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

The Atomic Weight of Rubidium

BY E. H. ARCHIBALD AND J. GILBERT HOOLEY

Some experiments have been described[1] on a redetermination of the atomic weight of rubidium through the measurement of the rubidium chloride–silver ratios. The value for the equivalent in question was found to be 85.482. We have since found it possible to make several determinations of the rubidium bromide–silver as well as the rubidium bromide–silver bromide ratios. These experiments are described below.

The purification of most of the chemicals used was carried out by standard methods, platinum and quartz vessels being used wherever advantageous.

Hydrobromic Acid.—The C. P. acid was distilled three times in quartz, a few crystals of potassium permanganate being added before the *initial* distillation. In each case, the first and last quarters were rejected.

Bromine.—Bromine (C. P.) was distilled once from a solution of purified calcium bromide, and then five times in quartz, with the usual rejection of the first and last quarters.

Samples of the hydrobromic acid and bromine were tested for chloride by preferential oxidation of the bromide with potassium persulfate in a boiling, dilute sulfuric acid solution. Excess silver nitrate was then added and comparison with a blank in the nephelometer showed equal turbidities, and hence the absence of chloride. That this treatment oxidizes no chloride was *proven* by applying it to a blank containing a known trace of chloride. No change in turbidity could be observed.

Rubidium Bromide.—The starting material was 45 g. of rubidium nitrate formed during the analysis of the chloride. The excess silver contained in a solution of this already pure salt was filtered off as the bromide. The solution was then evaporated with sulfuric acid until no trace of halogen was shown by the nephelometer. From this the hydroxide was prepared using barium hydroxide that had been fractionally recrystallized eight times in platinum. Conversion to the acid tartrate followed, using of course the purified tartaric acid. The rubidium bitartrate was now recrystallized four times in platinum vessels accompanied with centrifugal drainage. As the cesium acid tartrate is appreciably more soluble than the rubidium salt, impurity in the form of the heavier alkali should be eliminated from the less soluble end product.

The final yield of bitartrate was ignited to the carbonate. This was treated with hydrobromic acid, the solution filtered through platinum and part evaporated to give Sample I. The rest of the bromide in solution was converted to the tribromide by cooling the solution after adding excess bromine. The trihalide salt was then twice recrystallized and the less soluble fraction decomposed and evaporated with hydrobromic acid several times to convert it to the bromide. This gave Sample II. The mother liquor from these recrystallizations gave the material for Sample III.

Balance and weights have already been described as well as the method of weighing. Another comparison of the weights by the Richards' method showed no measurable changes.

Analysis of Rubidium Bromide

With a few variations which are noted below, the method of analysis was that described in the previous paper. Before any solution was withdrawn for the determination of the end-point, the flask containing the precipitate and supernatant liquid was allowed to remain packed in ice for a week. This flask was thoroughly shaken each day for the first four days. The analytical solutions used in the case of the bromide analyses were of much lower concentration than those employed for the chloride work. The three pairs of solutions contained 0.04, 0.08 and 0.12 mg. per liter, respectively, of silver or its equivalent. All were as before 0.025 N in rubidium nitrate and 0.10 N in nitric acid.

The nephelometric fields produced by the silver bromide suspensions were very much darker and somewhat more difficult to compare than those obtained with silver chloride; however, as the amount held in suspension was much less, analyses could be duplicated to 0.01 mg. of silver per liter.

In conjunction with the nephelometric analyses, three gravimetric determinations were carried out in the case of experiments 6, 7 and 9. The silver bromide precipitate was collected on a Gooch–Munroe crucible, washed with very dilute nitric acid, dried at 120° for six hours and then at 300° for sixteen hours in an electric furnace, provided with a quartz muffle, and weighed. It was found that after the silver bromide had been kept at 300° for eight hours a further heating for twelve hours did not change its weight by more than 0.01 mg., which is practically negligible with a balance of the sensitivity of the one used. The loss in weight of the silver bromide upon fusion was not determined, but it is worth noting that when the silver halide was fused and allowed to cool a transparent slightly amber-colored solid resulted.

The technique followed in collecting, washing and drying the precipitate, as well as in the treatment of the wash waters, was that described by C. R. Johnson.[2] The mother liquor was analyzed nephelometrically for bromide. The correction to be applied for solubility was found in this way to be between +0.12 and +0.15 mg. The acid washings were combined with the ammonia washings of all surfaces which had contacted silver bromide, acidified and diluted to 500 ml. This solution was nephelometrically analyzed for bromide by comparison with a standard solution of similar composition. The magnitude

---

[1] Archibald, Hooley, and Phillips, THIS JOURNAL, **58**, 70 (1936).

[2] C. R. Johnson, *J. Phys. Chem.*, **37**, 928 (1933).

of this correction was between +0.06 and +0.08 mg., all as silver bromide.

Results

When making the corrections necessary for reducing the observed weights of silver, silver bromide and rubidium bromide to the vacuum standard, the specific gravity of silver was taken as 10.49, of silver bromide as 6.473 and that of rubidium bromide as 3.282.

TABLE I

NEPHELOMETRIC ANALYSES

Expt.	Rubidium bromide	Rubidium bromide in vac., g.	Silver in vac., g.	At. wt. of rubidium
1	I	3.67283	2.39554	85.485
2	I	3.27067	2.13320	85.488
3	II	4.04039	2.63537	85.479
4	II	3.20309	2.08916	85.485
5	II	4.00547	2.61245	85.488
6	II	6.66951	4.35022	85.480
7	II	4.69377	3.06150	85.481
8	II	3.33389	2.17458	85.477
9	III	3.62456	2.36409	85.483
			Average	85.483

TABLE II

GRAVIMETRIC ANALYSES

Expt.	Rubidium bromide in vac., g.	Silver bromide in vac., g.	At. wt. of rubidium
6	6.66951	7.57272	85.481
7	4.69377	5.32945	85.480
9	3.62456	4.11561	85.473
		Average	85.478

The equivalents used in making the calculations for the tables were Ag = 107.880 and Br = 79.916.

These values agree well with the value found from the study of the chloride. We then have three values as follows:

From Rubidium Chloride-Silver	85.482
From Rubidium Bromide-Silver	85.483
From Rubidium Bromide-Silver Bromide	85.478
Average	85.481

The atomic weight of rubidium cannot therefore be far from 85.481.

This research was greatly aided by an award to one of us in the form of a scholarship from Dr. Francis J. Nicholson.

Summary

The nephelometric determination of the rubidium bromide–silver ratios gave a value 85.483 for the atomic weight of rubidium and the gravimetric estimation of the ratios rubidium bromide–silver bromide gave the figure 85.478. When these values are combined with that obtained from the rubidium chloride analyses the average value 85.481 is obtained for the atomic weight in question.

VANCOUVER, B. C. RECEIVED JANUARY 28, 1936

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions of Electrolytes as a Function of the Concentration. III. Cesium Iodide and Potassium Permanganate

BY GRINNELL JONES AND HOLMES J. FORNWALT

This paper describes a continuation of the earlier researches[1] carried out in this Laboratory on the viscosity of solutions for the purpose of testing further the general validity of the following: (1) the law for the variation of the viscosity with the concentration, $\eta = 1 + A\sqrt{c} \pm Bc$, proposed by Jones and Dole; (2) the Falkenhagen and Vernon[2] equation for the coefficient of the square root term A; (3) the suggestion of Cox and Wolfenden[3] that the coefficient of the linear term ($\pm B$) is made up additively of parts characteristic of each ion; (4) the extension of the Jones and Dole equation proposed by Onsager and Fuoss,[4] $\eta = 1 + A\sqrt{c} - Bc + Dc \log c + \ldots$; (5) the Root[5] equation for the variation of the density of solutions with the concentration.

Cesium iodide was selected for study because the available data on other salts indicated that the cesium ion exceeds all other cations and the iodide ion all other anions, in their tendency to cause a decrease in the viscosity of water. It is,

---

(1) Grinnell Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933); *Physics*, **4**, 215 (1933); Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, **57**, 2041 (1935).

(2) H. Falkenhagen and M. Dole, *Z. physik. Chem.*, **B6**, 159 (1929); *Physik, Z.*, **30**, 611 (1929); H. Falkenhagen, *ibid.*, **32**, 365, 745 (1931); H. Falkenhagen and E. L. Vernon, *ibid.*, **33**, 140 (1932); *Phil. Mag.*, [7] **14**, 537 (1932).

(3) W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc. London*, **A145**, 475 (1934).

(4) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(5) W. C. Root, THIS JOURNAL, **55**, 850 (1933).