ADDENDUM.

Since the paper was written and presented, a letter from Sir William Crookes has been received, excerpts from which are given herewith. "I had not quite sufficient to enable me to photograph the whole ultraviolet spectrum, but I have taken that portion, between wave-lengths 3444.020 and 4071.903, which contain some very characteristic thorium lines. I compared the spectra with my standard thorium spectrum taken from the spark between the poles of metallic thorium. Making allowance for the fact that my spectrum is from the metal, while that from your material is from the chloride solutions, all five spectra are practically identical, all the prominent lines being seen in each spectrum, while there are no lines in one which are not seen in the others................ You must not attach too great importance to these spectrum results. All I can say is that they give no positive proof of the existence of anything new. But they by no means prove that such bodies do not exist. They may be there with their spectra, masked by the thorium, which is present."

As only a limited portion of the spectrum was examined, the question is still an open one. My sincere thanks are due Sir William Crookes.

June 18, 1904.

RUTHENIUM, VI: THE BROMIDES.

By Jas. Lewis Howe.

Received June 24, 1904.

In order to determine whether the bromides of ruthenium correspond to the chlorides, several members of the different series have been prepared and are described in this paper. It was found that the salts of the bromruthenite, X'_2RuBr_5, 'aquo'-bromruthenate, $X'_2Ru(H_2O)Br_5$, and bromruthenate, X'_2RuBr_6, series differ very slightly from the corresponding chlorides, but are rather more soluble and more easily decomposed. This has rendered their preparation, and especially their purification, more difficult, so that sufficient time only has been put upon them to learn their general character.

The bromruthenous acid was prepared by the action of hydrobromic acid upon ruthenium tetroxide, RuO_4. On covering the tetroxide with a solution (50 per cent.) of hydrobromic acid the solution at once becomes dark reddish purple, very distinct from the reddish brown of the chlorruthenous acid. The action of hydrobromic acid upon ruthenium tetroxide is much more violent than that of hydrochloric acid, but was, in every case, incomplete, a black residue being left, which is insoluble in acids, including aqua regia. This residue dissolves quite readily, as do metallic ruthenium and most ruthenium salts, in potassium hypobromite, giving, apparently, a solution of potassium ruthenate.[1]

On adding bromides of the alkalies to the solution of bromruthenous acid the corresponding bromruthenites are formed. These are very soluble in solution of hydrobromic acid, but less so in excess of the alkali bromides. The cesium and rubidium salts can be almost completely precipitated by excess of the bromide, even in solutions not strongly acid.

In one experiment the bromruthenous acid solution was precipitated by excess of potassium chloride. The salt formed proved, by analysis (No. 2), to be a nearly pure bromruthenite, showing that in the solution there is present not $RuBr_3$, but H_2RuBr_5, and $2\overset{+}{H},\overset{--}{RuBr_5}$ rather than $\overset{+++}{Ru}, 3\overset{-}{Br}$. While this would be expected from analogy to the salts of the type $X'_2M^{IV}Cl_6$, it has possibly not been shown for those of the type $X'_2M'''Cl_5$.

The bromruthenites, when treated with water, give an intensely dark blue solution, which becomes reddish brown and eventually reddish purple on warming with hydrobromic acid. This is unlike any of the chlorine compounds of ruthenium of similar type. On boiling with dilute alcohol in acid solution the bromruthenites undergo an analogous change to that shown by the chlorruthenites, the solution becoming less deeply colored (though still deeply colored in comparison with the aquo-chloride solution). This solution, which contains the aquo-bromruthenate, $X'_2Ru(H_2O)Br_5$, darkens on the addition of bromine water, forming the bromruthenate, X'_2RuBr_6. In this respect there is complete analogy between the chlorides and bromides of ruthenium.

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[1] A portion of this insoluble residue weighing 0.1105 gram, after drying to constant weight at 100°, lost, on heating in hydrogen, 0.0424 gram, of which 0.0062 gram was bromine. This bromine was doubtless from either HBr or H_2RuBr_5 which had not been completely removed from the insoluble compound. Allowing for this, the per cent. of ruthenium is in the former case 65.26, in the latter 64.73. This corresponds to $RuO_{3.4}$ or $RuO_{3.5}$. $Ru(OH)_3$ requires 66.6 per cent. ruthenium, and it is thus probable that the black residue is an insoluble hydroxide corresponding to either Ru_2O_3 or possibly RuO_2.

The bromruthenates, like the bromruthenites, are turned intensely blue by water, unless much hydrobromic acid is present. This blue solution of the bromruthenate, if quite dilute and no free acid is present, becomes purplish brown on boiling, and gives then a fugitive purple on the addition of a drop of hydrochloric acid. This reaction is also characteristic of the chlorruthenates. When boiled with acid alcohol the bromruthenate is changed back into the aquo-bromruthenate. The bromruthenates crystallize in minute octahedra, giving a black powder with a purplish sheen, while the chlorruthenates are similar except that the sheen is green. The aquo-bromruthenates are the most soluble of the ruthenium bromides and very difficult to crystallize. They resemble closely the aquo-chlorides. From experimental difficulties in preparation the analyses of the aquo-salts leave much to be desired. The bromine salts of ruthenium which have been prepared are the following:

K_2RuBr_5	$K_2Ru(H_2O)Br_5$	K_2RuBr_6
Rb_2RuBr_5,H_2O	$Rb_2Ru(H_2O)Br_5$	Rb_2RuBr_6
Cs_2RuBr_5,H_2O		

EXPERIMENTAL PART.

The analysis of these salts has been carried out as previously described,[1] except that in some cases the bromine was determined by collecting the hydrobromic acid evolved in a measured excess of N/5 $AgNO_3$ and titrating the excess with N/20 KSCN.

Only after the analyses were completed was it noted that in most cases the bromine removed in the hydrogen stream was high, while that left with the alkali metal after heating was correspondingly low. The hydrogen was dried by passing through two small sulphuric acid wash-bottles, but it evidently contained sufficient moisture to slightly decompose the alkali bromides at the temperature used. Unfortunately it was too late to verify this suggestion by testing the solution of the alkali bromide for free alkali.

Potassium Bromruthenite, K_2RuBr_5.—(1) Formed by addition of potassium bromine to solution of RuO_4 in hydrobromic acid and evaporation over concentrated sulphuric acid. Small brown crystals, very soluble in dilute hydrobromic acid and very soluble with decomposition in pure water. 0.3487 gram.

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[1] This Journal, **23**, 783 (1901).

(2) Precipitated by addition of concentrated solution of potassium chloride to a concentrated solution of H_2RuBr_5. Similar to (1). 0.4352 gram.

	1.	2.	Theory.
Ruthenium	17.49	17.05	17.54
Bromine (with ruthenium)	39.49	43.97	41.38
Potassium bromide	40.64	39.41	41.08

A double chloride and bromide of ruthenium and potassium, $2KCl.RuBr_3$, would require 20.73 per cent. ruthenium, 48.88 per cent. bromine, and 30.39 per cent. potassium chloride.

Rubidium Bromruthenite, Rb_2RuBr_5,H_2O.—(3) Precipitated by rubidium bromide from a solution of H_2RuBr_5, and recrystallized from dilute hydrobromic acid. 0.2830 gram.

	3.	Theory.
Ruthenium	15.48	14.73
Bromine (with ruthenium)	36.71	34.74
Rubidium bromide	46.18	47.91

Cesium Bromruthenite, Cs_2RbBr_5,H_2O.—(4) Precipitated by cesium bromide from solution of H_2RuBr_5. Fine black needles. 0.3053 gram.

	4.	Theory.
Ruthenium	14.59	12.95
Bromine (with ruthenium)	32.51	30.54
Cesium bromide	49.84	54.24
Water	2.46	2.29

Potassium Aquo-bromruthenate, $K_2Ru(H_2O)Br_5$.—(5) Potassium bromruthenite was boiled with alcohol and hydrobromic acid, and evaporated. Minute brown crystals separated out on standing. 0.5809 gram lost 0.0029 gram in sixteen hours at 90°, 0.0032 gram additional in six hours at 140°, 0.0011 gram on further heating sixteen hours at 140°. In twenty hours heating at from 200° to 240° it had not become completely dehydrated.

	5.	Theory.
Ruthenium	16.44	17.01
Bromine (with ruthenium)	43.41	40.13
Potassium bromide	38.60	39.84
Water	2.24	3.01

Rubidium Aquo-bromruthenate, $Rb_2Ru(H_2O)Br_5$.—(6) Ruthenium bromruthenite was boiled with dilute alcohol and hydrobromic acid, and evaporated over concentrated sulphuric acid. A brownish black crystalline mass, but no good crystals.

0.1506 gram lost 0.5 per cent. of water at 140° ; 2.06 per cent. in eight hours at 200° ; on further heating it began to lose bromine.

	6.	Theory.
Ruthenium	16.20	14.73
Bromine (with ruthenium)	35.78	34.74
Bromine (with rubidium)	21.32	23.17
Water	2.06	2.61

Potassium Bromruthenate, K_2RuBr_6.—(7) A concentrated solution of aquo-bromruthenate was cooled to 0°, and through this was passed a current of bromine gas. A precipitate of very minute crystals was formed, which was filtered by suction on a Hirsch funnel, and washed with a few drops of hydrobromic acid. As the acid touched the salt it became instantly indigo-blue. The salt when dry is black with purplish sheen, and consists of minute octahedra. It is very soluble. 0.2992 gram.

	7.	Theory.
Ruthenium	15.54	15.42
Bromine (with ruthenium)	48.27	48.48
Bromine (with potassium)	22.79	24.24

Rubidium Bromruthenate, Rb_2RuBr_6.—(8) A concentrated solution of aquo-bromruthenate was treated with several drops of bromine and allowed to stand over night. Gave minute black octahedra, resembling those of the potassium salt, but less soluble. 0.1288 gram.

	8.	Theory.
Ruthenium	13.97	13.52
Bromine (with ruthenium)	41.38	42.51
Bromine (with rubidium)	21.74	22.26

WASHINGTON AND LEE UNIVERSITY,
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