that 528 g. of 24.3% peroxide was concentrated at 0° to 102 g. of 91.1% material. The yield was, therefore, 65%; the time taken was four hours. It is interesting to notice that in comparison Maass and Hatcher cite an experiment of Wolfenstein's, in which he concentrated 802 g. of 4.5% peroxide to 66.6% and obtained a 28.3% yield. This experiment was not carried out under reduced pressure, as they state, but was performed in an evaporating dish on a water-bath at 75°.

Summary

A quantitative study has been made of the preparation of concentrated solutions of hydrogen peroxide. A simple method of concentrating hydrogen peroxide solutions to 90% has been described. The yields obtained are excellent.

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MOLYBDENUM THIOCYANATE AND THE QUALITATIVE DETECTION OF MOLYBDENUM

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The red color produced by the action of reducing agents on a soluble hexavalent molybdenum compound in the presence of a thiocyanate salt in acid solution appears to have been first noticed by Braun[2] in 1867. Skey[3] also described it in the same year.

In 1903, Chilesotti[4] electrolyzed a solution containing hexavalent molybdenum, obtaining as a consequence a solution of molybdenum trichloride. This salt, combined in water solution with potassium or ammonium salts, produced a red solution presumably of the composition K_3MoCl_6.

He found later that this double salt added to potassium thiocyanate yielded on crystallization an orange-red double potassium molybdenum salt of the composition $K_3Mo(SCN)_6.4H_2O$.[5] According to Sand and Burger,[6] hexavalent molybdenum electrolytically reduced in the presence of ammonium thiocyanate gave thiocyanate salts of quadrivalent molybdenum. These salts were obtained with pyridine or quinoline of crystallization by extracting the water solution with ether and extracting this ether

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[1] This material is taken from the thesis of Mr. C. E. Swartz presented in partial fulfilment of the requirements for the degree of Master of Science at the University of Wisconsin.

[2] Braun, *Z. anal. Chem.*, **6,** 86 (1867).

[3] Skey, *Chem. News*, Am. Reprint I, 296 (1867).

[4] Chilesotti, *Atti. accad. Lincei,* **12,** ii, 22, 67 (1903).

[5] Chilesotti, *Gazz. chim. ital.*, **34,** ii, 493 (1904).

[6] Sand and Burger, *Ber.*, **38,** 3384 (1905).

solution with pyridine, or quinoline. Noyes and Bray,[7] in their "A System of Qualitative Analysis" assumed the formula of the red thiocyanate of molybdenum used in its qualitative detection to be $Mo(SCN)_4$.

Later, Maas and Sand[8] determined that the compounds spoken of by Sand and Burger were compounds of tervalent rather than quadrivalent molybdenum, and the results of Rosenheim and Garfunkel[9] are in agreement with this view. This reaction was made use of by King[10] in the development of a colorimetric method for the quantitative determination of molybdenum in tungsten or tungsten ores.

The instability of molybdenum thiocyanate necessitates care in selecting the reducing agent used in its formation. If the reducing action is too rapid, the red color will be discharged almost as rapidly as formed and changed to a distinct blue often known as molybdenum blue. This will be replaced by a darker blue and finally by a black or gray, if the reducing atmosphere is maintained.

The composition of this compound of molybdenum, which gives the blue color, is not definitely known.

Experimental Part

To ascertain the optimum conditions for the qualitative detection of molybdenum as molybdenum thiocyanate the following experiments were performed.

Effect of Acid Concentration

To a solution containing a known quantity of molybdenum, as ammonium molybdate, was added a known quantity of a 10% solution of potassium thiocyanate. To a portion of this solution a small amount of granulated zinc was added together with a given quantity of hydrochloric, hydrobromic, sulfuric, phosphoric or acetic acid.

In similar experiments various reducing agents such as aluminum, copper, mercury, tin, magnesium, lead, stannous chloride, resorcinol and hydroquinol were used.

It was found that phosphoric and acetic acids would not produce a definite red color of molybdenum thiocyanate except with relatively large amounts of molybdenum.

When equivalent concentrations of the acids were the same, and other factors such as quantity of molybdenum, quantity of reducing agent, etc., were kept constant, the order of decreasing sensitivity of the acids used was as follows: hydrobromic, hydrochloric, sulfuric, phosphoric, acetic. This order held for all reducing agents tried. Hydrochloric acid was, therefore, selected as the most suitable acidifying reagent.

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[7] Noyes and Bray, THIS JOURNAL, **29**, 137 (1907).

[8] Maas and Sand, *Ber.*, **41**, 1861, 3369 (1908).

[9] Rosenheim and Garfunkel, *Ber.*, **41**, 2386 (1908); **42**, 149 (1909).

[10] King, *Ind. Eng. Chem.*, **15**, 350 (1923).

Effect of Reducing Agents

Resorcinol, hydroquinol and other organic reducing agents were found to be unsuitable, either because of a tendency to inhibit the reaction or because of a tendency to give a slight red color themselves on standing, either of which would be objectionable. This left only the metals and inorganic salts as suitable reducing agents. Magnesium was found to be so active that the reduction of the molybdenum to the blue stage occurred almost immediately, even when used with acetic acid. For this reason small amounts of molybdenum would remain undetected. Aluminum was also unsatisfactory. Zinc was found to be the most satisfactory metal to use for several reasons: (1) it is active enough to reduce the molybdate immediately and rapidly giving the red coloration; (2) it is also active enough to reduce any iron that has not been removed, to the ferrous condition, thus causing a disappearance of any red color due to ferric thiocyanate; (3) its reducing reaction is not so rapid but that the red stage of oxidation of the molybdenum can always be observed except in the presence of excessive amounts of acid; (4) the reducing action always begins at the surface of the zinc, whereas in the case of a salt solution, such as stannous chloride, used as a reducing agent, it would naturally begin simultaneously throughout the solution. Metallic tin developed a suitable red coloration except that its reaction was slower than that of zinc. Stannous chloride also gave good results but is too rapid in its reducing action. When exactly the right amount was not added the blue color was produced immediately, the intermediate red stage being either too quickly passed through or missed entirely. Metallic lead, copper and mercury gave very satisfactory results except that their action was very slow and the red color due to iron was not readily discharged. They were not sufficiently active, on the other hand, to reduce the molybdenum to the blue stage. It is quite possible that the amalgams described by K. Someya,[11] might be used to good advantage in the qualitative detection of molybdenum.

It should also be noted that when a solution of a thiocyanate is acidified, some thiocyanic acid is produced and that the greater the acidity, the more of this free acid is formed. This acid itself is a reducing agent, for when a solution containing molybdenum thiocyanate, is made up of 35% by volume of concd. hydrochloric acid, for example, no further reducing agent is needed to produce the red compound of molybdenum. The greater the concentration of acid and the higher the temperature, the more rapidly the red color of the solution develops.

The following procedure, then, is recommended for the qualitative detection of molybdenum by the thiocyanate method. The solution believed to contain molybdenum is evaporated to dryness with nitric acid.

[11] Someya, *Z. anorg. allgem. Chem.*, **138**, 291 (1924); **145**, 2614 (1925).

This converts any molybdenum present to molybdenum trioxide if it is not already in that state of oxidation. Upon reaching dryness care should be used in heating in order that molybdenum may not be lost by volatilization of the oxide.

The material is cooled, extracted with hot ammonium hydroxide and filtered to remove iron, and the residue washed with dil. aqueous ammonia. The filtrate is neutralized with hydrochloric acid, and 5 cc. of 10% solution of potassium thiocyanate is added. If at this point a slight red color appears, due to iron which escaped filtration, the solution is extracted with ether until colorless.

When a small piece of zinc is now placed in the solution no coloration should appear even though molybdenum is present. Concd. hydrochloric acid is now added drop by drop until hydrogen begins to be evolved and a red coloration, especially on the surface of the zinc, shows the presence of molybdenum. When no red color can be seen in the aqueous solution the latter is extracted with 2 to 5 cc. of ether and a red color in the ether layer indicates molybdenum.

If it is feared that small quantities of iron may be interfering with this color reaction, the color of the iron thiocyanate may be destroyed before the ether extraction by the addition of a few cubic centimeters of a 10% solution of phosphoric acid. For small quantities of molybdenum, this procedure is not to be recommended, however, because the presence of the phosphoric acid reduces the sensitivity of the reaction with respect to molybdenum.

Determination of the Sensitivity of the Reaction with Respect to Small Quantities of Molybdenum

Solutions were prepared by weighing out ammonium molybdate in such amounts as to give concentrations as low as one part of molybdenum to fifty million parts of solution. Using the procedure described above it was found that when other substances were absent the reaction was easily sensitive to about one part in one million parts of solution. With a little practice one part of molybdenum in fifty million parts of solution can be detected.

Small amounts of substances which are but slightly ionized, such as mercuric chloride, phosphoric acid, certain organic compounds, etc., are known to reduce the sensitivity of the reaction in the same way that they affect the thiocyanate test for iron. This fact should be considered when phosphoric acid is used to prevent the interference of ferric iron with this color reaction.[12]

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[12] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons Inc., vol. I, 5th ed., p. 548. Hopkins, "Chemistry of the Rarer Elements," D. C. Heath and Co., **1923**, p. 260.

The Isolation, if Possible, of the Molybdenum Thiocyanate Produced by the Reducing Reactions Described, and its Comparison with the Similar Compound Produced by Electrolytic Reduction

Although Chilesotti[5] prepared electrolytically and isolated the compound $K_3Mo(CNS)_6.4H_2O$, it was found impossible to isolate the compound produced by reducing reactions as described above. Under the conditions of these reactions the compound was very unstable. Neither the water nor the ether solution could be concentrated by heating, even under reduced pressure, without decomposition. Evaporation in an atmosphere of hydrogen gave no better results. Attempts to freeze out the compound did not give a homogeneous solid, and salting-out methods also failed to yield any precipitate of definite composition. Extractions from the water solution could not be made with other solvents.

According to Chilesotti, the red thiocyanate of molybdenum has the following formula in water solution: $K_3Mo(CSN)_6$. When an aqueous solution of molybdenum thiocyanate was extracted with ether and the resulting solution thoroughly washed with water, it was found that on adding this solution to a few cubic centimeters of water and evaporating the ether, only a trace of potassium could be detected by spectroscopic examination. Hence, if Chilesotti's results were correct, and if the compound produced by electrolytic reduction was analogous to that produced by reduction methods herein used, the double salt breaks down when ether extraction is made, and the ether dissolves only the molybdenum thiocyanate. One would thus suspect the formula of molybdenum thiocyanate in the ether solution to be $Mo(SCN)_3$ rather than $Mo(SCN)_4$.[4]

Since it seemed impossible to isolate the molybdenum compound which dissolved in the ether and determine its composition from the solid state, it was thought of interest to determine the relative amounts of molybdenum and thiocyanate present in the ether solution.

A solution of ammonium molybdate was cooled to 5–10° and to this was added a solution of potassium thiocyanate acidified with hydrochloric acid and having the same temperature. The beaker was kept in ice water and stirred until the temperature was 10° or below. Zinc was then added and allowed to react until the solution became intensely red due to the formation of molybdenum thiocyanate. The red material was completely extracted from this solution with ether, and the ether solution washed five to ten times with an equal volume of distilled water to remove any potassium thiocyanate or other water-soluble impurity. The ether solution, freed as far as possible from water, was poured through a dry filter into a 50% solution of potassium hydroxide. On shaking this solution the molybdenum thiocyanate was extracted from the ether. Without decanting or separating the ether, the potassium hydroxide solution was placed in an ice-water pack and cooled again to 5–10°. The alkali was then neutralized by adding at intervals of several minutes a few cubic centimeters of nitric acid, while the temperature was kept below 10°. When neutralization was effected the solution was treated with fuming nitric acid and allowed to stand in the ice water for one hour. The solution was then boiled very gently for two hours on an electric hot-plate. The molybdenum had thus been oxidized to molybdate and the sulfur of the thiocyanate had been oxidized to sulfate. The nitrates and nitric acid present were decomposed by evaporating to dryness several times with hydrochloric acid. The solution was diluted and portions were analyzed quantitatively for sulfate and molybdate. The sulfate was first determined as barium sulfate according to the procedure given by Blair[13] for the determination of sulfur in molybdenum steel. The molybdate was then determined in the filtrate as lead molybdate as given by Bonardi.[14]

The results of these analyses are given in Table I.

TABLE I

RATIO OF MOLYBDENUM TO SULFUR IN MOLYBDENUM THIOCYANATE

Portion	$PbMoO_4$, g.	$BaSO_4$, g.	MO, g.	S, g.	Ratio of molybdenum to sulfur Calcd. for $Mo(SCN)_3$ 1:1.002 Found
			SAMPLE 1		
1	0.7703	1.4776	0.2014	0.2029	1:1.008
2	.7713	1.4788	.2016	.2031	1:1.007
3	.7753	1.4660	.2027	.2013	1:0.9933
4	.7863	1.4723	.2056	.2022	1:0.9936
			SAMPLE 2		
1	1.6163	3.0837	.4226	.4235	1:1.002
2	1.6046	3.0693	.4195	.4314	1:1.028
3	1.6239	3.0964	.4246	.4253	1:1.002
4	1.6255	3.0994	.4250	.4257	1:1.002

These results indicate that molybdenum is tervalent in this compound rather than quadrivalent. The formula, therefore, would be $Mo(SCN)_3$.

The reactions between tervalent molybdenum and thiocyanate are apparently very similar to those between ferric iron and thiocyanate which forms the other known red thiocyanate. According to Krüss and Moraht,[15] ferric thiocyanate in aqueous solution exists as a double salt $K_3Fe(SCN)_6$, but when extracted from the water solution with ether, decomposition occurs and $Fe(SCN)_3$ only is dissolved in the ether.

Summary

1. The condition most favorable for the qualitative detection of molybdenum by the thiocyanate method was reduction by zinc in hydrochloric acid solution.

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[13] Blair, "The Chemical Analysis of Iron," J. B. Lippincott and Co., 8th ed., 1918, p. 228.

[14] Bonardi, *Bur. Mines Bull.*, **212,** 98–103 (1923).

[15] Krüss and Moraht, *Ann.*, **260,** 204 (1890).

2. The sensitivity of the reaction with respect to molybdenum was also found in the case where no interfering substances were present, the sensitivity being about one part of molybdenum per million parts of solution. Many substances such as mercuric chloride, phosphoric acid and organic compounds were found to decrease the sensitivity.

3. The ratio between the molybdenum and the sulfur in the thiocyanate radical, when the compound was dissolved in ether, was found to be such as to correspond to the formula, $Mo(SCN)_3$.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 30]

THE CATALYTIC SYNTHESIS OF WATER VAPOR IN CONTACT WITH METALLIC SILVER

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Introduction

One type of contact catalysis having a relatively simple mechanism consists in the interaction of two gases in contact with a solid under such conditions that no compounds are formed involving the catalyst and only one of the gases is measurably adsorbed. The formation of water vapor from hydrogen and oxygen in contact with metallic silver appears to be an example of this kind.

The reaction has been studied by Bone and Wheeler[2] who used a number of different catalysts, including silver foil and gauze. Their method consisted in continuously circulating the gas mixture over the catalyst held at constant temperature (usually 400°), condensing the water thus formed and measuring the rate of steam formation by the pressure decrease in the system. The results indicated that with silver foil the rate of reaction was roughly proportional to the pressure of the hydrogen but independent of the oxygen pressure; with silver gauze the results appeared to be less simple. It was also found that the activity of the catalyst was greatly stimulated by previous heating in hydrogen, but not in oxygen. Bone and Wheeler interpreted these results to mean that the hydrogen becomes activated by association with the silver surface, probably by forming an unstable hydride which reacts with oxygen to form water and regenerate the catalyst. As evidence for this view they state that an active silver surface was found to absorb hydrogen both at 400° and at dull red heat.

The conclusions of Bone and Wheeler have been criticised in another

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[1] DuPont Fellow in Chemistry.

[2] Bone and Wheeler, *Phil. Trans.*, **206A,** 1 (1906).