5. The ionization of this complex as an extremely strong acid has been discussed.
6. Evidence has been offered as to the existence in concentrated solutions of a substance more complex than $H_2UO_2(C_2O_4)_2$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF BRITISH COLUMBIA]

The Atomic Weight of Rubidium

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Somewhat over thirty years ago, one of the authors studied the atomic weight of rubidium through the determination of the silver chloride and bromide equivalents of rubidium chloride and bromide, as well as the silver equivalent of these salts. During the intervening years, several investigators have developed improvements that allow more precise measurements to be made of the quantities involved. In particular the technique of approaching and attaining the exact endpoint of the reaction concerned, has received a lot of attention. With these considerations in mind, it was decided that a new study of the equivalent in question was advisable.

Materials

In the preparation or purification of the chemicals necessary for this investigation, platinum and quartz vessels were used almost exclusively; only when such containers would be attacked did we resort to the use of Pyrex ware.

The water, the several acids, invert sugar, sodium hydroxide, calcium oxide, barium hydroxide, tartaric acid and silver were purified by standard methods.

Iodine Monochloride.—The iodine for this reagent had been sublimed three times, a thorough grinding with potassium iodide preceding the first sublimation. The chlorine was prepared from redistilled hydrochloric acid and potassium permanganate that had been three times recrystallized. The gas was passed over the solid iodine until the mass had been completely liquid for several minutes. The product was then distilled from quartz and came over at a constant boiling point of 101°.

Rubidium Chloride.—The starting material was C. P. rubidium salts, chiefly the carbonate, with small amounts of sulfate and bromide. These were dissolved in water and the solutions filtered. All were then converted to the chloride, and from a warm, saturated solution of this salt the dichloroiodide was precipitated by the addition of the pure iodine monochloride. The rubidium dichloroiodide was then fractionally recrystllaized ten times in quartz vessels, the crystals being drained each time on porcelain in the centrifuge at the usual 1500 r. p. m. As the compound is appreciably soluble in water, even at low temperatures, a second crop of crystals was taken from the mother liquor each time, and there was still a considerable amount of salt left in the residual liquor; but it must be an efficient method of eliminating alkali metals of lower atomic mass.

In making these crystallizations it is very necessary to use water containing about 5% of hydrochloric acid when dissolving the halide salt. Otherwise, decomposition takes place and too much iodine is set free.

The final product of dichloroiodide was converted through the sulfate to the hydroxide by means of the purified barium hydroxide. The pure tartaric acid was then used to convert the rubidium hydroxide to acid tartrate and the acid salt was recrystallized five times with the usual drainage in the centrifuge, in order to eliminate any cesium that might have accumulated during the double halide crystallizations. As the cesium acid tartrate is appreciably more soluble than the rubidium salt, recrystallization should leave the former tartrate in the mother liquor.

The final fraction of acid tartrate was ignited in platinum, and the carbonate obtained treated with pure hydrochloric acid. The chloride solution was diluted and filtered through a Gooch–Munroe crucible. Three crystallizations as chloride followed, the first from hydrochloric acid solution and the last two from water. After the centrifuge draining, the last crop of crystals was dried at 150° and placed in a desiccator over fused potassium hydroxide.

During the treatment outlined above, silica beakers of 250–300 cc. capacity were used for the halide crystallizations, and platinum and silica dishes in the later procedure, whichever were considered the better for the purpose in hand.

That the final product of rubidium chloride was free from the impurities most difficult to get rid of, sodium, potassium, and cesium was indicated by the spectrum photographs; samples examined in the copper arc showed no indications of the lines pertaining to these three metals.

Balance and Weights

The balance used was a No. 10 Troemner with which weighings could be duplicated to 0.02 mg. The weights were corrected according to the method suggested by Richards.[1] Independent comparisons by two observers gave corrections identical within the errors of the experiment. This gave us additional assurance of the constancy of the weights. The weighings were made by substitution using counterpoises of glass and platinum similar to the objects being weighed.

The Analysis of Rubidium Chloride

The analyses were made by the conventional titration method, first devised by Richards and

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(1) Richards, THIS JOURNAL, 22, 144 (1900).

Wells.[2] However, in their work and subsequent investigations at the Harvard laboratories, the end-point was followed by the "equal opalescence method," whereas, in the present work, the "standard solution method" of C. R. Johnson[3] was employed.

Following this procedure, a 2 or 3 gram pellet of silver was carefully weighed. It was then dissolved in such a volume of 6.4 N nitric acid that, when diluted to 0.025 N as regards silver nitrate, the nitric acid concentration was 0.1 N. The pellet was dissolved in a special apparatus from which oxides of nitrogen and acid spray could escape only by means of a baffle and water trap.

On the basis of an assumed atomic weight for rubidium, an amount of the chloride 2 or 3 mg. greater than the weight equivalent to the above pellet of silver was weighed in a platinum boat. The salt was then fused in a current of pure nitrogen in a quartz Richards bottling apparatus. The boat and contents were cooled, the nitrogen displaced by dry air, and the boat finally bottled. The salt was weighed by substitution, using counterpoise of weighing bottle and platinum as stated above. The boat containing the chloride was lowered into a 3-liter Pyrex flask and shaken with 100 ml. of water until the salt was dissolved. The boat was then removed with a Pyrex rod and washed with water until the washings, when examined in the nephelometer, showed no indications of silver or chloride ion.

The volume of water necessary to bring this solution of rubidium chloride but slightly below the dilution finally required, 0.05 N, was then calculated and in the dark room, in an atmosphere free of dust, this was added from a sample of water recently tested in the nephelometer.

The silver nitrate solution was now added to the chloride solution, in the light of a Wratten Safe Light, at the rate of about 6 ml. per minute, the contents of the flask meantime being kept constantly in motion.

As, during the fusion, a trace of salt was volatilized, and varying amounts of water were lost, exact equivalence on the basis of the assumed atomic weight was not, in general, attained at this point; so the requisite volume of a standard solution of rubidium chloride or silver nitrate, whichever was necessary, was now added to attain this equivalence. These standard solutions contain rubidium chloride or silver nitrate equivalent to 0.1 mg. of silver per ml. The analytical solution was then diluted to 0.025 N as regards rubidium nitrate and the flask and contents packed in ice in a dark room.

Recent experiments by Johnson[4] have shown that any hydrolysis that may take place when potassium chloride is fused, under the conditions outlined above, is not significant in the measurements we are here describing; such hydrolysis would probably be less when rubidium chloride is fused under the same conditions.

When the solution had stood in the ice-bath from twenty-four to thirty hours, a 50-ml. sample was pipetted off, filtered through a platinum mat and allowed to come to the temperature of the standard solutions described below.

As has been said, Johnson's[3] (p. 832) standard solution method was followed in making the analysis. Four solutions were necessary. Two of these contained silver nitrate equivalent to 0.7 and 0.5 mg. per liter of silver, respectively. The other two contained potassium chloride equivalent to 0.7 and 0.5 mg. per liter of silver, respectively. All four were made 0.025 N with rubidium nitrate and 0.1 N with nitric acid, these being the concentrations of these compounds in the solution to be analyzed. Two precipitating solutions were also necessary. These contained as is customary potassium chloride and silver nitrate in concentrations equivalent to 1.0 g. per liter of silver.

When preparing the nephelometric suspensions for the turbidity measurements, the device suggested by Scott and Hurley[5] to be used in mixing the solutions, was employed. The solutions appeared to mix uniformly and constant turbidities could be obtained.

The suspensions having been prepared, the cups and plungers of the nephelometer, previously rinsed with water, were now rinsed with the suspension with which they were to come in contact. Comparisons were then made. If the analysis showed an excess of either silver or chloride ion, suitable additions of the standard solution of rubidium chloride or silver nitrate were made. The flask and contents were again packed in ice and the following day another sample was withdrawn and analyzed, and if necessary, another addition of standard solution made. This procedure was continued until the end-point was reached. The

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[2] Richards and Wells, THIS JOURNAL, **27**, 502 (1905).

[3] C. R. Johnson, *J. Phys. Chem.*, **35**, 830 (1931).

[4] Johnson, *ibid.*, **39**, 781 (1935).

[5] Scott and Hurley, THIS JOURNAL, **56**, 333 (1934).

time necessary to reach this end-point varied between four and eight days. The necessity of waiting for this equilibrium was evident, as we have found, in confirmation of the statements of Johnson, that when the system is not at equivalence, analysis of the supernatant liquid cannot be trusted to indicate the correct excess of chlorine or silver ion present in the system as a whole.

Results

For the purpose of reducing the observed weights of silver and rubidium chloride to the vacuum standard, the specific gravity of silver was taken as 10.49 and that of rubidium chloride as 2.753. There is therefore a correction of −0.000031 per g. for the silver and +0.00028 per g. for the alkali salt.

The equivalents used in making the necessary calculations for the following tables were Ag = 107.880 and Cl = 35.457.

TABLE I

Experiment	Silver in vacuum, g.	Rubidium chloride in vacuum, g.	Atomic weight of rubidium
1	2.15167	2.41226	85.488
2	2.47848	2.77942	85.519
3	2.59105	2.90458	85.479
4	2.23897	2.51028	85.495
5	2.71636	3.04508	85.478
6	2.01411	2.25778	85.474
7	2.18166	2.44580	85.484
8	2.31509	2.59528	85.479

Average of last *six* results 85.482

The first two results, as they were obtained from the first measurements made, may be regarded as preliminary and have not been included when computing the average value. There seems little excuse for making a more extended series of analyses, as any constant error would be repeated without finding a value for the atomic weight more nearly correct. The practice followed in the past of making a large number of analyses, following the same procedure, has not always been helpful; an unwarranted reliance on the value obtained was engendered.

The value for the atomic weight of rubidium found by early investigators[6] was considerably below the number we have obtained; approximately 85.37. The value found some years ago by one of the authors was 85.44.[7] It appears likely, that, assuming the atomic masses of silver and of chlorine to be as above, that of rubidium cannot be far from 85.48.

It seems useless to speculate as to the reason for a higher value in the present case. It is doubtful if there was an appreciable amount of sodium in the material used in 1903. The authors consider that the end-point of the reaction between the chloride and silver has been more correctly attained in the experiments here described than heretofore.

Summary

Re-investigation of the atomic weight of rubidium through the determination of the silver–rubidium chloride ratio has given a slightly higher value for this constant (85.482) than that accepted by the International Committee.

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(6) Bunsen, *Pogg. Ann.*, **113**, 339 (1861); Piccard, *J. prakt. Chem.*, **86**, 454 (1862); Godeffroy, *Ann. Chem. Pharm.*, **181**, 185 (1876).

(7) *J. Chem. Soc.*, **85**, 776 (1904).