VOL. XXXIX. MARCH, 1917. NO. 3.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

TWENTY-FOURTH ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1916.

BY GREGORY PAUL BAXTER.

Received February 1, 1917.

Determinations of atomic weights published during 1916 are chiefly confirmatory.

Hydrogen.—Burt and Edgar[1] have completed a long series of determinations of the combining ratios by volume of hydrogen and oxygen.

Series.	Number of experiments.	Ratio.
1	14	2.00289
2	12	2.00287
3	10	2.00287
4	10	2.00289
5	13	2.00287
6	4	2.00287
	Average,	2.00288

Using Morley's density ratio of oxygen and hydrogen, 1.42900/0.089873, hydrogen has the atomic weight 1.00772. If the density of oxygen is 1.42905, hydrogen becomes 1.00769.

Argon.—Schultze[2] by the globe method, working at 735 mm. has obtained the following values for the density of argon:

[1] *Phil. Trans.*, **216**, 393 (1916).

[2] *Ann. Physik*, [4] **48**, 269 (1915).

1.78374 1.78371 1.78367 Average, 1.78371

By the method of limiting densities argon is found to have the atomic weight 39.945.

Zinc.—Baxter and Grose[1] determined the zinc in anhydrous zinc bromide by depositing the metal electrolytically in a weighed mercury cathode, either directly or after changing the bromide to sulfate. A small amount of metal undeposited was estimated by evaporating the electrolyte and weighing the residue of zinc sulfate. Br = 79.916. Weights are corrected to vacuum.

Weight of $ZnBr_2$.	Weight of Zn.	At. wt. Zn.
6.88781	1.99917	65.362
6.79973	1.97324	65.345
7.67096	2.22712	65.389
8.02839	2.33122	65.402
7.18458	2.08517	65.356
7.55005	2.19181	65.380
7.71332	2.23937	65.387
7.11551	2.06599	65.395
7.44099	2.16047	65.393
7.18828	2.08727	65.401
	Average, omitting the first two analyses,	65.381

Bromine.—Moles[2] has determined the density of hydrobromic acid gas prepared by different methods and purified by fractional distillation at low temperatures. The gas was weighed in globes filled at 0° and about one atmosphere.

	Globe I. 352.06 cc.	Globe II. 602.60 cc.	Globe III. 603.09 cc.	Average.
I	3.6450	3.6453	3.6453	3.6452
II	3.6436	3.6430	3.6461	3.6442
III	3.6437	3.6453	3.6440	3.6443
IV	3.6457	3.6437	3.6444	3.6446
V	3.6449	3.6447	3.6442	3.6446
VI	3.6460	3.6444	3.6436	3.6447
VII	3.6440	3.6435	3.6448	3.6441
VIII	3.6440	3.6441	3.6437	3.6439
IX	3.6442	3.6437	3.6448	3.6443
X	3.6442	3.6442	3.6448	3.6444
XI	3.6448	3.6433	3.6450	3.6444
Average	3.6446	3.6441	3.6446	3.6444

Experiments performed at lower pressures gave the following results calculated to 760 mm.:

[1] THIS JOURNAL, **38**, 868 (1916).

[2] *Compt. rend.*, **162**, 686; **163**, 94 (1916).

P (mm.).	Globe I.	Globe II.	Globe III.	Average.
497.0	....	3.6332	3.6343	3.6337
509.1	3.6338	3.6330	3.6348	3.6338
506.96	3.6347	3.6312	3.6338	3.6332
486.1	3.6338	3.6305	3.6315	3.6319
Average.....	3.6341	3.6319	3.6336	3.6331
257.1	3.6260	3.6227	3.6229	3.6239
246.0	3.6269	3.6193	3.6209	3.6224
251.7	3.6205	3.6218	3.6204	3.6209
254.7	....	3.6209	3.6220	3.6215
251.5	3.6238	3.6206	3.6220	3.6219
251.4	3.6210	3.6195	3.6219	3.6208
Average.....	3.6236	3.6207	3.6217	3.6219

By a method of limiting densities HBr = 80.934. If H = 1.008, Br = 79.926.

Yttrium.—Hopkins and Balke[1] have continued the purification and examination of yttrium material begun by Egan and Balke. Partially purified material was fractionated (1) as chromate, (2) as hydroxide with ammonia and (3) with sodium nitrite. The atomic weight was found by converting weighed amounts of oxide to anhydrous chloride by fusion in hydrochloric acid gas in a quartz flask. Vacuum weights are used.

Wt. of Y_2O_3.	Wt. of YCl_3.	At. wt. Y.
0.56492	0.97718	88.89
0.51059	0.88348	88.80
0.64232	1.11092	88.92
0.82157	1.42087	88.93
0.68246	1.17975	89.06
0.54164	0.93688	88.89
		Average, 88.91

Columbium.—Smith and van Haagen[2] have obtained a low value for the atomic weight of columbium by converting sodium metacolumbate into sodium chloride. The carefully purified and dried salt was heated in a quartz tube in a current of carbon dioxide and sulfur monochloride. Weights are corrected to vacuum. Na = 23.00; Cl = 35.46.

Wt. of $NaCbO_3$.	Wt. of NaCl.	At. wt. Cb.
0.36419	0.12975	93.089
0.69113	0.24617	93.128
1.04904	0.37368	93.116
1.64337	0.58516	93.180
1.33367	0.47487	93.185
0.88051	0.31366	93.110
1.29947	0.46289	93.115
		Average, 93.13

[1] THIS JOURNAL, **38**, 2332 (1916).

[2] *Ibid.*, **37**, 1783 (1915). This work was overlooked in the 1915 Report.

Cadmium.—Baxter, Grose and Hartmann[1] have obtained further evidence in favor of the higher value for cadmium, by the determination of the metal in the bromide. Weighed amounts of fused salt were dissolved and the cadmium was deposited electrolytically in a weighed mercury cathode, in some experiments directly from the bromide solution, in some after conversion of the bromide to sulfate. Since deposition was always incomplete the electrolyte was evaporated to dryness and the residue, consisting chiefly of cadmium sulfate, was weighed. Br = 79.916. Vacuum weights are given.

Wt. of $CdBr_2$.	Wt. of Cd.	At. wt. Cd.
16.55663	6.83575	112.395
6.83764	2.82342	112.419
7.16223	2.95626	112.387
6.71886	2.77414	112.402
10.31855	4.26112	112.434
9.40020	3.88142	112.412
8.21123	3.39038	112.406
10.51504	4.34154	112.403
10.22411	4.22157	112.409
10.99613	4.54013	112.401
11.05166	4.56317	112.405
19.67134	8.12244	112.411
		Average, 112.407

In three similar experiments the cadmium in cadmium chloride was determined. Cl = 35.457.

Wt. of $CdCl_2$.	Wt. of Cd.	At. wt. Cd.
6.49746	3.98430	112.425
6.62682	4.06348	112.415
7.35812	4.51165	112.399
		Average, 112.413

Tin.—Baxter and Starkweather[2] have confirmed Briscoe's recent value, 118.70, obtained by comparing stannic chloride with silver, by the electrolytic determination of the tin in stannic chloride with the use of a mercury cathode. The chloride was synthesized from the partially purified elements, and after fractional distillation at room temperature in a vacuum, was collected in small, sealed glass bulbs. These bulbs were weighed and broken under hydrochloric acid solution. The glass was collected on a filter, ignited and weighed. Then the solution was electrolyzed and the residual electrolyte was evaporated to dryness to determine a small amount of undeposited tin. The two series of fractions represent different preparations.

Cl = 35.457. All weights are corrected to vacuum.

[1] THIS JOURNAL, **38**, 857 (1916).

[2] *Proc. Nat. Acad. Sci.*, **2**, 718 (1916).

Series.	Fraction.	Wt. of $SnCl_4$.	Wt. of Sn.	At. wt. Sn.
I.....	5	11.64269	5.30498	118.717
I.....	7	13.5943	6.1935	118.691
I.....	8	10.0897	4.5971	118.705
I.....	9	11.4319	5.2080	118.678
I.....	11	12.2869	5.5983	118.709
I.....	12	12.20889	5.56286	118.713
I.....	13	10.7469	4.8965	118.703
I.....	14	11.54233	5.25846	118.684
			Average,	118.700
II.....	2	15.65437	7.13198	118.689
II.....	3	16.23310	7.39664	118.718
II.....	4	17.29151	7.87850	118.707
II.....	7	15.04889	6.85695	118.715
II.....	8	18.36074	8.36507	118.692
II.....	9	21.58929	9.83676	118.709
II.....	10	17.22210	7.84718	118.716
II.....	11	15.70516	7.15589	118.713
			Average,	118.707
			Average of Series I and II,	118.703

Neodymium.—Further analyses of neodymium chloride have been made by Baxter, Whitcomb, Stewart and Chapin.[1] Material was fractionally crystallized as nitrate from concentrated nitric acid through 158 series of 2606 fractions in all. Certain fractions were converted to chloride and the salt was carefully dehydrated and fused in an atmosphere of dry hydrochloric acid. After being weighed the chloride was compared with pure silver and the silver chloride was collected in the usual way. Traces of samarium and praseodymium in the head and tail of the series, were estimated by photographic comparison of the absorption spectra with those of known mixtures, and suitable corrections were computed. Cl = 35.457. All weights are corrected to vacuum. The result is essentially identical with that found some years ago by Baxter and Chapin, 144.27.

Fraction.	Wt. of $NdCl_3$.	Wt. of Ag.	At. wt. Nd.	Wt. of AgCl.	At. wt. Nd.
2590–1–2	3.34038	4.31287	144.293	.....	.....
2590–1–2	4.03869	5.21445	144.294	6.92786	144.310
			Average, 144.294		
2593–4	4.48251	5.78760	144.289	7.69005	144.281
2593–4	3.75204	4.84458	144.282	6.43738	144.262
2593–4	6.00909	7.75892	144.280	10.30876	144.287
			Average, 144.284	Average,	144.277

[1] THIS JOURNAL, **38**, 302 (1916).

Fraction.	Wt. of $NdCl_3$.	Wt. of Ag.	At. wt. Nd.	Wt. of AgCl.	At. wt. Nd.
2595–6	4.96466	6.41045	144.276	8.51634	144.307
2595–6	4.15431	5.36392	144.285	7.12743	144.266
2595–6	5.53210	7.14338	144.268	9.49134	144.264
		Average,	144.276	Average,	144.279
2597–8	4.73995	6.12054	144.267	8.13232	144.262
2597 8	4.22430	5.45444	144.278	7.24714	144.279
2597–8	5.93271	7.66088	144.261	10.17891	144.258
		Average,	144.269	Average,	144.266
2599–2600	5.60324	7.23524	144.268	9.61299	144.275
2599–2600	7.22817	9.33359	144.264	12.40098	144.270
		Average,	144.266	Average,	144.273
2601–2	5.16230	6.66603	144.262	8.86147	(144.134)
2601–2	4.50348	5.81558	144.250	7.72718	144.244
		Average,	144.256		
2603–4	6.42333	8.29438	144.262	11.02284	(144.209)
2603–4	7.59534	9.80822	144.251	.....	.....
		Average,	144.256		

Fraction.	Average of all analyses.	Average of all analyses corrected for impurity.
2590–1–2	144.299	144.263
2593–4	144.280	144.256
2595–6	144.278	144.266
2597–8	144.268	144.262
2599–2600	144.269	144.269
2601–2	144.252	144.254
2603–4	144.256	144.259
		Average, 144.261

Dysprosium.—Engle and Balke[1] purified dysprosium material by fractional crystallization of (1) the bromate, (2) the nitrate, (3) the ethyl sulfate. Weighed quantities of oxide were converted to anhydrous chloride in a quartz flask. Weights are corrected to vacuum. Cl = 35.46.

Sample.	Wt. of Dy_2O_3.	Wt. of $DyCl_3$.	At. wt. Dy.
1	0.50996	0.73300	164.354
2	1.05741	1.51988	164.357
3	0.65617	0.94352	164.116
4	1.22603	1.76297	164.104
5	1.96935	2.83135	164.207
			Average, 164.228

This value is considerably higher than the one selected by the International Committee on Atomic Weights.

[1] THIS JOURNAL, **39**, 53 (1917).

Radioactive Lead.—Richards and Wadsworth[1] have continued the investigation begun by Richards and Lembert upon radio-lead by the analysis of lead chloride prepared from various selected radioactive minerals. Vacuum weights are given. Cl = 35.459.

Source.	Wt. of $PbCl_2$.	Wt. of Ag.	At. wt. Pb.	Radioactivity referred to UO_3 β-rays.
Common.....	3.72918	2.89325	207.179	....
	5.35111	4.15151	207.188	
		Average,	207.183	
Carnotite, Australia.....	4.64010	3.61118	206.318	1.36
	5.35517	4.16711	206.359	
	6.15608	4.79072	206.334	
	4.14770	3.22748	206.359	
		Average,	206.342	
Carnotite, U. S. A.....	5.31585	4.12670	207.015	9.42
	4.65899	3.61707	206.994	
		Average,	207.004	
Bröggerite, Norway.....	4.29104	3.34187	206.122	3.91
Cleveite, Norway.....	3.92736	3.05913	206.079	2.91
	4.45270	3.46818	206.090	
		Average,	206.084	

The value for Norwegian bröggerite lead is almost identical with Hönigschmid's, 206.07.

Lead.—DeConinck and Gérard[2] ignited weighed quantities of lead nitrate and weighed the resulting oxide. N_2O_5 = 108.

Wt. of $Pb(NO_3)_2$.	Wt. of PbO.	At. wt. Pb.
0.9054	0.6099	206.91
0.7243	0.4880	207.03
0.8149	0.5490	206.98
0.6338	0.4270	206.99
	Average,	206.98

Lead extracted from uranium minerals was found to have the atomic weight 206.71 as the mean of three experiments.

Bismuth.—DeConinck and Gérard[3] reduced bismuth chloride to metal in a current of hydrogen. Cl = 35.5.

[1] THIS JOURNAL, **38**, 2613 (1916).
[2] *Compt. rend.*, **163**, 514 (1916).
[3] *Ibid.*, **162**, 252 (1916).

Wt. of $BiCl_3$.	Wt. of Bi.	At. wt. Bi.
0.6100	0.4038	208.55
0.5490	0.3634	208.52
0.4880	0.3230	208.48
0.4930	0.3263	208.46
		Average, 208.50

Thorium-Ionium.—Hönigschmid[1] compared thorium with its isotope ionium, by analyzing the bromides of common thorium and of thorium extracted from uranium ores. The bromide was prepared by heating the oxide mixed with carbon in an atmosphere of nitrogen and bromine, and was resublimed into a quartz boat and fused. The salt was dissolved and compared with silver in the usual way, and the silver bromide was weighed. Weights are corrected to vacuum. Br = 79.916.

Wt. of $ThBr_4$.	Wt. of Ag.	At. wt. Th.	Wt. of AgBr.	At. wt. Th.
5.11577	4.00046	232.162	6.96402	232.155
3.85077	3.01126	232.160	5.24210	232.142
4.89327	3.82643	232.167	6.66091	232.174
4.70546	3.67975	232.140	6.40573	232.134
5.12854	4.01057	232.144	6.98157	232.143
4.18710	3.27425	232.162	5.69982	232.157
3.66181	2.86343	232.172	4.98479	232.153
3.74590	2.92948	232.117	5.09931	232.148
4.47249	3.49762	232.131	6.08888	232.106
5.02409	3.92861	232.184	6.83873	232.195
5.34994	4.18375	232.139	7.28310	232.133
4.32353	3.38105	232.143	5.88552	232.159
	Average,	232.152	Average,	232.150

Wt. of Th-$IoBr_4$.	Wt. of Ag.	At. wt. Th-Io.	Wt. of AgBr.	At. wt. Th-Io.
3.21504	2.51702	231.525	4.38166	231.517
2.73569	2.14178	231.515	3.72848	231.501
4.27574	3.34762	231.494	5.82751	231.492
	Average,	231.507	Average,	231.503

Guye[2] discusses significant figures in weighing with reference to the balance, weights, adsorption on objects and weights, and vacuum corrections. Guye and Germann[3] give further evidence as to the presence of gases in silver and their effect upon atomic weights obtained through comparisons with silver.

Further information as to the purity of the silver deposits in a coulometer is furnished by Vinal and Bovard,[4] who have found that the presence

[1] *Z. Elektrochem.*, **22**, 18 (1916).

[2] Guye, *J. chim. phys.*, 14, 25 (1916); Renard and Guye, *Ibid.*, **14**, 55 (1916); Guye, *Ibid.*, **14**, 83 (1916).

[3] *Ibid.*, 14, 195, 204 (1916); see Report for 1915.

[4] THIS JOURNAL, **38**, 496 (1916); see also Richards and Anderegg, *Ibid.*, 2044; Rosa and Vinal, *Bur. Stand. Sci. Paper*, **283**, 447; **285**, 479 (1916).

of platinum black upon the surface of the electrode markedly increases the proportion of impurity. With clean electrodes the average per cent. of impurities is 0.004. A fairly large discrepancy thus remains between the ratio of silver and iodine determined by direct combination and by coulometers.[1]

In "Atomic Weights"[2] E. F. Smith outlines the researches upon atomic weights carried out in the John Harrison Laboratory of the University of Pennsylvania.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

IMPROVEMENTS IN CALORIMETRIC COMBUSTION, AND THE HEAT OF COMBUSTION OF TOLUENE.

BY THEODORE W. RICHARDS AND HAROLD S. DAVIS.

Received December 21, 1916.

This paper is one of a series, the object of which is to secure further knowledge of a more precise nature concerning the heats of combustion of typical compounds of carbon, and further development of the methods of determination.[3] The work herein described followed directly after that detailed in the recent communication published with Dr. Frederick Barry; and the methods and apparatus resembled in most respects those already explained. Having profited by the experience of the earlier work, we were able to improve upon some of its details. Especial emphasis will be laid upon the improvements.

The method depends on the successive combustions of toluene and of a standard substance in the Berthelot bomb as modified by Atwater and Benedict, in oxygen under about 22 atmospheres pressure. The rise of temperature of the calorimeter containing the bomb was paralleled in the environment, so that no correction for cooling was needed. That this adiabatic method is capable of giving excellent relative results is shown by the series of investigations conducted at Harvard University, while the accuracy of its absolute results is proved by the recent careful work of the Bureau of Standard by H. C. Dickinson and his assistants.[4] The general assemblage of apparatus is adequately described and depicted in the most recent of the preceding papers, and the reader is referred to this as regards minutiae.

The details in which improvements were instituted were as follows: the mode of sealing the bomb, the mode of providing for the well-regulated

[1] See Report for 1914.

[2] Monograph, University of Pennsylvania.

[3] For references, see Richards and Barry, THIS JOURNAL, 37, 993 (1915).

[4] *Bull. Bur. Stand.*, 11, 243 (1914).