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TENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1902.

By F. W. CLARKE.

Received October 16, 1902.

DURING 1902 there has been a fair amount of activity in the determination of atomic weights, and some of the work published is highly important. One new metal, radium, appears as a definite element for the first time, taking its proper place in the periodic system as a member of the calcium, strontium, barium group. The recorded investigations are summarized below. The work on iodine, calcium, selenium, lanthanum, and uranium is especially worthy of notice.

IODINE.

In order to establish more exactly the relative positions of tellurium and iodine under the periodic law, Ladenburg¹ has re-determined the atomic weight of the latter element. His process consisted in transforming silver iodide to silver chloride, by heating in chlorine, and a preliminary series of experiments gave the following results. All weights were reduced to a vacuum, and the calculations are based upon $O = 16$.

¹ *Ber. d. chem. Ges.*, **35**, 2275.

Weight AgI.	Weight AgCl.	Atomic weight I.
31.2558	19.0817	126.93
33.7357	20.5930	126.96
49.88229	30.4525	126.94
47.8830	29.2262	126.98
60.1435	36.7154	126.95
41.3649	25.2448	127.01
50.8916	31.0664	126.95
41.3233	25.2200	126.98
80.8139	49.3181	127.02
89.5071	54.6367	126.96
		Mean, 126.97

This value is notably higher than that given by Stas, 126.85, and therefore additional determinations were necessary. Three experiments, conducted with the utmost care and with all needful precautions, gave as follows:

Weight AgI.	Weight AgCl.	Atomic weight I.
62.6608	38.2496	126.957
63.8351	38.9656	126.961
74.7516	45.6288	126.963
		Mean, 126.960

This result serves to vindicate the preliminary series, but the cause of the difference from Stas' value is yet to seek. One careful experiment by Stas' method, the synthesis of silver iodide, was made by Ladenburg, whose data, with all corrections applied, are these:

50.3147 Ag gave 109.4608 AgI. Hence $I = 126.87$.

Here Stas is corroborated, and the difference is evidently due to the different methods. Ladenburg regards the synthesis of the iodide from silver as attended by much greater errors than affect the other method, and says that their tendency is to lower the apparent atomic weight of iodine. The new data, therefore, are entitled to very respectful consideration.

Two syntheses of silver iodide are also given by Scott,¹ incidentally to his research upon tellurium. The data are subjoined, and represent reductions to a vacuum, and calculations based upon $O = 16$ and $Ag = 107.93$.

Weight Ag.	Weight AgI.	Atomic weight I.
4.6240	10.0634	126.96
6.39978	13.92913	126.98

¹ *Proc. Chem. Soc. (London)*, 18, 112, May 7, 1902.

Here again there is a variation from Stas, and an agreement with the higher value obtained by Ladenburg. It seems clear that the atomic weight of iodine should be most carefully scrutinized.

CALCIUM.

An important preliminary notice by Richards¹ describes a number of experiments upon the atomic weight of calcium. The compound studied was the chloride, and the results, reduced to a vacuum, were as follows: ($O = 16$, $Cl = 35.455$.)

Weight $CaCl_2$.	Weight $AgCl$.	Atomic weight.
1.56454	4.0409	40.121
3.57630	9.2361	40.130
3.59281	9.2788	40.129
5.00880	12.9364	40.124
9.00246	23.2506	40.125
		<hr/>
		Mean, 40.126

Still another paper upon this subject, by Hinrichsen,² is supplementary to the memoir which he published in 1901.³ Transparent calcite from Russia was reduced to lime by ignition. After reduction to a vacuum and correction for known impurities in the original material, the subjoined data were obtained.

Weight $CaCO_3$.	Weight CaO .	Atomic weight.
31.20762	17.49526	40.139
22.00588	12.33642	40.136

The value found in 1901 was $Ca = 40.142$. These figures harmonize with those of Richards, and prove that the formerly accepted number, $Ca = 40$, is too low.

SELENIUM.

Atomic weight redetermined by Julius Meyer.⁴ Silver selenite, scrupulously pure, was analyzed electrolytically. The data, with all weights reduced to a vacuum, are as follows:

Weight Ag_2SeO_3 .	Weight Ag .	Per cent. Ag .	Atomic weight.
0.5152	0.3241	62.907	79.28
0.5237	0.3295	62.915	79.24
1.8793	1.1826	62.928	79.17
2.1460	1.3503	62.922	79.20
1.6964	1.0672	62.910	79.27
			<hr/>
			Mean, 79.23

¹ This Journal, 24, 374.

² *Ztschr. phys. Chem.*, 40, 746.

³ *Ibid.*, 39, 311.

⁴ *Ztschr. anorg. Chem.*, 31, 391; *Ber. d. chem. Ges.*, 35, 1591.

From the sum of the weights, corrected for a trace of silver which remained in solution after electrolysis, the final result becomes

$$\text{Se} = 79.21.$$

This figure is nearly in accord with Lenher's determination, but notably higher than that obtained by Pettersson and Ekman.

TELLURIUM.

Guthier,¹ in order to determine the atomic weight of tellurium, has studied telluric acid and tellurium dioxide. His analyses depended upon the precipitation of tellurium by hydrazine hydrate, and special precautions were taken to avoid any oxidation of the precipitated metal. The latter was found to be extremely oxidizable. First, two direct determinations were made of water in telluric acid, as follows:

Weight H_6TeO_6 .	Weight H_2O .	Per cent. H_2O .	Atomic weight.
0.4937	0.1162	23.54	127.60
0.9910	0.2335	23.56	127.70
			<hr/>
			Mean, 127.65

All weights were reduced to a vacuum, and calculations were based upon $\text{O} = 16$ and $\text{H} = 1.008$.

Secondly, Guthier gives six determinations of tellurium in telluric acid, after several fractional crystallizations of the latter. Three separate fractions were studied, with duplicate determinations on each. The data are given below:

Weight H_6TeO_6 .	Weight Te .	Per cent. Te .	Atomic weight.
0.9380	0.5204	55.48	127.20
0.4963	0.2754	55.49	127.25
1.0485	0.5829	55.60	127.80
0.8865	0.4915	55.44	127.00
0.4339	0.2411	55.56	127.60
0.3492	0.1937	55.48	127.34
			<hr/>
			Mean, 127.365

From tellurium dioxide, similarly reduced, the following data were obtained.

Weight TeO_2 .	Weight Te .	Per cent. Te .	Atomic weight.
0.1662	0.13287	79.94	127.50
0.3136	0.2507	79.94	127.50
0.2799	0.2238	79.95	127.60
			<hr/>
			Mean, 127.53

¹ *Ann. Chem.* (Liebig), **320**, 52.

The average of the three series of determinations is

$$\text{Te} = 127.51.$$

The low results of the second series are probably ascribable to traces of mother-liquor retained in some crystals of the telluric acid.

A preliminary notice upon the atomic weight of tellurium has also been published by Scott.¹ The substances studied were trimethyl tellurium iodide, $\text{Te}(\text{CH}_3)_3\text{I}$, and the corresponding bromide. Analyses of the iodide were as follows:

Weight $\text{Te}(\text{CH}_3)_3\text{I}$.	Weight AgI .	Atomic weight.
1.7461	1.3688	127.70
6.6425	5.20575	127.66
8.0628	6.3181	127.69

The bromide was titrated with silver solution, and gave these results:

Weight $\text{Te}(\text{CH}_3)_3\text{Br}$.	Weight Ag .	Atomic weight.
2.4294	1.0373	127.77
6.8424	2.9201	127.78

The second sample of bromide was not so pure as the first. Rejecting it, the mean of the other four determinations gives $\text{Te} = 127.70$. The mean of all five is 127.74. All weights are reduced to a vacuum, and the antecedent values are $\text{O} = 16$, $\text{C} = 12.00$, $\text{H} = 1.0075$, $\text{I} = 126.85$, $\text{Br} = 79.95$, $\text{Ag} = 107.93$.

LANTHANUM.

The determinations of atomic weight by Jones² were made upon material of remarkable purity. The only contamination which could be detected with the Rowland spectroscope of the Johns Hopkins University, was a trace of cerium, amounting to not more than 0.01 per cent. and probably much less. Furthermore, some of the lanthanum oxide was ignited in hydrogen in order to make sure that no oxide higher than La_2O_3 was present. The method of determination was the usual synthesis of sulphate from oxide, and careful experiments showed that under the conditions of the investigation no acid sulphate was formed. The sulphate which was finally weighed was perfectly soluble in water and absolutely neutral in reaction. Twelve determinations are given, as follows: The atomic weight was calculated with $\text{O} = 16$, and $\text{S} = 32.06$.

¹ *Proc. Chem. Soc. (London)*, 18, 112, May 7, 1902.

² *Am. Chem. J.*, 28, 23.

Weight La_2O_3 .	Weight $\text{La}_2(\text{SO}_4)_3$.	Atomic weight.
1.0122	1.7592	138.72
1.1268	1.9581	138.78
0.94585	1.6437	138.77
1.0675	1.8553	138.73
0.9030	1.5692	138.78
1.1273	1.9589	138.79
0.9407	1.6347	138.78
1.0455	1.8168	138.78
1.1271	1.9586	138.78
1.3074	2.2720	138.77
1.3389	2.3267	138.77
1.2012	2.0874	138.78
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		Mean, 138.77

An attempt was also made to use the oxalate method, but that proved to be unsatisfactory.

A second memoir upon lanthanum, by Brauner and Pavlicek,¹ is even more elaborate than that of Jones. The method of determination was the same in both cases, but there are many differences of detail. The Bohemian authors find a serious difficulty in the presence of the acid sulphate, for which measured corrections are applied, and they also note another source of error in the hygroscopic character of $\text{La}_2(\text{SO}_4)_3$. The latter error was guarded against by special precautions in weighing. The final results (omitting a preliminary series), with vacuum weights, and all corrections applied, are as follows: The calculations depend upon $\text{O} = 16$ and $\text{S} = 32.06$.

Weight La_2O_3 .	Weight $\text{La}_2(\text{SO}_4)_3$.	Atomic weight.
1.06562	1.85054	139.036
1.00694	1.74856	139.053
1.12553	1.95457	139.038
1.70276	2.95707	139.026
1.02460	1.77943	139.009
1.28650	2.23419	139.024
1.06488	1.84910	139.068
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		Mean, 139.036

The reverse method of determination, the ignition of sulphate to oxide, gave bad results. A series of determinations by the oxalate method gave in mean, $\text{La} = 139.07$, but the individual measurements show a wide range of variation, namely, from 138.67 to 139.66. The value for the atomic weight of lanthanum derived

¹ *J. Chem. Soc.*, 81, 1243.

from the sulphate syntheses is doubtless not far from the truth. The mean of the Jones and Brauner values is

$$\text{La} = 139.905,$$

and, pending further evidence, this value may properly be adopted; although Brauner, in a later communication,¹ criticizes the work of Jones and argues in favor of his own determinations. Brauner insists strongly upon the presence of acid sulphate in the lanthanum sulphate studied by Jones, and also suggests that the latter overlooked the hygroscopic nature of his material. If further investigation sustains these criticisms, then the Brauner value is to be preferred.

YTTERBIUM.

Atomic weight redetermined by Astrid Cleve,² with very pure material. The method employed was the synthesis of the sulphate from the oxide. The data are as follows, when O = 16 and S = 32.06.

Weight Yb ₂ O ₃ .	Weight Yb ₂ (SO ₄) ₃ .	Atomic weight.
0.7791	1.2535	173.22
0.5190	0.8353	173.05
0.4905	0.7894	173.07

These figures confirm the earlier determination by Nilson.

URANIUM.

The work of Richards and Merigold³ upon the atomic weight of uranium is rich in details, and also in matter relative to probable sources of error. The substance finally chosen for study was uranous bromide prepared by sublimation, and scrupulously protected from the oxidizing action of the air. It contained a minute quantity of sodium bromide, but the amount of this was determined, and the necessary correction was applied. All weights refer to a vacuum, and the antecedent atomic weights were O = 16, Ag = 107.93, and Br = 79.955. A preliminary series of analyses gave as follows, all corrections included:

Weight UBr ₄ .	Weight AgBr.	Atomic weight.
2.2058	2.9699	238.36
1.4418	1.9401	238.69
1.4050	1.8910	238.56
1.1749	1.5818	238.39

Mean, 238.50

¹ *Ztschr. anorg. Chem.*, **33**, 317.

² *Ibid.*, **32**, 129.

³ *Proc. Amer. Acad.*, **37**, 365.

In another and final set of experiments, the uranous bromide was titrated with known amounts of pure silver, and the precipitated silver bromide was also weighed. Hence two ratios were determined, with the following results:

Weight UBr ₄ .	Weight AgBr.	Atomic weight.
1.7999	2.4226	238.54
1.0662	1.4352	238.50
1.8551	2.4967	238.59
		<hr/> Mean, 238.54
Weight UBr ₄ .	Weight Ag.	Atomic weight.
1.7999	1.3918	238.49
1.0662	0.8245	238.46
1.8551	1.4342	238.60
		<hr/> Mean, 238.52
	Average of all determinations,	238.52
	Average of last six determinations,	238.53

This result is notably lower than the usually accepted value for the atomic weight of uranium.

From series 2 and 3 the ratio between silver and bromine may be deduced. It gives for the percentage of Ag in AgBr the number 57.447. Stas found 57.445. This agreement is eminently satisfactory.

RADIUM.

By many fractional crystallizations, Madame Curie¹ has succeeded in preparing radium chloride sufficiently pure for determinations of the atomic weight of the metal. According to Demarcay, who examined the spectrum of the material, it contained a minimum quantity of barium, incapable of exerting any appreciable influence upon the atomic weight. Three analyses were made, the chlorine being weighed as silver chloride, with the following values deduced for the atomic weight of radium.

225.3
225.8
224.0
<hr/> Mean, 225.0

MISCELLANEOUS NOTES.

Several papers have appeared during the year, dealing with numerical relations between the atomic weights of the various

¹ *Compt. Rend.*, **135**, 161.

elements. Three of them, by Bilecki,¹ Marshall,² and Hollins,³ relate to possible modifications of "Prout's law"; that is, they point out relations analogous to, but not identical with, those assumed by Prout. Schmidt⁴ and Stoney⁵ discuss the connection of the atomic weights in a more purely mathematical way, and so too does Vincent.⁶ The logarithmic spiral of Stoney is especially suggestive. There is also an elaborate memoir by Lord Kelvin⁷ on the "weights of atoms"; and a discussion by Clarke⁸ of the best method for the reduction and combination of atomic weight determinations. Ebaugh's work on the atomic weight of arsenic,⁹ which was cited in the report of your committee for 1901, has appeared in full in this Journal.

INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

This committee, which was too large for effective working, has appointed a smaller body for action. This smaller committee, consisting of F. W. Clarke, T. E. Thorpe and Karl Seubert, has already reported, and its report has appeared in this Journal.¹⁰ The table of atomic weights, there given, need not be repeated here.

THE DISTRIBUTION OF HYDROGEN SULPHIDE TO LABORATORY CLASSES.

BY CHARLES LATHROP PARSONS.

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SO MUCH has been written regarding new forms of generators for hydrogen sulphide and their use in the laboratory that one must needs approach the subject with trepidation and, at least, the semblance of an apology. There are, however, few teachers of chemistry who have not experienced the many inconveniences in the use of this most important laboratory reagent, inconveniences that are too frequently little understood by the student himself and which are generally the direct result of wasteful use. It is

¹ *Chem. Ztg.*, **26**, 399.

² *Ibid.*, **26**, 663, and *Chem. News*, **86**, 88.

³ *Chem. News*, **86**, 147.

⁴ *Ztschr. anorg. Chem.*, **31**, 147.

⁵ *Phil. Mag.* (6), **4**, 411 and 504.

⁶ *Ibid.*, (6), **4**, 103.

⁷ *Ibid.*, (6), **4**, 177 and 281.

⁸ *Am. Chem. J.*, **27**, 321.

⁹ This Journal, **24**, 489, June, 1902.

¹⁰ V. **25**, p. 1, January, 1903; and *Ztschr. angew. Chem.*, **15**, 1305.