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TWENTY-SIXTH ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS.

DETERMINATIONS PUBLISHED DURING 1918 AND 1919.

BY GREGORY PAUL BAXTER.

Received February 12, 1920.

For the first time since 1916 the International Committee on Atomic Weights[1] recommends changes in its table. In the case of elements affected by the report the old and new values are given below:

	1916.	1920.
Argon	39.88	39.9
Boron	11.0	10.9
Columbium	93.5	93.1
Gallium	69.9	70.1
Nitrogen	14.01	14.008
Thorium	232.4	232.15
Yttrium	88.7	89.33

The individual determinations published during the last two years are as follows:

Helium.—Guye[2] continues his discussion of general errors affecting atomic weight determinations, with especial reference to exact weighing and the microbalance. Taylor's[3] results on the density of helium are recalculated, with the result 3.998 for the atomic weight of this element.

[1] THIS JOURNAL, 41, 1881 (1919).

[2] *J. chim. phys.*, 16, 46 (1918).

[3] *Phys. Rev.*, 10, 653 (1917).

Boron and Fluorine.—Smith and van Haagen[1] converted weighed quantities of very carefully dehydrated borax into a number of different sodium salts, by evaporation in a platinum flask with methyl alcohol and acid. In some cases the acid used during the expulsion of the methyl borate corresponded to the sodium salt finally weighed. In others formic acid was employed in the preliminary evaporation and the formic acid was eventually displaced by the acid finally combined with the sodium. In 3 experiments the sodium fluoride which was first obtained was weighed and then was converted to sulfate quantitatively, and in one experiment a similar process was adopted with sodium chloride. Except in the case of sodium fluoride and sulfate, one experiment only of each sort was completed. The same specimen of borax was used throughout. This was prepared by combining sodium carbonate with a slight excess of boric acid, and crystallizing the product many times with one intermediate fusion. Vacuum weights are given. C = 12.005; N = 14.010; Na = 22.997; S = 32.069; Cl = 35.457.

Expt.	Wt. of $Na_2B_4O_7$.	Wt. of salt.	At. wt. B.	At. wt. F.
		NaCl		
IV	0.89853	0.52112	10.896	19.002
		Na_2SO_4		
		0.63313	10.905	
		NaF		
V	0.69695	0.29042		19.005
		Na_2SO_4		
		0.49113	10.901	19.006
		Na_2SO_4		
VI	1.59374	1.12315	10.898	
		$NaNO_3$		
VII	1.86458	1.57250	10.900	
		Na_2CO_3		
VIII	1.97702	1.03946	10.903	
		NaF		
IX	1.99197	0.83003		19.004
		NaF		
X	1.60201	0.66757		19.006
		Na_2SO_4		
		1.12889	10.902	19.008
		NaF		
IX	2.64768	1.10329		19.005
		Na_2SO_4		
		1.86597	10.896	19.002
		Average,	10.900	19.005

The International Committee on Atomic Weights has adopted this new value for boron.

Carbon.—Stahrfoss[2] has determined the densities of acetylene, ethylene

[1] *Carnegie Inst. Publication*, 267, 1918.

[2] *J. chim. phys.*, 16, 175 (1918).

and ethane. Acetylene was prepared by dropping a mixture of calcium carbide, potassium dichromate and ferrous chloride into water, and, after scrubbing and drying, was fractionally distilled. The numbers represent the weight of the liter in grams. In the last column the correction for deviation from Boyle's law is applied.

Globe A. 349.58 cc.	Globe B. 578.80 cc.	Globe C. 893.10 cc.	Average.	Corrected average.
1.17876	1.17905	1.17871	1.17884	1.17926
1.17849	1.17897	1.17921	1.17889	1.17925
1.17842		1.17841	1.17842	1.17879
			Average,	1.17910

Ethylene was prepared from ethyl alcohol and phosphoric acid, and also, after purification and drying, was purified by fractional distillation.

Globe A.	Globe B.	Globe C.	Average.	Corrected average.
1.26030	1.26031	1.25997	1.26019	1.26094
1.26177	1.26078	1.26183	1.26146	1.26210
1.26031	1.26001	(1.26396)	1.26016	1.26096
			Average,	1.26133

Stahrfoss prefers to reject the second series. If this is done the average is 1.26095.

One sample of ethane was made by allowing ethyl bromide to act upon magnesium and decomposing the product with water. The gas was purified and fractionated.

Globe A.	Globe B.	Globe C.	Average.	Corrected average.
1.35466	1.35430	1.35502	1.35466	1.35632
1.35400	1.35482		1.35411	1.35621
	1.35416	1.35521	1.35468	1.35668
	1.35399	1.35381	1.35390	1.35585
			Average,	1.35629

A second sample of ethane, resulting from the action of ethyl cyanide upon sodium, was purified as above.

Globe A.	Globe B.	Globe C.	Average.	Corrected average.
1.35493	1.35459	1.35525	1.35492	1.35684
1.35450	1.35456	1.35525	1.35477	1.35701
1.35450	1.35440	1.35489	1.35460	1.35687
			Average,	1.35690
			Average of both series,	1.35660

If the results of the last 7 experiments are averaged with 12 previously obtained by Baume and Perrot[1] and corrected, the final value 1.3565 is obtained.

It is stated that by the method of critical constants the atomic weight of carbon is calculated to be 12.00, but details of the treatment of results are lacking.

[1] *J. chim. phys.*, **7**, 369 (1909).

Batuecas[1] also has determined the density of ethylene, prepared by the reaction of alcohol on (1) phosphoric acid, (2) boric acid, (3) sulfuric acid, and (4) by the catalytic decomposition of alcohol. After purification and drying the ethylene was fractionally distilled. In the following table the correction for deviation from Boyle's law has been applied:

Method of preparation.	Globe RT. 615.23.	Globe 3. 602.69.	Globe 4. 793.70.	Average.
1 preliminary	1.25985	1.26033		1.26009
1	1.26047	1.25999	1.26041	1.26029
1	1.26002	1.26022	1.26052	1.26025
2		1.26045		1.26045
3	1.26029	1.26003	1.26031	1.26021
3	1.26047	1.26050	1.26052	1.26050
4	1.26012	1.26037	1.26047	1.26032
4	1.26029	1.26046	1.26031	1.26035
Average,	1.26022	1.26029	1.26042	1.26031

By comparison with oxygen the molecular weight of ethylene and the atomic weight of carbon (H = 1.0077) are computed.

By the molecular volume method	C = 11.996
By the limiting density method	C = 11.999
By the critical constant method	C = 12.005

Argon.—Leduc[2] finds the specific gravity of argon referred to air at 0° to be 1.3787, and the coefficient of deviation from Boyle's law at 14° to be 10.2×10^{-6} per cm. of mercury between one and five atmospheres. The molecular and atomic weight of argon by the method of limiting densities is found to be 39.91. The International Committee has adopted the value 39.9.

Gallium.—Richards, Craig and Sameshima[3] purified gallium trichloride by 3 distillations in chlorine at 220–230°, 3 in chlorine at 175°, 3 in nitrogen at 90–110° and 5 at 65–80° in vacuum. In one preliminary experiment 0.43947 g. of the chloride was weighed in an exhausted glass bulb, and, after solution, was compared with silver. The chloride required 0.80587 g. of silver and yielded 1.07087 g. of silver chloride, all in vacuum. These data give the values 70.09 and 70.11 for the atomic weight of gallium. The value 70.1 has been provisionally adopted by the International Committee on Atomic Weights.

Bromine.—Guye[4] discusses the calculation of the deviation of a gas from Avogadro's rule by the method of compressibilities, with special reference to hydrobromic acid, and from the data of Moles[5] and Reiman[6]

[1] *J. chim. phys.*, **16**, 322 (1918).
[2] *Compt. rend.*, **167**, 70 (1918); *Ann. Phys.*, **9**, 5 (1918).
[3] THIS JOURNAL, **41**, 131 (1919).
[4] *J. chim. phys.*, **17**, 141 (1919).
[5] *Ibid.*, **14**, 389 (1916).
[6] *Ibid.*, **15**, 293 (1917).

finds the value of $1 + \lambda$ at one atmosphere to be 1.00934. On the basis of this value Guye[1] computes the atomic weight of bromine to be 79.920, using the average corrected weight of the normal liter as found by Moles and Reiman, 3.64423, and that of oxygen, 1.42904 ($1 + \lambda = 1.00097$). If the individual values of Moles, 3.64441, and Reiman, 3,64404, are used, however, the values 79.924 and 79.915 are obtained for bromine.

Yttrium.—Kremers and Hopkins[2] have determined the ratio of yttrium chloride to silver, using yttrium salt which had been purified for a previous investigation.[3] Vacuum weights are given. Ag = 107.88; Cl = 35.46.

Sample.	Wt. of YCl_3.	Wt. of Ag.	Ratio. $YCl_3 : 3$ Ag.	At. wt. Y.
O_{4-6}.....	3.31143	5.47636	0.60468	89.32
O_{4-6}.....	2.31979	3.83587	0.60476	89.34
O_{4-6}.....	2.26815	3.75045	0.60477	89.35
O_{4-6}.....	2.29376	3.79302	0.60473	89.33
T_{11}.....	2.00731	3.31977	0.60465	89.31
R_4.....	1.97610	3.26827	0.60463	89.30
R_4.....	2.17949	3.60389	0.60476	89.34
			Average,	89.33

This value has been adopted by the International Committee on Atomic Weights.

Tin.—Brauner and Krepelka[4] have compared tin tetrabromide, distilled in vacuum, with silver.

Wt. of $SnBr_4$.	Wt. of Ag.	Ratio, $SnBr_4 : 4$ Ag.	At. wt. Sn.
	Preliminary Series.		
1.11964	1.10206	1.01595	118.73
1.97428	1.94359	1.01579	118.67
2.35469	2.31788	1.01588	118.71
		Average,	118.70
	Final Series.		
5.11788	5.03796	1.01586	118.702
2.46875	2.43035	1.01580	118.674
0.99510	0.97961	1.01581	118.679
1.69834	1.67172	1.01592	118.727
3.54265	3.48737	1.01585	118.697
3.82180	3.76199	1.01590	118.717
		Average,	118.699

This value is in close agreement with the recent results of Briscoe, and Baxter and Starkweather.

Dysprosium.—Kremers, Hopkins and Engle[5] purified dysprosium material by fractionation of the (1) bromate and (2) ethyl sulfate. Then

[1] *J. chim. phys.*, **17**, 171 (1919).

[2] THIS JOURNAL, **41**, 718 (1919).

[3] *Ibid.*, **38**, 2332 (1916).

[4] *Rozpravy Ceské Akademie věd a uměné.* The data have been communicated privately to Dr. Krepelka.

[5] THIS JOURNAL, **40**, 598 (1918).

weighed quantities of oxide were converted to chloride in a weighed quartz flask. As the oxide was subsequently found to contain carbonate, the results of this series of experiments are rejected by the authors, and therefore are not given here. Next, the chloride, which had been rendered anhydrous by fusion in a current of hydrogen chloride, was compared with silver in the usual way. Weights are corrected to vacuum. Ag = 107.880.

Sample.	Wt. of $DyCl_3$.	Wt. of Ag.	Ratio, 3 Ag : $DyCl_3$.	At. wt. Dy.
Ethyl sulfate....	1.04979	1.26301	1.20309	162.62
	1.95604	2.35380	1.20334	162.57
	1.47475	1.77504	1.20362	162.51
	1.26253	1.51991	1.20386	162.45
	0.99677	1.20033	1.20421	162.38
	2.25129	2.70992	1.20371	162.49
Bromate.....	2.23374	2.68806	1.20338	162.56
	1.20763	1.45325	1.20339	162.56
			Average,	162.52

Erbium.—Wichers, Hopkins and Balke[1] made a comparative study of methods for the separation of yttrium from erbium, and completed preliminary experiments in which a weighed quantity of erbium oxide was converted to chloride, which was weighed. The subsequent discovery that erbium oxide made from oxalate contains carbonate even after ignition at 900°, not only makes the results of these experiments of doubtful value, but also, as the authors point out, throws suspicion on all experiments where the weight of a rare earth oxide made by ignition of the oxalate has entered into the computation of the atomic weight.

Radioactive Lead.—Hönigschmid[2] found the atomic weight of thorium-lead used by Soddy in density determinations to be 207.77.

In another investigation upon thorium-lead, Hönigschmid[3] has determined the atomic weight of lead from 3 specimens of Ceylon thorianite, of the following composition:

	I.	II.	III.
Thoria and rare earths.....	78.2	79.11	72.52
Uranium oxide.....	11.9	12.2	18.1
Pb.....	2.34	3.11	3.5
At. wt. Pb.....	207.21	206.91	206.84

Fayans, Richter, and Rauchenberger[4] separated the lead from thorite containing 30.1% of thorium, only 0.44% of uranium, and 0.35% of lead. Three determinations of the atomic weight of the lead by Hönigschmid gave an average value of 207.90.

[1] THIS JOURNAL, 40, 1615 (1918).

[2] *Physik. Z.*, 18, 114 (1917).

[3] *Ibid.*, 19, 436 (1918); *Z. Elektrochem.*, 25, 91 (1919).

[4] *Sitzb. Heidelberger Akad. Wiss.*, 1918, p. 28; *J. Chem. Soc.*, 116, II, 7.

Davis[1] purified ordinary lead and lead from samarskite by crystallization of the nitrate and chloride. Analysis of the chloride gave the value 207.27 for the atomic weight of common lead and 206.30 for that of radioactive lead.

The samarskite was found to contain 12.21% uranium and 1.03% thorium.

J. J. van Laar[2] applies a method of critical constants to the determination of the atomic weights of several elements, using the density data of various experimenters, with the following results: H = 1.00770; He = 4.000; C = 12.001; N = 14.004; S = 32.060; Cl = 35.460; Br = 79.922.

Moles[3] discusses critically revisions of atomic weights published in 1917.

Guye and Renard[4] consider the distribution of errors in determinations of atomic weights.

Guichard[5] briefly compares methods of atomic weight investigation.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

A SIMPLE, RAPID METHOD FOR THE DETERMINATION OF HALOGEN IN ORGANIC SUBSTANCES.[6]

BY W. A. VAN WINKLE AND G. MCP. SMITH.

Received November 22, 1919.

Introduction.—The present investigation is a continuation of work taken up by G. McP. Smith at the request of the Bureau of Mines shortly after our entry into the war, which led to a scheme for the rapid, approximate determination of certain gases (*e. g.*, of chloropicrin) in the air by a method of simple combustion.

In view of the difficulties involved in many of the available methods for the determination of halogen in organic compounds, this method of simple combustion was considered worthy of further investigation. And it will be shown in the experimental part that the method in its simplest form is capable of wide application, and that it can be depended upon to furnish reliable values.

Previous Work.—This method of analysis has frequently been proposed, and nothing could be simpler in principle. Trouble has always been met with, however, in carrying out the combustion, and often in

[1] *J. Phys. Chem.*, **22**, 631 (1918).

[2] *J. chim. phys.*, **17**, 266 (1919); *Chem. Weekblad*, **16**, 1243 (1919).

[3] *J. chim. phys.*, **16**, 350 (1918).

[4] *Arch. sci. phys. nat.*, **44**, 402 (1918).

[5] *Bull. soc. chim.*, **21**, 238 (1917).

[6] Excerpt from a thesis submitted to the Graduate Faculty of the University of Illinois by W. A. Van Winkle, in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.