2. The dissociation pressure of sodium vapor from solid sodium carbide is represented approximately by the equation: $\log p = 9059 - 6609/T$.
3. The dissociation pressure becomes one atmosphere at about 800°. It follows that any sodium carbide which is formed as a step in the fixation of nitrogen as cyanide can exist only in the gas phase, since considerably higher temperatures are required for the fixation.
4. At 700°, sodium carbide in the gas phase is largely dissociated, the partial pressure of gaseous sodium carbide over solid sodium carbide being about 0.6 mm. of mercury as compared with 191 mm. dissociation pressure of sodium.

WASHINGTON, D. C.

THE POLYSULFIDES AND POLYSELENIDES OF LITHIUM, SODIUM AND POTASSIUM

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Introduction

In connection with an investigation of the action of liquid ammonia solutions of the alkali metal amides—bases of the ammonia system—upon elements more electronegative than cobalt or nickel, it was necessary to study the action of solutions of the alkali metals upon sulfur and selenium, previous work of Hugot along these lines having been found inaccurate in many details.[2]

Procedure and Preparation of Materials

The solubility of sulfur and selenium in solutions of the alkali metals was determined essentially according to the method of Kraus and Chiu.[3] Briefly a weighed stick of sulfur or selenium was suspended in a liquid ammonia solution containing a known weight of alkali metal at —33°. At the end of the stages of the reaction corresponding to the disappearance of the blue color of the alkali metal solution, to the disappearance of a precipitate, or at the point corresponding to the saturation of the solution with respect to the more electronegative element, the stick was raised, washed with liquid ammonia and weighed. The volume of the solution was determined with sufficient accuracy from graduations on the bulb of the reaction tube.

Weighed quantities of sodium and potassium were enclosed in glass capsules according to the method of Kraus and Chiu.[3] Lithium, as it could not be melted into capsules of the glass on hand, was weighed rapidly from a weighing bottle. Sulfur, a special preparation of Kahlbaum, was

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[1] National Research Fellow.

[2] Hugot, *Compt. rend.*, **129**, 299 (1899).

[3] Kraus and Chiu, THIS JOURNAL, **44**, 2002 (1922).

used without further purification. Commercial selenium was dissolved in concd. nitric acid, the excess of acid expelled by evaporation, and the resulting selenium dioxide sublimed twice in glass. Selenium was prepared by passing sulfur dioxide through the hydrochloric acid solution of this purified dioxide. The precipitate was washed and fused in a vacuum.

Selenium and sulfur were cast in stick form in the mold shown in Fig. 1.

A drop of glass was fused on one end of a coil of Nichrome wire about half the diameter of the stick it was to support; this drop was then fused into the bottom of the soft glass tube A (about 10 mm. internal diameter). The upper part of the tube was filled with coarsely powdered sulfur or selenium, after which it was attached to the vacuum line and evacuated.[4] By the use of a hand torch, the material was melted into the mold A, and there allowed to solidify. The tube, while still very warm, was suddenly chilled in cold water, this serving partially to separate the stick from the walls. In order to remove the stick completely from the glass, it was generally necessary to crack the latter in a number of places by application of a hot tip of glass to a number of file scratches. The glass was removed by the judicious use of a pair of pliers. The excess wire at the top was bent in the form of a loop, so that the stick could be suspended in the reaction tube. Without the wire centers the sticks would readily have been broken.

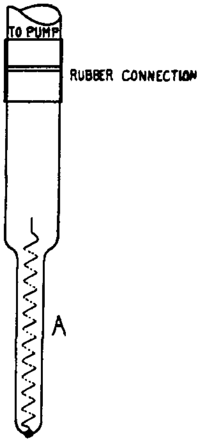

Fig. 1.

The Polysulfides of the Alkali Metals

Sulfur reacts very rapidly with solutions of lithium, sodium and potassium at —33° with the initial production of white, apparently amorphous precipitates of the corresponding monosulfides. Further reaction with sulfur leads to the formation of light yellow or orange disulfides, and these in turn react with sulfur to form tetrasulfides, which are readily soluble in ammonia, giving orange-yellow solutions. The tetrasulfides at first readily dissolve further quantities of sulfur with the formation of red solutions of the higher polysulfides. In attempting to determine the composition of the solution in equilibrium with sulfur, it was found that large quantities of this element were slowly dissolved with lapse of time, indicating that a side reaction was taking place. Ruff and Geisel[5] have found that sulfur dissolves slowly in liquid ammonia at room temperatures to form derivatives of ammonium sulfide and sulfur nitride. The rate of solution of crystalline sulfur while very slow at —33° in pure ammonia is probably much greater under the conditions of the experiments.

Due to the rapidity of the action of solutions of the alkali metals on sulfur, it was difficult to obtain accurately the end-point corresponding to the formation of the monosulfide. The following experiment, carried out

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[4] The pressure should not be reduced to the point where the sulfur boils.

[5] Ruff and Geisel, *Ber.*, **38**, 2659 (1905).

in a reaction tube at —33°, shows that the slightly soluble yellow precipitate formed by the action of sulfur on sodium monosulfide is sodium disulfide.

Sodium in solution, 0.5797 g. Sulfur necessary for formation of Na_2S, 0.4040 g.; for the formation of Na_2S_2, 0.8080 g. The solution was colored a light lavender after the addition of 0.4020 g. of sulfur, and was colorless after the addition of 0.0015 g. more. When a total of 0.8026 g. of sulfur had been added, a yellow precipitate was formed that was nearly as bulky as the original monosulfide, and the solution was orange-yellow. Disulfides were likewise formed by the further action of sulfur upon lithium and potassium monosulfides.

The end-point corresponding to the disappearance of the disulfide pre-

Table I

Weight of Selenium Dissolved by Known Weights of Alkali Metal in Ammonia Solution

Metal, M	Wt. of M G.	Concn. of M *N*	Selenium dissolved A[a]	B[b]	Atomic ratios A	B
Li	0.1678	0.69	0.9690	5.1377	1.012	5.36
Li	.0173[c]	.070	.0922	0.5171	0.976	5.47
Li	.0634[c]	.21	.3412	1.8884	.985	5.45
Na	.0620	.067	...	0.6031	..	5.65
Na	.0486	.10	...	.4678	..	5.59
Na	.1406	.25	...	1.4022	..	5.79
Na	.2061	.37	.3535	1.9686	.996	5.55
Na	.0487	.054	.0829	0.4776	.989	5.70
K	.0506	.037	...	.2557	..	4.99
K	.1299	.14	.1300	.6632	.988	5.04
K	.1127	.12	.1110	.5758	.972	5.04
K	.1206	.13	.1203	.6034	.985	4.94

[a] At end of first stage, corresponding to disappearance of blue color of the alkali metal solution.

[b] Maximum amount of selenium dissolved by polyselenide solution.

[c] 4.2% iron in lithium. Corrected weights of lithium given.

Weight of Sulfur Dissolved by Known Weights of Alkali Metal in Ammonia Solution

Metal, M	Wt. of M G.	Sulfur dissolved A[d]	B[e]	Atoms of S per 2 M A	B
Na	0.2228	...	0.5995	...	3.86
Na	.3330	0.2570	.8867	1.107	3.82
K	.1118	.0519	.1841	1.132	4.02
K	.2852	.1161	.4900	0.993	4.19
K	.1402	.0554	.2383	.964	4.15
K	.4851	...	.8020	...	4.03
K	.4626	.2065	...	1.09	..
Li	.0944	...	.8676	...	3.98
Li	.0989	.2648	.9186	1.16	4.02

[d] At end of first stage, corresponding to disappearance of blue color of alkali metal solution.

[e] S dissolved to point where the disulfide ppt. has just disappeared.

cipitate and the formation of the tetrasulfide solution was difficult to obtain accurately because of the rapidity of the reaction. The sticks of sulfur became so badly corroded at this stage that it was considered better to add most of the sulfur to the reaction mixture in lump form, using the stick merely to determine the end-point.

The experimental data are given in Table I.

The Polyselenides of the Alkali Metals

Selenium reacts very readily with solutions of lithium, sodium[2,6] and potassium at —33°, initially to give white, sparingly soluble and apparently amorphous precipitates of the corresponding monoselenides. Further reaction with an excess of selenium leads to the formation of soluble diselenides, and then to the formation of very soluble polyselenides of higher selenium content. The average compositions of the polyselenides whose solutions were in equilibrium with selenium were found to be, within the concentration ranges studied, $K_2Se_{5.0}$, $Na_2Se_{5.7}$ and $Li_2Se_{5.4}$ (see Table I). Inasmuch as solutions of the selenides of the formulas K_2Se_2 and K_2Se_4 are red, while a solution of the selenide K_2Se_3 is green, polyselenides of these compositions must be definite chemical compounds (see Table II).

The time necessary for the formation of the initial precipitate of monoselenide varied from less than five to about 20 minutes, being shorter, the greater the initial concentration of the alkali metal. The composition of the solution in equilibrium with the monoselenide could not be determined accurately by observing the point of complete disappearance of the precipitate, for the solution was too intensely colored. In order to show that this solution contained the diselenide, the product of the reaction of two atomic parts of potassium with one and one-half atomic parts of selenium[7] was washed several times, the soluble matter on analysis proving to be potassium diselenide.

Anal. Subs. (dried in a vacuum at 20°): 0.2232; (dried in a vacuum at 150°) 0.2215: NH_3 ($^1/_2$),[8] 0.00077; KCl ($^1/_2$), 0.0720. Calcd. for K_2Se_2: K, 33.1. Found at 150°: K, 34.1; NH_3, 0.7.

The high value for potassium is due to the presence of a small amount of monoselenide transferred in solution with the diselenide. Potassium diselenide is slightly soluble in ammonia at room temperature, but much more soluble at —33°.

Equilibrium between the polyselenide solutions and selenium was generally reached in one or two days. The stick frequently gained a very little in weight when allowed to remain in contact with the solution after equilibrium had been reached, perhaps because of absorption of the prod-

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[6] Kraus, unpublished observations.

[7] In a 2-legged glass reaction tube, at room temperature. Franklin, THIS JOURNAL, **27**, 831 (1905); **29**, 1694 (1907); **35**, 1460 (1913); *J. Phys. Chem.*, **15**, 915 (1911).

[8] Refers to the proportion of substance taken for analysis.

ucts of the reaction by the selenium. The exact value of the equilibrium ratio is therefore in doubt.

TABLE II

COLOR OF LIQUID AMMONIA SOLUTIONS OF THE POTASSIUM POLYSELENIDES AT 20°

Salt	Very dil. soln.	Moderate concns.	Very concd.
K_2Se	colorless	very slightly soluble	
K_2Se_2	pale red	transparent red[a]	transparent red[a]
K_2Se_3	pale greenish-yellow	deep green[a]	deep green[a]
K_2Se_4	pale yellow	brownish-red[a]	deep red[a]
K_2Se_5	pale yellow	olive-green and reddish-brown mixed color (daylight); red, transmitted electric light	deep red[a]

When ammonia free, K_2Se_3, K_2Se_4 and K_2Se_5 are gray or grayish-black in appearance.

[a] To daylight.

Table II shows the variation in the color of potassium polyselenide solutions with concentration. Polyselenides of the desired composition were prepared by the action of the calculated quantity of selenium on weighed amounts of potassium[3] in two legged reaction tubes.[7] The selenides of the formulas K_2Se, K_2Se_2 and K_2Se_3 dissolve completely in a small volume of water in the absence of air, while the substances K_2Se_4 and K_2Se_x invariably leave some residue, probably because of the fact that solutions of the higher polyselenides are unstable in water. Solutions of all polyselenides in water are deep red and, as is well known, readily absorb oxygen from the air with separation of selenium. The corresponding polyselenide solutions in ammonia are not oxidized to any great extent by a current of dry air.

Ammonia Retained by the Polysulfides and Polyselenides.—The polyselenides, K_2Se_2-K_2Se_5 inclusive, dried in a vacuum at 20°, retained from 0.3 to 0.7% of ammonia, some of which was given off during heating in a vacuum at 140–150°. Sodium tetrasulfide, as prepared in ammonia solution, retains slightly more than one molecular proportion of ammonia when dried in a vacuum at room temperature. This was not entirely given off on heating at 140° in a vacuum. Potassium tetrasulfide and monosulfide retain less than 0.1 molecular proportion of ammonia after being dried in a vacuum at room temperature. The lithium polysulfides with four or more atoms of sulfur retain several molecular proportions of ammonia under similar conditions. In the case of lithuim tetrasulfide, nearly all the ammonia was given off in a vacuum at 140°.

Discussion

According to Hugot[2] the products of the action of solutions of the alkali metals (M) in liquid ammonia on an excess of sulfur, selenium or tellurium have the respective formulas, M_2S_5, M_2Se_4, and M_2Te_3. Kraus and Chiu[3] have previously shown that the final product of the action of an excess of tellurium on a solution of sodium has the composition represented by the formula Na_2Te_4. Inasmuch as the highest polyselenides obtained in the present work contained from 5.0 to 5.8 atoms of selenium for two atoms of alkali metal, it is evident that Hugot failed to attain equilibrium in his experiments. The reaction between sulfur and solutions of potassium or sodium in liquid ammonia was found to be more complex than stated by Hugot. Recognizing the fact that sulfur "dissolves" in liquid ammonia,[2] this author separated the alkali metal polysulfide from the uncombined sulfur, after removal of solvent ammonia, by the action of water vapor. Consequently, the polysulfide obtained was the highest one stable in aqueous solution under the conditions of the experiment.

Solutions of the polysulfides of sodium and potassium in water and in ethyl alcohol have been extensively investigated.[9] The compounds with formulas from Na_2S to Na_2S_5, from K_2S to K_2S_6 inclusive, and Na_2Se, Na_2Se_2, Na_2Se_3, Na_2Se_4 and Na_2Se_6 have been shown to exist by thermal analysis.[10] The mixed color of a solution in liquid ammonia of a substance of the composition M_2Se_5 suggests a mixture of M_2Se_4 with a higher polyselenide, perhaps M_2Se_6 (M = Na, K, or Li).

In conclusion, the author wishes to express his thanks to Dr. C. A. Kraus for his kind and helpful interest in this work.

Summary

An investigation has been made of the reactions between sulfur and selenium and solutions of lithium, sodium, and potassium in liquid ammonia. Letting M represent an alkali metal, the reactions may be expressed by the following equations.

$2M + S = M_2S$, $M_2S + S = M_2S_2$, $M_2S_2 + 2S = M_2S_4$, $M_2S_4 + (x - 4)\ S = M_2S_x$; $2M + Se = M_2Se$, $M_2Se + Se = M_2Se_2$, $M_2Se_2 + Se = M_2Se_3$, $M_2Se_3 + Se = M_2Se_4$, $M_2Se_4 + (x - 4)\ Se = M_2Se_x$. ($x$ = 5 to 6.)

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[9] Küster and Heberlein, *Z. anorg. Chem.*, **43**, 53 (1905). Küster, *ibid.*, **44**, 431 (1905). Thomas and co-workers, *J. Chem. Soc.*, **125**, 2207 (1924); **123**, 1181 (1923); **123**, 1726 (1923).

[10] Thomas and Rule, *J. Chem. Soc.*, **111**, 1063 (1917). Mathewson, THIS JOURNAL, **29**, 867 (1907).