

LVI.—*The Polysulphides of the Alkali Metals.*  
*Part II. Lithium.*

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A SURVEY of the literature of the sulphides of lithium (see Thomas and Jones, J., 1924, **125**, 2207) makes it evident that only one polysulphide had been previously identified, *viz.*,  $\text{Li}_2\text{S}_2\cdot\text{Aq}$  (Berzelius, *Pogg. Ann.*, 1826, **6**, 439). These workers, by evaporating an alcoholic solution of the hydrosulphide containing excess of sulphur, also obtained but one compound, *viz.*,  $\text{Li}_2\text{S}_2\cdot\text{C}_2\text{H}_5\cdot\text{OH}$ , and that in impure condition. Since it seemed probable that higher sulphides should be obtainable, the present work was undertaken, and it demonstrates, *inter alia*, the existence of a somewhat unstable *tetrasulphide*.

EXPERIMENTAL.

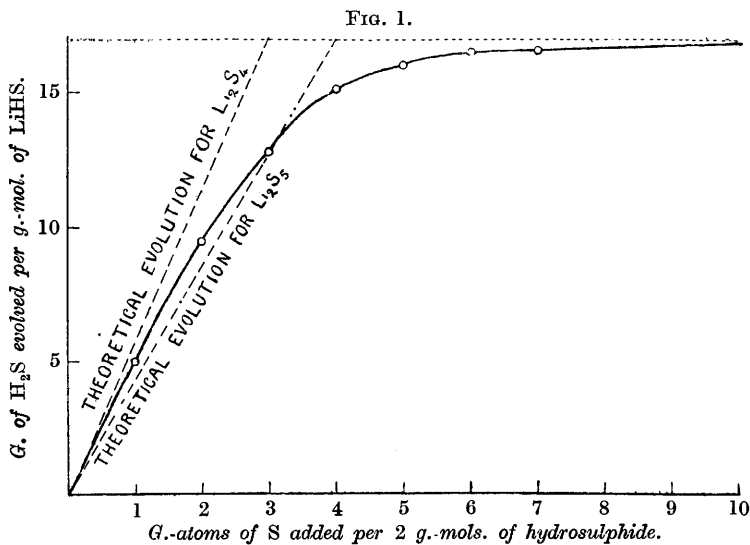
*Preparation of Materials.*—The lithium (in large sticks preserved under dry paraffin, from Messrs. Harrington Bros.) was evidently purer in parts than that used by Jones and Thomas (J., 1923, **123**, 3288), for it yielded with alcohol a pure, white ethoxide. Other portions, however, particularly those which appeared to come from the end of the electrolytic sticks, contained much carbide and some free carbon, and were rejected. The preparation of the other materials and the analytical processes employed were on the lines previously described (Pearson and Robinson, J., 1930, 1474).

*Preparation of Polysulphides from Solution.*

1. *The Action of Sulphur on Lithium Monosulphide in Alcoholic, Aqueous-alcoholic, and Aqueous Solutions.*—The procedure was substantially that employed by us with sodium (*loc. cit.*), except that, owing to its low solubility, the ethoxide suspension was not divided into two parts. Two-gram portions of lithium were cleaned by scraping with a knife under paraffin, washed in toluene, dried, weighed, and rapidly transferred to a measured quantity of alcohol, aqueous alcohol, or water. The resulting suspension of ethoxide was converted to hydrosulphide by saturation with hydrogen sulphide, excess of which was removed by boiling in a stream of nitrogen. To this colourless solution was added a suspension of ethoxide from a further 2 g. of lithium, and in the monosulphide solution so obtained various amounts of sulphur were dissolved. These solutions were evaporated in a vacuum or cooled in freezing mixtures. Evaporation was very slow and hard glassy crusts formed on the surface of the liquids. Analysis showed these to be mixtures of ethoxide, polysulphide, and possibly thiosulphate, with

much alcohol [Found : (I) Li, 13.38, 13.96; (S)\*, 1.01, 1.22; S, 3.74, 3.09; (II) Li, 5.04, 5.02; (S), 2.03, 2.01; S, 5.39, 5.74 mols.]. Although the whole mass occasionally set in either a glassy or a semi-crystalline form, definitely crystalline products could not be separated.

*The Action of Sulphur on Anhydrous Alcoholic Solutions of Lithium Hydrosulphide.*—Contrary to the experience of previous workers (see above), we have now shown, by (a) measuring the hydrogen sulphide evolved during the dissolution of the sulphur, and (b) crystallising the polysulphide solutions so produced, that the chief and primary product of this reaction is *tetrasulphide*. The striking similarity between the form of the lithium curve (Fig. 1) and the



corresponding sodium curve (Rule and Thomas, J., 1914, 105, 179) is consistent with the close relationships existing between these metals.

The high viscosity of the sulphide solutions at the crystallising point rendered difficult the separation and accurate identification of solid products. Nevertheless, the deductions from Fig. 1 are corroborated by the facts that (1) samples of centrifuged crystals obtained by evaporation at room temperature of solutions with a tetrasulphide ratio gave analyses close to the tetrasulphide dialcoholate, and (2) unchanged hydrosulphide could be separated from solutions treated with sulphur in quantities sufficient only to form disulphide (*i.e.*,  $2\text{LiHS} + \text{S} \rightarrow \text{Li}_2\text{S}_2 + \text{H}_2\text{S}$ ).

\* (S) = Polysulphide sulphur.

The formation of disulphide by evaporation at the boiling point is consistent with the lower thermal stability of the higher lithium sulphides than that of the corresponding sodium compounds: indeed, the argument put forward by Rule and Thomas (*ibid.*, pp. 185, 186) applies equally well to lithium, except that in this case the disulphide, not the tetrasulphide, is stable under the experimental conditions.

(a) *Measurement of hydrogen sulphide evolved.* 0.9 G. of metallic lithium, when treated with 100 c.c. of absolute alcohol under nitrogen, gave lithium ethoxide, which was converted into a hydrosulphide solution of which the lithium content was immediately determined by titration with standard acid.

This solution (50 c.c.) was placed in a 250-c.c. round-bottomed flask and through an attached reflux condenser a weighed quantity of sulphur in a small bottle was added. The hydrogen sulphide produced was removed by an hour's gentle boiling in a current of nitrogen delivered below the surface, and was trapped in a series of absorption vessels containing 0.2*N*-iodine solution. Titration of the residual iodine with 0.2*N*-thiosulphate solution gave a measure of the hydrogen sulphide thus evolved.

As it was noted that the hydrosulphide of lithium underwent alcoholysis to a much greater extent than those of the other alkali metals, the magnitude of this effect was estimated by measuring the hydrogen sulphide evolved when an aliquot portion of the solution was boiled in nitrogen under the standardised conditions. Evidently the correction is applicable only when small quantities of sulphur have been added, for otherwise the residual hydrosulphide is small.

The results (Table I) are plotted in Fig. 1, the point at the composition corresponding to disulphide being corrected for the hydrolysis of the unchanged hydrosulphide known to be present.

TABLE I.

Atoms S added per 2LiHS.	G. of H <sub>2</sub> S evolved per g.-mol. of LiHS.			
	Expt. 1.	Expt. 2.	Expt. 3.	Mean.
0	2.02	1.90	1.82	1.91
1	7.43	6.90	6.46	6.93
2	9.81	9.46	9.38	9.55
3	12.95	12.98	12.70	12.88
4	15.47	15.20	14.90	15.19
5	—	—	16.28	16.28
6	—	16.46	16.66	16.56
7	—	16.61	—	16.61
10	16.98	—	—	16.98

(b) *Crystallisation of solutions prepared from hydrosulphide.* 2-G. portions of lithium dissolved in 75 c.c. of absolute alcohol

were converted into the hydrosulphide, and the required weights of sulphur dissolved in the gently boiling solutions.

When sulphur was used in the proportion required for disulphide, a yellow solution, brownish-red when hot, was formed; on evaporation at room temperature in a vacuum desiccator over phosphoric oxide, this became filled with a mass of colourless, nacreous plates. So viscous had the solution become, and so sensitive were the crystals to moisture and oxidation, that only a part of the liquor could be removed by filtration. Furthermore, their great solubility prevented efficient washing. A specimen of centrifuged crystals appeared under the microscope as a suspension of rectangular, colourless plates with straight extinction in all positions and a typical biaxial optical figure. Such crystals, optically identical with those of the alcoholated hydrosulphide prepared by the crystallisation of pure hydrosulphide solutions, gave  $\text{Li} : (\text{S}) : \text{S} = 1 : 0.05 : 1.15$ , the polysulphide sulphur being undoubtedly due to adhering mother-liquor.

With sulphide in the tetrasulphide proportion, evaporation at the room temperature gave a mass of yellow, bi-prismatic, embryo crystals, showing straight extinction in two positions. It was impossible to grow crystals large enough to give an optical figure but the symmetry of the small crystals suggested the monoclinic system. Their crystalline form, together with their complete solubility in both alcohol and water to give clear light yellow solutions, showed that the crystals were not sulphur. A suspension of crystals in mother-liquor was centrifuged on a cotton-wool filter pad for 15 mins. at 4000 r.p.m., the mother-liquor poured off from the felted mass, the crystals centrifuged again, and then washed on the centrifuge with several small quantities of absolute alcohol [Found : (I) Li, 6.46; (S), 38.42; S, 55.58; (II) Li, 6.08; (S), 37.67; S, 55.70.  $\text{Li}_2\text{S}_4 \cdot 2\text{C}_2\text{H}_5 \cdot \text{OH}$  requires Li, 5.98; (S), 41.07; S, 54.70%].

With sufficient sulphur for the pentasulphide, a deep red viscous solution was obtained, which, when evaporated at room temperature to the consistency of thick treacle, deposited minute crystals that consisted almost entirely of sulphur (Found :  $\text{Li} : \text{S} = 1 : 76$ ). The remaining liquor was, without further concentration, cooled in a freezing mixture of ice and salt, whereupon a mass of tiny, transparent crystals, typical of the tetrasulphide, was deposited. These were separated as completely as possible from mother-liquor, and the lithium and polysulphide sulphur determined in a sample without weighing [Found :  $\text{Li} : (\text{S}) = 2 : 2.78, 2 : 2.65$ ]. The low value for polysulphide sulphur is probably due to loss of the very volatile hydrogen persulphide formed in quantity on addition of the mineral acid. The evidence as a whole left no doubt that the material so produced is *lithium tetrasulphide dialcoholate*.

A saturated solution of sulphur in hydrosulphide was prepared by digesting excess of sulphur with a solution of the hydrosulphide, and by following the manipulation described by Thomas and Jones (*loc. cit.*, p. 2212) results were obtained which confirmed theirs in every detail, the only polysulphide separating being one approximating to the formula  $\text{Li}_2\text{S}_2\cdot\text{C}_2\text{H}_5\cdot\text{OH}$ . This material was invariably contaminated by varying amounts of hydrolysis products.

*Preparation of Polysulphides by Dry Methods.*

(1) *Reaction between Sulphur and Lithium Carbonate or Hydroxide.*—These reactions have not previously been examined. The products corresponded with those obtained from the analogous sodium compounds.

4.8 G. of sulphur and 7.4 g. of anhydrous lithium carbonate were heated under nitrogen. Very slow reaction commenced at about  $200^\circ$ , giving thiosulphate and polysulphide; at  $400^\circ$ , the product contained some sulphate in addition to thiosulphate, whilst at  $700^\circ$  much sulphate and small quantities of thiosulphate and sulphite were produced. The reaction, as judged from the weight of carbon dioxide evolved, was completed at  $700^\circ$  after about 30 mins.

Analogous reactions were observed with the hydroxide, but similar experiments in aqueous solution led to the formation of only thiosulphate and polysulphide.

(2) *Action of Lithium on Sulphur.*—The reaction between these elements (compare Troost, *Ann. Chim. Phys.*, 1857, **51**, 107), either being molten, is very violent (compare J., 1930, 1485); even under an organic liquid, serious decomposition of the liquids occurs, and the product is contaminated with carbon and metallic carbide. However, a material of very low sulphur content, less than that required by disulphide, was obtained and a small amount of unchanged metal detected.

Lithium (1 g.) was melted under 150 c.c. of boiling naphthalene, and sulphur added in 0.5-g. lots through a reflux condenser. No reaction occurred until 0.5 g.-atom had been added per atom of lithium, whereupon one started with explosive violence. Further quantities of sulphur did not appear to react. The material was filtered off from the liquid naphthalene, thoroughly washed with boiling toluene, and strongly heated in a vacuum to expel the residual solvent (see J., 1930, 1486).

The product on treatment with water evolved a mixture of hydrogen and hydrocarbons, from free metal and carbides in quantities too small to alter the S : 2Li ratio, and deposited free carbon. On acidification, the filtrate gave a small amount of polysulphide sulphur, which was estimated as follows. The material was treated

with dilute hydrochloric acid and boiled until the sulphur had coagulated. The mass of carbon and sulphur was filtered off, dried, and weighed, and then extracted with carbon disulphide, the sulphur being determined by difference. It is clear from the results (Table II) that the polysulphide is only present in minute amount, the chief product being monosulphide.

TABLE II.

Reactants : S, %.	Products, %.				S : 2Li, mols.
	C.	S.	(S).	Li.	
95.2	11.7	65.1	—	23.2	1.23
92.1	18.4	54.8	6.0	26.8	0.90
90.4	18.9	58.2	7.0	22.9	1.11

*The System Lithium Monosulphide-Sulphur.*

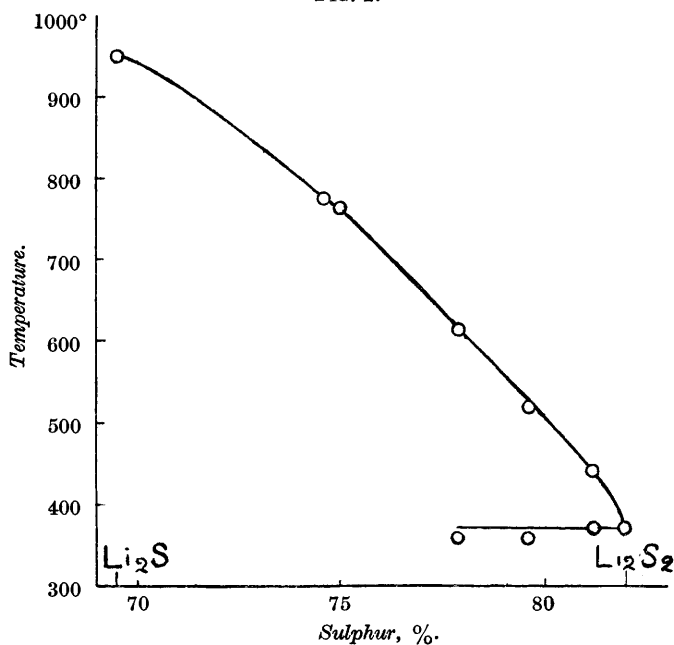
Lithium polysulphides are so unstable that only a small portion of the diagram, *viz.*, that between mono- and di-sulphide, could be investigated: with greater sulphur content, the melting of the mixtures caused severe decomposition into disulphide with rapid loss of free sulphur. Nevertheless, the limited results accorded well with those obtained by working with solutions.

The large quantities of polysulphide required were prepared by sintering anhydrous monosulphide with the appropriate quantity of sulphur at as low a temperature as possible. 14-G. portions of metallic lithium were dissolved in 500 c.c. of absolute alcohol in a stream of nitrogen on a water-bath, and the solution was saturated by a rapid stream of pure dry hydrogen sulphide. About 400 c.c. of alcohol were then distilled off in hydrogen sulphide, and the remainder was removed in a vacuum. When quite dry, the mass was broken up to a fine powder and exposed to hydrogen sulphide for 3 hours. The flask was then evacuated and placed in a furnace at 450°. After 4 hours, the buff powder was re-gassed for several hours, and again heated at 450° for 2 hours (Found: Li, 29.92, 29.98, 30.13. Calc. for  $\text{Li}_2\text{S}$ : Li, 30.44%).

To prepare polysulphides from this material, it was mixed with the appropriate quantity of finely powdered sulphur, and cautiously heated until it sintered, and then melted. In all cases in which the sulphur was added in excess of that required for disulphide, large quantities of the element were lost by distillation: even at disulphide composition, this occurred unless special precautions were taken. The material which gave the arrest was analysed immediately after solidification. In the region of the disulphide, much free sulphur was always liberated; this was removed by extraction with ice-cold carbon disulphide, and the residual solid dried in a vacuum and analysed.

The arrangements employed for the thermal measurements have already been described (J., 1930, 1490). Supercooling occurred very readily, and all the precautions there described were taken to ensure correct arrest temperatures, but even these were of little avail, especially in the vicinity of monosulphide. The measurements

FIG. 2.



were further vitiated by the extremely rapid reaction of the melts with both glass and porcelain. Most of the higher temperatures, however, have an error less than  $\pm 10^\circ$ , whilst those relating to the disulphide region are probably correct to within  $\pm 1^\circ$ . The results recorded in Table III and Fig. 2 show that monosulphide is stable at its melting point.

TABLE III.

S, %.	Arrests.		Solid.	Fracture.
	Upper.	Lower.		
69.5	900—975°	—	Li <sub>2</sub> S	Light chocolate
74.6	774	—		
75.0	765	—		
77.9	618	355°		
79.6	520	353		Dark yellow
81.2	444	369.5		
82.0	369.5	—	Li <sub>2</sub> S <sub>2</sub>	Brownish-yellow

*Summary.*

A critical investigation of the formation and properties of the lithium polysulphides has yielded the following results.

1. The action of sulphur on aqueous, aqueous-alcoholic, and anhydrous alcoholic solutions of lithium monosulphide gave polysulphide solutions from which crystalline products could not be isolated.

2. By the dissolution of various proportions of sulphur in alcoholic solutions of lithium hydrosulphide, only one compound, *viz.*,  $\text{Li}_2\text{S}_4$ , was formed ( $2\text{NaHS} + 3\text{S} \longrightarrow \text{Na}_2\text{S}_4 + \text{H}_2\text{S}$ ); on crystallisation at room temperature this separated as  $\text{Li}_2\text{S}_4 \cdot 2\text{C}_2\text{H}_5 \cdot \text{OH}$ . With less sulphur, the products were mixtures of tetrasulphide and unchanged hydrosulphide. Higher polysulphides may also have been formed, but could not be separated by crystallisation. At the boiling point of the solutions, only an alcoholated disulphide,  $\text{Li}_2\text{S}_2 \cdot \text{C}_2\text{H}_5 \cdot \text{OH}$ , was separable.

3. Sulphur reacted with lithium 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.

4. Sulphur reacted with molten lithium under naphthalene to give monosulphide mixed with a little polysulphide.

5. A phase-rule study of the system  $\text{Li}_2\text{S}-\text{S}$  indicated that only two sulphides of lithium are stable at atmospheric pressure, *viz.*, the monosulphide, stable at its melting point,  $900-975^\circ$ , and the disulphide, slightly decomposed at its melting point,  $369.5^\circ$ .

6. Only two polysulphides of lithium could be formed, the tetra- and the di-sulphide, of which the latter is by far the more stable.

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