may be crystallised: $K_2S_2,3H_2O$; K_2S_3; $K_2S_4,3H_2O$; $K_2S_4,2H_2O$; K_2S_5,H_2O.

Solutions of the hydroxide for conversion into the monosulphide were prepared by the action of clean metallic potassium on aqueous alcohol or water. One-half of each of the solutions was saturated with hydrogen sulphide, giving pearly crystals which redissolved as saturation proceeded. After removal of the excess of hydrogen sulphide, the addition of the second half of the hydroxide immediately produced a crystalline precipitate. In this suspension the requisite weight of sulphur was dissolved by gentle heating on the water-bath for the minimum time. Within a certain range of concentration, a dark thick oil separated 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 by evaporation at room temperature in a vacuum over phosphoric oxide. This process, impossible in the case of sodium, was much more convenient than freezing out the crystals, since it gave solutions which, on account of their low viscosity, could be filtered easily. Only small fractions of crystals were removed in order to alter the composition of the liquid phase as little as possible from its original state; these were washed with ice-cold absolute alcohol, then with dry ether, exposed to phosphoric oxide in a vacuum desiccator, and analysed.

The results are shown in Table I and Fig. 1, the S : K ratios being here, as elsewhere, atomic ratios. The "polysulphide sulphur" is denoted throughout by (S).

The oils which separated were concentrated aqueous polysulphide solutions. These also were crystallised by evaporation. Filtration was in these cases difficult owing to the viscosity of the liquid phase, so that a high accuracy cannot be claimed for the analysis.

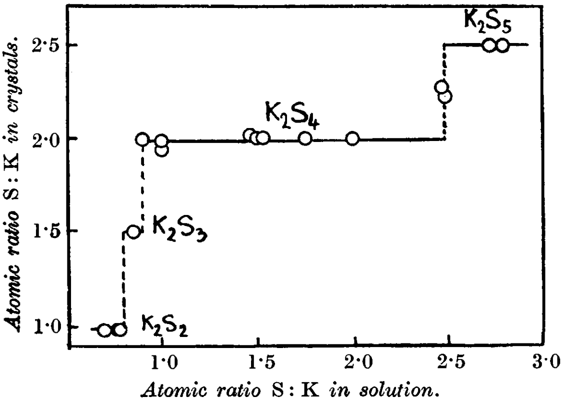
The behaviour of the oils was so similar to that of the liquids that the results are recorded together.

TABLE I.

	Solutions.				Crystals.			
No.	K, g.	Water, c.c.	Alcohol, c.c.	S : K.	K, %.	(S), %.	S, %.	S : K.
1	4	40	—	0·700	40·05	15·80	32·74	0·995
2	4	40	—	0·752	40·05	17·64	32·67	0·994
3	4	40	—	0·775	39·77	16·20	32·64	1·000
4	5·4	40	—	0·860	43·98	37·32	53·98	1·496
5	5·4	40	—	0·860	44·29	36·76	54·54	1·504
6	5·4	40	—	0·875	30·69	37·28	50·09	1·990
7*	4	20	54	1·000	32·30	37·90	48·75	1·840
8	4	20	54	1·000	32·11	37·15	52·15	1·980
9	5·4	20	54	1·483	30·72	36·88	51·28	2·035
10*	4	20	54	1·512	29·41	34·00	48·78	2·022
11	4	20	54	1·526	32·19	38·53	51·46	1·949
12	4	40	—	1·750	32·23	37·47	52·54	1·987
13	4	20	54	2·000	30·02	36·60	49·27	2·001
14	4	20	54	2·473	29·67	46·49	55·56	2·283
15	4	25	50	2·500	30·55	46·12	55·57	2·217
16	4	20	54	2·750	29·56	46·08	60·60	2·500
17	4	20	54	2·800	29·23	45·23	60·24	2·513

* Oils.

FIG. 1.



Samples of the products were tested for alcohol by the methods previously outlined (J., 1930, 1479), and the quantities present were as minute as those in the sodium compounds. Thiosulphate was also detected, in quantities slightly smaller than recorded in the sodium compounds, as might be expected from the greater stability of the potassium compounds in water.

Properties of the polysulphides. The *disulphide trihydrate* is a cream-coloured, acicularly crystalline compound, very similar in appearance to sodium disulphide hexahydrate. Like the other hydrated sulphides, it is very soluble in water and less so in alcohol [Found: K, 39·90; (S), 16·61; S, 32·67; H_2O, 27·50 ± 0·5. $K_2S_2,3H_2O$ requires K, 39·79; (S) 16·33; S, 32·65; H_2O, 27·55%].

The anhydrous *trisulphide* separated from aqueous solution as orange-red prismatic crystals [Found: K, (*a*) 43·85, 44·00, (*b*) 44·36, 44·21; (S), (*a*) 37·62, 37·01, (*b*) 36·89, 36·63; S, (*a*) 53·89, 54·06, (*b*) 54·19, 54·89. K_2S_3 requires: K, 44·83; (S), 36·80; S, 55·20%]. The very minute range of the S : K ratio for the solutions from which trisulphide could be crystallised made the preparation of the material in a pure state difficult, as this involved precise regulation of the composition of the solutions.

The trihydrated tetrasulphide formed golden-yellow glistening tabular crystals [Found: K, 30·48; (S), 36·93; S, 50·21; H_2O, 20·50. Calc.: K, 30·01; (S), 36·99; S, 49·32; H_2O, 20·77%]. The dihydrated tetrasulphide formed slightly lighter-coloured glistening tabulæ [Found: K, 32·18; (S), 37·72; S, 52·05. Calc. K, 32·23; (S), 39·68; S, 52·90%].

The *pentasulphide monohydrate* was an orange-red, minutely crystalline material [Found, in separate preparations: K, 29·56, 29·23; (S), 46·08, 45·23; S, 60·60, 60·24. K_2S_5,H_2O requires K, 30·47; (S), 46·86; S, 62·50. $K_2S_5,2H_2O$ requires K, 28·89: (S), 44·43; S, 59·25%].

(ii) *The action of sulphur on anhydrous alcoholic solutions of potassium monosulphide.* A solution of potassium (2·5 g.) in 36 c.c. of absolute alcohol was converted into hydrosulphide, the excess of hydrogen sulphide removed by boiling for 30 mins. in a stream of nitrogen, and the solution added to 2·5 g. of potassium in 36 c.c. of absolute alcohol. To this liquid was added the requisite weight of sulphur, which dissolved on gentle boiling, a polysulphide being precipitated. The reaction was complete after 30 mins. and the polysulphide was then filtered off, washed with absolute alcohol, centrifuged, and analysed.

The results, recorded in Table II and Fig. 2, make it evident that over the considerable S : K range studied the yellow trisulphide separates in the pure condition up to an S : K ratio of 1·63, and red pentasulphide from 2·00 to 2·50. Between the ratios 1·63 and 2·00, mixtures of the two sulphides, each of which could be readily identified, result, and from about 3·00 upwards free sulphur is present with the pentasulphide.

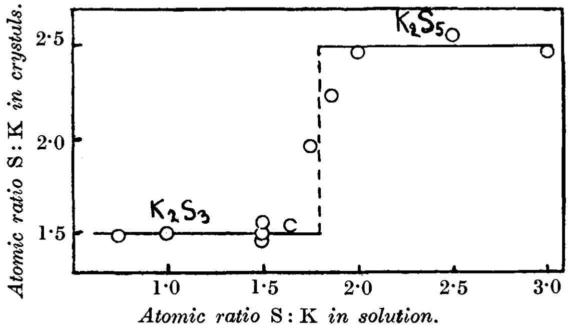
(iii) *The action of sulphur on potassium hydrosulphide.* Rule and Thomas (J., 1914, **105**, 2821) dissolved various proportions of sulphur in a solution of potassium hydrosulphide and found pure pentasulphide to be formed only when the elements were present in the ratio required by $2KHS + 4S \longrightarrow K_2S_5 + H_2S$. With less

TABLE II.

	Original comp.,	Crystals.						
No.	S : K, mols.	K, %.	(S), %.	S, %.	(S) : K, mols.	S : K, mols.	Colour.	Description.
1	0·75	41·41	39·58	50·14	1·17	1·48	Yellow	Trisulphide
2	1·00	43·80	38·80	53·68	1·08	1·50	Yellow	,,
3	1·00	42·56	42·60	52·33	1·23	1·50	Yellow	,,
4	1·50	41·73	39·10	49·85	1·15	1·46	Yellow (orange)	,,
5	1·50	44·04	39·49	55·96	1·10	1·56	Yellow (ochre)	,,
6	1·50	44·86	37·04	55·11	1·01	1·50	Yellow (orange)	,,
7	1·63	43·61	38·01	54·36	1·07	1·53	Yellow	,,
8	1·75	38·99	43·10	60·31	1·35	1·89	Mixture (yellow and red)	—
9	1·88	35·15	47·30	64·82	1·65	2·26	Mixture (yellow and red)	—
10	2·00	33·61	52·25	67·43	1·90	2·46	Red	Pentasulphide
11	2·50	32·87	52·66	69·22	1·96	2·58	Red	,,
12	3·00	33·64	53·09*	67·57	1·93	2·46	Red	,,

* These results have been corrected for free sulphur present with the polysulphide.

FIG. 2.



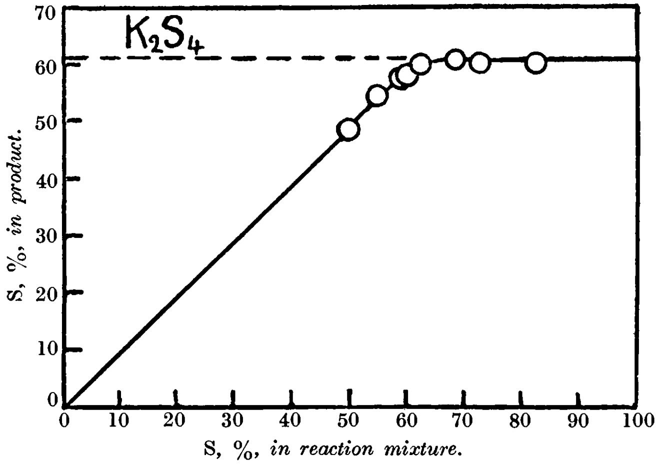
sulphur the products were considered to be mixtures of unchanged hydrosulphide with pentasulphide. These authors confirmed their results by estimating the hydrogen sulphide evolved during the dissolution of the sulphur in hydrosulphide solutions.

We have repeated and confirmed these results, and find no evidence of Bloxam's tetrapotassium polysulphides (*loc. cit.*). It seems clear that his materials were fortuitous mixtures of simple dipotassium compounds.

4-G. portions of potassium dissolved in 100 c.c. of pure dry alcohol were converted into the hydrosulphide; in the gently boiling solutions the required weights of sulphur were dissolved, and the solutions evaporated to crystallisation or precipitated with dry ether. In appearance, composition, and properties, the products were identical with those described by Rule and Thomas (*loc. cit.*), pentasulphide being the only definite polysulphide. ·The action of metallic potassium on alcoholic pentasulphide solutions was also confirmed, and further support for our results has been obtained by measuring the hydrogen sulphide evolved during the dissolution of the sulphur.

Preparation of Polysulphides by Dry Methods.—(i) *Reaction between sulphur and potassium carbonate or hydroxide.* This reaction has been known since the earliest times (Schöne, *loc. cit.*), and it is generally recognised that the chief products are polysulphides with, at low temperatures, thiosulphate, and at high temperatures, sulphate. This we have confirmed.

FIG. 3.



6·4 G. of sulphur and 6·9 g. of anhydrous potassium carbonate were heated in nitrogen. Reaction was slow at 250°, producing only polysulphide and thiosulphate. Above 600°, a loss of 2·2 g. was observed, corresponding to the whole of the carbon dioxide in the carbonate, and the product contained only sulphate and polysulphide. Analogous reactions were observed with potassium hydroxide, but similar experiments in boiling aqueous solutions led only to thiosulphate and polysulphide.

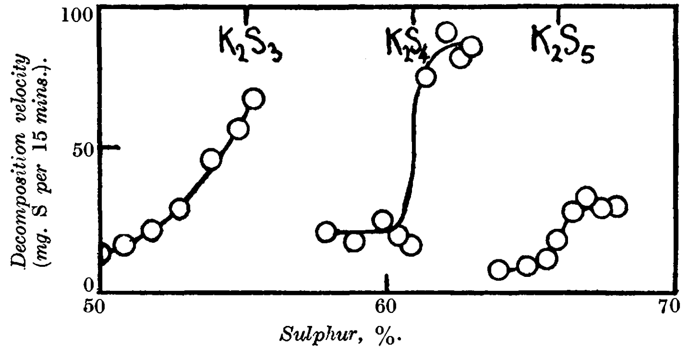
(ii) *The action of potassium on sulphur.* The reaction between metallic potassium and molten sulphur, as in the cases of the other alkali metals, is extremely violent, and useless for the preparation of polysulphides (compare J., 1930, 1484), but it seemed likely that the reaction could be moderated by carrying it out under organic liquids (*ibid.*, p. 1485).

The experimental procedure was identical with that already described for the preparation of the corresponding sodium compounds (*loc. cit.*, pp. 1485, 1486), with the obvious variations consequent on the formation of tetra- in the place of tri-sulphide.

Our findings (Fig. 3) indicate that no compound higher than the tetrasulphide is produced. Free potassium is present in diminishing quantities until this composition is reached, but not afterwards, provided that the reactants have been brought into intimate contact by crushing. The reaction is essentially similar to those occurring in the case of lithium and sodium, and again apparently a polysulphide was the first product of the reaction.

The following table enables the proportion of sulphur originally used to be compared with that found in the final product after melting. There are no results for compositions below 50% of sulphur because the violence of the combination of so much free potassium with the polysulphide during melting rendered the process impracticable.

FIG. 4.



S, %, in reactants......	50·0	55·2	59·0	60·3	62·1	68·2	73·5	81·9
S, %, in products	49·5	55·1	58·4	59·5	61·4	62·2	61·0	61·9

(Calc. for K_2S_4 : S, 62·2%.)

(iii) *Desulphurisation of the polysulphides.* Rule and Thomas (J., 1917, **111**, 1071) measured the loss in weight when potassium pentasulphide was heated for consecutive ½-hour periods, the temperature being raised 50° between each period. The results, when plotted as time against composition, indicated that disulphide is the most stable polysulphide at high temperatures; a slight change in decomposition velocity also occurred at trisulphide.

We have applied to the polysulphides of potassium the method previously described (J., 1930, 1487), but here porcelain was used in all but the penta–tetra-transition on account of the high temperatures necessary to give measurable decomposition velocities. The results involving high temperatures may have been somewhat vitiated by some reaction between the polysulphides and the containing vessels. The results shown graphically in Fig. 4, of which some typical ones are tabulated below, indicate the presence of di-, tetra-, and penta-sulphides by clearly defined changes in the rates of evolution of sulphur, and give some evidence of formation of trisulphide. The low rate of evolution of sulphur at trisulphide composition made the use of high temperatures essential; this introduced complicating factors which did not allow of the accurate determination of the possible change of decomposition velocities in the region K_2S_3—K_2S_2.

At 345°.

Rate of loss of S (mg./15 mins.)	28	28	32	27	18	10	8	7
S, %, in material	68·0	67·5	67·0	66·5	66·0	65·5	65·0	64·0

At 600°.

Rate of loss of S (mg./15 mins.)	85	80	90	75	15	18	23	15	20
S, %, in material	63·0	62·5	62·0	61·5	61·0	60·5	60·0	59·0	58·0

At 1000°.

Rate of loss of S (mg./15 mins.)	65	55	43	28	20	15	12
S, %, in material	55·5	55·0	54·0	53·0	52·0	51·0	50·0

The System Potassium Monosulphide–Sulphur.—This system has been studied by Rule and Thomas (J., 1917, **111**, 1077), who obtained evidence of di-, tri-, tetra-, penta-, and hexa-sulphides. We have repeated this work, and, although our results are occasionally higher by a few degrees, there is general agreement. Only a few measurements were therefore necessary, except in the region from mono- to di-sulphide, which had not previously been studied. The curve (Fig. 5) shows our results by small circles on Rule and Thomas's curve (continuous line) and our curve from mono- to di-sulphide by a broken line.

The initial materials used for these measurements were prepared under hot toluene, p. 1310; for preparations of higher sulphur content than tetrasulphide, this element was added to the compound, and for those of lower sulphur content, potassium was added, the mixture being carefully melted with thorough mixing. The thermal arrangement was identical with that employed in the case of sodium (J., 1930, 1490).

Owing to the intense supercooling in the region tri–tetra-sulphide, which had also been noticed by the previous workers, we took special precautions to ensure accuracy by many repetitions of the cooling and heating curves.

The close agreement between our results (Table III) and those of Rule and Thomas made microphotography superfluous, but

FIG. 5.

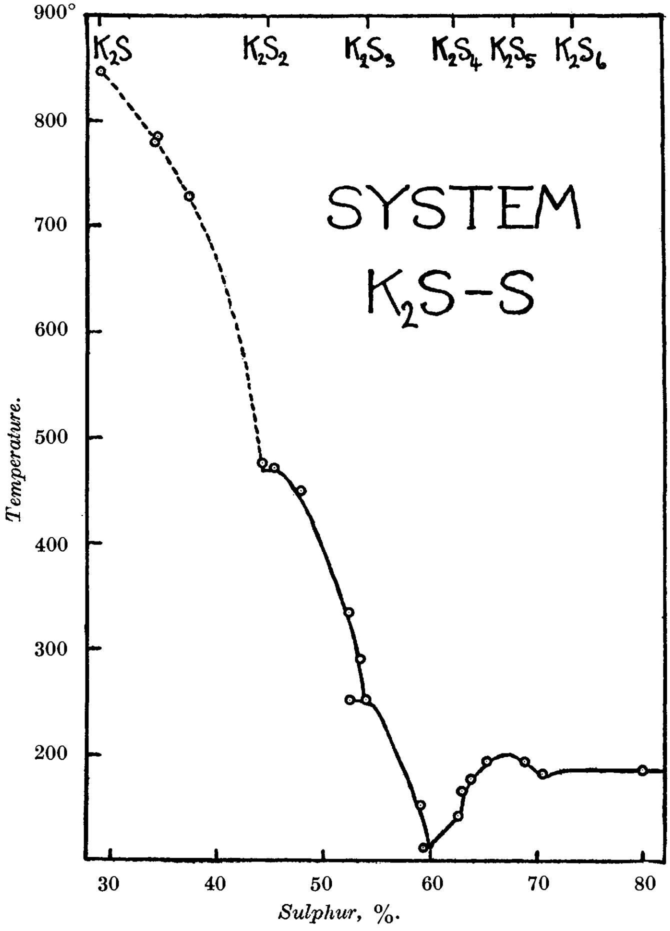


TABLE III.

S, %.	Upper arrest.	Lower arrest.	Approx. comp.
29·10	840 ± 20°	—	K_2S
34·41	782	—	
34·48	791	—	
37·50	731	—	
44·50	480	—	
44·83	475	—	K_2S_2
48·23	442—448	—	
52·40	336	245—248°	
53·80	288°	249·5°	K_2S_3
59·55	156·5	108—112	
62·75	167·5	140—144	K_2S_4
63·85	180·0	—	
65·05	198·0	—	
69·00	196·7	—	K_2S_5
70·42	182·9	—	
80·00	188·2	—	

micro-examination of the melts confirmed the form of the equilibrium diagram. The crystals of disulphide have the same form as those of sodium disulphide [J., 1930, Plate I (*a*), facing p. 1494], and the other sulphides show normal, polygonal, grained structures.

Summary.

Studies of the formation and properties of the potassium polysulphides have been repeated and extended, with the following results.

(1) The action of sulphur on aqueous or aqueous-alcoholic solutions of potassium monosulphide gives polysulphide solutions from which may be crystallised $K_2S_2,3H_2O$; K_2S_3; $K_2S_4,2H_2O$; $K_2S_4,3H_2O$; and K_2S_5,H_2O.

(2) The action of sulphur on anhydrous alcoholic solutions of potassium monosulphide results, according to the proportion of each used, in the formation of either tri- or penta-sulphide: no other sulphide separates.

(3) By the dissolution of various proportions of sulphur in alcoholic solutions of potassium hydrosulphide, only one compound, *viz.*, the pentasulphide, is obtained, with the elements present in the calculated proportions: $2KHS + 4S \longrightarrow K_2S_5 + H_2S$. With less sulphur the products are mixtures of penta- and unchanged hydrosulphide.

(4) Metallic potassium reacts with solutions of potassium pentasulphide to give mixtures of lower polysulphides.

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

(6) Sulphur reacts with molten potassium under toluene to give the tetrasulphide, possibly mixed with minute traces of some lower sulphide.

(7) On desulphurising the polysulphides of potassium in a stream of nitrogen at definite temperatures, changes in the decomposition velocity indicate the existence of penta-, tetra-, di-, and probably tri-sulphide.

(8) A phase-rule study of the system sulphur–monosulphide indicates the existence of the latter as a compound stable at its m. p., *i.e.*, 840°; di-, tri-, and tetra-sulphides slightly decompose as indicated by hidden maxima at 45·0, 55·1 and 62·1% of sulphur respectively; pentasulphide is stable at its m. p., 206°, and hexasulphide largely decomposed, as shown by a very flat maximum at 189°; a saturated solid solution occurs with material containing 74% of sulphur at 188·2°; finally, tetra-sodium compounds are not formed.

The authors wish to thank Mr. J. H. Smith for his very valuable assistance, and to acknowledge grants from the Research Committee of this College for the purchase of the potentiometer and special centrifuge.

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[*Received, February* 19*th*, 1931.]