Summary

The instantaneous coefficients of expansion of aluminum, copper, silver, rock salt, quartz parallel to the optic axis, and Pyrex glass have been determined by an interference method for temperatures between 90° and 315°K.

The coefficients of expansion of the crystalline solids approach zero at low temperatures, in agreement with the prediction of the third law of thermodynamics. The coefficients of expansion change slightly more rapidly with temperature than do the specific heats.

Guided by a semi-theoretical expression due to Grüneisen, terms depending on the constraints between atoms are introduced into the equation for the entropy of solids. The entropies of six monatomic solid metals are satisfactorily represented by the equation $S_{p,\,298} = 3/2 R ln M + R ln V - 3/2 R ln\ (C_p/3\alpha)_{T\,=\,160} + 26.5$. A simple extension to binary compounds proves successful.

It is pointed out that data at still lower temperatures are required before adequate tests of theories of lattice mechanics can be made.

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[Contribution from the Chemical Laboratories of Brown and Stanford Universities]

SOLUTIONS OF THE ELECTRONEGATIVE ELEMENTS IN LIQUID AMMONIA. I. THE ACTION OF SELENIUM, TELLURIUM, ARSENIC AND A SOLUTION OF SULFUR IN LIQUID AMMONIA UPON CYANIDES

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Introduction

Chlorine dissolves readily in water in accordance with the equation, $Cl_2 + HOH \rightleftharpoons HCl + ClOH$. A solution of chlorine in water contains, therefore, in addition to free chlorine, hydrochloric and hypochlorous acids, which contain, in terms of the valence theory respectively, univalent negative and univalent positive chlorine. It is known that liquid ammonia reacts with the halogens in the same manner that water does, although more energetically. Chlorine and bromine, for instance, readily react with liquid ammonia, even at —40°, to form ammonium chloride or bromide and nitrogen gas in the same manner that fluorine reacts with water to give hydrofluoric acid and ozonized oxygen.[2] Iodine is very

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[1] National Research Fellow.

[2] There is evidence for the formation during these reactions of the very unstable chloro- and bromo-amines, the hypochlorous and hypobromous acids of the ammonia system (Franklin, unpublished work).

soluble in a small volume of liquid ammonia, but reacts reversibly with it on dilution in the sense of the equation $I_2 + 2NH_3 \rightleftharpoons INH_2 + NH_4I$ to form iodine-amine or a deammonation product and ammonium iodide.[3] Since the iodine-amine may be regarded as a hypo-iodous acid of the ammonia system,[4] this reaction is entirely analogous to the reaction between chlorine and water.

Ruff and Geisel,[5] Franklin and Kraus,[6] Moissan[7] and others have found that sulfur slowly dissolves in liquid ammonia at ordinary temperatures without evolution of gas. The first two authors have suggested that sulfur reacts with ammonia in the same manner that chlorine reacts with water, perhaps in accordance with the equation

$$10S + 4NH_3 \rightleftharpoons 6H_2S + N_4S_4 \qquad (1)$$

for it was found that silver iodide in ammonia solution reacts with dissolved sulfur to give a precipitate of silver sulfide and a solution of sulfur nitride, N_4S_4. Both of the substances on the right-hand side of the equation are combined with the solvent, hydrogen sulfide forming ammonium sulfide and nitrogen sulfide a mixture of the two acids, $S(NH)_2$ and $S_2(NH)_2$, which may be regarded, respectively, as a sulfurous and a thiosulfuric acid of the ammonia system.[4,8] The products of the reaction of sulfur and liquid ammonia therefore contain sulfur in different states of nitridation (oxidation), just as do the products of the action of chlorine on water or of iodine on ammonia. In support of Equation 1, Ruff and Geisel have found that small quantities of ammonium sulfide may be volatilized by passing a current of dry hydrogen through a saturated solution of sulfur in ammonia.[3] Furthermore, hydrogen sulfide and sulfur nitride dissolved in liquid ammonia were found to react to give a solution identical with the solution of elementary sulfur in ammonia.

Some years later, Ruff and Hecht[9] upon examining the freezing-point curve of solutions of sulfur in liquid ammonia found one compound, $S \cdot 6NH_3$, m. p. —78.5°, characterized by a flat maximum and obtained evidence for the existence of $S \cdot 3NH_3$. These authors conclude, therefore, that the previously assumed equilibrium between sulfur nitride and hydrogen sulfide in liquid ammonia, as represented by Equation 1, is of minor importance, as the sulfur for the most part is present in the form of the solvates mentioned above.

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[3] Ruff, *Ber.*, **33**, 3025 (1900). Hugot, *Compt. rend.*, **130**, 505 (1900).

[4] Franklin, THIS JOURNAL, **46**, 2142 (1924), and unpublished work.

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

[6] Franklin and Kraus, *Am. Chem. J.*, **20**, 830 (1898).

[7] Moissan, *Compt. rend.*, **132**, 510 (1901).

[8] Sulfur nitride may be regarded as a mixed anammonide of sulfurous and thiosulfuric acids; $N_4S_4 + 2NH_3 = 2S(NH)_2 + S_2(NH)_2$.

[9] Ruff and Hecht, *Z. anorg. Chem.*, **70**, 49 (1911). Hecht, "Dissertation," Danzig, **1911**.

Now, certain objections may be raised to the theories of Ruff and Geisel and of Ruff and Hecht in regard to the constitution of solutions of sulfur at temperatures far removed from the freezing point of the solvent. Ammonium monosulfide should not exist in the presence of an excess of sulfur, and indeed the author found that these two substances readily react in liquid ammonia to form very soluble ammonium polysulfides. If sulfur nitride, S_4N_4, is to be regarded as a mixed anammonide of sulfurous and thiosulfuric acid, and if aquosulfurous acid reacts with sulfur to form aquothiosulfuric acid,[9a] one would expect the sulfurous acid part of sulfur nitride to take up additional sulfur, in accordance with the equation $S + S(NH)_2 = S_2(NH)_2$ to form ammonothiosulfuric acid. It was found that sulfur nitride did react very slowly with sulfur solution to form a deep blue solution which, however, appeared to contain in addition some other sulfur acids of the ammonia system.[10] Franklin and Kraus[11] have found that a solution of sulfur in liquid ammonia conducts the electric current as well as many salts in this solvent. It would seem logical that the ions taking part in the conduction process were derived in some such manner as indicated by Equation 1, although it is possible that the sulfur is all in the anion and the cation is some sort of a solvent complex associated with a positive charge.[12] If the latter alternative were true, we should not expect gas to be liberated at either electrode upon electrolysis, for sulfur dissolves in ammonia without evolution of gas, and the solution is not decomposed in the presence of a catalytic surface such as a platinum electrode. Preliminary experiments indicated that nitrogen and hydrogen were liberated during electrolysis of a solution of sulfur in liquid ammonia in such volumes as to indicate very appreciable quantities of dissolved sulfur nitride and ammonium sulfide.[13]

It was with the hope of obtaining further evidence concerning the constitution of solutions of sulfur in ammonia that the present investigation was undertaken. As a first step in the study of the chemical properties of sulfur solutions an investigation has been made of the action upon this solution of a number of metallic cyanides. In conjunction with this work it was of interest to see whether selenium, tellurium and arsenic would react with cyanides in the same manner as sulfur.

[9a] In small amounts only, due to the instability of the free acid. Aloy, *Compt. rend.*, **137**, 51 (1903); *J. Chem. Soc.*, **61**, 199 (1892).

[10] Ruff and Hecht (Ref. 9 p. 55) have obtained evidence for the existence of three compounds formed by the interaction of ammonia solutions of sulfur nitride and sulfur.

[11] Franklin and Kraus, *Am. Chem. J.*, **24**, 89 (1900).

[12] Iodine, iodine mono- and trichloride form conducting solutions in which all of the halogen appears to be in the anion. Bruns, *Z. physik. Chem.*, **118**, 89 (1925). Bruner and Galecki, *ibid.*, **84**, 513 (1913). Bruner and Bekier, *ibid.*, **84**, 570 (1913).

[13] These results will be published at a later date.

Purification of Materials and Manipulation

Selenium and sulfur were prepared as described in a preceding article.[14] Tellurium was purified according to the method of Kraus and Chiu.[15] Arsenic was chemically pure material, the oxide coat of which had been sublimed away by strong heating in a current of ammonia.

The reactions described in this paper were carried out in two-legged glass reaction tubes according to the methods of Franklin.[16] The manipulations may be understood from the description of a typical experiment, in which aluminum selenocyanide was prepared.

Aluminum cyanide was prepared in one leg of a reaction tube by the action of a solution of mercuric cyanide in liquid ammonia upon aluminum wire.[17] The resulting solution of aluminum cyanide was decanted into the other leg of the reaction tube, in which had been placed selenium in excess of the amount theoretically required for the reaction. The leg of the reaction tube containing the residue of amalgamated aluminum was opened, cleaned out and resealed. Into this leg was decanted the solution of aluminum selenocyanate. As this substance was so soluble in ammonia that it could not be purified by crystallization, analyses were made of the crude solid remaining after evaporation of the solvent from the reaction tube.

Thiocyanates were similarly prepared by the action of a solution of sulfur in liquid ammonia upon a cyanide. The soluble cyanides of potassium and aluminum were carefully titrated with sulfur solution so as to obtain a thiocyanate as pure as possible. Magnesium cyanide was used in excess, for it is only slightly soluble in ammonia.

For the purpose of analysis, specimens were treated with water and then with dil. sulfuric acid. Selenocyanates were thus decomposed with the formation of red selenium, hydrocyanic acid and salts of ammonia and the metal present in the specimen. The selenium was removed by filtration and the remainder of the analyses made upon the filtrate. It was generally found that a small additional quantity of selenium could be precipitated from a portion of this filtrate by boiling. It was necessary to remove hydrocyanic acid by precipitation as silver cyanide prior to the determination of ammonia. The sulfuric acid solution of a thiocyanate was treated with silver nitrate to precipitate silver thiocyanate and the remainder of the analyses were made upon the filtrate from this precipitate.

Equilibria in the Solution of Sulfur in Liquid Ammonia

Sulfur solution was found to react very readily with solutions of the cyanides of potassium, aluminum and magnesium in liquid ammonia to give

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[14] Bergstrom, This Journal, **48**, 146 (1926).

[15] Kraus and Chiu, *ibid.*, **44**, 2001 (1922).

[16] Franklin, *ibid.*, **27**, 831 (1905); **29**, 1694 (1907); **35**, 1460 (1913); **46**, 1545 (1924); *J. Phys. Chem.*, **15**, 510 (1911); **19**, 539 (1915).

[17] Bergstrom, This Journal, **46**, 1559 (1924).

the corresponding thiocyanates to the exclusion of appreciable quantities of by-products. It is therefore evident that if a solution of sulfur in liquid ammonia contains sulfur nitride and ammonium sulfide, as the work of Ruff and Geisel would indicate,[3] these two substances must either be capable of reacting separately with cyanide solutions to give thiocyanates or, failing to do this, they must react with one another, in accordance with Equation 1, read from right to left, to give sulfur, which in turn reacts with the cyanides. The following experiments showed the latter alternative to be correct.

A solution of sulfur nitride, N_4S_4, in liquid ammonia was mixed with a solution of aluminum or zinc cyanide in excess in a two-legged reaction tube. At the end of a month the yellow color of the sulfur nitride solution had not appreciably lightened, showing that sulfur nitride was not to any great extent converted to thiocyanate. A solution of ammonium sulfide, prepared by passing dry hydrogen sulfide into liquid ammonia in a reaction tube cooled to —40°, failed to react in a week with aluminum cyanide to form appreciable quantities of thiocyanate. It was found, however, that ammonium polysulfide, prepared by the action of sulfur upon ammonium monosulfide solution, slowly became colorless when poured into a solution of aluminum cyanide. The blue solution resulting from the very slow action of sulfur nitride upon sulfur, reacts with aluminum cyanide to form some thiocyanate and a yellow solution of sulfur nitride. Cyanides, therefore, may react with polysulfide sulfur or with such extra sulfur as may have entered into combination with sulfur nitride, to form thiocyanate, ammonium sulfide and sulfur nitride. These latter two substances then react with each other to form sulfur, which in turn reacts with cyanides to form thiocyanates. When sulfur dissolves in liquid ammonia one is concerned with a number of reactions and equilibria, among which are the following: $10S + 6NH_3 \rightleftharpoons S_4N_4 + 6H_2S$; $H_2S + 2NH_3 = (NH_4)_2S$; $S_4N_4 + 2NH_3 = 2S(NH)_2 + S_2(NH)_2$; $(NH_4)_2S + xS = (NH_4)_2S_{x+1}$; $(NH_4)_2S_{x+1} \rightleftharpoons (NH_4)_2S_x + S$, etc., $S_4N_4 + S \rightleftharpoons$ other sulfur acids of the ammonia system.

From our knowledge of the reactions between sulfur solutions and the cyanides of potassium, magnesium and aluminum, we should expect silver and mercuric cyanides to react with dissolved sulfur to form thiocyanates alone. While some thiocyanate is obtained, silver and mercuric sulfides are precipitated in considerable quantities at the same time and the solution is found to contain sulfur nitride. These reactions may reasonably be interpreted by assuming in solution sulfide ions formed in accordance with Equation 1, read from left to right. That mercuric sulfide is not instantaneously precipitated when sulfur solution is poured into a solution of mercuric cyanide, affords evidence for the existence in solution of ammonium polysulfide, for the mercuric polysulfide first formed may exist for a very short length of time before it decomposes into sulfur and the more stable mercuric monosulfide.

The Action of Selenium, Tellurium and Arsenic on Solutions of Cyanides in Liquid Ammonia

Pure selenium very slowly attacks the elements arsenic, zinc, copper and magnesium and readily reacts with the cyanides of magnesium, aluminum, zinc and potassium to form the corresponding selenocyanates. An excess of selenium was found to precipitate nearly all of the silver from a solution of silver cyanide, the precipitate containing silver selenide and selenium nitride or a silver salt of this substance, while the solution contained ammonium selenocyanate. Mercuric cyanide and selenium react in a similar manner. Obviously, these reactions are closely analogous to the corresponding reactions of a solution of sulfur and one may conclude that selenium has an extremely slight solubility in liquid ammonia, such a solution resembling in its character the solution of sulfur in the same solvent. In other words, selenium tends to react with ammonia to form selenium nitride and ammonium selenide.

Tellurium failed to react with magnesium, arsenic or copper in liquid ammonia, but did dissolve very slowly in solutions of aluminum and potassium cyanides. Evaporation of these solutions to dryness appeared to cause decomposition into cyanide and elementary tellurium. No definite compounds were isolated. Arsenic failed to react with solutions of potassium or aluminum cyanides over a long period of time.

Nitridizing Properties of Sulfur and Selenium

Sodium in liquid ammonia solution precipitates, or reduces silver from a solution of silver iodide just as any element, in general, displaces, or reduces, a less electropositive element from solutions of its salts.[18] In a similar manner sulfur precipitates, or nitridizes (oxidizes), lead from a solution of potassium polyplumbide in liquid ammonia in accordance with the equation, $K_4^{++++}Pb_9^{----} + 2S = 2K_2S + 9Pb$, just as any element, in general, displaces, or nitridizes, a less electronegative element from a solution containing this latter as an anion.[19] The halogens are strong nitridizing or oxidizing agents in reactions that do not involve the replacement of one element by another. Even selenium slowly nitridizes cuprous cyanide in liquid ammonia solution to form a precipitate of cupric selenide and a solution of cupric selenocyanate. Sulfur or selenium precipitates a copper sulfide or selenide from a solution of cuprous thiocyanate in ammonia, at the same time nitridizing a portion of the cuprous salt to the cupric condition. The action of sulfur and selenium upon solu-

[18] Kraus and Kurtz, THIS JOURNAL, **47**, 54 (1925).

[19] Bergstrom, *ibid.*, **47**, 1503 (1925).

tions of cyanides may be regarded as a nitridation, inasmuch as a carbonite of the ammonia system is converted to a mixed thio- or selenocarbonate.[20]

Preparations of Thiocyanates and Selenocyanates

Potassium Thiocyanate.—The reaction between potassium cyanide and sulfur solution is noticeably slower than the reaction between sulfur and the cyanides of magnesium or aluminum, in spite of the low solubility of magnesium cyanide. Calcd. for KSCN:-SCN, 59.8. Found: 59.0.

Magnesium Thiocyanate.—Preparation 1. Subs. (20°),[21] 0.4135: (1/1)[22] 0.6687 AgSCN; (1/4) of filtrate from AgSCN, 0.03393 NH_3; (1/2) 0.1110 $Mg_2P_2O_7$.

Preparation 2. Subs. (−33°), 0.7219: (20°) 0.6189, (136°) 0.5479. A portion of the salt liquefied at this temperature. (1/1) 0.9916 AgSCN; (2/5) 0.05324 NH_3; (3/5) 0.2006 $Mg_2P_2O_7$. Calcd. for $Mg(SCN)_2 \cdot 4NH_3$: Mg, 11.7; SCN, 55.7; NH_3, 32.7. Found (20°): Mg, 11.7, 11.8; SCN, 56.6, 56.1; NH_3, 32.8, 33.0.

Aluminum Thiocyanate.—In Preparations 1 and 3 approximately the calculated amount of sulfur was used; in Preparation 2 a slight excess.

Preparation 1. Subs. (20°), 0.5166: (1/1) 0.8903 AgSCN; (1/4) 0.03908 NH_3; (1/2) 0.0490 Al_2O_3.

Preparation 2. Subs. (20°), 0.6476: (77°) 0.5719; (1/4) 0.02813 NH_3; (3/4) 0.0828 Al_2O_3.

Preparation 3. Subs. (30°), 0.9245: (1/4) 0.06864 NH_3; (1/2) 0.0879 Al_2O_3.

Calcd. for $Al(SCN)_3 \cdot 5NH_3$: Al, 9.4; SCN, 60.8; NH_3, 29.7. Found: (20°): Al, 10.0, 9.0, 10.1; SCN, 60.3; NH_3, 30.2, 29.9, 29.7.

Potassium Selenocyanate.—Calcd. for KSeCN: K, 27.1; Se, 54.9. Found (20°): K, 27.6, 27.5; Se, 53.3, 54.5; NH_3, 1.0,—.

Magnesium Selenocyanate. *Preparation 1.*—Subs. (20°), 0.2648: (1/2) 0.0493 $Mg_2P_2O_7$; (1/2) 0.03037 NH_3.

Preparation 2. Subs. (−33°), 0.5905: (20°) 0.5370; (135°) 0.5033: (2/5) 0.03570 NH_3; (3/5) 0.1221 $Mg_2P_2O_7$.

Calcd. for $Mg(SeCN)_2 \cdot 4NH_3$: Mg, 8.0; NH_3, 22.5. Found (20°): Mg, 8.1, 8.3; NH_3, 22.9, 22.9. Magnesium selenocyanate darkens when heated in a vacuum at 135°, indicating slight decomposition. Approximately six molecules of ammonia are retained by the salt at −33°.

Aluminum Selenocyanate.—Aluminum selenocyanate decomposes slightly when heated in a vacuum at 75°. Subs. (20°), 0.6662, 0.7113, 0.9722; (70°) —, 0.6445; 0.8915: Al_2O_3, (4/5) 0.0657, (3/5) 0.0508, (2/5) 0.0468; Se, No. 3, (1/1) 0.5411. Calcd. for $Al(SeCN)_3 \cdot 5NH_3$: Al, 6.3; Se, 55.5. Found: Al, 6.3, 6.3, 6.4; Se 55.7. Dried in a vacuum at 70°, this salt retained from 2.0 to 2.5 molecules of ammonia.

Zinc Selenocyanate.—This salt melts in a vacuum around 100° with slight decomposition. The zinc cyanide used in Preparation 1 was prepared by the action of an ammonia solution of mercuric cyanide on zinc; that used in Preparation 2 was prepared by adding potassium cyanide to a solution of zinc chloride in water.

Preparation 1. Subs. (20°), 1.1925: (1/5) 0.04764 NH_3; (2/5) 0.2099 $Zn_2P_2O_7$.

Preparation 2. Subs. (20°), 0.8014: (1/1) 0.3721 Se; (2/5) 0.1449 $Zn_2P_2O_7$.

Calcd. for $Zn(SeCN)_2 \cdot 4NH_3$: Zn, 19.0; Se, 46.1; NH_3, 19.8. Found: Zn, 18.9, 19.4; NH_3, 20.0; Se, 46.4.

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[20] Potassium cyanide may be regarded as a potassium ammonocarbonite [Franklin, *J. Phys. Chem.*, **27**, 167 (1923)]. Iodine nitridizes potassium cyanide to potassium cyanamide, a potassium ammonocarbonate, for mixed iodocarbonates do not exist.

[21] That is, dried in a vacuum at 20°.

[22] Refers to proportion of substance taken for analysis.

Cupric Selenocyanate.—Copper slowly precipitates mercury from a solution of mercuric cyanide in liquid ammonia with the formation of a mixture of cuprous and cupric cyanides. In contact with an excess of copper, the cupric salt is reduced to cuprous cyanide, which forms colorless crystals moderately soluble in liquid ammonia at room temperatures. Selenium reacts slowly with a solution of this salt to form a strongly-colored blue solution of cupric selenocyanate and a black precipitate of cupric selenide, perhaps in accordance with the equation $2CuCN + 3Se = Cu(SeCN)_2 + CuSe$. The cupric salt was not prepared entirely free from cuprous selenocyanate.

Reactions of Potassium Tetrasulfide, Pentaselenide and Tetratelluride Solutions[22a] with Potassium Cyanide.—The first two salts react with potassium cyanide solution at room temperature to form potassium thio- or selenocyanate and a precipitate, probably of potassium disulfide or diselenide. Potassium tetratelluride and potassium cyanide do not appear to react with each other. It will be remembered that cyanide solutions react with the polysulfide sulfur of ammonium polysulfides to form thiocyanates.

Previous Preparation of Selenocyanates.—Crookes[23] prepared in water solution and analyzed the selenocyanates of potassium, silver, lead and mercury. The selenocyanates of sodium, ammonium, barium, strontium, calcium, magnesium, zinc, iron and copper were prepared but not analyzed. Very little work has subsequently been done on the preparation of selenocyanates.[24]

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

Summary

1. According to Ruff and Geisel, sulfur dissolves in liquid ammonia in accordance with the reaction $10S + 4NH_3 \rightleftharpoons 6H_2S + N_4S_4$. An entirely analogous reaction takes place when chlorine dissolves in water, $Cl_2 + H_2O \rightleftharpoons HCl + ClOH$. The existence of the first equilibrium has been confirmed by a study of the action of solutions of metallic cyanides upon a solution of sulfur in liquid ammonia. Sulfur dissolves in liquid ammonia in a more complex manner than indicated by the first equation. Preliminary experiments indicate that sulfur solutions contain very appreciable quantities of ammonium polysulfide and sulfur nitride, or the products of the action of sulfur nitride upon an excess of sulfur.

2. Selenium must have an extremely slight solubility in liquid ammonia, such solutions resembling solutions of sulfur in constitution.

[22a] Prepared by the action of a liquid ammonia solution of potassium upon the calculated amounts of sulfur, selenium or tellurium.

[23] Crookes, *Ann.*, **78**, 177 (1851).

[24] Cameron and Davy, *Chem. News*, **44**, 63 (1881). Rosenheim and Pritze, *Z. anorg. Chem.*, **63**, 275 (1909). Muthmann and Schröder, *Ber.*, **33**, 1765 (1900).

3. Sulfur and selenium behave in liquid ammonia as weak nitridizing (oxidizing, de-electronizing) agents.

4. Solutions of cyanides in liquid ammonia react very readily with sulfur and selenium, much more slowly with tellurium, and not at all with arsenic. The following new compounds have been prepared: $Al(SCN)_3 \cdot 5NH_3$, $Mg(SCN)_2 \cdot 4NH_3$, $Mg(SeCN)_2 \cdot 4$ and $6(?)NH_3$, $Zn(SeCN)_2 \cdot 4NH_3$, $Al(SeCN)_3 \cdot 5NH_3$.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 107]

THE CRYSTAL STRUCTURE OF SODIUM PERIODATE

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Introduction

The similarity of crystal form of sodium periodate, $NaIO_4$, and calcium tungstate, $CaWO_4$, as well as of some periodates of other univalent metals and tungstates and molybdates of other bivalent metals, was recognized by Hiortdahl.[1] To these Barker[2] added the compounds $KRuO_4$ and $KOsO_3N$ and discussed the bearing of such cases of isomorphism on valence theory. These crystals are all tetragonal[3] and have axial ratios ranging from 1:1.521 to 1:1.634. Crystallographers have not, however, assigned all of these compounds to the same *class* of symmetry. Thus sodium periodate is given[3] as ditetragonal bipyramidal (D_{4h}), calcium tungstate as tetragonal bipyramidal (C_{4h}), and lead molybdate as tetragonal pyramidal (C_4). The present work casts doubt upon the reality of these differences in symmetry.

From some x-ray-spectrometer measurements it was concluded[4] that in wulfenite, $PbMoO_4$, and scheelite, $CaWO_4$, the metal atoms were placed on two interpenetrating "diamond" arrangements elongated in the direction of the tetragonal axis. These data were theoretically discussed by Niggli and Faesy,[5] and an attempt was made to determine the space-group symmetry; owing, however, to an omission[6] in the space-group tables used, the space group C_{4h}^6 was incorrectly eliminated. In some unpublished work in this Laboratory, Dr. R. M. Bozorth and one of us (R. G. D.) found that symmetrical, basal-plane Laue photographs of wulfenite showed

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[1] Hiortdahl, *Z. Kryst. Min.*, **12**, 411 (1887).

[2] Barker, *J. Chem. Soc.*, **101**, 2487 (1912).

[3] Groth, "Chemische Krystallographie," Engelman, Leipzig, **1908**, vol. 2, pp. 175, 393.

[4] Dickinson, THIS JOURNAL, **42**, 85 (1920).

[5] Niggli and Faesy, *Z. Kryst.*, **59**, 473 (1924).

[6] This omission has since been corrected by K. Weissenberg, *ibid.*, **63**, 173 (1926).