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# FIFTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1897.

BY F. W. CLARKE.

Received January 20, 1898.

*To the Members of the American Chemical Society:*

During 1897 comparatively few new determinations of atomic weights have appeared. The data given are as follows:

*Carbon.*—Scott[1] has carefully studied the determinations of the atomic weight of carbon which depend upon the combustion of the element and the weight of the dioxide formed, and has discovered an important correction. This is due to the considerable change of volume in the potash solution produced by the absorption of carbon dioxide, which involves a notable change in the reduction of the weighings to a vacuum. Scott has measured the amount of this change, and has applied it to the work of his predecessors with the subjoined results. In each case the values given are the means of the several experiments recorded.

| | Uncorrected. | Corrected. |
|---|---|---|
| Dumas and Stas | 11.9975 | 11.9938 |
| Erdmann and Marchand | 12.0093 | 12.0054 |
| Roscoe | 12.0029 | 11.9973 |
| Friedel | 12.0112 | 12.0056 |
| Van der Plaats | 12.0031 | 12.0018 |
| Mean, | 12.0048 | 12.0008 |

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[1] *J. Chem. Soc.*, 71, 550, May, *1897*.

These values are based upon O = 16; with O = 15.879, the corrected mean result becomes C = 11.910.

Scott further criticises in detail the determinations by Stas which depend upon the combustion of carbon monoxide, and shows that they require possible corrections and involve various uncertainties. He concludes "that the atomic weight of carbon is by no means one of those most accurately known, and that a careful revision of it is imperative."

*Nitrogen, Chlorine, and Silver.*—Leduc[1], on the basis of his density determinations, assumes N = 14.005 when O = 16. Applying this to the determinations by Stas of the ratios Ag : Cl, AgCl : $O_3$, and AgCl : $NH_4Cl$, he finds a discrepancy of about one part in 320. That is, the work of Stas gives N = 14.044 instead of 14.005. This disagreement Leduc attributes to the presence of occluded oxygen, as pointed out by Dumas, in the silver used by Stas. For this he assumes a correction, and then, combining his value for nitrogen with the data given by Stas, he computes H = 1.0076, Cl = 35.470, and Ag = 107.916. The correction applied by Leduc seems to be somewhat uncertain; and it is doubtful whether his determination of the density of nitrogen is entitled to greater weight than the other data which are involved in the calculations.

*Aluminum.*—In the third and fourth reports of this committee Thomsen's data for the atomic weight of oxygen are given. In these determinations oxygen and hydrogen were compared with aluminum as an intermediary; but the aluminum used was not absolutely pure. Had it been pure, the atomic weight of the metal, with reference to the two gases, could have been computed.

Thomsen now[2] gives the data necessary for the comparison, and deduces the atomic weight of aluminum. The impurities are determined, and corrections for them applied. There is also a correction for the change in volume of the potash solution in which the metal was dissolved. Applying the corrections, Thomsen finds that 0.99897 gram pure aluminum correspond to 0.11195 gram of hydrogen. Hence, with H = 1,

$$Al = 26.770.$$

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[1] *Compt. rend.*, 125, 299, August 2, *1897*.

[2] *Ztschr. anorg. Chem.*, 15, 447.

Again, 0.99897 gram of metal is equivalent to 0.88824 gram of oxygen. Hence, with O = 16,

$$Al = 26.992.$$

These two values, referring to the two standard units, are determined independently of each other, and are independent of any measured ratio between O and H. They are notably lower than the values computed by myself from Mallet's data, 26.91 and 27.11, and possibly should supplant the latter. This question, however, needs further discussion, and probably some additional experiments.

*Nickel.*—Atomic weight determined by Richards and Cushman,[1] from analyses of the anhydrous, sublimed bromide, $NiBr_2$. This substance is shown by the authors to be perfectly suited to the purpose of the investigation. The method of analysis was in all essential respects that used by Richards in other researches of the same kind, and was partly gravimetric and partly volumetric. On the one hand, the ratio $2AgBr : NiBr_2$ was determined; on the other, the ratio $2Ag : NiBr_2$. All weighings were reduced to a vacuum. The results, in three series, were as follows:

### FIRST SERIES.

| Weight $NiBr_2$. | Weight AgBr. | Atomic weight Ni. |
|---|---|---|
| 2.26113 | 3.88769 | 58.646 |
| 2.80668 | 4.82431 | 58.708 |
| 1.41317 | 2.42880 | 58.716 |
| 1.71759 | 2.95307 | 58.650 |
| 2.48565 | 4.27357 | 58.651 |
| 4.32997 | 7.44280 | 58.700 |
| 2.18072 | 3.74856 | 58.693 |
| | Mean, | 58.680 |

### SECOND SERIES.

| Weight $NiBr_2$. | Weight AgBr. | Atomic weight Ni. |
|---|---|---|
| 3.28039 | 5.63892 | 58.691 |
| 2.70044 | 4.64208 | 58.686 |
| 3.38230 | 5.81391 | 58.698 |
| 1.33459 | 2.29435 | 58.670 |
| 1.25054 | 2.14963 | 58.693 |
| 1.32778 | 2.27384 | 58.690 |
| 2.24452 | 3.85805 | 58.705 |
| | Mean, | 58.690 |

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[1] *Proc. Amer. Acad.*, **33**. 97, November, *1897*.

### THIRD SERIES.

| Weight $NiBr_2$. | Weight Ag. | Atomic weight Ni. |
|---|---|---|
| 3.28039 | 3.23910 | 58.701 |
| 2.70044 | 2.66636 | 58.709 |
| 3.38230 | 2.33990 | 58.689 |
| 1.33459 | 1.31787 | 58.689 |
| 1.25054 | 1.23482 | 58.698 |
| 1.32278 | 1.30629 | 58.675 |
| 2.24452 | 2.21652 | 58.676 |
| | | Mean, 58.691 |

From all these data the authors conclude that the atomic weight of nickel cannot be far from 58.69 when O = 16, or 58.25 if O = 15.88.

From series two and three 15.32086 grams of silver give 26.67078 grams of bromide. Hence the percentage of silver in silver bromide is 57.444, which agrees with the value 57.445 found by Stas. This is a good check upon the accuracy of the work.

*Cobalt.*—The atomic weight determinations by Richards and Baxter[1] are in all essential respects like those of nickel which have just been cited. The three series of data are as follows:

### FIRST SERIES.

| Weight $CoBr_2$. | Weight AgBr. | Atomic weight Co. |
|---|---|---|
| 2.25295 | 3.86818 | 58.950 |
| 2.88763 | 4.95732 | 58.975 |
| 1.88806 | 3.24056 | 59.026 |
| | | Mean, 58.984 |

### SECOND SERIES.

| Weight $CoBr_2$. | Weight AgBr. | Atomic weight Co. |
|---|---|---|
| 1.33564 | 2.29296 | 58.975 |
| 2.58129 | 4.43095 | 58.998 |
| 2.84382 | 4.88135 | 59.009 |
| 1.83722 | 3.15368 | 59.000 |
| 2.68584 | 4.61046 | 58.996 |
| 3.18990 | 5.47607 | 58.982 |
| 2.88914 | 4.95943 | 58.997 |
| 2.32840 | 3.99706 | 58.987 |
| 1.91703 | 3.29053 | 59.010 |
| | | Mean, 58.995 |

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[1] *Proc. Amer. Acad.*, 33, 115, December, *1897*.

THIRD SERIES.

| Weight $CoBr_2$. | Weight Ag. | Atomic weight Co. |
|---|---|---|
| 1.33564 | 1.31702 | 59.002 |
| 2.58129 | 2.54585 | 58.955 |
| 2.84382 | 2.80449 | 58.977 |
| 1.83722 | 1.81170 | 58.991 |
| 2.68584 | 2.64879 | 58.969 |
| 2.88914 | 2.84891 | 58.998 |
| 2.32840 | 2.29593 | 59.003 |
| 1.91703 | 1.89033 | 58.999 |
| | Mean, | 58.987 |

If O = 16, Co = 58.99, as the outcome of all the series. If O = 15.88, Co = 58.55. From the data in series two and three the percentage of silver in silver bromide is 57.446, while Stas gives 57.445. The last five experiments, which are the best, give 57.447. This check on the accuracy of the work is therefore satisfactory.

*Tungsten.*—The investigation by Hardin[1] is rather the scrutiny of a method than an attempt to accurately fix an atomic weight. Most of the determinations of the atomic weight of tungsten have been based upon analyses or syntheses of the trioxide; and this substance is now shown to be exceedingly untrustworthy as regards the measurement of this constant. Hardin has made sixty-four determinations with the trioxide, in seventeen groups or series, using material from various sources, and working under a great variety of conditions. The values found range from W = 183.51 to W = 185.00, when O = 16, the average of all being 184.106. The same discordance appears upon comparing the results obtained by previous investigators, and it seems to be partly due to absorptions of tungsten or its oxide by the boat in which the reductions or oxidations were effected, and partly to the presence of nitrogen in the trioxide when the latter was prepared from ammonium tungstate. At all events, the method is unsuited to its purpose, and the atomic weight of tungsten needs thorough reinvestigation by means of other processes.

*Cerium.*—The atomic weight of this metal has been redetermined by Wyrouboff and Verneuil,[2] upon material purified by

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[1] This Journal, 19, 657, August, *1897*.

[2] *Bull. Soc. Chim.* [3], 17, 679.

an elaborate process and with extreme care. From this material the oxide $CeO_2$ was obtained perfectly white—a result in corroboration of the researches of Wolf and of Wing, but contrary to later investigators who have always found the substance to be more or less colored. The existence of a white oxide is also confirmed by the recent investigations of Moissan.[1]

The salt chosen for the atomic weight determinations was the sulphate, $Ce_2(SO_4)_3.8Aq$, a compound which is perfectly definite and stable, and which is easily obtained in a state of purity. At 250° it loses its water with facility, and up to 500° it undergoes no further decomposition. By ignition at a white heat, 1500° approximately, all sulphuric acid is expelled, and the pure oxide remains. The other hydrated sulphates of cerium are less manageable. The material studied was derived from three distinct sources, partly from monazite, partly from cerite; and the results attained confirm one another. The weights were as follows, but nothing is said as to their reduction to a vacuum. Probably the reduction was not made.

| Hydrous salt. | Anhydrous salt. | $CeO_2$. |
|---|---|---|
| | FIRST SAMPLE. | |
| 1.2385 | 0.9875 | 0.5977 |
| 1.2730 | 1.0148 | 0.6138 |
| 1.2030 | 0.9590 | 0.5794 |
| 1.5420 | 1.2295 | 0.7430 |
| | SECOND SAMPLE. | |
| 0.9642 | 0.7685 | 0.4642 |
| 1.3260 | 1.0571 | 0.6389 |
| 1.1429 | 0.9112 | 0.5518 |
| 0.9072 | 0.7232 | 0.4372 |
| | THIRD SAMPLE. | |
| 1.2114 | 0.9658 | 0.5840 |
| 1.2411 | 0.9894 | 0.5984 |

From these data the following atomic weights are derived, when $O = 16$ and $S = 32$, cerium being regarded by the authors as a dyad, with the oxide obtained having the formula $Ce_3O_4$.

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[1] *Compt. rend.*, **124**, 1233.

| | From per cent. $H_2O$. | From "$Ce_3O_4$" in hydrate. | From $Ce_3O_4$ in anhydrous salt. |
|---|---|---|---|
| | FIRST SERIES. | | |
| | 92.84 | 93.08 | 93.16 |
| | 92.65 | 92.88 | 92.95 |
| | 92.65 | 92.64 | 92.63 |
| | 92.85 | 92.74 | 92.70 |
| Mean, | 92.74 | 92.84 | 92.86 |
| | SECOND SERIES. | | |
| | 92.49 | 92.55 | 92.56 |
| | 92.69 | 92.72 | 92.73 |
| | 92.76 | 93.17 | 93.30 |
| | 92.66 | 92.77 | 92.80 |
| Mean, | 92.65 | 92.80 | 92.85 |
| | THIRD SERIES. | | |
| | 92.75 | 92.84 | 92.87 |
| | 92.68 | 92.88 | 92.93 |
| Mean, | 92.71 | 92.86 | 92.90 |
| Mean of all, | 92.70 | 92.83 | 92.87 |

The extreme variation is 0.75, which becomes 1.125 when cerium is regarded as a triad.

From the entire series of determinations, the salt $Ce_2(SO_4)_3.8Aq$ gives in mean 20.278 per cent. of water, and 48.205 $CeO_2$. The mean percentage of $CeO_2$ in the anhydrous sulphate is 60.467. From these data, with $H = 1$, $O = 15.879$, and $S = 31.83$, the following mean values for $Ce'''$ are deduced:

| | |
|---|---|
| From percentage of water | $Ce = 138.14$ |
| From $CeO_2$ in hydrated salt | $Ce = 138.35$ |
| From $CeO_2$ in $Ce_2(SO_4)_3$ | $Ce = 138.42$ |

The mean of these is $Ce = 138.30$. With $O = 16$, this becomes $Ce = 139.35$.

These figures are adopted in the table at the close of this report, as being probably more trustworthy than the older determinations, but they are still subject to a good deal of uncertainty.

Still another investigation upon cerium is reported by Boudouard,[1] who, following Schutzenberger, fractionates the salts of the metal. His atomic weight determinations are made by ignition of the sulphate; but the values assigned to O and S are

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[1] *Compt. rend.*, **125**, 772.

not stated. By fractionation of the acetate he gets an oxide giving from Ce = 135.1 to 140.7. From fractionations of the sulphate he finds Ce = 133.0 to 138.75. Hydrogen peroxide precipitates an oxide giving Ce = 137.15 to 137.6, while the unprecipitated portion ranges from 137.85 to 139.9. He concludes that the oxide of cerium is accompanied by small quantities of another earth of lower atomic weight.

Wyrouboff and Verneuil[1] criticise the work of Boudouard, and suggest that his high values for Ce are due to the presence of thoria, while the lower values are ascribable to the other earths of the cerium-yttrium groups. To this criticism Boudouard[2] replies, defending the purity of his material. He now states that his $CeO_2$ was *white*. Wyrouboff and Verneuil[3] reiterate their objections, and show that the variations in successive portions obtained by Boudouard are irregular, sometimes high, sometimes low, and not systematic in one direction as they should be with material representing an orderly fractionation.

It is evident from the discussion thus summarized that Boudouard's figures relate to mixtures, and not to one earth, whatever the mixtures may be. They are therefore unavailable as determinations of a definite atomic weight. It may be suggested here that a careful scrutiny of the supposed $CeO_2$ is necessary in order to prove that it is not contaminated by higher or lower oxides of cerium, and that it does not contain, like certain other oxides, occluded gaseous impurities. Until these questions have been settled, all atomic weight determinations based upon weighings of ceric oxide are uncertain.

*Gaseous Densities.*—Lord Rayleigh[4] has continued his investigation upon the density of the principal gases, and now gives data for CO, $CO_2$, and $N_2O$. His results, air being taken as unity, are tabulated as follows :

| | |
|---|---|
| Oxygen | 1.10535 |
| Atmospheric nitrogen, plus argon | 0.97209 |
| Nitrogen | 0.96737 |
| Argon | 1.37752 |
| Carbonic oxide | 0.96716 |
| Carbon dioxide | 1.52909 |
| Nitrous oxide | 1.52951 |

[1] *Compt. rend.*, **125**, 950.

[2] *Ibid*, **125**, 1096.

[3] *Ibid*, **125**, 1180.

[4] *Nature*, December 30, *1897*. *Chem. News*, December 31.

Calculated from the density of $CO$, with O = 16, C = 11.9989.

*Mathematical Relations.*—Rummel,[1] in a paper upon "The Spectra of the Alkalies and their Atomic Weights," works out a series of relations which seem to be significant. For the formulae developed, which are algebraic, the original paper must be consulted. When Na = 23, as the starting-point, the spectral relations give He = 3.64, K = 39.05, Rb = 85.15, and Cs = 133.47. These values are near enough to the actual determinations to show that the mathematical process deserves careful consideration.

*Miscellaneous Notes.*—At the Toronto Meeting of the British Association for the Advancement of Science, Brauner presented a paper on the atomic weight of thorium. Also at the Washington meeting of the American Chemical Society, Venable gave the preliminary results of an investigation upon zirconium. These determinations are as yet unpublished.

A memoir upon the atomic weight of molybdenum, by A. Vandenberghe, has been awarded the Stas prize of the Belgian Academy. It will appear in the quarto form adopted by the Academy for its more important publications.

The following table of atomic weights is essentially that given in Clarke's "Recalculation," a new edition of which was published by the Smithsonian Institution in January. The names of elements which represent changes from the table of 1896 are italicized.

| | H = 1. | O = 16. |
|---|---|---|
| Aluminum | 26.91 | 27.11 |
| Antimony | 119.52 | 120.43 |
| Argon | ? | ? |
| Arsenic | 74.44 | 75.01 |
| Barium | 136.39 | 137.43 |
| Bismuth | 206.54 | 208.11 |
| Boron | 10.86 | 10.95 |
| Bromine | 79.34 | 79.95 |
| Cadmium | 111.10 | 111.95 |
| Calcium | 39.76 | 40.07 |
| *Carbon* | 11.91 | 12.00 |
| *Cerium* | 138.30 | 139.35 |
| Cesium | 131.89 | 132.89 |
| Chlorine | 35.18 | 35.45 |
| Chromium | 51.74 | 52.14 |

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[1] *Proc. Roy. Soc.* of Victoria (Australia), 10, Part I, page 75.

| | H = 1. | O = 16. |
|---|---|---|
| *Cobalt* | 58.55 | 58.99 |
| Columbium | 93.02 | 93.73 |
| Copper | 63.12 | 63.60 |
| Erbium | 165.06 | 166.32 |
| Fluorine | 18.91 | 19.06 |
| Gadolinium | 155.57 | 156.76 |
| Gallium | 69.38 | 69.91 |
| Germanium | 71.93 | 72.48 |
| Glucinum | 9.01 | 9.08 |
| Gold | 195.74 | 197.23 |
| Helium | ? | ? |
| Hydrogen | 1.000 | 1.008 |
| Indium | 112.99 | 113.85 |
| Iodine | 125.89 | 126.85 |
| Iridium | 191.66 | 193.12 |
| Iron | 55.60 | 56.02 |
| Lanthanum | 137.59 | 138.64 |
| Lead | 205.36 | 206.92 |
| Lithium | 6.97 | 7.03 |
| Magnesium | 24.10 | 24.28 |
| Manganese | 54.57 | 54.99 |
| Mercury | 198.49 | 200.00 |
| Molybdenum | 95.26 | 95.99 |
| Neodymium | 139.70 | 140.80 |
| Nickel | 58.24 | 58.69 |
| Nitrogen | 13.93 | 14.04 |
| Osmium | 189.55 | 190.99 |
| Oxygen | 15.88 | 16.00 |
| Palladium | 105.56 | 106.36 |
| Phosphorus | 30.79 | 31.02 |
| Platinum | 193.41 | 194.89 |
| Potassium | 38.82 | 39.11 |
| Praseodymium | 142.50 | 143.60 |
| Rhodium | 102.23 | 103.01 |
| Rubidium | 84.78 | 85.43 |
| Ruthenium | 100.91 | 101.68 |
| Samarium | 149.13 | 150.26 |
| Scandium | 43.78 | 44.12 |
| Selenium | 78.42 | 79.02 |
| Silicon | 28.18 | 28.40 |
| Silver | 107.11 | 107.92 |
| Sodium | 22.88 | 23.05 |
| Strontium | 86.95 | 87.61 |
| Sulphur | 31.83 | 32.07 |
| Tantalum | 181.45 | 182.84 |

| | H = 1. | O = 16. |
|---|---|---|
| Tellurium | 126.52 | 127.49 |
| Terbium | 158.80 | 160.00 |
| Thallium | 202.61 | 204.15 |
| Thorium | 230.87 | 232.63 |
| Thulium | 169.40 | 170.70 |
| Tin | 118.15 | 119.05 |
| Titanium | 47.79 | 48.15 |
| Tungsten | 183.43 | 184.83 |
| Uranium | 237.77 | 239.59 |
| Vanadium | 50.99 | 51.38 |
| Ytterbium | 171.88 | 173.19 |
| Yttrium | 88.35 | 89.02 |
| Zinc | 64.91 | 65.41 |
| Zirconium | 89.72 | 90.40 |

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 26.]

# THE VOLUMETRIC DETERMINATION OF COBALT.[1]

By HARRY B. HARRIS.

Received January 14, 1898.

## INTRODUCTION.

ZINC, manganese, nickel, and cobalt constitute an analytical group of more than ordinary importance. The methods for the quantitative determination of these metals are mainly gravimetric. The volumetric methods applied in the estimation of zinc have won a permanent place with the analyst, and are used daily, where zinc determinations are of prime interest.

The estimation of manganese by means of potassium permanganate according to the recommendation of Volhard has almost completely supplanted the methods ordinarily used with that metal. When nickel and cobalt are brought to the front, and when the methods proposed at various times for their determination are carefully examined, it will be found that volumetric processes must be relegated to a very subordinate position.

Accurate, rapid, volumetric methods, giving satisfactory results for these two metals, would be welcomed by all analysts. It is true that volumetric methods have from time to time been brought forward, yet they seem not to have met with favor:

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[1] From a thesis presented for the degree of Doctor of Philosophy, 1897.