washed with water or dried without decomposition, make the determination of its composition a matter of extraordinary difficulty, as everything must be found by ratios, and the ammonia determination is complicated by the ammonium sulphate present. But from the preceding determinations and others by other workers, there seems to be no doubt that the ratio of bismuth to molybdenum is as one is to two and that if the formula is not $BiNH_4(MoO_4)_2$, the variation is extremely slight and not such as to prevent the use of this precipitate for the volumetric determination of bismuth.

QUANTITATIVE LABORATORY,
June 20, 1903.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE CONSTITUTION OF POTASSIUM RUTHENIUM NITROSO-CHLORIDE IN AQUEOUS SOLUTION.

BY S. C. LIND.

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THIS salt is the one which led Claus in 1845 to identify ruthenium as a new metallic element. He supposed it, however, to have the formula K_2RuCl_6, and, therefore, to belong to the well-known class of salts represented by K_2PtCl_6. In 1888, A. Joly[1] showed that this is not the case, but that the compound is a mononitroso salt of the formula K_2RuCl_5NO. The properties of this salt and analyses of it by several authors are presented in Freeny's "Encyclopedie Chimique."[2] J. L. Howe[3] has confirmed this interesting discovery and has described the salt very fully, and given new analytical data in regard to it.

The properties presented by this salt, its rather unique formula, and also its relation to several other analogous ruthenium salts, have made a study of its constitution in aqueous solution of interest. Such an investigation was undertaken at the suggestion of Dr. Jas. L. Howe, to whom the author is indebted for the salt used in the following measurements. His analyses were made on this same sample; they will be found in his article referred to above. The author also desires to acknowledge his indebtedness

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[1] *Compt. Rend.*, **107**, 994 (1888).

[2] "Encyclopedie Chimique," III, **17**, 1, 179-181.

[3] This Journal, **16**, 388 (1894).

to Dr. Arthur A. Noyes for his supervision of, and assistance in, this investigation.

The following determinations have been made. First, the electrical conductivity of the salt at 22°, at various concentrations from $^1/_{20}$ to $^1/_{2560}$ normal; second, the lowering produced by the salt in the freezing-point of water; third, the direction of the migration of the ruthenium during electrolysis.

I. CONDUCTIVITY MEASUREMENTS.

The apparatus used was the ordinary slide wire-bridge arrangement of Kohlrausch. The temperature employed was 22° (corrected), kept constant within 0.1° by means of a thermostat. The amount of salt required to make 100 cc. of an N/20 solution (that is, one containing $^1/_{40}$ K_2RuCl_5NO per liter) was dissolved in a weighed amount of water. This was used as a stock solution for making the more dilute solutions.

The salt was found to be perfectly stable in water solution at all the various concentrations, the conductivity of the solutions not changing at all in two weeks.

In the following table, the conductivity values obtained at the various dilutions, are given, expressed in reciprocal ohms. For comparison are also given the corresponding values for potassium platinic chloride at the same dilutions. These values were obtained from Walden's measurements at 25° by applying a temperature correction of 2.2 per cent. per degree, to the values for the different dilutions, obtained by interpolations from plots. The change from the Siemen's unit to the reciprocal ohm was effected by dividing each value by 1.063.

The specific conductivity of the water used in dissolving the salt and making the dilutions was 1.4×10^{-6} reciprocal ohms. This was subtracted in each case from the specific conductivity of the solution before calculating the equivalent conductivity.

TABLE I.—CONDUCTIVITY VALUES AT 22°.

Liters per equivalent.	Equivalent K_2RuCl_5NO.	Conductivity. K_2PtCl_6.
20	99.8	....
40	106.4	96.6
80	110.3	101.5
160	115.4	105.4
320	118.5	108.5
640	121.9	111.1
1280	126.0	113.4
2560	127.5	....

II. FREEZING-POINT LOWERING.

The method employed was the usual one described by Raoult. A correction was applied to the observed lowering for the increased concentration of the solution by the ice separated from it. This correction was calculated from the heat of fusion and the supercooling of the solution, which was 1.5 to 3.5°.

TABLE II.—FREEZING-POINT LOWERING.

	Weight of solvent. Grams.	Weight of salt. Gram.	Liters per mol.	Observed lowering.	Corrected lowering.	Molecular lowering.	van't Hoff's coëfficient i.	Percentage dissociation.
I.	20	0.4084	18.9	0.261°	0.251°	47.59	2.56	78.0
II.	20	0.4001	19.9	0.251°	0.242°	46.87	2.52	76.0
III.	20	0.2240	34.6	0.153°	0.148°	51.17	2.75	87.5
IV.	20	0.1052	73.4	0.071°	0.069°	50.59	2.72	86.0

By making a plot, using the conductivity values as abscissas and the cube roots of the corresponding concentrations as ordinates, a straight line is obtained. If this line be continued to zero concentration, a value is obtained for conductivity at infinite dilution, which in this case is found to be 133.5. This maximum conductivity of the salt represents its complete dissociation; therefore, from the ratio $\frac{\Lambda_{20}}{\Lambda_\infty}$, the percentage dissociation of the N/20 solution is found to be 74.7 per cent., slightly lower than the value found by the freezing-point method. From the above table, it appears that the salt is partially dissociated into *three ions*, as would be expected if we assign to it the formula $2K/RuCl_5NO$.

III. MIGRATION OF THE RUTHENIUM ION.

The solutions of this salt have a very characteristic violet-red color, which is due to the ruthenium ion. This seemed to offer a good opportunity of investigating the direction of motion of the colored ions under the influence of a direct electric current.

The form of apparatus used was suggested to the author by Mr. A. C. Melcher, and is so simple and so well adapted to experiments of this kind, that it may be briefly described.

A 2 per cent. solution of agar jelly in water was prepared, and to it was added a quantity of potassium chloride, sufficient to make an N/20 solution. Two 3-inch U-tubes were exactly filled with the jelly solution, which was then congealed by immersion in an ice-bath. An approximately N/20 solution of the potassium ruthenium nitrosochloride was prepared in a small beaker. One arm of each of the two inverted U-tubes was dipped into this solution to a depth of about 6 mm. The other arm of one of the tubes was immersed in a beaker containing a hydrochloric acid solution, and that of the other tube into a similar beaker containing a caustic potash solution. Into these two beakers were introduced platinum electrodes, and a direct current was passed so that the *anode* was in the beaker containing the *acid* solution, and the cathode in that containing the alkaline solution. The purpose of these two solutions was to neutralize the products of electrolysis set free at the electrodes. Their concentration is immaterial.

A 110-volt current was then passed through the system. After its passage for a few minutes, a pink layer appeared above the surface of the solution, in the arm on the anode side, and moved steadily toward that electrode. This extension of the color zone continued regularly, with a well-defined and perfectly level boundary, at a rate of about 5 cm. per hour. On the other hand, in the cathode arm, not a trace of color appeared either above or below the surface of the solution.

This decisive result shows that the ruthenium is a constituent of the negative ion, and that there are no positive ions containing ruthenium in the solution. This consideration, together with the facts already shown in regard to the number of ions into which the salt dissociates, shows its structure to be $2K^+/RuCl_5NO^{--}$.

SUMMARY.

By way of summary, the following points in regard to the structure and properties of this salt may be mentioned, as having been established by the foregoing experiments.

(1) It is perfectly stable in aqueous solution, as is shown by the fact that its conductivity does not change at all in two weeks.

(2) It has a molecular conductivity very close to that of the analogous salt, potassium platinic chloride.

(3) The salt is partially dissociated into three ions as shown by its effect on the freezing-point of water. The value of van't Hoff's coëfficient i, is 2.52-2.72 in $^1/_{20}$-$^1/_{70}$ molar solution.

(4) The degree of dissociation of the salt, derived from the freezing-point lowering, agrees well with that obtained by conductivity measurements; it also agrees with the value for potassium platinic chloride.

(5) The direction of migration of the colored ions shows that the ruthenium is present in the negative ion, and in that alone.

(6) It will be seen from Table I, that the values for the ruthenium salt are uniformly about 10 per cent. greater than those for the platinum salt. It is evident, therefore, that the dissociation relations are entirely similar.

THE ACTION OF FUMING SULPHURIC ACID UPON ISOAMYL CHLORIDE.

BY R. A. WORSTALL.

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SOME years ago, while the author was engaged upon an investigation of aliphatic sulphonic acids, some preliminary work was done upon the products of the reaction between isoamyl chloride and fuming sulphuric acid. It was the author's intention to make an extended study of the action of sulphuric acid of various degrees of concentration upon different alkyl haloids, but owing to pressure of other work this investigation was dropped, and neither the opportunity nor the facilities have since been available for completing this work. As it does not seem probable that opportunity will be afforded for any further work along this line, it may not be amiss to publish the results of the investigation so far as it was carried.

The following is a brief résumé of the literature upon the subject of the reactions between sulphuric acid and alkyl haloids. Williamson,[1] by the action of sulphuric anhydride upon ethyl chloride, obtained chlorethyl sulphuric acid, a heavy oil, decomposed by water into hydrochloric acid, sulphuric acid and ethyl sulphuric acid. Methyl chloride gave a similar result. By the action of chlorsulphuric acid upon the alcohols, the same compounds resulted.

Oppenheim[2] states that amyl chloride with concentrated sulphuric acid gave amyl sulphuric acid, and that all alkyl chlorides, by similar treatment, lose hydrochloric acid and form alkyl sulphuric acids. The same author,[3] by acting upon ethylene chloride and its homologues with concentrated sulphuric acid in sealed

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[1] *J. prakt. Chem.*, **73**, 73.

[2] *Am. Chem. J.*, **6**, 353.

[3] *Ber. d. chem. Ges.*, **2**, 212.