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TWENTIETH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1912.

BY F. W. CLARKE.

Received January 16, 1913.

During 1912 a number of investigations upon atomic weights have been published, covering a rather wide field. The numerical data are as follows:

Nitrogen.—Wourtzel,¹ by the oxidation of NO to N_2O_4 , has obtained the following figures for nitrogen:

Weight NO.	O taken up.		At. wt. N.
1.3653	0.72805		14.005
1.76655	0.9419		14.008
1.5983	0.85225		14.006
1.9562	1.04305		14.007
2.1854	1.1652		14.008
			·····-
		Mean,	14.0068

Chlorine.—The synthesis of NOCl, by the direct union of $2NO + Cl_2$ gave Wourtzel² the subjoined results. The atomic weight of chlorine was computed with N = 14.008.

Weight Cl ₂ .		At. wt. Cl.
2.1667		35.461
I.775I		35.400
2.5632		35 . 459
2.25875		35.461
2.8994		35 · 457
	Mean,	35.4596
	Weight Cl ₂ . 2.1667 1.7751 2.5632 2.25875 2.8994	Weight Cl ₂ . 2.1667 1.7751 2.5632 2.25875 2.8994 Mean,

¹ Compt. rend., 154, 115. ² Ibid., 155, 345. Wourtzel¹ has also determined the density of nitrosyl chloride, and found the weight of the normal liter to be 2.9919 grams. Hence he deduces a molecular weight of 65.456, which is probably too low.

The ratio between NH_3 and HCl, previously studied by Thomsen, has been remeasured by Baume and Perrot.² After rejecting several failures, the following results are regarded as satisfactory. Computed with N = 14.008 and H = 1.008.

Weight HCl.	Weight NH_3 .		At. wt. Cl.
1.50409	0.70245		35 · 459
1.28613	0.60046		35.471
0.56776	0.26514		35.462
I . 47740	o.68995		35.461
2.08181	0.97219		35 . 462
		Mean,	35.463

Bromine.—The complete synthesis of hydrobromic acid has been effected by Weber,³ with all the refinements suggested by his former work with Noyes on chlorine. The hydrogen was weighed in palladium, and the bromine in potassium bromoplatinate. For the details involved in collecting and weighing the hydrobromic acid the original memoir must be consulted. The corrected weights are given in the following table, with the atomic weight of bromine referred to H = I:

Weight H	Weight Br.	Weight HBr.	H : Br.	H:HBr.
0.77300	61.28837	63.06052	79.2863	80.2853
o.8606o	68.25033	69.11144	79.3055	80.3061
0.7 7607	61.54733	62.32198	79.3064	80.3046
0.96927	76.88221	77.85135	79.3197	80.3195
1.07545	85.29562	86.37092	79.3114	80.3114
0. 99689	79.06834	80.06424	79.3150	80.3140
0.74966	59.45275	60.20500	79.3063	80.3097
0.98161	77.85554	78.83758	79.3141	80.3145
1.00131	79.39633	80.39658	79.2915	80.2914
0.81983	65.02140	65.83867	79.3108	80.3077
		Mean,	79.3067	80.3 06 4

The two series of values combined give Br = 79.3066, when H = 1, or 79.924 with O = 16.

Fluorine.—McAdam and Smith⁴ have sought to determin the atomic weight of fluorine by a new method, namely, by converting sodium fluoride into chloride by heating in a current of dry, gaseous hydrochloric acid. Two determinations only are given, the work so far being regarded as

³ THIS JOURNAL, 34, 1294.

4 Ibid., 34, 592.

¹ Compt. rend., 155, 152.

² Ibid., 155, 461.

preliminary. The atomic weight of fluorine was computed with Na = 23.00, and Cl = 35.46.

Weight NaF.	Weight NaCl.	At. wt. F.
4.3274	6.0208	19.0176
3.39398	4.72260	19.0133

Phosphorus.—Two important memoirs on the atomic weight of phosphorus have been published from the Harvard laboratory. First, Baxter, Moore and Boylston^I have made three series of analyses of the tribromide, PBr_{s} , by the usual Harvard methods. The results, with vacuum weights, are as follows:

Weight PBr ₈ . Weight Ag. At. wt. P. Weight Ag. 5.95293 7.11504 31.031 12.38 4.71056 5.63022 31.028 9.800 4.72373 5.64583 31.034 9.824 6.47622 7.74048 31.031 13.474 4.61956 5.52140 31.030 9.612 7.62060 9.10849 31.025 3.83321 4.58163 31.030 9.832 4.72578 5.64835 31.030 9.832	AgBr. At. wt. P. 560 31.035 058 31.039 830 31.031 428 31.036 143 31.034 563 261 31.025 261 31.029
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3.83321 4.58163 31.025 7.975 4.72578 5.64835 31.030 9.832	563 31.025 261 31.029
4.72578 5.64835 31.030 9.833	261 31.029
	21 022
Mean, 31.031	31.033
Series II.	
Weight PBr ₃ . Weight Ag. At. wt. P. Weight	AgBr. At. wt. P
3.21808 3.84649 31.018 6.69	553 31.034
5.77604 6.90379 31.025 12.01	761 31.034
5.51730 6.59456 31.024 11.47	946 31.030
7.15048 8.54653 31.026	
7.94753 9.49930 31.023 16.53	569 31.032
4.30924 5.15074 31.018 8.96	595 31. 029
Mean, 31.022	31.032
SERIES III.	
Weight PBr ₃ . Weight Ag. At. wt. P. Weight	AgBr. At. wt. P
4.39626 5.25447 31.032 9.14	663 31.040
7.07758 8.45957 31.021 14.72	2642 31.019
4.19854 5.01851 31.013 8.73	586 31.022
7.26540 8.68405 31.021 15.11	725 31.018
7.75072 9.26406 31.023 16.12	31.013
Mean, <u>31.022</u>	31.022

The mean of all, when Ag = 107.88, is P = 31.024.

The second memoir, by Baxter and Moore,² deals with analyses of phosphorus trichloride, PCl_3 . The results obtained may be massed in two series, as follows:

¹ This Journal, 34, 259.

² Ibid., 34, 1644.

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		SERIES I.		
Weight PCl ₃ .		Weight Ag.		At. wt. P.
3.60 897		8.50148		31.018
3.49255		8.22734		31.016
3.80549		8.96427		31.020
4.64502		10.94 2 12		31.017
3.99011		9 · 39 943		31.016
3.38036		7.96 30 1		1 31.017
			Mea	n , 31.017
		Series II.		
Weight PCl ₈ .	Weight Ag.	At. wt. P.	Weight AgCl.	At. wt. P.
4 - 59507	10.82441	31.017	14.38118	31.026
4 40117	10.36771	31.016	13.77494	31.020
5.71561	13.46408	31.017	17.88933	31.020
5 . 18668	12.21814	31.016	16.23430	31.019
5.15583	12.14555	31.015	16.13727	31.017
5.13108	12.08725	31.015	16.05962	31.018
4.85457	11.43585	31.016	15.19245	31.0 3 4
3.58844	8.45324	31.016	11.23091	31.024
5.91915	13.94377	31.015	18.52592	31.020
	Mean,	31.016		31.022

The mean of all, when Ag = 107.88, is P = 31.018.

Iron.—Baxter and Hoover¹ have redetermined the atomic weight of iron by reduction of ferric oxide in hydrogen. Two series of analyses were made, one with artificial the other with meteoric iron. The data, with vacuum weights, are subjoined:

	SERIES I.		
Weight Fe ₂ O ₈ .	Weight Fe.		At. wt. Fe.
4.86111	3 - 39995		55.845
7.59712	5.31364		55.847
6.50945	4.55298		55.841
8.00040	5.59576		55.849
7.27260	5.08661		55.846
7.69441	5.38155		55.843
7.33754	5.13213		55.849
	SERIES II.		
4.46431	3.12240		55.844
4.85179	3.39351		55.849
5.21397	3.64674		55.845
5.99087	4.19030		55.853
6.70197	4.68752		55.847
		Mean of all,	55.847

Uranium.--Lebeau² has redetermined the atomic weight of uranium

¹ This Journal, 34, 1657.

² Compt. rend., 155, 161.

by calcination of uranyl nitrate, $UO_2(NO_3)_2.2H_2O$ to UO_2 . His figures are as follows:

Weight nitrate.	Weight UO ₂ .	At. wt. U.
0.9657	0.6067	238.48
1.6038	1.0077	238.56
1.8226	1.1451	238.51
2.1934	1.3783	238.64
2.7473	1.7262	238.57
3.9402	2.4755	238.50

Mean, 238.54

Lebeau rejects the fourth determination, and then U = 238.52.

Another determination of this atomic weight has been published by Oechsner de Coninck.¹ He calcined uranic oxalate to UO_2 , and in seven analyses obtained values for U ranging from 238.16 to 238.91; in mean 238.44.

Copper, Zinc, Lead.—Pecheux² has sought to determin the atomic weights of these metals by their simultaneous electrolytic precipitation in circuit with silver. He gives inadequate details, and only single values which are stated to be the means of pairs. He finds, when Ag = 107.88, Cu = 63.43, Zn = 65.44, Pb = 206.86.

Mercury.—Easley and Brann³ have redetermined the atomic weight of mercury, by analysis of mercuric bromide. The data, with vacuum weights and referred to Ag = 107.88 and Br = 79.92, are as follows:

Weight HgBr ₂ .	Weight AgBr.	At. wt. Hg.
8.93958	9.31480	200.63
14.36691	14.96940	200,64
10.13638	10.56230	200.61
9.94452	10.36218	200.62
12.60142	13.13051	200.63
12.16157	12.67122	200.65
11.19762	11.66809	200,62
16.16607	16.84235	200.68
11.28487	11.75970	200,59
17.25074	17.97597	200.61
14.20924	14.80685	200.61

Mean, 200.64

This confirms Easley's former work with mercuric chloride.

Tellurium.—The controversy over the integrity of tellurium as an element still continues. Pellini⁴ has published figures, which need not be reproduced in detail, representing numerous analyses of fractionated ma-

- * THIS JOURNAL, 34, 137.
- * Atti accad. Lincei, [5] 21, 218.

¹ Compt. rend., 155, 1511.

² Ibid., 154, 1419.

terial, all the fractions giving practically the same atomic weight. In a brief paper, Flint¹ defends his evidence showing that tellurium is complex. Morgan² reports a number of experiments which show that the atomic weight of tellurium is constant. A paper by Dudley and Jones³ on the spectrum of tellurium also bears on the controversy, which still seems to be unsettled, but with the weight of evidence so far, adverse to Flint.

Ruthenium.—Vogt⁴ has given a series of analyses of ruthenium dioxide, by the usual reduction method, which confirm the accepted value for the atomic weight of this metal. The following figures are reported:

Weight RuO.	Weight Ru.	At. wt. Ru.
1.11748	0.84998	101.68
0.39454	0.30009	101.67
0.67499	0.51315	101.46
0.74681	0.56800	101.65
0.57902	0.44043	101.69
0.40827	0.31049	101.61
		······

Mean, 101.63

Palladium.—Shinn⁵ has reinvestigated the atomic weight of palladium, by analysis of the well known chloride, $Pd(NH_3Cl)_2$. This salt was reduced in aqueous solution by ammonium formate, which precipitated the palladium quantitatively. The results obtained vary more than is satisfactory, which leads Shinn to suppose that the chloride used is less definit than it has been assumed to be. The actual results are as follows: when Cl = 35.46 and N = 14.01:

Weight chloride.	Weight Pd.	At. wt. Pd.
1.03021	0.51923	106.685
1.45506	0.73323	106.675
1.10384	0.55645	106.705
0.88141	0.44448	106.804
1, 53091	0.771 60	106.688
1.98887	1.00212	106.625
1.45102	0.73174	106.808
1.57909	0.79563	106.620
1.61705	0.81583	106.779

Mean, 106.709

This mean is practically identical with the accepted International value.

Osmium.—Seybold⁶ has determined the atomic weight of osmium by eight analyses of ammonium osmichloride, $(NH_4)_2OsCl_6$. Five of the

- ⁴ Sitzungsb. phys. med. Soz. Erlangen, 43, 268.
- ⁵ This Journal, 34, 1448.
- ⁸ Inaug. Diss., Erlangen, 1912.

¹ THIS JOURNAL, 34, 1325.

² Ibid., 34, 1669.

^a Ibid., 34, 995.

analyses gave percentages of metal ranging from 43.203 to 43.221. From the mean of these Seybold finds Os = 189.4; a very low value. In the other three experiments the percentage of osmium was from 43.412 to 43.452; or 43.437 in mean. Hence, Os = 191.1. Seybold prefers the lower figure, on the ground that the osmium in the higher series had probably absorbed oxygen. The investigation is by no means conclusive.

Platinum.--Atomic weight redetermined by Schulz, I by reduction of ammonium chloroplatinate in hydrogen. The figures obtained are as follows

Weight N ₂ H ₈ PtCl ₆ .	Weight Pt.	At. wt. Pt.
3.53199	1.54910	194.41
2.31493	1.01537	194.43
3.84762	1.68867	194.63
1.52569	0.66953	194.59
2.20900	0.96880	194.39

Mean, 194.49

The value is evidently too low.

Scandium.—A new measurement of the atomic weight of scandium is due to Meyer and Goldenberg.² Three determinations by the sulfate method gave the subjoined results:

Weight sulfate.	Weight oxide.	At. wt. Sc.
1.5924	0.5766	44.11
2.4207	0.8765	44.11
2.6394	0.9565	44.20

Mean, 44.14

This agrees with the accepted value. The higher figure previously reported by Meyer and Winter was due to the presence of a little thoria in the material employed.

Radium.-Gray and Ramsay⁸ determined the atomic weight of radium by converting the bromide into the chloride by heating in a current of gaseous hydrochloric acid. The weighings, in milligrams, were made with a microbalance, and corrected to a vacuum. Omitting some rejected experiments, the following figures are available:

137	aight	DoDe.	***
w	eight	RaBr ₂₁	mg.

Weight RaCl ₂ , mg.	At. wt. Ra.
2.19586	226.40
2.12492	226.25
2.00988	226.35
1.87275	226.35
1.81711	226.45
	Weight RaCl ₂ , mg. 2.19586 2.12492 2.00988 1.87275 1.81711

Mean, 226.36

¹ Inaug. Diss., Erlangen, 1912.

³ Proc. Roy. Soc., 86A, 270.

² Chem. News, 106, 12.

As a check upon the radium determinations, Ramsay and Gray redetermined, by the same method, the atomic weight of barium. Two measurements gave Br = 137.37 and 137.32. This agrees fairly well with the accepted value.

Ramsay and Gray's value for radium agrees with that of Mme. Curie, but is much higher than that found by Hönigschmid. In his first paper¹ he reports the results of a series of analyses of radium chloride, by what may be called the "Harvard method." More than a gram of material was available for this work. The following results were obtained:

Weight RaCl ₂ .	Weight AgCl.	At. wt. Ra.	Weight Ag.	At. wt. Ra.
1.06167	1.02534	225.92		
1.03300	0.99751	225.96		
1.01687	0.98205	225.93	· · · · •	
0.99905	0.96473	225.96	0.72626	225.89
0.98555	0.95166	225.97	0.71630	225.95
0.97142	0.93804	225.96	0.70600	225.96
0. 603 85	0.58316	225.93		
		<u></u>		
	Mean,	225.95		225.93

In a second paper,² written in consequence of Ramsay and Gray's research, Hönigschmid gives several analyses of radium bromide, a salt of which he had 1.2 grams to work with. The data, reduced to a vacuum, are as follows:

Weight RaBr ₂ .	Weight AgBr.	At. wt. Ra.
1.17016	1.13940	225.90
0.9965 9	0.97022	225.97
0.90111	0.87733	225.94
0.75505	0.73504	225.98

Mean, 225.96

Between the lower and the higher value for Ra it would be premature to decide.

Miscellaneous Notes.—Hinrichs,³ in one paper, seeks to show that Ag = 108 exactly; and in another he discusses systematic errors in atomic weight determinations. LeChatelier,⁴ however, has criticized Hinrichs' mathematical method, and claims that it is fallacious. The question of KCl in KClO₃, as bearing upon the molecular weight of chlorine, has been considered by Meyer and Staehler⁵ and also by Guye.⁶

On the nature of atomic weight, see Katayama,⁷ whose memoir is

¹ Monatsh. Chem., 33, 253.

² Anzeiger Akad. Wien, No. 18, July 11, 1912.

³ Compt. rend., 154, 211 and 1227.

⁴ Ibid., 155, 110.

^o Z. anorg. Chem., 77, 255.

⁶ J. chim. phys., 10, 145.

⁷ Science Rep., Tôhuku Imperial University, Sendai, Japan, 1, 3.

purely mathematical. Feilmann¹ has discussed the approximation of atomic weights to integral and semi-integral numbers.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE RARE EARTHS OF THE CAROLINA MONAZITE SANDS.

BY C. JAMES.

Received January 10, 1913.

According to some writers, the yttrium earths, derived from the monazite sands of Carolina, contain an element, which prevents the rapid fractionation of this mixture. It occurred to the writer that it would be extremely interesting to apply the bromate method to these earths. It is true that the yttrium metals from monazite have been submitted to this method, but in previous work they were added to euxenite earths and the whole treated together. The conditions were therefore different and no conclusions could be drawn.

The material used in this work was obtained by treating a solution of monazite earths with potassium sulfate. The latter salt was added in an insufficient quantity to precipitate all the cerium metals. It was hoped that, by leaving a fair amount of neodymium, etc., in solution, nearly all the samarium and gadolinium, contained in the original mineral, would be left unprecipitated. The filtrate was treated with oxalic acid and the resulting oxalate was the starting point for this study.

These earths were prepared in this manner by Dr. H. S. Miner, to whom the author desires to express his sincere thanks.

The oxalates were converted into oxides by ignition, after which they were dissolved in nitric acid. Since cerium was present in considerable amount, some of the original oxalate was boiled with the solution to reduce all cerium in the ceric condition. The nitrate solution was then poured into large earthenware vessels, and the whole allowed to settle. The clear liquid was syphoned off and mixed with magnesium nitrate. (The magnesium nitrate was prepared from ignited magnesite by dissolving it in nitric acid. The neutral solution was then treated with a slight excess of magnesite at the boiling point. This threw down the small quantities of iron and aluminium that were present. These hydroxides were separated from the solution by filtration through cloth.)

The double magnesium nitrates were fractionally crystallized from water acidified with nitric acid. Lanthanum, cerium and praseodymium rapidly passed into the less soluble fractions. The intermediate crystals carried nearly all the neodymium together with very small quantities of praseodymium. The mother liquors, which crystallized badly, owing to the accumulation of iron and aluminium in addition to

¹ Proc. Chem. Soc., 28, 283.

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