KOH, the mixture was heated to boiling, shaken well while hot, cooled, and filtered. Two cc. of this reagent were added to 1 cc. NaCl solution containing 3 mg. Na: no precipitate separated in a day, showing that the KOH must not be added to the solution until after it is cooled.

Behavior of Potassium Antimonate Reagent towards Various Substances.—In the following experiments the substance was dissolved in 1 cc. water and 1 to 2 cc. of the antimonate reagent added.

With 1 mg. NH_4 as NH_4NO_3, no precipitate over night. With 2 mg. NH_4, a turbidity in 1½ hours. With 5 mg. NH_4, turbidity in a few minutes. With 10 mg. NH_4, turbidity at once.

With 1.0 mg. Ca as nitrate, a large white gelatinous precipitate at once. With 0.2 mg. Ca, marked turbidity at once. With 0.1 mg. Ca: slight turbidity at once.

With 0.2 mg. Ba as nitrate, a slight turbidity at once.

With 0.1 mg. Mg as nitrate, a slight turbidity at once. With 0.3 mg. Mg, a marked turbidity.

In a number of experiments 400 mg. Mg as nitrate were precipitated as magnesium ammonium carbonate by P. 81, and the (neutral) filtrate tested for Na by P. 93: in one or two cases a perfect blank was obtained, but in others a small flocculent precipitate separated corresponding to 0.1 to 0.3 mg. Mg. But this turbidity was probably not due to magnesium since in another experiment no precipitate separated when KOH was added before testing for Na, and yet a small flocculent precipitate was obtained on adding the antimonate.

A few drops of alcohol were added to 1 cc. of reagent: a large white precipitate separated at once.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEVADA.]

THE REDUCTION OF COPPER SULPHATE WITH HYDROXYLAMINE.

BY MAXWELL ADAMS AND ELIZA OVERMAN.

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In the test for free hydroxylamine with Fehling's solution, varying results, depending upon the concentration and temperature of the reagents, are obtained. If a few drops of Fehling's solution are added, to a cold dilute solution of hydroxylamine, a bright green precipitate, which soon changes brown, is formed. If the solutions are warm, the precipitate is yellow, and if they are warm, and also somewhat concentrated, the precipitate is red.

These observations induced the authors to undertake a study of the different stages which take place in the reduction of copper sulphate. This work led to the separation and identification of the following compounds:

$CuSO_4.NH_2OH$.—By adding an alcoholic solution of hydroxylamine to a solution of cupric chloride, Feldt[1] obtained violet-colored crystals, which, when removed from the solution, turned brown and decomposed before he was able to determine their composition. His experiments

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[1] *Ber.*, **27**, 401.

with cupric chloride suggested to us the advisability of mixing cupric sulphate and hydroxylamine in the presence of alcohol.

A saturated solution of cupric sulphate was prepared by dissolving the anhydrous salt in methyl alcohol. A solution of hydroxylamine in methyl alcohol was also prepared by treating sodium methylate, in molecular proportions, with hydroxylamine hydrochloride, cooling the mixture and filtering out the precipitated salt. The solutions of cupric sulphate and hydroxylamine were both cooled to —10° and mixed. The cupric sulphate was maintained in excess. Pale green, microscopic crystals were formed at once and filtered out, washed with alcohol, then with ether and dried. Analysis showed the salt to have the composition $CuSO_4.NH_2OH$.

Calculated: Cu, 33.02 ; SO_4, 49.84 ; N, 7.27.
Found: Cu, 33.05, 32.97; SO_4, 49.91, 49.73; N, 7.11.

$CuSO_4.2NH_2OH$.—When solutions of copper sulphate and hydroxylamine, prepared as described above, are mixed, and the hydroxylamine is kept in slight excess, a deep green precipitate, showing a distinct crystalline structure under the microscope, separates. This precipitate was washed, dried and analyzed in the same manner as that obtained in the preceding experiment.

Calculated: Cu, 28.19 ; SO_4, 42.55 ; N, 12.41.
Found: Cu, 28.18, 27.92; SO_4, 42.35, 42.52; N, 11.95, 12.44.

The salts $CuSO_4.NH_2OH$ and $CuSO_4.2NH_2OH$ are both changed into copper oxide when warmed with water, to which a drop of alkali has been added, but both are stable when kept dry. They are both stable at 65° in the presence of methyl alcohol, but when either salt is treated with an excess of free hydroxylamine in alcoholic solution at 15° it turns darker in color, and when allowed to stand in contact with this reagent, at 15° for a few hours, becomes violet in color, and analysis shows it to have absorbed considerable hydroxylamine. The amount absorbed appears to depend chiefly upon the concentration of the hydroxylamine solution. There is doubtless present here, mixed with the $CuSO_4.NH_2OH$ and $CuSO_4.2NH_2OH$, salts containing more than two molecules of hydroxylamine to one of copper sulphate, contaminated more or less with ammoniated copper salts, resulting from slight decomposition of the hydroxylamine into ammonia. All attempts to separate, from this mixture, a pure compound were unsuccessful.

$CuSO_4.5NH_2OH$.—An effort was made to prepare the salt $CuSO_4.5NH_2OH$, which would correspond to crystallized copper sulphate, but with only partial success. For use in the following experiment, pure hydroxylamine was prepared by distilling the phosphate under diminished pressure, after the method of Uhlenhuth.[1]

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[1] *Ann.*, 307, 332.

When a saturated solution of anhydrous copper sulphate in methyl alcohol is treated with a large excess of pure hydroxylamine, a dark green precipitate, rapidly changing to violet, separates out. Kept in contact with the original solutions, and examined under the microscope, this violet-colored compound is seen to consist of well-formed acicular crystals. They, however, lose their form and luster when dried, even though kept in an atmosphere of hydrogen.

Calculated for $CuSO_4.5NH_2OH$: Cu, 19.58 ; SO_4, 29.57 ; N, 21.53.
Found: Cu, 18.92, 18.42; SO_4, 29.51, 29.63; N, 16.34, 15.92.

The analysis indicates that $CuSO_4.5NH_2OH$ probably exists when kept in contact with a concentrated solution of hydroxylamine, but when dried ready for analysis some copper oxide is doubtless present, due to slight decomposition. In direct sunlight this compound changes in color from violet to light brown, and when heated to about 74° it decomposes with explosive violence.

$Cu_2OSO_4.2NH_2OH$.—If the compound $CuSO_4.2NH_2OH$ is treated with a cold aqueous solution of hydroxylamine, and allowed to stand for an hour, it is changed into a bright green, insoluble non-crystalline compound, which analysis shows to have the composition $Cu_2OSO_4.2NH_2OH$.

Calculated: Cu, 41.67 ; SO_4, 31.45 ; N, 9.17.
Found: Cu, 41.34, 41.28; SO_4, 31.38, 31.32; N, 9.02, 8.82.

This compound is readily formed in a number of ways, and in the presence of water appears to be the most stable of the salts described in this paper. It may be made by mixing water solutions of cupric sulphate and hydroxylamine, provided the solutions are kept cool. It is formed in an excess of either cupric sulphate or hydroxylamine. Cupric hydroxide is somewhat soluble in a solution of hydroxylamine hydrosulphate, forming a light green solution. When this solution is treated with alcohol, a small yield of $Cu_2OSO_4.2NH_2OH$ is separated, the salt being formed according to the following reaction:

$$2Cu(OH)_2 + (NH_2OH)_2H_2SO_4 = Cu_2OSO_4.2NH_2OH + 3H_2O.$$

The cupric hydroxide must be entirely free from alkali or it will be immediately reduced to cuprous oxide.

These compounds of copper and hydroxylamine are all stable in pure alcohol or ether, except $CuSO_4.5NH_2OH$. In the absence of free hydroxylamine or alkali, with the exception of the one just mentioned, they are stable in water at zero, but decomposition begins at about 15° and proceeds rapidly as the temperature rises. A drop of potassium or sodium hydroxide in water solution is sufficient to change any of them over into the yellow hydrated cuprous oxide and finally into the red cuprous oxide. They are readily soluble in acids. When gently warmed with dilute nitric acid, nitric oxide is given off, and part of the copper is deposited in the metallic form.

From the above experiments, the steps represented by the following reactions appear to take place in the reduction of cupric sulphate with hydroxylamine.

Hydroxylamine in alcoholic solution at —10°, added to an excess of cupric sulphate, produces reaction I.

$$\text{I. } CuSO_4 + NH_2OH = CuSO_4.NH_2OH.$$

When a slight excess of hydroxylamine is added to this same cold solution reaction II occurs.

$$\text{II. } CuSO_4.NH_2OH + NH_2OH \longrightarrow CuSO_4.2NH_2OH.$$

Adding a concentrated solution of hydroxylamine produces reaction III:

$$\text{III. } CuSO_4.2NH_2OH + 3NH_2OH \longrightarrow CuSO_4.5NH_2OH.$$

The addition of water produces reaction IV:

$$\text{IV. } 2[CuSO_4.5NH_2OH] + H_2O \longrightarrow Cu_2OSO_4.2NH_2OH + (NH_2OH)_2H_2SO_4 + 6NH_2OH.$$

The addition of sodium hydroxide in water solution produces reaction V:

$$\text{V. } Cu_2OSO_4.2NH_2OH + 2NaOH \longrightarrow Cu_2O + Na_2SO_4 + 4H_2O + N_2.$$

Continued boiling with an excess of hydroxylamine completes the reduction to metallic copper as shown in reaction VI.

$$\text{VI. } Cu_2O + 2NH_2OH \longrightarrow 2Cu + 3H_2O + N_2.$$

When a salt of hydroxylamine is added to a solution of copper sulphate, and sodium hydroxide added to free the hydroxylamine, the various steps as outlined in the above reactions doubtless take place, but they are passed over so rapidly that only the evolution of nitrogen and the production of cuprous oxide and metallic copper are observed.

RENO, NEV.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 165.]

DOES THORIUM EXIST AS THORIUM SILICATE IN MONAZITE?

BY O. KRESS AND F. J. METZGER.

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Monazite, as is well known, is essentially a phosphate of cerium, lanthanum, neo- and praseodidymium, with varying amounts of thorium. The form in which the thorium exists in monazite has never been definitely decided, some authorities stating that the thorium is present as a silicate, either as orangite or thorite, while others claim that it is present as a phosphate, either replacing a part of the cerium earths or being pres-