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ELEVENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1903.

By F. W. Clarke.

Received January 15, 1904.

During the year 1903 comparatively few determinations of atomic weight have been published, but some of the work done is of notable importance. Other work is known to be in progress, and the output for the coming year should be of considerable magnitude. The results which have appeared so far are summarized below.

POTASSIUM AND CAESIUM.

The review by Richards and Archibald[1] relates primarily to caesium, but some determinations in regard to potassium were made incidentally. First, potassium chloride, dried at 700°, was precipitated by silver nitrate. The latter had been prepared from a known quantity of pure silver, so that two distinct ratios were determined. Vacuum weights are given throughout, and the reductions were made with $Ag = 107.930$, and $Cl = 35.455$. $O = 16$. For the ratio between KCl and AgCl we have

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[1] *Proc. Am. Acad.*, **38**, 443; also *Ztschr. anorg. Chem.*, **34**, 353.

Weight KCl.	Weight AgCl.	Atomic weight K.
2.50019	4.80600	39.137
2.50391	4.81325	39.136

For the ratio Ag : KCl the data are

Weight KCl.	Weight Ag.	Atomic weight K.
2.50019	3.61747	39.140
2.50391	3.62283	39.141

Mean of both series, K = 39.139.

Another set of measurements was made by an entirely new method. Potassium nitrate was ignited with weighed quantities of silica; K_2O as silicate remained, and N_2O_5 (or rather, its decomposition products) was driven off. From the ratio thus ascertained, $K_2O : N_2O_5$, the atomic weight of potassium was calculated, with $O = 16$ and $N = 14.040$. The data are as follows:

Weight KNO_3.	N_2O_5 lost.	Atomic weight K.
1.81034	0.96692	39.138
3.14564	1.68005	39.142
2.55598	1.36512	39.142
	Mean,	39.141

For the work on caesium, the material was purified by repeated recrystallization of the dichloriodide, $CsCl_2I$. By heating this salt to from 90° to 100° in an electric oven it was reduced to CsCl, which was spectroscopically free from other alkaline salts. Several samples of chloride were prepared, and several series of determinations were made, similar to the two sets of chloride analyses given under potassium. The data thus obtained are as follows:

RATIO AgCl : CsCl.

First Series.

Weight CsCl.	Weight AgCl.	Atomic weight Cs.
3.83054	3.26240	132.901
3.95120	3.36532	132.892
2.27237	1.93555	132.882
3.02935	2.58003	132.901
3.19774	2.72382	132.878
	Mean,	132.891

Second Series.

Weight CsCl.	Weight AgCl.	Atomic weight Cs.
2.35068	2.00253	132.858
2.06245	1.75678	132.878
2.56372	2.18358	132.892
	Mean,	132.876

Third Series.

Weight CsCl.	Weight AgCl.	Atomic weight Cs.
2.01881	1.71972	132.868
1.77391	1.51093	132.886
		Mean, 132.877

Fourth Series.

3.08160	2.62484	132.881
3.13117	2.66720	132.872
5.06656	4.31570	132.876
		Mean, 132.876

RATIO Ag : CsCl.

First Series.

Weight CsCl.	Weight Ag.	Atomic weight Cs.
3.83054	2.45600	132.880
3.95120	2.53351	132.871
2.27237	1.45686	132.891
3.02935	1.94244	132.868
3.19774	2.05023	132.883
		Mean, 132.878

Second Series.

2.35068	1.50720	132.876
2.06245	1.32251	132.862
		Mean, 132.869

Third Series.

2.01881	1.29434	132.886
1.77391	1.13743	132.871
		Mean, 132.878

Fourth Series.

3.08160	1.97590	132.872
3.13117	2.00760	132.879
5.06656	3.24850	132.879
		Mean, 132.877

The general mean of these eight means gives Cs = 132.878.

By the ignition of calcium nitrate with silica the following data were obtained:

Weight $CsNO_3$.	N_2O_5 lost.	Atomic weight Cs.
3.76112	1.04273	132.882
5.33334	0.92416	132.876
4.81867	1.33590	132.886
5.04807	1.39960	132.871
		Mean, 132.879

Caesium bromide was also studied by Richards and Archibald, and two ratios are given by them. First, for the ratio CsBr : AgBr. Br = 79.955.

Weight CsBr.	Weight AgBr.	Atomic weight Cs.
3.49820	3.08815	132.878
6.20409	5.47673	132.883
7.17300	6.33213	132.880
		Mean, 132.880

Secondly, for the ratio CsBr : Ag.

Weight CsBr.	Weight Ag.	Atomic weight Cs.
3.49820	1.77402	132.873
6.20409	3.14606	132.885
7.17300	3.63740	132.884
		Mean, 132.881

The final values deduced by the authors from all their data are, with O = 16, K = 39.140, Cs = 132.879.

FLUORINE.

Julius Meyer[1] has redetermined the atomic weight of fluorine by a new and simple method. Calcium oxide was converted into fluoride, with suitable precautions, and from the ratio thus measured the atomic weight of fluorine was easily computed. First, the oxide, slaked with water, was converted by hydrochloric acid into chloride. The latter was then repeatedly evaporated with pure hydrofluoric acid, and the resulting fluoride was ignited to constant weight at a red heat. The data, with vacuum weights, are as follows:

Weight CaO.	Weight CaF_2.	Atomic weight F.
6.1883	8.6215	19.036
4.2736	5.9548	19.042
6.2931	8.7658	19.029
5.7767	8.0485	19.038
4.9836	6.9426	19.033
		Mean, 19.036

Calculated by Meyer with O = 16 and Ca = 40.136.

IRON.

A new determination of the atomic weight of iron, by Baxter,[2] is based upon the analysis of ferrous bromide. This salt was

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[1] *Ztschr. anorg. Chem.*, **39**, 313.

[2] *Proc. Am. Acad.*, **39**, 245.

sublimed in porcelain tubes, dissolved in acidulated water, oxidized by potassium dichromate, and then mixed with a solution of silver nitrate. The silver bromide was collected on a Gooch filter and weighed. In two experiments the ferrous bromide was also balanced against silver alone. The data, as published, involve a number of corrections, which complicate the table of results. The following corrected weights have kindly been supplied to me by Dr. Baxter. They are reduced to a vacuum, and the calculations represent O = 16, Ag = 107.93, and Br = 79.955.

Weight $FeBr_2$.	Weight AgBr.	Weight Ag.	Atomic weight Fe.
3.55929	6.19873	......	55.856
3.07448	5.35450	......	55.852
2.96102	5.15696	......	55.849
4.00791	6.97983	......	55.862
2.96102	......	2.96234	55.854
4.00791	......	4.00937	55.871
		Mean,	55.857

One correction still remains to be applied. Ferrous bromide, like the corresponding bromides of cobalt and nickel, when sublimed in porcelain, becomes contaminated with small quantities of sodium bromide. In this case the contamination amounted to 0.138 per cent. Corrected for this impurity the final value for Fe becomes 55.871. This agrees fairly well with the value 55.883 previously determined by Richards and Baxter. The number 55.88 is probably quite nearly correct.

As a check upon the accuracy of his work, Dr. Baxter also redetermined the ratio between silver and bromine. In three independent experiments his data are as follows:

Weight Ag.	Weight AgBr.	Ratio Ag : AgBr.
4.77783	8.31754	57.4428
5.87977	10.23533	57.4459
4.82995	8.40809	57.4441
	Mean,	57.4443

This is nearly identical with the mean derived from Stas' experiments, *viz.*, 57.4445. From the two experiments of the ferrous bromide series in which both Ag and AgBr were determined, the values for the ratio became 57.444 and 57.442.

ANTIMONY.

The electrolytic method for determining the atomic weight of this element has been investigated by Cohen and Strengers.[1] Antimony and silver were thrown down simultaneously in the same circuit, the former from solutions of trichloride. It was found that the atomic weight thus obtained increased with the concentration of the antimony solution, varying from 120.78 to 121.92, when Ag = 107.93. The concentrations varied from 3.3 to 83.3 grams of chloride in 100 grams of solution, and the gain in apparent atomic weight was quite regular. The method, therefore, involves unknown uncertainties, and is not applicable to the purpose of measuring the atomic weight in question.

LANTHANUM.

In the report of this committee for 1902 a set of determinations, by Jones, of the atomic weight of lanthanum was given, and also certain criticisms of the work by Brauner, who claimed that it was vitiated by constant errors. In his reply[2] to Brauner, Jones claims to show that the alleged errors do not exist, and new data are given in corroboration of the former series. In the new work hygroscopic impurity was carefully guarded against, and the lanthanum sulphate was proved to be neutral. Five syntheses of sulphate from oxide, conducted in porcelain crucibles, gave the subjoined results, when O = 16 and S = 32.06.

Weight La_2O_3.	Weight $La_2(SO_4)_3$.	Atomic weight La.
1.2161	2.1132	138.79
1.6311	2.8342	138.81
1.7804	3.0938	138.79
1.4168	2.4619	138.80
1.9702	3.4235	138.80
	Mean,	138.80

The value found in 1902 was La = 138.77.

In these experiments the oxide used was perfectly white. Brauner and Pavliček heated their oxide, not in porcelain, but in platinum crucibles, and found a higher value for the atomic weight, 139.04. Jones now gives the results of two experiments in platinum, and obtains similar values, as follows:

Weight La_2O_3.	Weight $La_2(SO_4)_3$.	Atomic weight La.
1.2820	2.2264	139.02
1.3885	2.4110	139.07

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[1] *Proc. Amsterdam Acad.*, **5**, II, 543.

[2] *Ztschr. anorg. Chem.*, **36**, 92.

In this case the oxide was somewhat discolored, and most so near the wall of the platinum crucible. Jones regards this as due to a slight oxidation of the material, which would account for the higher atomic weight. The controversy, however, is probably not yet ended. Determinations of atomic weight by some process radically different from either the sulphate or the oxalate method may be necessary to settle the questions at issue.

CERIUM.

Upon the atomic weight of cerium two important and elaborate memoirs have appeared; one by Brauner and Batĕk,[1] the other by Brauner[2] alone. Only the results of the two investigations can be given here; for details, the original publications must be consulted.

First, the salt $Ce_2(SO_4)_3.8H_2O$ was dehydrated by heating to 440°. The *anhydrous* sulphate was then reduced by ignition, with suitable precautions, to Ce_2O_4. In this way, operating upon various fractions of material, Brauner and Batĕk found

Weight sulphate.	Weight oxide.	Atomic weight Ce.
1.5074	0.9130	140.12
1.7979	1.08945	140.32
1.5937	0.9665	140.13
2.6240	1.5895	140.18
1.2161	0.7370	140.38
1.4974	0.9130	140.12
1.2192	0.7386	140.21
	Mean,	140.21

Calculated with O = 16, S = 32.06, and reduction to a vacuum.

In the second paper Brauner gives a series of experiments in which the salt $Ce_2(SO_4)_3.8H_2O$ was directly reduced to Ce_2O_4. The data, with vacuum weights throughout, are as follows:

Weight octahydrate.	Weight oxide.	Atomic weight Ce.
1.98989	0.96175	140.26
1.99154	0.96251	140.25
2.33919	1.13027	140.17 (?)
1.95882	0.94679	140.28
1.20961	0.58453	140.21
1.54162	0.74504	140.24
1.67748	0.81074	140.25
2.02736	0.97985	140.26
	Mean,	140.24

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[1] *Ztschr. anorg. Chem.*, **34**, 103.

[2] *Ibid.*, **34**, 207.

Rejecting the third of these values, in which Brauner suspects a possible loss during the experiment, the mean of the remaining seven becomes 140.25.

For the determinations which the authors carried out by the oxalate method, the data are too complex for full citation here. Only results can be given. The method involves two steps: first, ignition of cerium oxalate to Ce_2O_4; and secondly, determination of C_2O_3 in another portion of oxalate by titration with potassium permanganate. From the ratio between C_2O_3 and Ce_2O_4 the atomic weight of cerium is calculated. By this process Brauner and Batěk made the following eighteen determinations:

140.28
140.465
140.45
140.165
140.29
140.43
140.38
140.075
140.33
140.075
140.075
140.20
140.10
140.32
140.30
140.37
140.42
140.05

Mean, 140.265

One more experiment by this method, cited by Brauner in the second paper, gave Ce = 140.246. As the final result of both investigations, Brauner gives

$$Ce = 140.25.$$

This agrees with earlier work by Brauner, and also with determinations by Robinson, and should replace all other measurements of this atomic weight.

RADIUM.

In the report of this committee for 1902, Madame Curie's determinations of the atomic weight of radium were cited. Her data have since appeared in full,[1] as follows:

Weight $RaCl_2$.	Weight AgCl.	Atomic weight Ra.
0.09192	0.08890	225.3
0.08936	0.08627	225.8
0.08839	0.08589	224.0

Calculated with Ag = 107.8 (?) and Cl = 35.4. Madame Curie regards the value Ra = 225 as correct to within about one unit. This conclusion finds confirmation in the work of W. Marshall

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[1] *Ann. chim. phys.*, [7], 30, 140.

Watts,[1] who has studied relations between the spectra of the elements and the squares of their atomic weights. By comparing the spectra of Ba and Ra he finds Ra = 225.05; 'and for the spectra of Hg and Ra, Ra = 224.63. Mean of all his observations, Ra = 224.89. Runge and Precht,[2] on the other hand, comparing the spectra of Ca, Sr, Ba and Ra, concluded that the atomic weight of radium is 257.8. The apparent instability of radium offers an argument in favor of this higher value. In a later paper[3] Runge criticizes Watts' method of calculation, and argues that it is entirely fallacious.

MISCELLANEOUS NOTES.

Krypton.—A new determination of the density of krypton, by Ramsay,[4] gives the value 40.81. The atomic weight, there fore, is 80.62.

Bismuth.—Adie,[5] seeking to determine the atomic weight of bismuth, obtained discordant results, which were found to be due to small quantities of silica in the material studied. To this impurity he ascribes the discrepancies between the measurements of previous observers. A preliminary experiment upon pure bismuth gave Bi = 208.8, approximately.

Tellurium.—The atomic weight of tellurium has been discussed by Koethner,[6] by Seubert,[7] and by Pellini.[8] Koethner, from an examination of all the published determinations, concludes that the most probable value is Te = 126.71, when H = 1. Seubert argues in favor of Te = 126.6, or 127.6 with O = 16. Pellini, considering the anomalous position of tellurium in the periodic system, suggests a possible impurity in the form of a radioactive element of higher atomic weight.

Numerical Relations.—This subject is discussed by Mills,[9] under the caption "Numerics of the Elements." An attempt is made to compute the atomic weights from a general mathematical formula, and arguments are adduced to show that the most probable value for O is 15.94 when H = 1. Another paper, by

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[1] *Phil. Mag.*, [6], **5**, 203; and (for radium) **6**, 64.

[2] *Physikal. Ztschr.*, **4**, 285.

[3] *Phil. Mag.*, [6], **6**, 698.

[4] *Chem. News*, **87**, 159.

[5] *Proc. Cambridge Phil. Soc.*, **12**, 240.

[6] *Ztschr. anorg. Chem.*, **34**, 403.

[7] *Ibid.*, **35**, 205.

[8] *Gazz. chim. ital.*, **33**, II, 35.

[9] *Phil. Mag.*, [6], **5**, 543.

Hughes,[1] develops relations which suggest that the elements may be constituted analogously to the organic radicals. Still a third paper, by Henry Wilde, also deserves attention.[2]

International Atomic Weights.—The report of the smaller International Committee for 1903[3] has been sharply criticized by Ostwald.[4] To this criticism, which related mainly to the standard of values, Seubert published a reply.[5] The subject of a standard has also been discussed by Winkler,[6] whose paper called forth a rejoinder by Landolt and Ostwald.[7] In a still later note, Winkler answers his critics.[8] For the purposes of this report, these references to literature are sufficient.

THE CHEMICAL COMPOSITION OF COOKED VEGETABLE FOODS.

By Miss Katharine I. Williams.

Received December 9, 1903.

The investigations described in the following pages were undertaken at the suggestion of Sir William Ramsay; during the course of the work I have received much kind assistance from Dr. S. Young, in the way of advice as to working-details. Most of the previous work published on this subject deals with analysis of raw foods; the main object of this investigation was to gain information regarding the composition of foods as served at table.

The fresh, green vegetables were bought when in full season, the leeks in April, the rhubarb in March, the broccoli and Brussels sprouts in January, asparagus in the middle of May, while the green artichokes were purchased in June.

General Preparation of the Samples Used.—The chief consideration was to obtain a sample of each vegetable food as it would be served at table, therefore, in the case of broccoli, Brussels sprouts, rhubarb, leeks, asparagus, and green artichokes the usual

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[1] *Chem. News*, **88**, 298.

[2] *Mem. Manchester Lit. Phil. Soc.*, 48, 1.

[3] This Journal, **25**, (1903)

[4] *Ztschr. phys. Chem.*, **42**, 637.

[5] *Ztschr. anorg. Chem.*, **35**, 45.

[6] *Chem. Ztg.*, **27**, 918.

[7] *Ber. d. chem. Ges.*, **36**, 3759.

[8] *Ibid.*, **36**, 4299.