3. By assuming that the additivity of entropy is due to translational and other forms of energy and by making use of the equation

$$S = 5/2\, R\, ln\, T - R\, ln\, p + 3/2\, R\, ln\, M + S_1 + \int_0^T C_R \frac{dT}{T}$$

the entropy of hydrogen chloride has been shown to be 43.40 using the Tetrode constant and 43.17 using the Lewis constant, in good agreement with the experimental value.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

THE POLYSULFIDES OF SODIUM AND POTASSIUM

BY CARL Z. DRAVES AND HERMAN V. TARTAR

RECEIVED FEBRUARY 24, 1926 PUBLISHED JUNE 5, 1926

Introduction

During an investigation[1] of the reaction of sulfur with alkali hydroxides in boiling aqueous solution, it seemed desirable to determine with how many atoms of sulfur the free alkali metals tend most readily to unite in the formation of polysulfides. Although Locke and Austell[2] had sought an answer to this question by allowing a boiling solution of sulfur in toluene to react with molten sodium in toluene, the results of their experiments were not conclusive. In the two trials in which they used the most sulfur the percentages of sodium in their product lay between the values corresponding to the trisulfide and the tetrasulfide.

Experimental Part

The method of combining sulfur and an alkali metal employed by Locke and Austell was essentially modified, in that the metal was added to the solution of sulfur rather than the sulfur to the metal. Such an amount of recrystallized and dried sulfur as to be in large excess for the reaction was dissolved in toluene contained in the reaction flask. All the toluene used in this work had been twice distilled over metallic sodium and subsequently kept dry by storage over more of the same metal. In order to keep oxygen and moisture away from the reacting substances a vigorous stream of commercial hydrogen, purified by passage through alkaline pyrogallol and concd. sulfuric acid, was introduced above the surface of the toluene. The hydrogen escaped through a calcium chloride tube at the upper end of the reflux condenser with which the reaction flask was equipped. A cube of metallic sodium or potassium was weighed approximately, trimmed quickly under dry toluene and then dropped through a large hole in the fiber cork of the flask into the vigorously boiling solution

[1] Tartar and Draves, THIS JOURNAL, **46**, 574 (1924).

[2] Locke and Austell, *Am. Chem. J.*, **20**, 592 (1898).

of sulfur. The hole from which toluene vapor was escaping was immediately closed with a small cork. The toluene was kept boiling until the reaction seemed complete. The insoluble polysulfide was then quickly filtered onto a Büchner funnel and washed free from excess of sulfur with a volume of boiling toluene nearly equal to the volume used for the reaction. The vapors of the hot wash liquid were depended upon to minimize the effect of air and moisture. The product, still wet with toluene, was transferred to a vacuum desiccator and dried overnight at about 20 mm. pressure in an atmosphere of hydrogen.

Since sodium and potassium polysulfides are hygroscopic and also oxidize readily, it was necessary to weigh the samples for analysis with the greatest dispatch, from a closed weighing bottle. Sulfur was precipitated as barium sulfate after oxidation with sodium peroxide, applying no correction for adsorption.[3] The percentages of sodium and potassium were determined by careful transformation to the respective sulfates with an excess of sulfuric acid in large platinum crucibles. The data are presented in Tables I and II. The low total percentages of alkali metal and sulfur were undoubtedly due mainly to moisture and thiosulfate in the samples for analysis.

Table I

Composition of Sodium Polysulfide Formed by Direct Union of the Elements in Toluene

					Theoretical composition		
	Expt. 1	2	3	4	Na_2S_2	Na_2S_3	Na_2S_4
Sulfur used, g.	5.0	8.0	9.0	9.0	...	...	...
Sodium used, g.	(a)	(a)	2.8	2.4	...	...	...
Toluene used, cc.	250	750	1000	1000	...	...	...
Total boiling, hrs.	1.0	1.0	2.0	1.3	...	...	...
Sodium, %	31.20	31.54	30.80	30.31	41.77	32.26	26.41
Sulfur, %	65.00	66.09	66.35	67.00	58.23	67.64	73.59
Total percentage	96.20	97.63	97.15	97.31	100.0	100.0	100.0
At. ratio, S:Na	2.989/2	3.007/2	3.091/2	3.172/2	2/2	3/2	4/2

[a] Less than enough to form pentasulfide.

Table II

Composition of Potassium Polysulfide Formed by Direct Union of the Elements in Toluene

			Theoretical composition	
	Expt. 1	2	K_2S_4	K_2S_5
Sulfur used, g.	8.0	9.0	...	...
Potassium used, g.	2.0	2.0	...	...
Vol. of toluene for reaction, cc.	1000	1000	...	...
Total time of boiling, hrs.	1.3	2.0	...	...
Potassium, %	33.24	32.75	37.87	32.80
Sulfur, %	64.60	64.82	62.13	67.20
Total percentage	97.84	97.57	100.00	100.00
Atomic ratio sulfur to potassium	4.740/2	4.828/2	4/2	5/2

[3] Allen and Johnston, This Journal, **32**, 588 (1910).

Discussion of Results

The data of Table I seem to show that sodium trisulfide was formed when metallic sodium was allowed to react in the absence of air with an excess of free sulfur in boiling toluene. That the trisulfide should have been the final product in the presence of an excess of sulfur, even after allowing one to two hours for attainment of equilibrium, is surprising in the light of previous work on the polysulfides. Thomas and Rule,[4] from the freezing-point curves for the system sodium sulfide and sulfur, concluded that the trisulfide should be quite unstable even below its melting point of 223.5°, while the tetrasulfide should be stable. In an earlier work Rule and Thomas[5] expressed the belief that, generally, under the conditions of their experiments, the tetrasulfide was always the chief product of the action of sulfur on alcoholic solutions of the hydrosulfide.

The very recent work of Bergstrom[6] gave indications of the formation of sodium tetrasulfide rather than trisulfide when sulfur was allowed to react with metallic sodium in liquid ammonia solution.

One would expect potassium to form a higher polysulfide more readily than sodium. The data of Table II confirm this generalization. In the two experiments tried the ratios of sulfur to metal indicated that the pentasulfide of potassium was formed in boiling toluene from metallic potassium and an excess of free sulfur.

Summary

1. Sodium trisulfide was formed by the reaction of metallic sodium with an excess of sulfur in dilute solution in boiling toluene.

2. The formation of potassium pentasulfide under like conditions was indicated.

PENNS GROVE, NEW JERSEY

[4] Thomas and Rule, *J. Chem. Soc.*, **111**, 1063 (1917).

[5] Rule and Thomas, *ibid.*, **105**, 177 (1914).

[6] Bergstrom, THIS JOURNAL, **48**, 146 (1926).