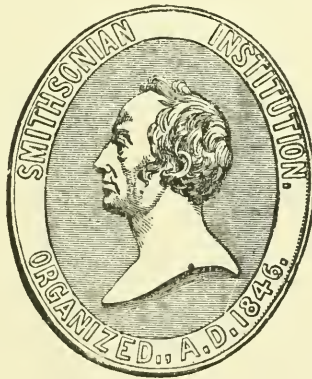# THE
CONSTANTS OF NATURE.

PART V.

A RECALCULATION

—OF—

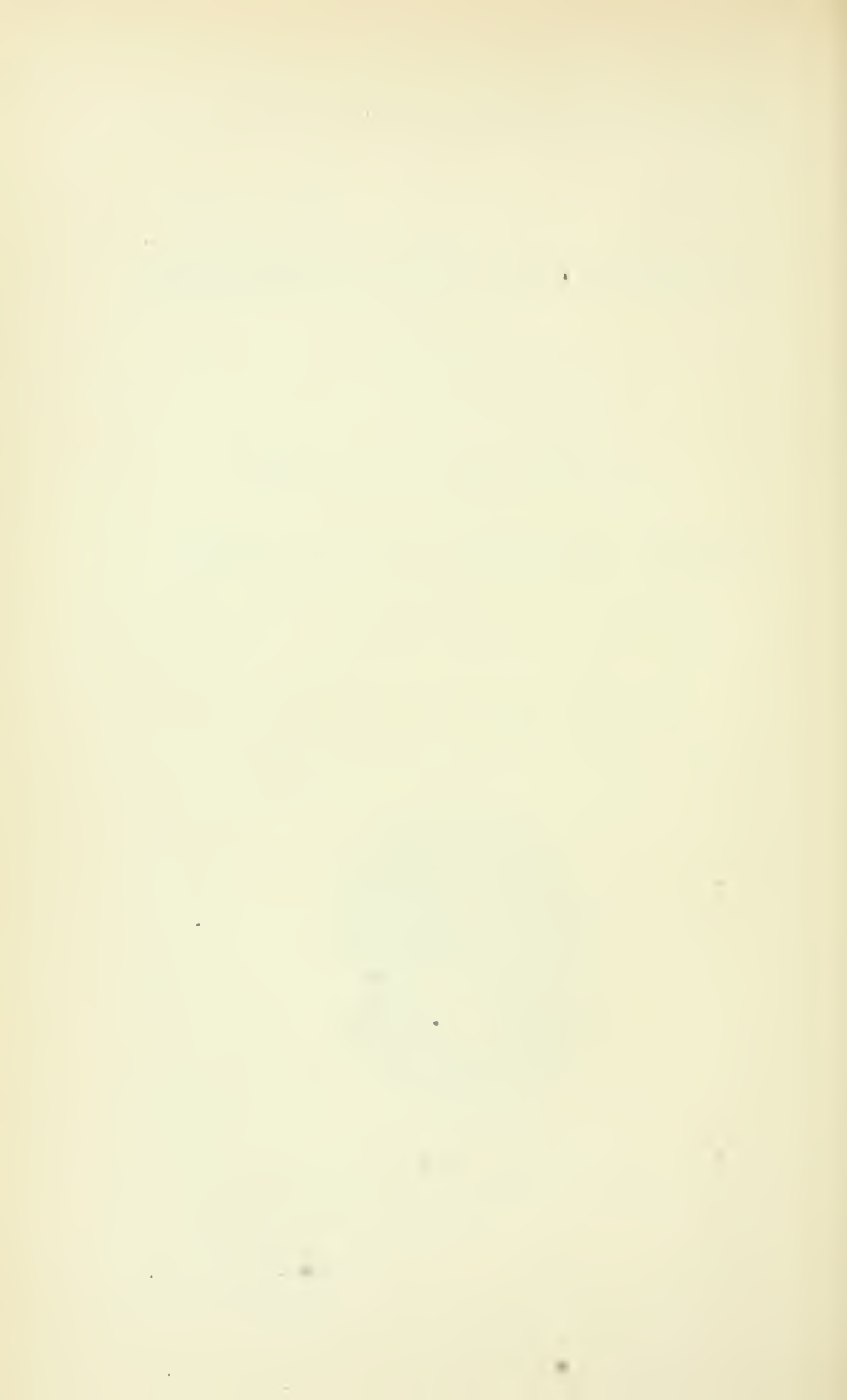# THE ATOMIC WEIGHTS.

BY

FRANK WIGGLESWORTH CLARKE, S. B.,

Professor of Chemistry and Physics in the University of Cincinnati.

ADVERTISEMENT.

The present publication is one of a series devoted to the discussion and more precise determination of various "Constants of Nature;" and forms the *Fifth* contribution to that subject published by this Institution.

The *First* number of the series, embracing tables of "Specific Gravities" and of Melting and Boiling Points of Bodies, prepared by the same author, Prof. F. W. Clarke, was published in 1873. The *Fourth* part of the series, comprising a complete digest of the various "Atomic Weight" determinations of the chemical elements published since 1814, commencing with the well-known "Table of Equivalents" by Wollaston, (given in the Philosophical Transactions for that year,) compiled by Mr. George F. Becker, was published by the Institution in 1880. The present work which may be regarded as practically supplementary to that digest, (or perhaps rather as the memoir to which that digest is introductory,) comprises a very full discussion and re-calculation of the "Atomic Weights" from all the existing data, and the assignment of the most probable value to each of the elements.

The manuscript of the work was presented to the Institution in its completed form by Prof. F. W. Clarke, the cost of publication only being at the expense of the Smithsonian fund.

<div style="text-align:right">

SPENCER F. BAIRD,
Secretary of Smithsonian Institution.

</div>

WASHINGTON, *January*, 1882.

TABLE OF CONTENTS.

INTRODUCTION.

In the autumn of 1877 the writer began collecting data relative to the determinations of atomic weights, with the purpose of preparing a complete resumé of the entire subject, and of recalculating all the estimations. The work was fairly under way, the material was collected and partly discussed, when I received from the Smithsonian Institution a manuscript by Professor George F. Becker, entitled "Atomic Weight Determinations: a Digest of the Investigations Published since 1814." This manuscript, which has lately been issued as Part IV of the "Constants of Nature," covered much of the ground contemplated in my own undertaking. It brought together all the evidence, presenting it clearly and thoroughly in compact form; in short, that portion of the task could not well be improved upon. Accordingly, I decided to limit my own labors to a critical recalculation of the data; to combine all the figures upon a common mathematical basis, and to omit everything which could as well be found in Professor Becker's "Digest."

At the very beginning of my work certain questions confronted me. Should I treat the investigations of different individuals separately, or should I combine similar data together in a manner irrespective of persons? For example, ought I, in estimating the atomic weight of silver, to take Stas' work by itself, Marignac's work by itself, and so on, and then average the results together; or should I rather combine all series of figures relating to the composition of potassium chlorate into one mean value, and all the data concerning the composition of silver chloride into another mean, and, finally, compute from such general means the constant sought to be established? The latter plan was finally adopted; in fact, it was rendered necessary by the method of least squares, which method was alone adequate to supply me with good processes for calculation.

The mode of discussion and combination of results was briefly as follows. The formulæ employed are given in another chapter. I began with the ratio between oxygen and hydrogen; in other words, with the atomic weight of oxygen referred to hydrogen as unity. Each series of experiments was taken by itself, its arithmetical mean was found, and the probable error of that mean was computed. Then the several means were combined according to the appropriate formula, each receiving a weight dependent upon its probable error. The general mean thus established was taken as the most probable value for the atomic weight of oxygen, and, at the same time, its probable error was mathematically asssigned.

Next in order came a group of elements which were best discussed together, namely, silver, chlorine, potassium, sodium, bromine, iodine, and sulphur. For these elements there were data from thirteen experimenters. All similar figures were first reduced to common standards, and then the means of individual series were combined into general means. Thus all the data were condensed into twenty ratios, from which several independent values for the atomic weight of each element could be computed. The probable errors of these values, however, all involved the probable error of the atomic weight of oxygen, and were, therefore, higher than they would have been had the latter element not entered into consideration. Here, then, we have suggested a chief peculiarity of this whole revision. The atomic weight of each element involves the probable errors of all the other elements to which it is directly or indirectly referred. Accordingly, an atomic weight determined by reference to elements whose atomic weights have been defectively ascertained will receive a high probable error, and its weight, when combined with other values, will be relatively low. For example, an atomic weight ascertained by direct comparison with hydrogen will, other things being equal, have a lower probable error than one which is referred to hydrogen through the intervention of oxygen; and a metal whose equivalent involves only the probable error of oxygen

will be more exactly known than one which depends upon
the greater errors of silver and chlorine. These points
will appear more clearly evident in the subsequent actual
discussions.

But although the discussion of atomic weights is osten-
sibly mathematical, it cannot be purely so. Chemical con-
siderations are necessarily involved at every turn. In as-
signing weights to mean values I have been, for the most
part, rigidly guided by mathematical rules; but in some
cases I have been compelled to reject altogether series of data
which were mathematically excellent, but chemically worth-
less because of constant errors. In certain instances there
were grave doubts as to whether particular figures should
be included or rejected in the calculation of means; there
having been legitimate reasons for either procedure. Prob-
ably many chemists would differ with me upon such points
of judgment. In fact, it is doubtful whether any two chem-
ists, working independently, would handle all the data in
precisely the same way, or combine them so as to produce
exactly the same final results. Neither would any two
mathematicians follow identical rules or reach identical con-
clusions. In calculating the atomic weight of any element
those values are assigned to other elements which have been
determined in previous chapters. Hence a variation in the
order of discussion might lead to slight differences in the
final results.

As a matter of course the data herein combined are
of very unequal value. In many series of experiments
the weighings have been reduced to a vacuum standard;
but in most cases chemists have neglected this correc-
tion altogether. In a majority of instances the errors thus
introduced are slight; nevertheless they exist, and interfere
more or less with all attempts at a theoretical consideration
of the results. For example, they affect seriously the in-
vestigation of Prout's hypothesis, and are often great enough
to account for seeming exceptions to it. Such questions as
these will be considered in the appendix.

Another serious source of error affecting many of the re-

sults was not discovered until recently. A large number of
computations had been actually finished, involving, among
other things, the greater part of Stas' work, when Dumas
published his investigation upon the occlusion of oxygen by
silver. Here it was shown that a very great number of
atomic weight determinations must have been vitiated by
constant errors, which, though constant for each series, were
probably of different magnitude in different series, and,
therefore, could not be systematically corrected for. At the
time of the announcement of this discovery of Dumas my
work was so far under way that I thought it best to com-
plete my discussion without reference to it, and then to
study its influence in the appendix. In the chapter upon
aluminum, however, it will be noted that Mallet eliminated
this error in great part from his experimental results.

Necessarily, this work omits many details relative to ex-
perimental methods, and particulars as to the arrangements
of special forms of apparatus. For such details original
memoirs must be consulted. Their inclusion here would
have rendered the work unwarrantably bulky. There is
such a thing as over-exhaustiveness of treatment, which is
equally objectionable with under-thoroughness.

Of course, none of the results reached in this revision
can be considered as final. Every one of them is liable to
repeated corrections. To my mind the real value of the
work, great or little, lies in another direction. The data
have been brought together and reduced to common stand-
ards, and for each series of figures the probable error has
been determined. Thus far, however much my methods
of combination may be criticized, I feel that my labors will
have been useful. The ground is now cleared, in a measure,
for future experimenters; it is possible to see more distinctly
what remains to be done; some clues are furnished as to the
relative merits of different series of results. I hope to be
able, from time to time, as new determinations are published,
to continue the task here begun, and perhaps, also, to add,
in the near future, some data of my own establishing.

In addition to the usual periodicals the following works

have been freely used by me in the preparation of this volume :

BERZELIUS, J. J. Lehrbuch der Chemie. 5 Auflage. Dritter Band. SS. 1147–1231. 1845.

VAN GEUNS, W. A. J. Prœve eener Geschiedenis van de Æquivalentgetallen der Scheikundige Grondstoffen en van hare Soortelijke Gewigten in Gasvorm, voornamelijk in Betrekking tot de vier Grondstoffen der Bewerktuigde Natuur. Amsterdam, 1853.

MULDER, E. Historisch-Kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van 13 Eenvoudige Ligchamen. Utrecht, 1853.

MULDER, L. Historisch-Kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van 24 Metalen. Utrecht, 1853.

OUDEMANS, A. C., Jr. Historisch-Kritisch Overzigt van de Bepaling der Æquivalent-Gewigten van Twee en Twintig Metalen. Leiden, 1853.

STAS, J. S. Untersuchungen über die Gesetze der Chemischen Proportionen über die Atomgewichte und ihre gegenseitigen Verhältnisse. Uebersetzt von Dr. L. Aronstein. Leipzig, 1867.

The four Dutch monographs above cited are especially valuable. They represent a revision of all atomic weight data down to 1853, as divided between four writers.

FORMULÆ FOR THE CALCULATION OF PROBABLE ERROR.

Although the ordinary formula for the probable error of an arithmetical mean is familiar to all physicists, it is perhaps best to reproduce it here, as follows:

(1.)
$$e = \pm .6745 \sqrt{\frac{S}{n(n-1)}}$$

Here n represents the number of observations or experiments in the series, while S is the sum of the variations of the individual results from the mean.

In combining several arithmetical means, representing several series, into one general mean each receives a weight indicated by its probable error; greater as the latter becomes less, and *vice versa*. Let A, B, C, etc., be such mean results, and a, b, c, their probable errors respectively. Then the general mean is determined by this formula:

(2.)
$$M = \frac{\frac{A}{a^2} + \frac{B}{b^2} + \frac{C}{c^2} \cdots}{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \cdots}$$

For the probable error of this general mean we have:

(3.)
$$m = \frac{1}{\sqrt{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \cdots}}$$

In the calculation of atomic and molecular weights the following formulæ have been employed. For assistance in connection with them my thanks are due to Professors H. T. Eddy and E. W. Hyde of the University of Cincinnati.

Using, as before, capital letters to represent known quantities and small letters for their probable errors respectively,

we have for the sum or difference of two quantities, A and B:

(4.) $$e = \sqrt{a^2 + b^2}$$

For the product of A multiplied by B the probable error is

(5.) $$e = \sqrt{(Ab)^2 + (Ba)^2}$$

For the product of three quantities, ABC:

(6.) $$e = \sqrt{(BCa)^2 + (ACb)^2 + (ABc)^2}$$

For a quotient, $\dfrac{B}{A}$, the probable error becomes

(7.) $$e = \frac{\sqrt{\left(\frac{Ba}{A}\right)^2 + b^2}}{A}$$

Given a proportion, $A : B :: C : x$, the probable error of the fourth term is as follows:

(8.) $$e = \frac{\sqrt{\left(\frac{BCa}{A}\right)^2 + (Cb)^2 + (Bc)^2}}{A}$$

This formula is used in nearly every atomic weight calculation, and is, therefore, exceptionally important. Rarely a more complicated case arises in a proportion of this kind:

$$A : B :: C + x : D + x$$

In this proportion the unknown quantity occurs in two terms. Its probable error is found by this expression, and is always large:

(9.) $$e = \sqrt{\frac{(C - D)^2}{(A - B)^4}(B^2 a^2 + A^2 b^2) + \frac{B^2 c^2 + A^2 d^2}{(A - B)^2}}$$

When several independent values have been calculated for an atomic weight they are treated like means, and combined according to formulæ (2) and (3.) Each final result

is, therefore, to be regarded as the general mean of all re-
liable determinations. This method of combination may
not be the best one theoretically possible, but it seemed to
be the only one practically available. The data are too im-
perfect to warrant the use of much more elaborate processes
of discussion.
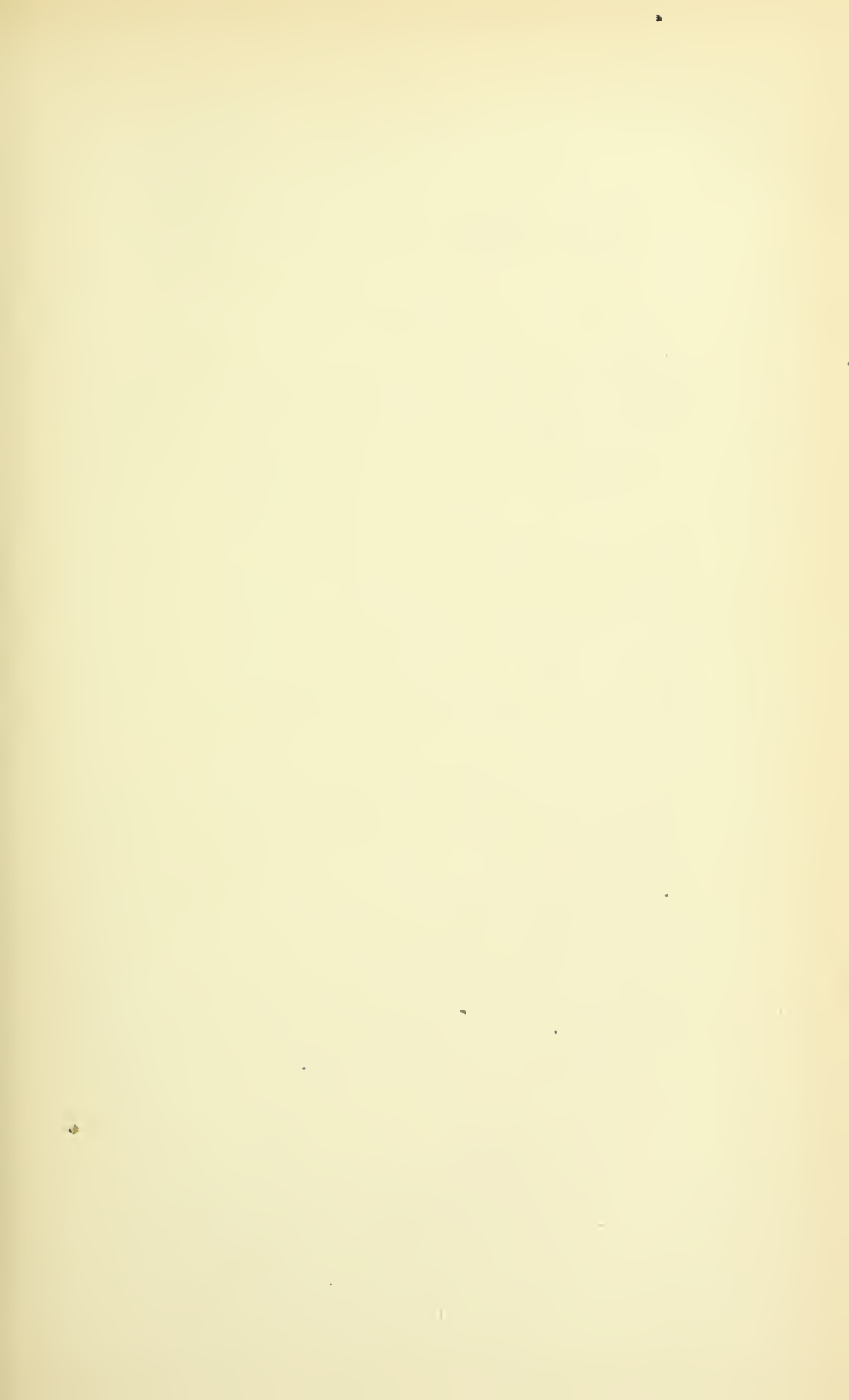
RECALCULATION OF THE ATOMIC WEIGHTS.

OXYGEN.

The ratio between oxygen and hydrogen is the foundation upon which the entire system of atomic weights depends. Hence, the accuracy of its determination has, from the beginning, been recognized as of extreme importance. A trifling error here may become cumulative when repeated through a moderate series of other ratios.

Leaving out of account the earliest researches, which have now only a historical value, we find that three methods have been employed for fixing this important constant. First, the synthesis of water, effected by passing hydrogen gas over red hot oxide of copper. Secondly, the exact determination of the relative density of the two gases. Thirdly, by weighing the quantity of water formed upon the direct union of a known volume of hydrogen with oxygen.

The first of these methods has been employed in three leading investigations, namely, by Dulong and Berzelius,[*] by Dumas, and by Erdmann and Marchand. The essential features of the method are in all cases the same. Hydrogen gas is passed over heated oxide of copper, and the water thus formed is collected and weighed. From this weight and the loss of weight which the oxide undergoes, the exact composition of water is readily calculated. Dulong and Berzelius made but three experiments, with the following results for the percentages of oxygen and hydrogen in in water:

O.	H.
88.942	11.058
88.809	11.191
88.954	11.046

---

[*] Thomson's Annals of Philosophy, July, 1821, p. 50.

These figures, rather roughly determined, and by no means exact enough to meet the requirements of modern science, give a mean value of 16.021 for the atomic weight of oxygen.   As the weighings were not reduced to a vacuum, this correction was afterwards applied by Clark,* who showed that these syntheses really make $O = 15.894$; or, in Berzelian terms, if $O = 100$, $H = 12.583$.

In 1842 Dumas† published his elaborate investigation upon the composition of water.   The first point was to get pure hydrogen.   This gas, evolved from zinc and sulphuric acid, might contain oxides of nitrogen, sulphur dioxide, hydrosulphuric acid, and arsenic hydride.   These impurities were removed in a series of wash bottles; the H_2S by a solution of lead nitrate, the H_3As by silver sulphate, and the others by caustic potash.   Finally, the gas was dried by passing through sulphuric acid, or, in some of the experiments, over phosphorus pentoxide.   The copper oxide was thoroughly dried, and the bulb containing it was weighed. By a current of dry hydrogen all the air was expelled from the apparatus, and then, for ten or twelve hours, the oxide of copper was heated to dull redness in a constant stream of the gas.   The reduced copper was allowed to cool in an atmosphere of hydrogen.   The weighings were made with the bulbs exhausted of air.   The following table gives the results:

Column A contains the symbol of the drying substance. B gives the weight of the bulb and copper oxide.   C, the weight of bulb and reduced copper.   D, the weight of the vessel used for collecting the water.   E, the same, plus the water.   F, the weight of oxygen.   G, the weight of water formed.   H, the crude equivalent of H when $O = 10,000$. I, the equivalent of H, corrected for the air contained in the sulphuric acid employed.   This correction is not explained, and seems to be questionable.

---

* Philosophical Magazine, 3d series, 20, 341.

† Compt. Rend., 14, 537.

A.	B.	C.	D.	E.	F.	G.	II.	I.
II₂SO₄	291.985	278.806	480.807	495.634	13.179	14.827	1250.5	1249.6
"	344.548	324.186	488.227	511.132	20.362	22.905	1249.0	1248.0
"	316.671	296.175	439.711	462.764	20.495	23.053	1248.1	1247.2
P₂O₅	625.829	568.825	884.190	948.323	57.004	64.044	1250.6	1249.0
H₂SO₄	804.546	728.182	887.331	973.291	76.364	85.960	1256.2	1254.6
"	533.726	490.155	867.159	916.206	43.571	49.047	1256.3	1255.0
P₂O₅	661.915	627.104	839.394	878.482	34.811	39.178	1254.6	1253.3
"	612.625	566.738	824.624	876.244	45.887	51.623	1250.0	1249.0
II₂SO₄	904.643	844.612	822.660	890.246	60.031	67.586	1258.3	1255.1
P₂O₅	642.325	590.487	741.095	799.417	51.838	58.320	1250.4	1248.8
"	587.645	535.137	874.832	933.910	52.508	59.078	1251.2	1249.0
II₂SO₄	673.280	613.492	931.487	998.700	59.789	67.282	1253.3	1250.8
"	660.855	598.765	682.374	752.273	62.090	69.899	1257.7	1254.8
"	642.325	590.487	741.097	799.455	51.838	58.360	1258.1	1256.2
P₂O₅	937.845	881.362	1064.762	1128.319	56.483	63.577	1255.8	1252.2
"	756.352	719.563	878.640	920.030	36.789	41.390	1250.6	1249.1
"	754.162	720.000	887.817	926.275	34.162	38.458	1257.3	1255.1
"	759.762	727.632	888.662	924.837	32.133	36.175	1257.5	1254.7
"	747.652	716.825	877.862	912.539	30.827	34.677	1248.8	1248.0
Means							1253.3	1251.5

In the sum total of these nineteen experiments, 840.161 grammes of oxygen form 945.439 grammes of water. This gives, in percentages, for the composition of water, oxygen 88.864; hydrogen, 11.136. Hence the atomic weight of oxygen, calculated in mass, is 15.9608. In the following column the values are given as deduced from the individual data given under the headings F and G:

$$
\begin{aligned}
&15.994\\
&16.014\\
&16.024\\
&15.992\\
&15.916\\
&15.916\\
&15.943\\
&16.000\\
&15.892\\
&15.995\\
&15.984\\
&15.958\\
&15.902\\
&15.987\\
&15.926\\
&15.992\\
&15.904\\
&15.900\\
&16.015
\end{aligned}
$$

Mean, 15.9607, with a probable error of ± .0070.

In calculating the above column several discrepancies were noted, probably due to misprints in the original memoir. On comparing columns B and C with F, or D and E with G, these anomalies chiefly appear. They were detected and carefully considered in the course of my own calculations; and, I believe, eliminated from the final result.

The paper by Erdmann and Marchand* followed closely after that of Dumas. The method of research was essentially the same as that of the latter chemist, varying only in points of comparatively unimportant detail. The results are given in two series, in one of which the weighings were

* Journ. f. Prakt. Chem., 1842, bd. 26, s. 461.

not actually made in vacuo, but were, nevertheless, reduced
to a vacuum standard. The second series represents actual
vacuum weighings. The quantity of water formed in each
experiment, was from 41.664 to 95.612 grammes. I give
below only the percentages of oxygen and hydrogen in
water as deduced from Erdmann and Marchand's data:

First Series.

O.	H.
88.836	11.164
88.821	11.179
88.874	11.126
88.868	11.132

Second Series.

O.	H.
88.887	11.113
88.898	11.102
88.895	11.105
88.899	11.101

Hence, the atomic weight of oxygen is, as follows:

First Series.	Second Series.
15.915	15.997
15.891	16.015
15.976	16.010
15.966	16.016
Mean, 15.9369, ± .0138	Mean, 16.0095, ± .0030

The effect of discussing these two series separately is
somewhat startling. It gives to the four experiments in
Erdmann and Marchand's second group a weight vastly
greater than their other four and Dumas' nineteen taken
together. For so great a superiority as this there is no
adequate reason; and it is highly probable that it is due
almost entirely to fortunate coincidences, rather than to
greater accuracy of work. We will, therefore, treat Erd-
mann and Marchand's experiments as one series, giving all
equal weight, and then combine them with the results ob-
tained by Dumas. We now have—

By Dumas _____ $O = 15.9607, \pm .0070$
By Erdmann and Marchand_____ $O = 15.9733, \pm .0113$

General mean_____ $O = 15.9642, \pm .0060$

In discussing the relative density of oxygen and hydrogen gases we need only consider the more modern researches of Dumas and Boussingault, and of Regnault. As the older work has some historical value, I may in passing just cite its results. For the density of hydrogen we have .0769, Lavoisier; .0693, Thomson; .092, Cavendish; .0732, Biot and Arago; .0688, Dulong and Berzelius. For oxygen there are the following determinations: 1.087, Fourcroy, Vauquelin, and Séguin; 1.103, Kirwan; 1.128, Davy; 1.088, Allen and Pepys; 1.1036, Biot and Arago; 1.1117, Thomson; 1.1056, De Saussure; 1.1026, Dulong and Berzelius; 1.106, Buff; 1.1052, Wrede.*

In 1841 Dumas and Boussingault† published their determinations of gaseous densities. For hydrogen they obtained values ranging from .0691 to .0695; but beyond this mere statement they give no details. For oxygen three determinations were made, with the following results:

1.1055
1.1058
1.1057

Mean, 1.10567, $\pm$ .00006

If we take the two extreme values given above for hydrogen, and regard them as the entire series, they give us a mean of .0693, $\pm$ .00013.

This mean hydrogen value, combined with the mean oxygen value, gives for the atomic weight of the latter element the number 15.9538, $\pm$ .031.

Regnault's researches, published four years later,‡ were of

---

* For Wrede's work, see Berzelius' Jahresbericht for 1843. For Dulong and Berzelius, see the paper already cited. All the other determinations are taken from Gmelin's Handbook, Cavendish edition, v. 1, p. 279.

† Compt. Rend., 12, 1005. Compare also with Dumas, Compt. Rend., 14, 537.

‡ Compt. Rend., 20, 975.

a more satisfactory kind. Indeed, they are among the classics of physical science; and probably approach as near to absolute accuracy as is possible for experiment.

For hydrogen three determinations of density gave the following results:

.06923
.06932
.06924

Mean, .069263, $\pm$ .000019

For oxygen four determinations were made, but in the first one the gas was contaminated by traces of hydrogen, and the value obtained, 1.10525; was, therefore, rejected by Regnault as too low. The other three are as follows:

1.10561
1.10564
1.10565

Mean, 1.105633, $\pm$ .000008

Now, combining the hydrogen and oxygen series, we have for the atomic weight of oxygen, 15.9628, $\pm$ .0044.*

Upon combining the result of Regnault's work with that from Dumas and Boussingault's we get the following value:

From Dumas and Boussingault _____. O = 15.9538, $\pm$ .031
From Regnault_____ O = 15.9628, $\pm$ .0044

General mean_____ O = 15.9627, $\pm$ .0043

This result, it will be seen, agrees remarkably well with that obtained in the experiments upon the synthesis of water.

---

* Since these computations were made, Professor John Le Conte has called my attention to the existence of slight numerical errors in Regnault's own reductions. As corrected by Le Conte, Regnault's figures give 1.105612 for the density of oxygen, and 0.069269 for that of hydrogen. Hence the atomic weight of O becomes 15.9611, instead of 15.9628. The difference is slight, but still it ought not to be ignored. All the computations in the body of this work, having been finished before I received Professor Le Conte's figures, must stand, nevertheless, as they are. For further details Le Conte refers to Phil. Mag., (4,) 27, p. 29, 1864; and also to the Smithsonian Report for 1878, p. 428.

The third method indicated at the beginning of this discussion has been recently employed in part by J. Thomsen[*] of Copenhagen. Unfortunately this chemist has not published the details of his work, but only the end results. These serve to confirm the values for oxygen fixed by other methods, but they cannot well be included in the systematic discussion. Partly by the oxidation of hydrogen over heated copper oxide, and partly by its direct union with oxygen, Thomsen finds that at the latitude of Copenhagen, and at sea level, one litre of dry hydrogen at 0° and 760 mm. pressure will form .8041 gramme of water. According to Regnault, at this latitude, level, temperature, and pressure, a litre of hydrogen weighs .08954 gramme. From these data, $O = 15.9605$. It will be seen at once that Thomsen's work depends in great part upon that of Regnault, and yet that it affords an admirable reinforcement of the latter.

It is now plain, in conclusion, that all the different lines of research point to an atomic weight for oxygen a little below 16.00. Five distinct investigations confirm each other wonderfully. Upon combining the values obtained by the two chief methods we get the following final results :

$$\text{From synthesis of water} \qquad O = 15.9642, \pm .0060$$
$$\text{From gaseous densities} \qquad O = 15.9627, \pm .0043$$

In the general mean the atomic weight of oxygen becomes 15.9633, with a probable error of $\pm$ .0035.[†]

---

[*] Ber. d. Deutsch. Chem. Gesellschaft, 1870, s. 928.

[†] Le Conte's correction of Regnault's figures introduced here would make $O = 15.9622$, instead of 15.9633. Difference, .0011.

SILVER, POTASSIUM, SODIUM, CHLORINE, BROMINE, IODINE, AND SULPHUR.

The atomic weights of these seven elements depend upon each other to so great an extent that they can hardly be considered independently. Indeed, chlorine, potassium, and silver have always been mutually determined. From the ratio between silver and chlorine, the ratio between silver and potassium chloride, and the composition of potassium chlorate, these three atomic weights were first accurately fixed. Similar ratios, more recently worked out by Stas and others, have rendered it desirable to include bromine, iodine, sulphur, and sodium in the same general discussion.

Several methods of determination will be left altogether out of account. For example, in 1842 Marignac* sought to fix the atomic weight of chlorine by estimating the quantity of water formed when hydrochloric acid gas is passed over heated oxide of copper. His results were wholly inaccurate, and need no further mention here. A little later Laurent† redetermined the same constant from the analysis of a chlorinated derivative of naphthalene. This method did not admit of extreme accuracy, and it presupposed a knowledge of the atomic weight of carbon; hence it may be properly disregarded. Maumené's‡ analyses of the oxalate and acetate of silver gave good results for the atomic weight of that metal; but they also depend for their value upon our knowledge of carbon, and will, therefore, be discussed further on with reference to that element.

Let us now consider the ratios upon which we must rely for ascertaining the atomic weights of the seven elements in question. After we have properly arranged our data we may then discuss their meaning. First in order we may

---

* Compt. Rend., 14, 570.   Also, Journ. f. Prakt. Chem., 26, 304.
† Compt. Rend., 14, 456.   Journ. f. Prakt. Chem., 26, 307.
‡ Ann. d. Chim. et d. Phys., (3,) 18, 41.   1846.

conveniently take up the percentage of potassium chloride obtainable from the chlorate.

The first reliable series of experiments to determine this percentage was made by Berzelius.* All the earlier estimations were vitiated by the fact that when potassium chlorate is ignited under ordinary circumstances a little solid material is mechanically carried away with the oxygen gas. Minute portions of the substance may even be actually volatilized. These sources of loss were avoided by Berzelius, who devised means for collecting and weighing this trace of potassium chloride. All the successors of Berzelius in this work have benefitted by his example; although for the methods by which loss has been prevented we must refer to the original papers of the several investigators. In short, then, Berzelius ignited potassium chlorate, and determined the percentage of chloride which remained. Four experiments gave the following results:

$$60.854$$
$$60.850$$
$$60.850$$
$$60.851$$

Mean, 60.851, with a probable error of $\pm$ .0006

The next series was made by Penny,† in England, who worked after a somewhat different method. He treated potassium chlorate with strong hydrochloric acid in a weighed flask, evaporated to dryness over a sand bath, and then found the weight of the chloride thus obtained. His results are as follows, in six trials:

$$60.825$$
$$60.822$$
$$60.815$$
$$60.820$$
$$60.823$$
$$60.830$$

Mean, 60.8225, $\pm$ .0014

---

* Poggend. Annalen, 1826, bd. 8, s. 1.
† Phil. Transactions, 1839, p. 20.

In 1842 Pelouze[*] made three estimations by the ignition of the chlorate, with these results :

<div align="center">

60.843
60.857
60.830

Mean, 60.843, ± .0053

</div>

Marignac, in 1842,[†] worked with several different recrystallizations of the commercial chlorate. He ignited the salt, with the usual precautions for collecting the material carried off mechanically, and also examined the gas which was evolved. He found that the oxygen from 50 grammes of chlorate contained chlorine enough to form .003 gramme of silver chloride. Here are the percentages found by Marignac :

In chlorate once crystallized	60.845
In chlorate once crystallized	60.835
In chlorate twice crystallized	60.833
In chlorate twice crystallized	60.844
In chlorate three times crystallized	60.839
In chlorate four times crystallized	60.839

<div align="center">

Mean, 60.8392, ± .0013

</div>

In the same paper Marignac describes a similar series of experiments made upon potassium perchlorate, $KClO_4$. In three experiments it was found that the salt was not quite free from chlorate, and in three more it contained traces of iron. A single determination upon very pure material gave 46.187 per cent. of oxygen and 53.813 of residue.

In 1845 two series of experiments were published by Gerhardt.[†] The first, made in the usual way, gave these results :

<div align="center">

60.871
60.881
60.875

Mean. 60.8757, ± .0020

</div>

* Compt. Rend., 15, 959.
† Ann. d. Chem. u. Pharm., bd. 44, s. 18.
‡ Compt. Rend., 21, 1280.

In the second series the oxygen was passed through a weighed tube containing moist cotton, and another filled with pumice stone and sulphuric acid. Particles were thus collected which in the earlier series escaped. From these experiments we get—

$$60.947$$
$$60.947$$
$$60.952$$

Mean, 60.9487, ± .0011

These last results were afterwards sharply criticized by Marignac,* and their value seriously questioned.

The next series, in order of time, is due to Maumené.† This chemist supposed that particles of chlorate, mechanically carried away, might continue to exist as chlorate, undecomposed; and hence that all previous series of experiments might give too high a value to the residual chloride. In his determinations, therefore, the ignition tube, after expulsion of the oxygen, was uniformly heated in all its parts. Here are his percentages of residue:

$$60.788$$
$$60.790$$
$$60.793$$
$$60.791$$
$$60.785$$
$$60.795$$
$$60.795$$

Mean, 60.791, ± .0009

The question which most naturally arises in connection with these results is, whether portions of chloride may not have been volatilized, and so lost.

Closely following Maumené's paper there is a short note by Faget,‡ giving certain mean results. According to this chemist, when potassium chlorate is ignited slowly, we get

---

* Supp. Bibl. Univ. de Genéve, Vol. I.
† Ann. d. Chim. et d. Phys., (3,) 18, 71.   1846.
‡ Ann. d. Chim. et d. Phys., (3,) 18, 80.   1846.

60.847 per cent. of residue.   When the ignition is rapid, we get 60.942.   As no detailed experiments are given, these figures can have no part in our discussion.

Last of all we have two series determined by Stas.*   In the first series we have the results obtained by igniting the chlorate.   In the second series the chlorate was reduced by strong hydrochloric acid, after the method followed by Penny :

First Series.

60.8380
60.8395
60.8440
60.8473
60.8450

Mean, 60.84276, $\pm$ .0012

Second Series.

60.850
60.853
60.844

Mean, 60.849, $\pm$ .0017

In these experiments every conceivable precaution was taken to avoid error and ensure accuracy.   All weighings were reduced to a vacuum standard ; from 70 to 142 grammes of chlorate were used in each experiment; and the chlorine carried away with the oxygen in the first series was absorbed by finely divided silver and estimated.   It is difficult to see how any error could have crept in.

Now, to combine these different series of experiments.

Berzelius, mean result		60.851,	$\pm$ .0006
Penny,	"	60.8225,	$\pm$ .0014
Pelouze,	"	60.843,	$\pm$ .0053
Marignac,	"	60.8392,	$\pm$ .0013
Gerhardt, 1st	"	60.8757,	$\pm$ .0020
" 2d	"	60.9487,	$\pm$ .0011
Maumené,	"	60.791,	$\pm$ .0009
Stas, 1st	"	60.8428,	$\pm$ .0012
" 2d	"	60.849,	$\pm$ .0017

General mean, from all nine series, representing forty experiments 60.846, $\pm$ .00038

* See Aronstein's Translation, p. 249.

This value is exactly that which Stas deduced from both of his own series combined, and gives great emphasis to his wonderfully accurate work. It also finely illustrates the compensation of errors which occurs in combining the figures of different experimenters.

Similar analyses of silver chlorate have been made by Marignac and by Stas. Marignac's figures I have not been able to find,* and Stas gives but two experiments. The following are his percentages of oxygen in silver chlorate :†

<div align="center">

25.081
25.078
_____
Mean, 25.0795, ± .0010

</div>

For the direct ratio between silver and chlorine there are seven available series of experiments. Here, as in many other ratios, the first reliable work was done by Berzelius.‡

He made three estimations, using each time twenty grammes of pure silver. This was dissolved in nitric acid. In the first experiment the silver chloride was precipitated and collected on a filter. In the second and third experiments the solution was mixed with hydrochloric acid in a flask, evaporated to dryness, and the residue then fused and weighed without transfer. One hundred parts of silver formed of chloride :

---

* Since all the calculations were finished I have secured a copy of Marignac's figures. They are as follows: The third column gives the percentage of O in $AgClO_3$.

24.510 grm. $AgClO_3$ gave	18.3616 AgCl.		25.103
25.809	"	"	19.3345 "	25.086
30.306	"	"	22.7072 "	25.074
28.358	"	"	21.2453 "	25.082
28.287	"	"	21.1833 "	25.113
57.170	"	"	42.8366 "	25.072

<div align="right">Mean, 25.088, ± .0044</div>

The introduction of these figures into the subsequent calculations could not produce any appreciable result. They would practically vanish from the general mean. However, they serve here as confirmation of Stas' work.

† Aronstein's Translation, p. 214.

‡ Thomson's Annals of Philosophy, 1820, v. 15, p. 89.

132.700
132.780
132.790
___
Mean, 132.757, ± .019

Turner's work* closely resembles that of Berzelius. Silver was dissolved in nitric acid and precipitated as chloride. In experiments one, two, and three the mixture was evaporated and the residue fused. In experiment four the chloride was collected on a filter. A fifth experiment was made, but has been rejected as worthless.

The results were as follows: In a third column I put the quantity of AgCl proportional to 100 parts of Ag.

28.407 grains Ag gave 37.737 AgCl.   132.844
41.917   "   "   55.678   "   132.829
40.006   "   "   53.143   "   132.837
30.922   "   "   41.070   "   132.818
                                                        ___
                        Mean, 132.832, ± .0038

The same general method of dissolving silver in nitric acid, precipitating, evaporating, and fusing without transfer of material was also adopted by Penny.† His results for 100 parts of silver are as follows, in parts of chloride:

132.836
132.840
132.830
132.840
132.840
132.830
132.838
___
Mean, 132.8363, ± .0012

In 1842 Marignac‡ found that 100 parts of silver formed 132.74 of chloride, but gave no available details. Later,‖

___
* Phil. Transactions, 1829, 291.
† Phil. Transactions, 1839, 28.
‡ Ann. Chem. Pharm., 44, 21.
‖ See Berzelius' Lehrbuch, 5th Ed., Vol. 3, pp. 1192, 1193.

in another series of determinations, he is more explicit, and gives the following data: The weighings were reduced to a vacuum standard.

79.853 grm. Ag gave	106.080 AgCl.	Ratio,	132.844
69.905	"	92.864	"		132.843
64.905	"	86.210	"		132.825
92.362	"	122.693	"		132.839
99.653	"	132.383	"		132.844

Mean, 132.839, ± .0024

The above series all represent the synthesis of silver chloride. Maumené* made analyses of the compound, reducing it to metal in a current of hydrogen. His experiments make 100 parts of silver equivalent to chloride:

132.734
132.754
132.724
132.729
132.741

Mean, 132.7364, ± .0077

By Dumas† we have the following estimations:

9.954 Ag gave	13.227 AgCl.	Ratio,	132.882
19.976	"	26.542	"		132.869

Mean, 132.8755, ± .0044

Finally, there are seven determinations by Stas,‡ made with his usual accuracy and with every precaution against error. In the first, second, and third, silver was heated in chlorine gas, and the synthesis of silver chloride thus effected directly. In the fourth and fifth silver was dissolved in nitric acid, and the chloride thrown down by passing hydrochloric acid gas over the surface of the solution. The whole was then evaporated in the same vessel, and the chloride fused, first in an atmosphere of hydrochloric acid,

---

* Ann. d. Chim. et d. Phys., (3,) 18, 49.   1846.
† Ann. Chem. Pharm., 113, 21.   1860.
‡ Aronstein's Translation, p. 171.

and then in a stream of air. The sixth synthesis was similar to these, only the nitric solution was precipitated by hydrochloric acid in slight excess, and the chloride thrown down was washed by repeated decantation. All the decanted liquids were afterwards evaporated to dryness, and the trace of chloride thus recovered was estimated in addition to the main mass. The latter was fused in an atmosphere of HCl. The seventh experiment was like the sixth, only ammonium chloride was used instead of hydrochloric acid. From 98.3 to 399.7 grammes of silver were used in each experiment, the operations were performed chiefly in the dark, and all weighings were reduced to vacuum. In every case the chloride obtained was beautifully white. The following are the results in chloride for 100 of silver:

$$132.841$$
$$132.843$$
$$132.843$$
$$132.849$$
$$132.846$$
$$132.848$$
$$122.8417$$

Mean, 132.8445, $\pm$ .0008

We may now combine the means of these seven series, representing in all thirty-three experiments. One hundred parts of silver are equivalent to chlorine, as follows:

Berzelius	32.757,	± .0190
Turner	32.832,	± .0038
Penny	32.8363,	± .0012
Marignac	32.839,	± .0024
Maumené	32.7364,	± .0077
Dumas	32.8755,	± .0044
Stas	32.8445,	± .0008

General mean 32.8418, ± .0006

Here, again, we have a fine example of the evident compensation of errors among different series of experiments. We have also another tribute to the accuracy of Stas, since this general mean varies from the mean of his results only within the limits of his own variations.

The ratio between silver and potassium chloride, or, in other words, the weight of silver in nitric acid solution which can be precipitated by a known weight of KCl, has been fixed by Marignac and by Stas. Marignac,[*] reducing all weighings to vacuum, obtained these results. In the third column I give the weight of KCl proportional to 100 parts of Ag.

4.7238 grm. Ag =		3.2626 KCl.		69.067
21.725	"	15.001	"	69.050
21.759	"	15.028	"	69.066
21.909	"	15.131	"	69.063
22.032	"	15.216	"	69.063
25.122	"	17.350	"	69.063

Mean, 69.062, ± .0017

Stas' experiments upon this ratio may be divided into two series.[†] In the first series the silver was slightly impure, but the impurity was of known quantity, and corrections could therefore be applied. In the second series pure silver was employed. The potassium chloride was from several different sources, and in every case was purified with the utmost care. From 10.8 to 32.4 grammes of silver were taken in each experiment, and the weighings were reduced to vacuum. The method of operation was, in brief, as follows: A definite weight of potassium chloride was taken, and the exact quantity of silver necessary, according to Prout's hypothesis, to balance it was also weighed out. The metal, with suitable precautions, was dissolved in nitric acid, and the solution mixed with that of the chloride. After double decomposition the trifling excess of silver remaining in the liquid was determined by titration with a normal solution of potassium chloride. One hundred parts of silver required the following of KCl:

---

[*] See Berzelius' Lehrbuch, 5th edition, Vol. 3, pp. 1192, 1193.
[†] Aronstein's Translation, pp. 250–257.

First Series.

69.105
69.104
69.103
69.104
69.102

Mean, 69.1036, ± .0003

Second Series.

69.105
69.099
69.107
69.103
69.103
69.105
69.104
69.099
69.1034
69.104
69.103
69.102
69.104
69.104
69.105
69.103
69,101
60.105
69.103

Mean, 69.1033, ± .0003

Now, combining the three series, with their thirty experiments, we get the following:

Marignac_____ 69.062, ± .0017
Stas, 1st series_____ 69.1036, ± .0003
Stas, 2d series _____ 69.1033, ± .0003

General mean_____ 69.1032, ± .0002

The quantity of silver chloride which can be formed from a known weight of potassium chloride has also been determined by Berzelius, Marignac, and Maumené. Berzelius[*] found that 100 parts of KCl were equivalent to 194.2 of

---

[*] Poggend. Annal., 8, 1. 1826.

AgCl; a value which, corrected for weighings in air, becomes 192.32. This experiment will not be included in our discussion.

In 1842 Marignac* published two determinations, with these results from 100 KCl:

$$192.33$$
$$192.34$$

Mean, corrected for weighing in air, 192.26, $\pm$ .003

In 1846 Marignac† published another set of results, as follows. The weighings were reduced to vacuum. The usual ratio is in the third column.

17.034 grm. KCl gave	32.761	AgCl.		192.327
14.427	"	27.749	"		192.341
15.028	"	28.910	"		192.374
15.131	"	29.102	"		192.334
15.216	"	29.271	"		192.370

Mean, 192.349, $\pm$ .006

Three estimations of the same ratio were also made by Maumené,‡ as follows:

10.700 grm. KCl gave	20.627	AgCl.		192.776
10.5195	"	20.273	"		192.716
8.587	"	16.556	"		192.803

Mean, 192.765, $\pm$ .017

The three series of ten experiments in all foot up thus:

Marignac, 1842	192.260,	$\pm$ .003
" 1846	192.349,	$\pm$ .006
Maumené	192.765,	$\pm$ .017
General mean	192.294,	$\pm$ .0029

These figures show clearly that the ratio which they represent is not of very high importance. It might be rejected altogether without impropriety, and is only retained for the

* Ann. Chem. Pharm., 44, 21. 1842.

† Berzelius' Lehrbuch, 5th Ed., Vol. 3, pp. 1192, 1193.

‡ Ann. d. Chim. et d. Phys., (3,) 18, 41. 1846.

sake of completeness. It will obviously receive but little weight in our final discussion.

In estimating the atomic weight of bromine the earlier experiments of Balard, Berzelius, Liebig, and Löwig may all be rejected. Their results were all far too low, probably because chlorine was present as an impurity in the materials employed. Wallace's determinations, based upon the analysis of arsenic tribromide, are tolerably good, but need not be considered here. In the present state of our knowledge, Wallace's analyses are better fitted for fixing the atomic weight of arsenic, and will, therefore, be discussed with reference to that element.

The ratios with which we now have to deal are closely similar to those involving chlorine. In the first place there are the analyses of silver bromate by Stas.* In two careful experiments he found in this salt the following percentages of oxygen:

20.351
20.347

Mean, 20.349, ± .0014

There are also four analyses of potassium bromate by Marignac.† The salt was heated, and the percentage loss of oxygen determined. The residual bromide was feebly alkaline. We cannot place much reliance upon this series. The results are as follows:

28.7016
28.6496
28.6050
28.7460

Mean, 28.6755, ± .0207

When silver bromide is heated in chlorine gas, silver chloride is formed. In 1860 Dumas‡ employed this method

---

* Aronstein's Translation, pp. 200–206.

† See E. Mulder's Overzigt, p. 117; or Berzelius' Jahresbericht, 24, 72.

‡ Ann. Chem. Pharm., 113, 20.

for estimating the atomic weight of bromine. His results are as follows: In the third column I give the weight of AgBr equivalent to 100 parts of AgCl.

2.028 grm. AgBr gave	1.547 AgCl.		131.092
4.237 "	3.235 "		130.974
5.769 "	4.403 "		131.024

Mean, 131.030, ± .023

This series is evidently of but little value.

But the two ratios upon which, in connection with Stas' analyses of silver bromate, the atomic weight of bromine chiefly depends are those which connect silver with the latter element directly and silver with potassium bromide.

Marignac,* to effect the synthesis of silver bromide, dissolved the metal in nitric acid, precipitated the solution with potassium bromide, washed, dried, fused, and weighed the product. The following quantities of bromine were found proportional to 100 parts of silver:

74.072
74.055
74.066

Mean, reduced to a vacuum standard, 74.077, ± .003

Much more elaborate determinations of this ratio are due to Stas.† In one experiment a known weight of silver was converted into nitrate, and precipitated in the same vessel by pure hydrobromic acid. The resulting bromide was washed thoroughly, dried, and weighed. In four other estimations the silver was converted into sulphate. Then a known quantity of pure bromine, as nearly as possible the exact amount necessary to precipitate the silver, was transformed into hydrobromic acid. This was added to the dilute solution of the sulphate, and, after precipitation was complete, the minute trace of an excess of silver in the clear supernatant fluid was determined. All weighings were re-

---

* E. Mulder's Overzigt, p. 116. Berzelius' Jahresbericht, 24, 72.
† Aronstein's Translation, pp. 154-170.

duced to a vacuum.   From these experiments, taking both series as one, we get the following quantities of bromine corresponding to 100 parts of silver :

$$74.0830$$

$$
\begin{array}{l}
74.0790 \\
74.0795 \\
74.0805 \\
74.0830
\end{array}
$$

Mean, 74.081, $\pm$ .0006

Combining this with Marignac's result, 74.077, $\pm$ .003, we get as a general mean the value 74.0809, $\pm$ .0006.*

The ratio between silver and potassium bromide was first accurately determined by Marignac.†   I give, with his weighings, the quantity of KBr proportional to 100 parts of Ag :

2.131 grm. Ag $=$	2.351 KBr.		110.324
2.559	"	2.823	"	110.316
2.447	"	2.700	"	110.339
3.025	"	3.336	"	110.283
3.946	"	4.353	"	110.314
11.569	"	12.763	"	110.321
20.120	"	22.191	"	110.293

Mean, corrected for weighing in air, 110.343, $\pm$ .005

Stas,‡ working in essentially the same manner as when he fixed the ratio between potassium chloride and silver, obtained the following results :

---

* O. W. Huntington, in his paper upon the atomic weight of cadmium, (Amer. Acad. Proc., 1881,) gives three analyses and three syntheses of silver bromide. These give a mean value of Ag : Br : : 100 : 74.064.   This figure I record here in order that other chemists may not overlook the work of Mr. Huntington, although it came out too late for use in my own calculations.

† E. Mulder's Overzigt, p. 116.   Berzelius' Jahresbericht, 24, 72.

‡ Aronstein's Translation, pp. 334–347.

$$110.361$$
$$110.360$$
$$110.360$$
$$110.342$$
$$110.346$$
$$110.338$$
$$110.360$$
$$110.336$$
$$110.344$$
$$110.332$$
$$110.343$$
$$110.357$$
$$110.334$$
$$110.335$$

Mean, 110.3463, $\pm$ .0020

Combining this with Marignac's mean result, 110.343, $\pm$ .005, we get a general mean of 110.3459, $\pm$ .0019.

The ratios upon which we must depend for the atomic weight of iodine are exactly parallel to those used for the determination of bromine.

To begin with, the percentage of oxygen in potassium iodate has been determined by Millon.[*] In three experiments he found :

$$22.46$$
$$22.49$$
$$22.47$$

Mean, 22.473, $\pm$ .005

Millon also estimated the oxygen in silver iodate, getting the following percentages:

$$17.05$$
$$17.03$$
$$17.06$$

Mean, 17.047, $\pm$ .005

The analysis of silver iodate has also been performed with extreme care by Stas.[†] From 76 to 157 grammes were used

[*] Ann. d. Chim. et d. Phys., (3,) 9, 400. 1843.
[†] Aronsteins' Translation, pp. 179–200.

in each experiment, the weights being reduced to a vacuum standard. As the salt could not be prepared in an absolutely anhydrous condition, the water expelled in each analysis was accurately estimated and the necessary corrections applied. In two of the experiments the iodate was decomposed by heat, and the oxygen given off was fixed upon a weighed quantity of copper heated to redness. Thus the actual weights, both of the oxygen and the residual iodide, were obtained. In a third experiment the iodate was reduced to iodide by a solution of sulphurous acid, and the oxygen was estimated only by difference. In the three percentages of oxygen given below the result of this analysis comes last. The figures for oxygen are as follows:

$$16.976$$
$$16.972$$
$$16.9761$$

Mean, 16.9747, ± .0009

This, combined with Millon's series above cited, gives us a general mean of 16.9771, ± .0009.

The ratio between silver and potassium iodide seems to have been determined only by Marignac,* and without remarkable accuracy. In five experiments 100 parts of silver were found equivalent to potassium iodide as follows:

1.616 grm. Ag =	2.483 KI.	Ratio,	153.651
2.503 "	3.846 "	， "	153.665
3.427 "	5.268 "	"	152.720
2.141 "	3.290 "	"	153.667
10.821 "	16.642 "	"	153.794

Mean, 153.6994, ± .0178

The synthesis of silver iodide has been effected by both Marignac and Stas. Marignac, in the paper above cited, gives these weighings. In the last column I add the ratio between iodine and 100 parts of silver:

15.000 grm. Ag gave	32.625 AgI.	117.500
14.790 "	32.170 "	117.512
18.545 "	40.339 "	117.519

Mean, corrected for weighing in air, 117.5335, ± .0036

---

* Berzelius' Lehrbuch, 5th Ed., 3, 1196.

Stas* in his experiments worked after two methods, which gave, however, results concordant with each other and with those of Marignac.

In the first series of experiments Stas converted a known weight of silver into nitrate, and then precipitated with pure hydriodic acid. The iodide thus thrown down was washed, dried, and weighed without transfer. By this method 100 parts of silver were found to require of iodine :

<div align="center">

117.529
117.536
———
Mean, 117.5325, ± .0024

</div>

In the second series a complete synthesis of silver iodide from known weights of iodine and metal was performed. The iodine was dissolved in a solution of ammonium sulphite, and thus converted into ammonium iodide. The silver was transformed into sulphate and the two solutions mixed. When the precipitate of silver iodide was completely deposited the supernatant liquid was titrated for the trifling excess of iodine which it always contained. As the two elements were weighed out in the ratio of 127 to 108, while the atomic weight of iodine is probably a little under 127, this excess is easily explained. From these experiments two sets of values were deduced; one from the weights of silver and iodine actually employed, the other from the quantity of iodide of silver collected. From the first set we have of iodine for 100 parts of silver :

<div align="center">

117.5390
117.5380
117.5318
117.5430
117.5420
117.5300
———
Mean, 117.5373, ± .0015

</div>

From the weight of silver iodide actually collected we

---

* Aronstein's Translation, pp. 136, 152.

get as follows.   For experiment number three in the above column there is no equivalent here:

$$117.529$$
$$117.531$$
$$117.539$$
$$117.538$$
$$117.530$$

Mean, 117.5334, ± .0014

Now, combining these several sets of results, we have the following general mean:

Marignac _____ ___   117.5335, ± .0036
Stas, 1st series_____   117.5325, ± .0024
  "   2d   "   _____   117.5373, ± .0015
  "   3d   "   _____   117.5334, ± .0014

General mean_____   117.5345, ± .0009

One other comparatively unimportant iodine ratio remains for us to notice.   Silver iodide, heated in a stream of chlorine, becomes converted into chloride; and the ratio between these two salts has been thus determined by Berzelius and by Dumas.

From Berzelius[*] we have the following data: In the third column I give the ratio between AgI and 100 parts of $AgCl$.

5.000 grm. AgI gave 3.062 AgCl.   163.292
12.212   "   7.4755 "   163.360

Mean, 163.326, ± .023

Dumas'[†] results were as follows:

3.520 grm. AgI gave 2.149 AgCl.   163.793
7.011   "   4.281 "   163.770

Mean, 163.782, ± .008

General mean from the combination of both series, 163.733, ± .0076.

We now come to the ratios connecting sulphur with silver

---

* 'Ann. d. Chim. et d. Phys., (2,) 40, 430.   1829.
† Ann. Chem. Pharm., 113, 28.   1860.

and chlorine. Other ratios have been applied to the determination of the atomic weight of sulphur, but they are hardly applicable here. The earlier results of Berzelius were wholly inaccurate, and his later experiments upon the synthesis of lead sulphate will be used in discussing the atomic weight of lead. Erdmann and Marchand determined the amount of calcium sulphate which could be formed from a known weight of pure Iceland spar; and later they made analyses of cinnabar, in order to fix the value of sulphur by reference to calcium and to mercury. Their results will be applied in this discussion towards ascertaining the atomic weights of the metals just named. For our present purposes only three ratios need be considered.

First in order let us take up the composition of silver sulphide, as directly determined by Dumas, Stas, and Cooke. Dumas'[*] experiments were made with sulphur which had been thrice distilled and twice crystallized from carbon disulphide. A known weight of silver was heated in a tube in the vapor of the sulphur, the excess of the latter was distilled away in a current of carbon dioxide, and the resulting silver sulphide was weighed.

I subjoin Dumas' weighings, and also the quantity of Ag_2S proportional to 100 parts of Ag, as deduced from them:

					Ratio,	
9.9393 grm. Ag =	1.473	S.			Ratio,	114.820
9.962	"	1.4755	"		"	114.811
·30.637	"	4.546	"		"	114.838
30.936	"	4.586	"		"	114.824
30.720	"	4.554	"		"	114.824

Mean, 114.8234, $\pm$ .0029

Dumas used from ten to thirty grammes of silver in each experiment. Stas,[†] however, in his work, employed from sixty to two hundred and fifty grammes at a time. Three of Stas' determinations were made by Dumas' method, while in the other two the sulphur was replaced by pure sulphu-

---

* Ann. Chem. Pharm., 113, 24. 1860

† Aronstein's Translation, p. 179.

retted hydrogen.   In all cases the excess of sulphur was ex-
pelled by carbon dioxide, purified with scrupulous care.
Impurities in the dioxide may cause serious error.   The
five results come out as follows for 100 parts of silver:

<div align="center">

114.854
114.853
114.854
114.851
114.849

Mean, 114.8522, ± .0007

</div>

The experiments made by Professor Cooke* with reference
to this ratio were only incidental to his elaborate researches
upon the atomic weight of antimony.   They are interesting,
however, for two reasons: they serve to illustrate the vola-
tility of silver, and they represent, not syntheses, but reduc-
tions of the sulphide by hydrogen.   Cooke gives three series
of results.   In the first the silver sulphide was long heated
to full redness in a current of hydrogen.   Highly concord-
ant and at the same time plainly erroneous figures were ob-
tained; the error being eventually traced to the fact that
some of the reduced silver, although not heated to its melt-
ing point, was actually volatilized and lost.   The second
series, from reductions at low redness, are decidedly better.
In the third series the sulphide was fully reduced below a
visible red heat.   Rejecting the first series we have from
Cooke's figures in the other two the subjoined quantities of
sulphide corresponding to 100 parts of silver:

7.5411 grm. Ag_2S lost	.9773 grm. S.	Ratio,	114.889
5.0364 "	.6524 "	"	114.882
2.5815 "	.3345 "	"	114.886
2.6130 "	.3387 "	"	114.892
2.5724 "	.3334 "	"	114.891

<div align="center">Mean, 114.888, ± .0012</div>

1.1357 grm. Ag_2S lost	.1465 S.	Ratio,	114.810
1.2936 "	.1670 "	"	114.823

<div align="center">Mean, 114.8165, ± .0044</div>

---

* Proc. American Acad. of Arts and Sciences, v. 12.   1877.

Now, combining all four series, we get the following results:

Dumas	114.8234, $\pm$ .0029
Stas	114.8522, $\pm$ .0007
Cooke's 2d	114.888, $\pm$ .0012
" 3d	114.8165, $\pm$ .0044
General mean	114.8581, $\pm$ .0006

Here again we encounter a curious and instructive compensation of errors, and another evidence of the accuracy of Stas.

The percentage of silver in silver sulphate has been determined by Struve and by Stas. Struve* reduced the sulphate by heating in a current of hydrogen, and obtained these results:

5.1860 grm. Ag_2SO_4 gave	3.5910 grm. Ag.		69.244 per cent.	
6.0543	"	4.1922	"	69.243 "
8.6465	"	5.9858	"	69.228 "
11.6460	"	8.0608	"	69.215 "
9.1090	"	6.3045	"	69.212 "
9.0669	"	6.2778	"	69.239 "

Mean, 69.230, $\pm$ .004

Stas,† working by essentially the same method, with from 56 to 83 grammes of sulphate at a time, found these percentages:

69.200
69.197
69.204
69.209
69.207
69.202

Mean, 69.203, $\pm$ .0012

Combining this mean with that from Struve's series we get a general mean of 69.205, $\pm$ .0011.

* Ann. Chem. Pharm., 80, 203. 1851.
† Aronstein's Translation, pp. 214-218.

The third and last sulphur ratio with which we have now to deal is one of minor importance. When silver chloride is heated in a current of sulphuretted hydrogen the sulphide is formed. This reaction was applied by Berzelius[*] to determining the atomic weight of sulphur. He gives the results of four experiments; but the fourth varies so widely from the others that I have rejected it. I have reason to believe that the variation is due, not to error in experiment, but to error in printing; nevertheless, as I am unable to track out the cause of the mistake, I must exclude the figures involving it entirely from our discussion.

The three available experiments, however, give the following results: The last column contains the ratio of silver sulphide to 100 parts of chloride.

6.6075 grm. AgCl gave	5.715 grm. Ag_2S.	86.478
9.2323 "	7.98325 "	86.471
10.1775 "	8.80075 "	86.472

Mean, 86.4737, $\pm$ .0015

We have also a single determination of this value by Svanberg and Struve.[†] After converting the chloride into sulphide they dissolved the latter in nitric acid. A trifling residue of chloride, which had been enclosed in sulphide, and so protected against change, was left undissolved. Hence a slight constant error probably affects this whole ratio. The experiment of Svanberg and Struve gave 86.472 per cent. of silver sulphide derived from 100 of chloride. If we assign this figure equal weight with the results of Berzelius, and combine, we get a general mean of 86.4733, $\pm$ .0011.

For sodium there are but two ratios of any definite value for present purposes. The early work of Berzelius we may disregard entirely, and confine ourselves to the consideration of the results obtained by Penny, Pelouze, Dumas, and Stas.

---

[*] Berzelius' Lehrbuch, 5th Ed., Vol. 3, p. 1187.
[†] Journ. für Prakt. Chem., 44, 320. 1848.

The percentage of oxygen in sodium chlorate has been determined only by Penny,* who used the same method which he applied to the potassium salt. Four experiments gave the following results:

$$
\begin{array}{l}
45.060 \\
45.075 \\
45.080 \\
45.067 \\
\hline
\end{array}
$$

Mean, 45.0705, ± .0029

The ratio between silver and sodium chloride has been fixed by Pelouze, Dumas, and Stas. Pelouze† dissolved a weighed quantity of silver in nitric acid, and then titrated with sodium chloride. Equivalent to 100 parts of silver he found of chloride:

$$
\begin{array}{l}
54.158 \\
54.125 \\
54.139 \\
\hline
\end{array}
$$

Mean, 54.141, ± .0063

By Dumas‡ we have seven experiments, with results as follows: The third column gives the ratio between 100 of silver and NaCl.

2.0535 grm. NaCl	=	3.788 grm. Ag.		54.211
2.169	"	4.0095	"	54.097
4.3554	"	8.0425	"	54.155
6.509	"	12.0140	"	54.178
6.413	"	11.8375	"	54.175
2.1746	"	4.012	"	54.202
5.113	"	9.434	"	54.187

Mean, 54.172, ± .0096

Stas,‖ applying the method used in establishing the similar ratio for potassium chloride, and working with salt from

---

* Phil. Transactions, 1839, p. 25.

† Compt. Rend., 20, 1047. 1845.

‡ Ann. Chem. Pharm., 113, 31. 1860.

‖ Aronstein's Translation, p. 274.

six different sources, found of sodium chloride equivalent to 100 parts of silver:

$$54.2093$$
$$54.2088$$
$$54.2070$$
$$54.2070$$
$$54.2070$$
$$54.2060$$
$$54.2076$$
$$54.2081$$
$$54.2083$$
$$54.2089$$

Mean, 54.2078, $\pm$ .0002

Now, combining these three series, we get the following result:

Pelouze	54.141,	$\pm$ .0063
Dumas	54.172,	$\pm$ .0096
Stas	54.2078,	$\pm$ .0002
General mean	54.2076,	$\pm$ .0002

Here the work of Stas is of such superior excellence that the other series might be completely rejected without appreciably affecting our calculations.

We have now before us the data establishing, with greater or less accuracy, twenty different ratios relating to the atomic weights of the seven elements under discussion. In these we are to discuss the results of about two hundred and fifty separate experiments. Before beginning upon our calculations we will tabulate our ratios, and number them for convenient future reference. Of course it will be understood that the probable errors given below relate to the last term of each proportion:

(1.)	Percentage of O in		$KClO_3$	39.154,	$\pm$ .00038
(2.)	"	"	$KBrO_3$	28.6755,	$\pm$ .0207
(3.)	"	"	KIO_3	22.473,	$\pm$ .0050
(4.)	"	"	$NaClO_3$	45.0705,	$\pm$ .0029
(5.)	"	"	$AgClO_3$	25.0795,	$\pm$ .0010
(6.)	"	"	$AgBrO_3$	20.349,	$\pm$ .0014
(7.)	"	"	$AgIO_3$	16.9771,	$\pm$ .0009
(8.)	"	Ag in	Ag_2SO_4	69.205,	$\pm$ .0011

3

(9.) Ag : NaCl :: 100 : 54.2076, $\pm$ .0002
(10.) Ag : KCl :: 100 : 69.1032, $\pm$ .0002
(11.) Ag : KBr :: 100 : 110.3459, $\pm$ .0019
(12.) Ag : KI :: 100 : 153.6994, $\pm$ .0178
(13.) Ag : Cl :: 100 : 32.8418, $\pm$ .0006
(14.) Ag : Br :: 100 : 74.0809, $\pm$ .0006
(15.) Ag : I :: 100 : 117.5345, $\pm$ .0009
(16.) Ag : Ag_2S :: 100 : 114.8581, $\pm$ .0006
(17.) KCl : AgCl :: 100 : 192.294, $\pm$ .0029
(18.) AgCl : AgBr :: 100 : 131.030, $\pm$ .023
(19.) AgCl : AgI :: 100 : 163.733, $\pm$ .0076
(20.) AgCl : Ag_2S :: 100 : 86.4733, $\pm$ .0011

Now, from ratios 1 to 7 inclusive, we can at once, by applying the known atomic weight of oxygen, deduce the molecular weights of seven haloid salts. Let us consider the first calculation somewhat in detail.

Potassium chlorate yields 39.154 per cent. of oxygen and 60.846 per cent. of residual chloride. For each of these quantities the probable error is $\pm$ .00038. The atomic weight of oxygen is 15.9633, $\pm$ .0035, so that the value for three atoms becomes 47.8899, $\pm$ .0105. We have now the following simple proportion: 39.154 : 60.846 :: 47.8899 : x, = the molecular weight of potassium chloride, = 74.4217. The probable error being known for the first, second, and third term of this proportion, we can easily find that of the fourth term by the formula given in our introduction. It comes out $\pm$ .0164. By this method we obtain the following series of values, which may conveniently be numbered consecutively with the foregoing ratios:

(21.) KCl, from (1,) = 74.4217, $\pm$ .0164
(22.) KBr, " (2,) = 119.117, $\pm$ .0962
(23.) KI, " (3,) = 165.210, $\pm$ .0529
(24.) NaCl, " (4,) = 58.366, $\pm$ .0137
(25.) AgCl, " (5,) = 143.062, $\pm$ .0320
(26.) AgBr, " (6,) = 187.453, $\pm$ .0432
(27.) AgI, " (7,) = 234.195, $\pm$ .0530

With the help of these molecular weights we are now able to calculate eight independent values for the atomic weight of silver:

First, from (10) and (21,) Ag = 107.696, ± .024
Second, " (11) " (22,) " = 107.948, ± .087
Third, " (12) " (23,) " = 107.488, ± .037
Fourth, " (9) " (24,) " = 107.671, ± .025
Fifth, " (13) " (25,) " = 107.694, ± .024
Sixth, " (14) " (26,) " = 107.681, ± .025
Seventh, " (15) " (27,) " = 107.659, ± .024
Eighth, " (8) " (16,) " = 107.712, ± .025

General mean, " = 107.675, ± .0096

It is noticeable that six of these values agree very well. The second and third, however, diverge widely from the average, but in opposite directions; they have, moreover, high probable errors, and consequently little weight. Of these two, one represents little and the other none of Stas' work. Their trifling influence upon our final results becomes curiously apparent in the series of silver values given a little further along.

When we consider closely, in all of its bearings, any one of the values just given, we shall see that for certain purposes it must be excluded from our general mean. For example, the first is derived partly from the ratio between silver and potassium chloride. From this ratio, the atomic weight of one substance being known, we can deduce that of the other. We have already used it in ascertaining the atomic weight of silver, and the value thus obtained is included in our general mean. But if from it we are to determine the molecular weight of potassium chloride, we must use a silver value derived from other sources only, or we should be assuming a part of our result in advance. In other words, we must now use a general mean for silver from which this ratio with reference to silver has been rejected. Hence the following series of silver values, which are lettered for reference:

A. General mean from all eight_____ 107.675, ± .0096
B. " rejecting the first _____ 107.671, ± .0105
C. " " second _____ 107.671, ± .0097
D. " " third _____ 107.679, ± .0100
E. " " fourth _____ 107.675, ± .0104
F. " " fifth _____ 107.671, ± .0105
G. " " sixth _____ 107.674, ± .0104
H. " " seventh_____ 107.678, ± .0105
I. " " eighth_____ 107.679, ± .0104

These values are essentially the same, both in magnitude and in weight. For all practical purposes any one of them is as good as any other. Still, on theoretical grounds, it may be well to keep them distinct and separate in the remainder of this discussion.

We are now in a position to determine more closely the molecular weights of the haloid salts which we have already been considering.

For silver chloride, still employing the formula for the probable error of the last term of a proportion, we get the following values:

From (5) _____ _____ AgCl = 143.062, ± .032
From (13) and (F) _____   "   = 143.032, ± .014
From (17) and (21) _____   "   = 143.108, ± .034
From (18) and (26) _____   "   = 143.061, ± .041
From (19) and (27) _____   "   = 143.035, ± .033

General mean ____   "   = 143.045, ± .0108

Subtracting from this the atomic weight of silver, 107.675, ± .0096, we get for the atomic weight of chlorine, Cl = 35.370, ± .014.

For silver bromide we have these results:

From (6) _____ AgBr = 187.453, ± .043
From (14) and (G) _____   "   = 187.440, ± .018
From (18) and (25) _____   "   = 187.454, ± .053

General mean _____   "   = 187.443, ± .016

Hence, using the general mean for silver as above, Br = 79.768, ± .019.

Silver iodide comes out as follows:

From (7) _____ _____ AgI = 234.195, ± .053
From (15) and (H) _____   "   = 234.237, ± .023
From (19) and (25) _____   "   = 234.240, ± .054

General mean _____   "   = 234.232, ± .019

Hence I = 126.557, ± .022.

For the molecular weight of sodium chloride we have:

From (4) _____ NaCl = 58.366, ± .0137
From (9) and (E) _____   "   = 58.368, ± .0056

General mean ____   "   = 58.3676, ± .0052

Hence, if chlorine = 35.370, ± .014, then Na = 22.998, ± .011.

For potassium chloride:

From (1)_____KCl = 74.4217, ± .016
From (10) and (B) _____ " = 74.4041, ± .007
From (17) and (25)_____ " = 74.3975, ± .017
_____
General mean_____ " = 74.4057, ± .0062

For potassium bromide we get:

From (2) _____KBr = 119.117, ± .096
From (11) and (C) _____ " = 118.810, ± .0118
_____
General mean_____ " = 118.815, ± .0117

And for potassium iodide:

From (3)_____KI = 165.210, ± .053
From (12) and (D)_____ " = 165.502, ± .029
_____
General mean _____ " = 165.432, ± .026

Now, taking the molecular weights of these three potassium salts in connection with the atomic weights just found for chlorine, bromine, and iodine, we get these values for potassium:

From the chloride _____K = 39.036, ± .016
From the bromide _____ " = 39.047, ± .022
From the iodide_____ " = 38.875, ± .034
_____
General mean _____ " = 39.019, ± .012

Finally, the three sulphur ratios give us three estimates for the atomic weight of sulphur. In the third of these I have applied the "A" value for silver and the general mean for silver chloride:

From (8) and (I)_____S = 31.968, ± .014
From (16) and (I)_____ " = 31.995, ± .032
From (20)_____ " = 32.041, ± .028
_____
General mean_____ " = 31.984, ± .012

We may now appropriately compare the results of this

discussion with the atomic weights deduced by Stas from his own experiments only. His values are given under two headings: one for oxygen = 16, the other for O = 15.96. As we have been using the figure 15.9633 for oxygen, here is at the outset a discrepancy. Starting from this value we found:

$$Ag = 107.675, \pm .0096$$
$$Cl = 35.370, \pm .014$$
$$Br = 79.768, \pm .019$$
$$I = 126.557, \pm .022$$
$$Na = 22.998, \pm .011$$
$$K = 39.019, \pm .012$$
$$S = 31.984, \pm .012$$

If we assume 16 to be the true figure for oxygen, we get the following results, which I have placed in a column parallel with the values found by Stas:

	The New Values.	Stas.	Differences.
Silver	107.923	107.930	.007
Chlorine	35.451	35.457	.006
Bromine	79.951	79.952	.001
Iodine	126.848	126.850	.002
Sodium	23.051	23.043	.009
Potassium	39.109	39.137	.028
Sulphur	32.058	32.074	.016

These differences are insignificant. No other criticism could more severely test the character of Stas' work, or more definitely illustrate his magnificent accuracy of manipulation.

NITROGEN.

The atomic weight of nitrogen has been determined from the density of the gas, from the ratio between ammonium chloride and silver, and from the composition of certain nitrates.

Upon the density of nitrogen a great many experiments have been made. In early times this constant was determined by Biot and Arago, Thomson, Dulong and Berzelius, Lavoisier, and others. But all of these investigations may be disregarded as of insufficient accuracy; and, as in the case of oxygen, we need consider only the results obtained by Dumas and Boussingault, and by Regnault.

Taking air as unity, Dumas and Boussingault* found the density of nitrogen to be—

.970
.972
.974
_____
Mean, .972, ± .00078

For hydrogen, as was seen in our discussion of the atomic weight of oxygen, the same investigators found a mean of .0693, ± .00013. Upon combining this with the above nitrogen mean, we find for the atomic weight of the latter element, N = 14.026, ± .0295.

By Regnault† much closer work was done. He found the density of nitrogen to be as follows:

.97148
.97148
.97154
.97155
.97108
.97108
_____
Mean, .97137, ± .000062

---

* Compt. Rend., 12, 1005. 1841.
† Compt. Rend., 20, 975. 1845.

For hydrogen, Regnault's mean value is .069263, ±
.000019. Hence, combining as before, N = 14.0244, ±
.0039.*

The value found by combining both series of experiments
is N = 14.0244, ± .0039.

In discussing the more purely chemical ratios for estab-
lishing the atomic weight of nitrogen, we may ignore, for
the present, the researches of Berzelius, of Anderson, and of
Svanberg. These chemists experimented chiefly upon lead
nitrate, and their work is consequently now of greater value
for fixing the atomic weight of lead. Their results will be
duly considered in the proper connection further on.

The ratio between ammonium chloride and silver has
been determined by Pelouze, by Marignac, and by Stas.
The method of working is essentially that adopted in the
similar experiments with the chlorides of sodium and potas-
sium.

For the ammonium chloride equivalent to 100 parts of
silver, Pelouze† found :

$$49.556$$
$$49.517$$

Mean, 49.5365, ± .013

Marignac‡ obtained the following results. The usual
ratio for 100 parts of silver is given also :

8.063 grm. Ag =	3.992 grm. NH_4Cl.	49.510
9.402 "	4.656 "	49.521
10.339 "	5.120 "	49.521
12.497 "	6.191 "	49.540
11.337 "	5.617 "	49.546
11.307 "	5.595 "	49.483
4.326 "	2.143 "	49.538

Mean, 49.523, ± .0055

---

* Professor Le Conte, in his corrections of Regnault's calculations, already
cited in a foot note to the chapter on oxygen, finds for the density of nitrogen the
value 0.971346. Hence N = 14.0225. This correction is very slight, but it
should be considered in any future revision of the atomic weights.

† Compt. Rend., 20, 1047.   1845.

‡ Berzelius' Lehrbuch, 5th Ed., 3d v., 1184, 1185.

But neither of these series can for a moment compare with that of Stas.* He used from 12.5 to 80 grammes of silver in each experiment, reduced his weighings to a vacuum standard, and adopted a great variety of precautions to ensure accuracy. He found for every 100 parts of silver the following quantities of NH_4Cl:

$$
\begin{aligned}
&49.600 \\
&49.599 \\
&49.597 \\
&49.598 \\
&49.597 \\
&49.593 \\
&49.597 \\
&49.5974 \\
&49.602 \\
&49.597 \\
&49.598 \\
&49.592
\end{aligned}
$$

Mean, 49.5973, $\pm$ .0005

Now, combining these three series, we get:

Pelouze	49.5365,	$\pm$ .013
Marignac	49.523,	$\pm$ .0055
Stas	49.5973,	$\pm$ .0005
General mean	49.597,	$\pm$ .0005

The quantity of silver nitrate which can be formed from a known weight of metallic silver has been determined by Penny, by Marignac, and by Stas. Penny† dissolved silver in nitric acid in a flask, evaporated to dryness without transfer, and weighed. One hundred parts of silver thus gave of nitrate:

$$
\begin{aligned}
&157.430 \\
&157.437 \\
&157.458 \\
&157.440 \\
&157.430 \\
&157.455
\end{aligned}
$$

Mean, 157.4417, $\pm$ .0033

---

* Aronstein's Translation, pp. 56–58.
† Phil. Trans., 1839.

Marignac's* results were as follows. In the third column they are reduced to the common standard of 100 parts of silver:

68.987 grm. Ag gave	108.608 grm. AgNO$_3$.				157.433
57.844	"	91.047	"		157.401
66.436	"	104.592	"		157.433
70.340	"	110.718	"		157.404
200.000	"	314.894	"		157.447

Mean, 157.4236, ± .0061

Stas,† employing from 77 to 405 grammes of silver in each experiment, made two different series of determinations at two different times. The silver was dissolved with all the usual precautions against loss and against impurity, and the resulting nitrate was weighed, first after long drying without fusion just below its melting point; and again, fused. Between the fused and the unfused salt there was in every case a slight difference in weight, the latter giving a maximum and the former a minimum value.

In Stas' first series there are eight experiments; but the seventh he himself rejects as inexact. The values obtained for the nitrate from 100 parts of silver are given below in two columns, representing the two conditions in which the salt was weighed. The general mean given at the end I have deduced from the means of the two columns considered separately:

Unfused.	*Fused.*
157.492	157.474
157.510	157.481
157.485	157.477
157.476	157.471
157.478	157.470
157.471	157.463
157.488	157.469

Mean, 157.4857   Mean, 157.472

General mean, 157.474, ± .0014

* Berzelius' Lehrbuch, 5th Ed., 3, pp. 1184, 1185.
† Aronstein's Translation, pp. 305 and 315.

In the later series there are but two experiments, as follows:

	Unfused.	*Fused.*
	157.4964	157.488
	157.4940	157.480
Mean,	157.4952	Mean, 157.484

General mean, 157.486, ± .0003

Now, to combine all four sets of results:

Penny _____ 157.4417, ± .0033
Marignac_____ 157.4236, ± .0061
Stas, 1st series_____ 157.4740, ± .0014
Stas, 2d series_____ 157.4860, ± .0003

General mean_____ 157.479, ± .0003

For the direct ratio between silver nitrate and silver chloride there are two series of estimations. A weighed quantity of nitrate is easily converted into chloride, and the weight of the latter ascertained. In two experiments Turner* found of chloride from 100 parts of nitrate:

84.357
84.389

Mean, 84.373, ± .011

Penny,† in five determinations, found the following percentages:

84.370
84.388
84.377
84.367
84.370

Mean, 84.3744, ± .0025

The general mean from both series is 84.3743, ± .0025.

The ratio directly connecting silver nitrate with ammonium chloride has been determined only by Stas.‡ The

---

* Phil. Trans., 1833, 537.
† Phil. Trans., 1839.
‡ Aronstein's Translation, p. 309.

usual method of working was followed; namely, nearly equivalent quantities of the two salts were weighed out, the solutions mixed, and the slight excess of one estimated by titration. In four experiments 100 parts of silver nitrate were found equivalent to chloride of ammonium as follows:

$$31.489$$
$$31.490$$
$$31.487$$
$$31.486$$

Mean, 31.488, $\pm$ .0006

The similar ratio between potassium chloride and silver nitrate has been determined by both Marignac and Stas.

Marignac[*] gives the following weights. I add the quantity of KCl proportional to 100 parts of $AgNO_3$:

1.849 grm. KCl =	4.218 grm. $AgNO_3$.		43.836
2.473 "	5.640 "		43.848
3.317 "	7.565 "		43.847
2.926 "	6.670 "		43.868
6.191 "	14.110 "		43.877
4.351 "	9.918 "		43.870

Mean, 43.858, $\pm$ .0044

Stas'[†] results are given in three series, representing silver nitrate from three different sources. In the third series the nitrate was weighed in vacuo, while for the other series this correction was applied in the usual way. For the KCl equivalent to 100 parts of $AgNO_3$ Stas found:

First Series.

$$43.878$$
$$43.875$$
$$43.875$$
$$43.874$$

Mean, 43.8755, $\pm$ .0005

---

* Berzelius' Lehrbuch, 5th Ed., 3d vol., 1184, 1185.
† Aronstein's Translation, p. 308.

Second Series.

43.864
43.869
43.876
_____
Mean, 43.8697. ± .0023

Third Series.

43.894
43.878
43.885
_____
Mean, 43.8857, ± .0031

Combining all four series we have:

Marignac____ _____ _____ 43.858, ± .0044
Stas, 1st series___ _____ ____ 43.8755, ± .0005
" 2d " _____ 43.8697, ± .0023
" 3d " _____ 43.8857, ± .0031
_____
General mean____ __ _____ 43.8715, ± .0004

There have also been determined by Penny and by Stas a series of ratios connecting the alkaline chlorides and chlorates with the corresponding nitrates. One of these, relating to the lithium salts, will be studied further on with reference to that metal.

The general method of working upon these ratios is due to Penny.* Applied to the ratio between the chloride and nitrate of potassium it is as follows: A weighed quantity of the chloride is introduced into a flask which is placed upon its side and connected with a receiver. An excess of pure nitric acid is added, and the transformation is gradually brought about by the aid of heat. Then, upon evaporating to dryness over a sand bath, the nitrate is brought into weighable form. The liquid in the receiver is also evaporated, and the trace of solid matter which had been mechanically carried over is recovered and also taken into account. In another series of experiments the nitrate was taken, and by pure hydrochloric acid converted into chloride; the process being the same. In the following columns of figures I

_____

* Phil. Trans., 1839.

have reduced both series to one standard; namely, so as to express the number of parts of nitrate corresponding to 100 of chloride :

First Series.— KCl treated with HNO_3.

135.639
135.637
135.640
135.635
135.630
135.640
135.630

Mean, 135.636, $\pm$ .0011

Second Series.— KNO_3 treated with HCl.

135.628
135.635
135.630
135.641
135.630
135.635
135.630

Mean, 153.633, $\pm$ .0011

Stas* results are as follows :

135.643
135.638
135.647
135.649
135.640
135.645
135.655

Mean, 135.6453, $\pm$ .0014

These figures by Stas represent weighings in the air. Reduced to a vacuum standard this mean really becomes 135.6423.

Now, combining, we have :

Penny, 1st series _____ 135.636, $\pm$ .0011
"   2d   "   _____ 135.633, $\pm$ .0011
Stas _____ 135.6423, $\pm$ .0014

General mean _____ 135.6363, $\pm$ .0007

---

* Aronstein's Translation, p. 270.

By the same general process Penny* determined how much potassium nitrate could be formed from 100 parts of chlorate. He found as follows:

82.505
82.497
82.498
82.500

Mean, 82.500, ± .0012

For 100 parts of sodium chlorate he found of nitrate:

79.875
79.882
79.890

Mean, 79.8823, ± .0029

For the ratio between the chloride and nitrate of sodium Penny made two sets of estimations as in the case of potassium salts. The subjoined figures give the amount of nitrate equivalent to 100 parts of chloride:

First Series.—NaCl treated with HNO_3.

145.415
145.408
145.420
145.424
145.410
145.418
145.420

Mean, 145.4164, ± .0015

Second Series.—$NaNO_3$ treated with HCl.

145.419
145.391
145.412
145.415
145.412
145.412

Mean, 145.410, ± .0026

* Phil. Trans., 1839.

Stas* gives the following series:

$$145.453$$
$$145.468$$
$$145.465$$
$$145.469$$
$$145.443$$

Mean, after reducing
to vacuum standard, $145.4526. \pm .0030$

Combining, we have as follows:

Penny, 1st series _____ $145.4164, \pm .0015$
   "   2d   " _____ $145.410, \pm .0026$
Stas _____ $145.4526, \pm .0030$

General mean_____ $145.4185, \pm .0012$

We have now, apart from the determinations of gaseous
density, nine ratios, representing one hundred and fourteen
experiments from which to calculate the atomic weight of
nitrogen. Let us first collect and number these ratios:

(1.) $Ag : AgNO_3 : : 100 : 157.479, \pm .0003$
(2.) $AgNO_3 : AgCl : : 100 : 84.3743, \pm .0025$
(3.) $AgNO_3 : KCl : : 100 : 43.8715, \pm .0004$
(4.) $AgNO_3 : NH_4Cl : : 100 : 31.488, \pm .0006$
(5.) $Ag : NH_4Cl : : 100 : 49.597, \pm .0005$
(6.) $KCl : KNO_3 : : 100 : 135.6363, \pm .0007$
(7.) $KClO_3 : KNO_3 : : 100 : 82.500, \pm .0012$
(8.) $NaCl : NaNO_3 : : 100 : 145.4185, \pm .0012$
(9.) $NaClO_3 : NaNO_3 : : 100 : 79.8823, \pm .0029$

From these ratios we are now able to deduce the molec-
ular weight of ammonium chloride and of the three nitrates
named in them. For these calculations we may use the
already determined atomic weights of silver, oxygen, potas-
sium, sodium, and chlorine, and the molecular weights of
silver chloride and sodium chloride. These two molecular
weights involve, respectively, the most probable values for
silver, sodium, and chlorine. We cannot, however, appro-
priately use the directly determined molecular weight of
potassium chloride, since the most probable value for the

---

* Aronstein's Translation, p. 278.

atomic weight of potassium is only in part derived from that salt. The following are the values which we shall employ:

$$Ag = 107.675, \pm .0096$$
$$K = 39.019, \pm .012$$
$$Na = 22.998, \pm .011$$
$$Cl = 35.370, \pm .014$$
$$O_3 = 47.8899, \pm .0105$$
$$AgCl = 143.045, \pm .0108$$
$$NaCl = 58.3676, \pm .0052$$

Now, from ratio number five we can get the molecular weight of ammonium chloride, $NH_4Cl = 53.4048, \pm .0048$, and $N = 14.0336, \pm .0153$.

From ratio number four an independent value for nitrogen can be calculated, namely, $N = 14.0330, \pm .015$.

For the molecular weight of silver nitrate three values are deducible, namely:

$$\text{From (1)} \quad AgNO_3 = 169.5655, \pm .0151$$
$$\text{From (2)} \quad " = 169.5362, \pm .0138$$
$$\text{From (3)} \quad " = 169.5612, \pm .0429$$

$$\text{General mean} \quad " = 169.5489, \pm .0099$$

Hence $N = 13.9840, \pm .0174$.

The molecular weight of potassium nitrate is twice calculable, as follows:

$$\text{From (6)} \quad KNO_3 = 100.8985, \pm .0255$$
$$\text{From (7)} \quad " = 100.8801, \pm .0178$$

$$\text{General mean} \quad " = 100.8863, \pm .0146$$

And $N = 13.9774, \pm .0216$.

So also for sodium nitrate we have:

$$\text{From (8)} \quad NaNO_3 = 84.8773, \pm .0076$$
$$\text{From (9)} \quad " = 84.8809, \pm .0099$$

$$\text{General mean} \quad " = 84.8785, \pm .0060$$

And $N = 13.9906, \pm .0163$.

We have now before us six estimates of the atomic weight of nitrogen. It only remains for us to combine these after

4

the usual method, as follows, in order to obtain the most probable value:

1. From specific gravity of N _____ N $= 14.0244, \pm .0039$
2. "   ammonium chloride _____ " $= 14.0336, \pm .0153$
3. "   ratio number four _____ " $= 14.0330, \pm .0150$
4. "   silver nitrate _____ " $= 13.9840, \pm .0174$
5. "   potassium nitrate _____ " $= 13.9774, \pm .0216$
6. "   sodium nitrate _____ " $= 13.9906, \pm .0163$

        General mean _____ " $= 14.0210, \pm .0035$

If oxygen is 16, this becomes 14.0291. Stas found N $=$ 14.044. The difference is .015, showing a remarkably close agreement.

CARBON.

Although there is a large mass of material relating to the atomic weight of carbon, much of it may be summarily set aside as having no value for present purposes. The density of carbon dioxide, which has been scrupulously determined by many investigators,[*] leads to no safe estimate of the constant under consideration. The numerous analyses of hydrocarbons, like the analyses of naphthalene by Mitscherlich, Woskresensky, Fownes, and Dumas, give results scarcely more satisfactory. In short, all the work done upon the atomic weight of carbon before the year 1840 may be safely rejected as unsuited to the present requirements of exact science. As for methods of estimation we need consider but three, as follows:

First.—The analysis of organic salts of silver.

Second.—The determination of the weight of carbon dioxide formed by the combustion of a known weight of carbon.

---

* Notably by Lavoisier, Biot and Arago, De Saussure, Dulong and Berzelius, Buff, Von Wrede, Regnault, and Marchand.   For details, Van Geuns' monograph may be consulted.

Third.—The method of Stas, by the combustion of carbon monoxide.

The first of these methods, which is also the least accurate, was employed by Liebig and Redtenbacher* in 1840. They worked with the acetate, tartrate, racemate, and malate of silver, making five ignitions of each salt, and determining the percentage of metal. From one to nine grammes of material were used in each experiment.

In the acetate the following percentages of silver were found:

$$64.615$$
$$64.624$$
$$64.623$$
$$64.614$$
$$64.610$$

Mean, 64.6172, ± .0018

After applying corrections for weighing in air this mean becomes 64.6065.

In the tartrate the silver came out as follows:

$$59.297$$
$$59.299$$
$$59.287$$
$$59.293$$
$$59.293$$

Mean, 59.2938, ± .0014
Or, reduced to a vacuum, 59.2806

In the racemate we have:

$$59.290$$
$$59.292$$
$$59.287$$
$$59.283$$
$$59.284$$

Mean, 59.2872, ± .0012
Or, corrected, 59.2769

---

* Ann. Chem. Pharm., 38, 137.   Mem. Chem. Soc., 1, 9.   Phil. Mag., (3,) 19, 210.

And from the malate:

<div style="text-align:center">

61.996
61.972
62.015
62.059
62.011

</div>

<div style="text-align:center">

Mean, 62.0106, ± .0096
Or, corrected, 62.0016

</div>

Now, applying to these mean results the atomic weights already found for oxygen and silver, we get the following values for carbon :

<div style="text-align:center">

From the acetate _____ C = 12.0306, ± .0047
   "   tartrate _____ " = 12.0356, ± .0064
   "   racemate _____ " = 12.0413, ± .0063
   "   malate_____ " = 12.0408, ± .0054
      General mean_____ " = 12.0363, ± .0028

</div>

Now these results, although remarkably concordant, are by no means unimpeachable. They involve two possible sources of constant error, namely, impurity of material and the volatility of the silver. These objections have both been raised by Stas, who found that the silver tartrate, prepared as Liebig and Redtenbacher prepared it, always carried traces of the nitrate, and that he, by the ignition of that salt, could not get results at all agreeing with theirs. In the case of the acetate a similar impurity would lower the percentage of silver, and thus both sources of error would reinforce each other and make the atomic weight of carbon come out too high. With the three other salts the two sources of error act in opposite directions, although the volatility of the silver is probably far greater in its influence than the impurity. Even if we had no other data relating to the atomic weight of carbon, it would be clear from these facts that the results obtained by Liebig and Redtenbacher must be decidedly in excess of the true figure.

A different method of dealing with organic silver salts was adopted by Maumené,* in 1846, for the purpose of estab-

---

* Ann. d. Chim. et d. Phys., (3,) 18, 41.

lishing, by reference to carbon, the atomic weight of silver. We will simply reverse his results and apply them to the atomic weight of carbon. He effected the combustion of the acetate and the oxalate of silver, and, by weighing both the residual metal and the carbon dioxide formed, he fixed the ratio between these two substances. In the case of the acetate his weighings show that for every gramme of metallic silver the weights of CO_2 were produced, which are shown in the third column:

8.083 grm. Ag =	6.585 grm. CO_2.		.8147
11.215 "	9.135 "		.8136
14.351 "	11.6935 "		.8148
9.030 "	7.358 "		.8148
20.227 "	16.475 "		.8145

Mean, .81448

The oxalate of silver, ignited by itself, decomposes too violently to give good results; and for this reason it was not used by Liebig and Redtenbacher. Maumené, however, found that when the salt was mixed with sand the combustion could be tranquilly effected. The oxalate employed, however, with the exception of the sample represented in the last experiment of the series, contained traces of nitrate, so that these results involve slight errors. For each gramme of silver the appended weights of CO_2 were obtained:

14.299 grm. Ag =	5.835 grm. CO_2.		.4081
17.754 "	7.217 "		.4059
11.550 "	4.703 "		.4072
10.771 "	4.387 "		.4073
8.674 "	3.533 "		.4073
11.4355 "	4.658 "		.4073

Mean, .40718

Now, one of these salts being formed by a bivalent and the other by a univalent acid, we have to reduce both to a common standard. Doing this, we have the following results for the ratio between the atomic weight of silver and the molecular weight of CO_2; if Ag = 1.00,

$$\text{From the acetate, } CO_2 = .40724, \pm .000076$$
$$\text{`` oxalate, `` } = .40718, \pm .000185$$
$$\text{General mean, `` } = .40723, \pm .000071$$

Here the slight error due to the impurity of the oxalate becomes of such trifling weight that it practically vanishes.

From these data, if $Ag = 107.675, \pm .0096$, $CO_2 = 43.8485, \pm .0086$.

Hence $C = 11.9219, \pm .0111$.

As has already been said, the volatility of silver renders all the foregoing results more or less uncertain. Far better figures are furnished by the combustion of carbon directly, as carried out by Dumas and Stas* in 1840 and by Erdmann and Marchand† in 1841. In both investigations weighed quantities of diamond, of natural graphite, and of artificial graphite were burned in oxygen, and the amount of dioxide produced was estimated by the usual methods. The graphite employed was purified with extreme care by treatment with strong nitric acid and by fusion with caustic alkali. I have reduced all the published weighings to a common standard, so as to show in the third column the amount of oxygen which combines with a unit weight (say one gramme) of carbon. Taking Dumas and Stas' results first in order we have from natural graphite:

1.000	grm. C gave	3.671	grm. CO_2.		2.6710
.998	``	3.660	``		2.6673
.994	``	3.645	``		2.6670
1.216	``	4.461	``		2.6686
1.471	``	5.395	``		2.6676

Mean, $2.6683, \pm .0005$

With artificial graphite:

.992	grm. C gave	3.642	grm. CO_2.		2.6714
.998	``	3.662	``		2.6682
1.660	``	6.085	``		2.6654
1.465	``	5.365	``		2.6744

Mean, $2.66985, \pm .0013$

---

* Compt. Rend., 11, 991–1008. Ann. Chim. Phys., (3,) 1, 1.
† Journ. f. Prakt. Chem., 23, 159.

And with diamond:

.708 grm. C gave	2.598 grm. CO_2.		2.6695
.864 "	3.1675 "		2.6661
1.219 "	4.465 "		2.6628
1.232 "	4.519 "		2.6680
1.375 "	5.041 "		2.6662

Mean, 2.6665, $\pm$ .0007

Erdmann and Marchand's figures for natural graphite give the following results:

1.5376 grm. gave	5.6367 grm. CO_2.	2.6659
1.6494 "	6.0384 "	2.6609
1.4505 "	5.31575 "	2.6647

In one experiment 1.8935 grm. of artificial graphite gave 6.9355 grm. CO_2. Ratio for O, 2.6628. This, combined with the foregoing series, gives a mean of 2.6636, $\pm$ .0007.

With diamond they found:

.8052 grm. gave	2.9467 grm. CO_2.	2.6596
1.0858 "	3.9875 "	2.6632
1.3557 "	4.9659 "	2.6629
1.6305 "	5.97945 "	2.6673
.7500 "	2.7490 "	2.6653

Mean, 2.6637. $\pm$ .0009

Now, combining all these series, we get the following result:

Dumas and Stas, 1st set	2.6683,	$\pm$ .0005
" 2d "	2.66985,	$\pm$ .0013
" 3d "	2.6665,	$\pm$ .0007
Erdmann and Marchand, 1st	2.6636,	$\pm$ .0007
" 2d	2.6637,	$\pm$ .0009
General mean	2.66655,	$\pm$ .0003

Hence, if O = 15.9633, $\pm$ .0035, C = 11.973, $\pm$ .0030.

Another very exact method for determining the atomic weight of carbon was employed by Stas[*] in 1849. Carefully purified carbon monoxide was passed over a known weight

---

[*] Bull. Acad. Bruxelles, 1849. (1,) 31.

of copper oxide at a red heat, and both the residual metal and the carbon dioxide formed were weighed. The weighings were reduced to a vacuum standard, and in each experiment a quantity of copper oxide was taken representing from eight to twenty-four grammes of oxygen. The method, as will at once be seen, is in all essential features similar to that usually employed for determining the composition of water. The figures in the third column, deduced from the weights given by Stas, represent the quantity of carbon monoxide corresponding to one gramme of oxygen :

9.265 grm. O $=$	25.483 CO_2.	1.75046
8.327	" 22.900 "	1.75010
13.9438	" 38.351 "	1.75040
11.6124	" 31.935 "	1.75008
18.763	" 51.6055 "	1.75039
19.581	" 53.8465 "	1.74994
22.515	" 61.926 "	1.75043
24.360	" 67.003 "	1.75053

Mean, 1.75029, $\pm$ .00005

Hence the molecular weight of carbon monoxide is 27.9404, $\pm$ .0062. And C $=$ 11.9771, $\pm$ .0071.

Now, in order to complete our discussion, we must combine the four values we have found for carbon :

1. By Liebig and Redtenbacher__C $=$ 12.0363, $\pm$ .0028
2. By Maumené's figures _____ " $=$ 11.9219, $\pm$ .0111
3. By combustion of carbon_____ " $=$ 11.9730, $\pm$ .0030
4. By Stas' method _____ " $=$ 11.9771, $\pm$ .0071

General mean_____ " $=$ 12.0021, $\pm$ .0019

But values one and two are hardly reliable enough to be included in our final estimate. They involve dangerous constant errors, and ought, therefore, to be disregarded. Rejecting them altogether, and taking a general mean from values three and four, we get for the most probable figure for the atomic weight of carbon, C $=$ 11.9736, $\pm$ .0028. If oxygen is 16, then carbon becomes 12.0011. In other words, the ratio between oxygen and carbon is almost exactly 16 to 12.

BARIUM.

For determining the atomic weight of barium we have a series of six ratios, established by the labors of Berzelius, Turner, Struve, Pelouze, Marignac, and Dumas. Andrews* and Salvetat,† in their papers upon this subject, gave no details nor weighings; and, therefore, their work may be properly disregarded. First in order in point of importance, if not first chronologically, is the ratio between silver and anhydrous barium chloride, as determined by Pelouze, Marignac, and Dumas.

Pelouze,‡ in 1845, made the three subjoined estimations of this ratio, using his well known volumetric method. A quantity of pure silver was dissolved in nitric acid, and the amount of barium chloride needed to precipitate it was accurately ascertained. In the last column I give the quantity of barium chloride proportional to 100 parts of silver:

3.860 grm. BaCl$_2$ ppt.	4.002 grm. Ag.		96.452
5.790 "	6.003 "		96.452
2.895 "	3.001 "		96.468

Mean, 96.4573, $\pm$ .0036

Essentially the same method was adopted by Marignac‖ in 1848. His experiments were made upon four samples of barium chloride, as follows. A, commercial barium chloride, purified by recrystallization from water. B, the same salt, calcined, redissolved in water, the solution saturated with carbonic acid, filtered, and allowed to crystallize. C, the preceding salt, washed with alcohol, and again recrystallized. D, the same, again washed with alcohol. For 100 parts of silver the following quantities of chloride were required:

---

* Chemical Gazette, October, 1852.
† Compt. Rend., 17, 318.
‡ Compt. Rend., 20, 1047. Journ. für Prakt. Chem., 35, 73.
‖ Arch. d. Sci. Phys. et Nat., 8, 271.

A.

96.356
96.345
96.362

Mean, 96.3543, ± .0033

B.

96.356
96.452

Mean, 96.354. ± .0013

C.

96.358
96.363

Mean, 96.3605, ± .0017

D.

96.346
96.384
96.361
96.377

Mean, 96.367, ± .0057

Dumas* employed barium chloride prepared from pure barium nitrate, and took the extra precaution of fusing the salt at a red heat in a current of dry hydrochloric acid gas. Three series of experiments upon three samples of chloride gave the following results:

Series A.

1.7585 grm. BaCl$_2$ =	1.826 grm. Ag.	Ratio, 96.303
3.842 "	3.988 "	96.339
2.1585 "	2.2405 "	96.340
4.0162 "	4.168 "	96.358

Mean, 96.3325. ± .0068

Series B.

1.6625 grm. $BaCl_2$ =	1.727 grm. Ag.		Ratio,	96.265
2.4987	"	2.5946	"	96.304
3.4468	"	3.579	"	96.306
4.0822	"	4.2395	"	96.290
4.2062	"	4.3683	"	96.289
4.4564	"	4.629	"	96.271
8.6975	"	9.031	"	96.307

Mean, 96.2902, ± .0043

Series C.

2.2957 grm. $BaCl_2$ =	2.3835 grm. Ag.		Ratio,	96.316
4.1372	"	4.293	"	96.371
4.2662	"	4.430	"	96.303
4.4764	"	4.647	"	96.329
5.6397	"	5.852	"	96.372

Mean, 96.3382, ± .0096

We have now eight series of experiments upon this ratio, representing thirty distinct estimations. Combining, we get a general mean as follows:

Pelouze	96.4573, ± .0036
Marignac, A	96.3543, ± .0033
" B	96.3540, ± .0013
" C	96.3605, ± .0017
" D	96.3670, ± .0057
Dumas, A	96.3325, ± .0068
" B	96.2902, ± .0043
" C	96.3382, ± .0096
General mean	96.3596, ± .0009

The ratio between silver and crystallized barium chloride has also been fixed by Marignac.* The usual method was employed, and two series of experiments were made; in the second of which the water of crystallization was determined previous to the estimation. Five grammes of chloride were taken in each determination. The following quantities of $BaCl_2.2H_2O$ correspond to 100 parts of silver:

---

* Journ. f. Prakt. Chem., 74, 212. 1858.

A.	B.
113.109	113.135
113.135	113.122
113.097	113.060

Mean, 113.114, ± .0074   Mean, 113.106, ± .0154

The general mean from both series is 113.113, ± .0067.

The direct ratio between the chlorides of silver and barium was early established both by Berzelius* and Turner.† Berzelius found that 100 parts of dry barium chloride gave of silver chloride:

138.06
138.08

Mean, 138.07, ± .007

Turner made five experiments, with the following results:

137.45
137.54
137.70
137.62
137.64

Of these, Turner regards the fourth and fifth as the most exact. These give a mean of 137.63, ± .007, while the other three are in mean 137.563, ± .049. Combining Berzelius' figures with those of Turner, we get as follows:

Berzelius_____ 138.07, ± .007
Turner, 1, 2, 3_____ 137.563, ± .049
    "   4, 5_____ 137.63, ± .007

General mean_____ 137.841, ± .0047

Incidentally to some of his other work Marignac‡ determined the percentage of water in crystallized barium chloride. Two sets of three experiments each were made, the first upon five grammes and the second upon ten grammes of salt. The following are the percentages obtained:

* Poggend. Annal., 8, 177.
† Phil. Trans., 1829, 291.
‡ Journ. f. Prakt. Chem., 74, 212.   1858.

A.	B.
14.790	14.80
14.796	14.81
14.800	14.80

Mean, 14.795, ± .0019   Mean, 14.803, ± .002

General mean of both series, 14.799, ± .0014

The ratio between barium nitrate and barium sulphate has been determined only by Turner.* According to his experiments 100 parts of sulphate correspond to the following quantities of nitrate:

112.060
111.990
112.035

Mean, 112.028, ± .014

For the similar ratio between the sulphate and the chloride there are experiments by Turner, Berzelius, Struve, and Marignac. Turner† found that 100 parts of chloride ignited with sulphuric acid gave 112.19 parts of sulphate. By the common method of precipitation and filtration a lower figure was obtained, because of the slight solubility of the sulphate. This point bears directly upon many other atomic weight determinations.

Berzelius,‡ treating barium chloride with sulphuric acid, obtained the following results in $BaSO_4$ for 100 parts of $BaCl_2$:

112.17
112.18

Mean, 112.175, ± .0034

Struve,‖ in two experiments, found:

112.0912
112.0964

Mean, 112.0938, ± .0018

* Phil. Trans., 1833, 538.
† Phil. Trans., 1829, 291.
‡ Poggend. Annal., 8, 177.
‖ Ann. Chem. Pharm., 80, 204. 1851.

Marignac's[*] three results are as follows:

8.520 grm. $BaCl_2$ gave 9.543 $BaSO_4$.   Ratio, 112.007
8.519   "   9.544   "   112.032
8.520   "   9.542   "   111.995

Mean, 112.011, $\pm$ .0071

Rejecting Turner's single result as unimportant, we may combine the other series:

Berzelius _____ _____ 112.175, $\pm$ .0034
Struve _____ ____ 112.0938, $\pm$ .0018
Marignac _____. _____ 112.011, $\pm$ .0071

General mean _____ 112.106, $\pm$ .0015

The data from which we are to calculate the atomic weight of barium may now be tabulated as follows:

(1.) $Ag_2 : BaCl_2 :: 100 : 96.3596, \pm .0009$
(2.) $Ag_2 : BaCl_2.2H_2O :: 100 : 113.113, \pm .0067$
(3.) $BaCl_2 : 2AgCl :: 100 : 137.841, \pm .0047$
(4.) Per cent. of H_2O in $BaCl_2.2H_2O$, 14.799, $\pm .0014$
(5.) $BaSO_4 : BaN_2O_6 :: 112.028, \pm .014$
(6.) $BaCl_2 : BaSO_4 :: 100 : 112.106, \pm .0015$

From these ratios, with the aid of the atomic weights already established, we can immediately calculate four independent values for the molecular weight of $BaCl_2$:

From (1) _____ $BaCl_2 = 207.510, \pm .019$
From (2) _____ " $= 207.662, \pm .027$
From (3) _____ " $= 207.536, \pm .017$
From (4) _____ " $= 206.837, \pm .045$

General mean____ " $= 207.505, \pm .011$

We have here an interesting example of the compensation of constant errors. Ratios (2) and (4) both represent work done by Marignac upon barium chloride containing water of crystallization. If now, as is not improbable, the salt contained a trifling excess of water, the molecular weight of barium chloride as calculated from (2) would come out too high, while on the other hand the result from ratio (4) would err in the opposite direction. In point of fact, the

---

[*] Journ. f. Prakt. Chem., 74, 212. 1858.

two results in the present calculation nearly compensate each other, and, on account of their relatively high probable errors, they exert but an unimportant influence upon the general mean.

In conclusion, we have three independent values for the atomic weight of barium :

From mol. wt. of $BaCl_2$ ____ Ba $= 136.765, \pm .031$
From ratio (5) _____ " $= 136.795, \pm .364$
From ratio (6) _____ " $= 136.595, \pm .309$

General mean _____ " $= 136.763, \pm .031$

If $O = 16$, then $Ba = 137.007$. In other words, the ratio between oxygen and barium is almost an exact ratio between two whole numbers.

In the above discussion it will at once be noticed that the second and third values for Ba have very high probable errors, and that they therefore exert almost no influence upon the general mean. This fact by no means renders them worthless however, for, at the lowest estimate, they are useful in confirmation of the better determinations. It is also highly probable that the method of discussion, rigidly carried out, does not do them absolute justice.

STRONTIUM.

The ratios which fix the atomic weight of strontium resemble in general terms those relating to barium, only they are fewer in number and represent a comparatively small amount of work. The early experiments of Stromeyer,[*] who measured the volume of CO_2 evolved from a known weight of strontium carbonate, are hardly available for the present discussion. So also we may exclude the determination by Salvétat,[†] who neglected to publish sufficient details.

Taking the ratio between strontium chloride and silver first in order, we have series of figures by Pelouze and by Dumas. Pelouze[‡] employed the volumetric method already described under barium, and in two experiments obtained the subjoined results. In another column I append the ratio between $SrCl_2$ and 100 parts of silver:

1.480 grm. $SrCl_2$ =	2.014 grm. Ag.		73.486
2.210 "	3.008 "		73.471

Mean, 73.4781, $\pm$ .0050

Dumas,[||] by the same general method, made sets of experiments with three samples of chloride which had previously been fused in a current of dry hydrochloric acid. His results, expressed in the usual way, are as follows:

Series A.

3.137 grm. $SrCl_2$ =	4.280 grm. Ag.	Ratio,	73.2944
1.982 "	2.705 "		73.2717
3.041 "	4.142 "		73.4186
3.099 "	4.219 "		73.4534

Mean, 73.3595, $\pm$ .0303

---

[*] Schweigg. Journ., 19, 228. 1816.
[†] Compt. Rend., 17, 318. 1843.
[‡] Compt. Rend., 29, 1047. 1845.
[||] Ann. Chim. Phys., (3.) 55, 29. 1859.   Ann. Chem. Pharm., 113, 34.

Series B.

3.356 grm. $SrCl_2$ =	4.574 grm. Ag.	Ratio, 73.3713
6.3645 "	8.667 "	73.4327
7.131 "	9.712 "	73.4246

Mean, 73.4095, $\pm$ .0130

Series C.

7.213 grm. $SrCl_2$ =	9.811 grm. Ag.	Ratio, 73.5195
2.206 "	3.006 "	73.3866
4.268 "	5.816 "	73.5529
4.018 "	5.477 "	73.3613

Mean, 73.4551, $\pm$ .0321

Combining, we have:

Pelouze _____ 73.4781, $\pm$ .0050
Dumas, A_____ 73.3595, $\pm$ .0303
   "   B_____ 73.4095, $\pm$ .0130
   "   C _____ 73.4551, $\pm$ .0321
   General mean_____ 73.4655, $\pm$ .0046

The foregoing figures apply to anhydrous strontium chloride. The ratio between silver and the crystallized salt, $SrCl_2.6H_2O$, has also been determined in two series of experiments by Marignac.* Five grammes of salt were used in each estimation, and, in the second series, the percentage of water was first determined. The quantities of the salt corresponding to 100 parts of silver are given in the last column:

Series A.

5 grm. $SrCl_2.6H_2O$ =	4.0515 grm. Ag.	123.411
" "	4.0495 "	123.472
" "	4.0505 "	123.442

Mean, 123.442, $\pm$ .012

Series B.

5 grm. $SrCl_2.6H_2O$ =	4.0490 grm. Ag.	123.487
" "	4.0500 "	123.457
" "	4.0490 "	123.487

Mean, 123.477, $\pm$ .007

General mean of both series, 123.470, $\pm$ .006

---

* Journ. Prakt. Chem., 74, 216. 1858.

5

In the same paper Marignac gives two sets of determinations of the percentage of water in crystallized strontium chloride. The first set, corresponding to " B " above, comes out thus:

$$40.556$$
$$40.568$$
$$40.566$$

Mean, 40.563, $\pm$ .0024

In the second set ten grammes of salt were taken at a time, and the following percentages were found:

$$40.58$$
$$40.59$$
$$40.58$$

Mean, 40.583, $\pm$ .0020

General mean, from both series, 40.575, $\pm$ .0015

The chloride used in the series of estimations last given was subsequently employed for ascertaining the ratio between it and the sulphate. Converted directly into sulphate, 100 parts of chloride yield the quantities given in the third column:

5.942 grm. $SrCl_2$ gave 6.887 grm. $SrSO_4$.	115.932
5.941 ``     6.8855    ``	115.949
5.942 ``     6.884    ``	115.927

Mean, 115.936, $\pm$ .004

Now, to sum up the ratios and calculate the atomic weight of strontium.

(1.) $Ag : SrCl_2 :: 100 : 73.4655, \pm .0046$
(2.) $Ag : SrCl_2.6H_2O :: 100 : 123.470, \pm .006$
(3.) Per cent. of H_2O in $SrCl_2.6H_2O, 40.575, \pm .0015$
(4.) $SrCl_2 : SrSO_4 :: 100 : 115.936, \pm .004$

We now have the molecular weight of $SrCl_2$, as follows:

From (1)_____$SrCl_2$ = 158.208, $\pm$ .017
From (2)_____ `` = 158.113, $\pm$ .034
From (3)_____ `` = 157.852, $\pm$ .032

General mean_____ `` = 158.124, $\pm$ .014

And for the atomic weight of strontium itself we have two values, as follows:

1. From mol. wt. of $SrCl_2$____Sr $= 87.384$, $\pm$ .032
2. From (4)_____ " $= 86.765$, $\pm$ .244

General mean___ _____ " $= 87.374$, $\pm$ .032

If $O = 16$, then $Sr = 87.575$.

CALCIUM.

For determining the atomic weight of calcium we have sets of experiments by Berzelius, Erdmann and Marchand, and Dumas. Salvétat[*] also has published an estimation, but without the details necessary to enable us to make use of his results. I also find a reference[†] to some work of Marignac; which, however, seems to have been of but little importance. The earlier work of Berzelius was very inexact as regards calcium, and it is not until we come down to the year 1842 that we find any material of decided value.

The most important factor in our present discussion is the composition of calcium carbonate, as worked out by Dumas and by Erdmann and Marchand.

In 1842 Dumas[‡] made three ignitions of Iceland spar, and determined the percentages of carbon dioxide driven off and of lime remaining. The impurities of the material were also determined, the correction for them applied, and the weighings reduced to a vacuum standard. The percentage of lime came out as follows:

56.12
56.04 .
56.06

Mean, 56.073, $\pm$ .016

[*] Compt. Rend., 17, 318. 1843.
[†] See Oudeman's monograph, p. 51.
[‡] Compt. Rend., 14, 537. 1842.

About this same time Erdmann and Marchand* began their researches upon the same subject. Two ignitions of spar, containing .04 per cent. of impurity, gave respectively 56.09 and 56.18 per cent. of residue; but these results are not exact enough for us to consider further. Four other results obtained with artificial calcium carbonate are more noteworthy. The carbonate was precipitated from a solution of pure calcium chloride by ammonium carbonate, was washed thoroughly with hot water, and dried at a temperature of 180°. With this preparation the following residues of lime were obtained:

<div align="center">

56.03
55.98
56.00
55.99
_____

Mean, 56.00, ± .007

</div>

It was subsequently shown by Berzelius that calcium carbonate prepared by this method retains traces of water even at 200°, and that minute quantities of chloride are also held by it. These sources of error are, however, in opposite directions, since one would tend to diminish and the other to increase the weight of residue.

In the same paper there are also two direct estimations of carbonic acid in pure Iceland spar, which correspond to the following percentages of lime:

<div align="center">

56.00
56.02
_____

Mean, 56.01, ± .007

</div>

In a still later paper† the same investigators give another series of results based upon the ignition of Iceland spar. The impurities were carefully estimated, and the percentages of lime are suitably corrected:

---

* Journ. für Prakt. Chem., 26, 472.   1842.
† Journ. für Prakt. Chem., 31, 269.   1844.

4.2134 grm. CaCO₃ gave	2.3594 grm. CaO.		55.997 per cent.	
15.1385 "	8.4810	"	56.022	"
23.5503 "	13.1958	"	56.031	"
23.6390 "	13.2456	"	56.032	"
42.0295 "	23.5533	"	56.044	"
49.7007 "	27.8536	"	56.042	"

Mean, 56.028, ± .0047

Six years later Erdmann and Marchand[*] published one more result upon the ignition of calcium carbonate. They found that the compound began giving off carbon dioxide below the temperature at which their previous samples had been dried, or about 200°, and that, on the other hand, traces of the dioxide were retained by the lime after ignition. These two errors do not compensate each other, since both tend to raise the percentage of lime. In the one experiment now under consideration these errors were accurately estimated, and the needful corrections were applied to the final result. The percentage of residual lime in this case came out 55.998. This agrees tolerably well with the figures found in the direct estimation of carbonic acid, and, if combined with those two, gives a mean for all three of 56.006, ± .0043.

Combining all these series we get the following result:

Dumas		56.073,	± .016
Erdmann and Marchand		56.006,	± .007
"	"	56.028,	± .0047
"	"	56.006,	± .0043
General mean		56.0198,	± .0029

For reasons given above this mean is probably vitiated by a slight constant error, which makes the figure a trifle too high.

In the earliest of three papers by Erdmann and Marchand there is also given a series of determinations of the ratio between calcium carbonate and sulphate. Pure Iceland

---

[*] Journ. für Prakt. Chem., 50, 237. 1850.

spar was carefully converted into calcium sulphate, and the gain in weight noted. One hundred parts of spar gave of sulphate:

$$136.07$$
$$136.06$$
$$136.02$$
$$136.06$$

Mean, $136.0525, \pm .0071$

In 1843 the atomic weight of calcium was redetermined by Berzelius,* who investigated the ratio between lime and calcium sulphate. The calcium was first precipitated from a pure solution of nitrate by means of ammonium carbonate, and the thoroughly washed precipitate was dried and strongly ignited in order to obtain lime wholly free from extraneous matter. This lime was then, with suitable precautions, treated with sulphuric acid, and the resulting sulphate was weighed. Correction was applied for the trace of solid impurity contained in the acid, but not for the weighing in air. The figures in the last column represent the percentage of weight gained by the lime upon conversion into sulphate:

1.80425 grm. CaO gained	2.56735 grm.	142.295	
2.50400 "	3.57050 "	142.592	
3.90000 "	5.55140 "	142.343	
3.04250 "	4.32650 "	142.202	
3.45900 "	4.93140 "	142.567	

Mean, $142.3998, \pm .0518$

Last of all we have the ratio between calcium chloride and silver, as determined by Dumas.† Pure calcium chloride was first ignited in a stream of dry hydrochloric acid, and the solution of this salt was afterwards titrated with a silver solution in the usual way. The $CaCl_2$ proportional to 100 parts of Ag is given in a third column:

* Journ. für Prakt. Chem., 31, 263. Ann. Chem. Pharm., 46, 241.
† Ann. Chim. Phys., (3,) 55, 129. 1859. Ann. Chem. Pharm., 113, 34.

2.738 grm. CaCl$_2$ =	5.309 grm. Ag.		51.573
2.436 "	4.731 "		51.490
1.859 "	3.617 "		51.396
2.771 "	5.3885 "		51.424
2.240 "	4.3585 "		51.394

Mean, 51.4554, ± .0230

We have now four ratios to calculate from, as follows:

(1.) Per cent. of CaO in CaCO$_3$, 56.0198, ± .0029
(2.) CaO : SO$_3$: : 100 : 142.3998, ± .0518
(3.) CaCO$_3$: CaSO$_4$: : 100 : 136.0525, ± .0071
(4.) Ag : CaCl$_2$: : 100 : 51.4554, ± .0230

These give us the subjoined values for calcium:

From (1)------------------Ca = 39.955, ± .011
From (2)------------------ " = 40.139, ± .023
From (3)------------------ " = 39.925, ± .068
From (4)------------------ " = 40.069, ± .058

General mean-------- " = 39.990, ± .010

If O = 16, then Ca = 40.082.

A glance at the above figures will show that, if, as is probable, the value deduced from the composition of calcium carbonate is a trifle too high, the general mean must be too high also. It is, therefore, interesting to see what result the very latest of Erdmann and Marchand's experiments will lead to. They found, after taking every precaution, in a single experiment that calcium carbonate yielded 55.998 per cent. of lime. From this we get Ca = 39.905; or, if O = 16, Ca = 39.997. It is possible, then, that "Prout's law" may hold good for calcium.

LEAD.

For the atomic weight of lead we have to consider experiments made upon the oxide, chloride, nitrate, and sulphate. The researches of Berzelius upon the carbonate and various organic salts need not now be considered, nor is it worth while to take into account any work of his done before the year 1818. The results obtained by Döbereiner* and by Longchamp† are also without special present value.

For the exact composition of lead oxide we have to depend upon the researches of Berzelius. His experiments were made at different times through quite a number of years; but were finally summed up in the last edition of his famous "Lehrbuch."‡ In general terms his method of experiment was very simple. Perfectly pure lead oxide was heated in a current of hydrogen, and the reduced metal weighed. From his weighings I have calculated the percentages of lead thus found and given them in a third column:

Earlier Results.

8.045 grm. PbO gave 7.4675 grm. Pb.			92.8217 per cent.	
14.183	"	13.165	"	92.8224	"
10.8645	"	10.084	"	92.8160	"
13.1465	"	12.2045	"	92.8346	"
21.9425	"	20.3695	"	92.8313	"
11.159	"	10.359	"	92.8309	"

Latest.

6.6155	"	6.141	"	92.8275	"
14.487	"	13.448	"	92.8280	"
14.626	"	13.5775	"	92.8313	"

Mean, 92.8271, $\pm$ .0013

For the synthesis of lead sulphate we have data by Berzelius, Turner, and Stas. Berzelius,‖ whose experiments

---

* Schweig. Journ., 17, 241. 1816.
† Ann. Chim. Phys., 34, 105. 1827.
‡ Bd. 3, s. 1218.
‖ Lehrbuch, 5th Ed., 3, 1187.

were intended rather to fix the atomic weight of sulphur,
dissolved in each estimation ten grammes of pure lead in
nitric acid, then treated the resulting nitrate with sulphuric
acid, brought the sulphate thus formed to dryness, and
weighed.   One hundred parts of metal yield of $PbSO_4$:

$$146.380$$
$$146.400$$
$$146.440$$
$$146.458$$

Mean, 146.419, $\pm$ .012

Turner,[*] in three similar experiments, found as follows:

$$146.430$$
$$146.398$$
$$146.375$$

Mean, 146.401, $\pm$ .011

In these results of Turner's *absolute* weights are implied.

The results of Stas' syntheses,[†] effected after the same
general method, but with variations in details, are as follows.
Corrections for weighing in air were applied:

$$146.443$$
$$146.427$$
$$146.419$$
$$146.432$$
$$146.421$$
$$146.423$$

Mean, 146.4275, $\pm$ .0024

Combining, we get the subjoined result:

Berzelius	146.419,	$\pm$ .012
Turner	146.401,	$\pm$ .011
Stas	146.4275,	$\pm$ .0024
General mean	146.4262,	$\pm$ .0023

Turner, in the same paper, also gives a series of syntheses
of lead sulphate, in which he starts from the oxide instead

---

* Phil. Trans., 1833, 527–538.
† Aronstein's Translation, 333.

of from the metal. One hundred parts of PbO, upon conversion into $PbSO_4$, gained weight as follows:

$$35.84$$
$$35.71$$
$$35.84$$
$$35.75$$
$$35.79$$
$$35.78$$
$$35.92$$

Mean, 35.804, ± .018

These figures are not wholly reliable. Numbers one, two, and three represent lead oxide contaminated with traces of nitrate. The oxide of four, five, and six contained traces of minium. Number seven was free from these sources of error, and, therefore, deserves more consideration. The series as a whole undoubtedly gives too low a figure; and this error would tend to slightly raise the atomic weight of lead.

Still a third series by Turner establishes the ratio between the nitrate and the sulphate; a known weight of the former being in each experiment converted into the latter. One hundred parts of sulphate represent of nitrate:

$$109.312$$
$$109.310$$
$$109.300$$

Mean, 109.307, ± .002

In all these experiments by Turner the necessary corrections were made for weighing in air.

For the ratio between lead chloride and silver we have a series of results by Marignac and one experiment by Dumas. There are also unavailable data by Turner and by Berzelius.

Marignac,* applying the method used in his researches upon barium and strontium, and working with lead chloride which had been dried at 200°, obtained these results.

---

* Journ. für Prakt. Chem., 74, 218. 1858.

The third column gives the ratio between $PbCl_2$ and 100 parts of Ag :

4.9975 grm. $PbCl_2$ =	3.8810 grm. Ag.	128.768
4.9980 "	3.8835 "	128.698
5.0000 "	3.8835 "	128.750
5.0000 "	3.8860 "	128.667

Mean, 128.721, $\pm$ .016

Dumas,* in his investigations, found that lead chloride retains traces of water even at 250°, and is sometimes also contaminated with oxychloride. In one estimation 8.700 grammes $PbCl_2$ saturated 6.750 of Ag. The chloride contained .009 of impurity ; hence, correcting, Ag : $PbCl_2$: : 100 : 128.750. If we assign this figure equal weight with those of Marignac, we get as the mean of all, 128.7266, $\pm$ .013. The sources of error indicated by Dumas, if they are really involved in this mean, would tend slightly to raise the atomic weight of lead.

The synthesis of lead nitrate, as carried out by Stas,† gives excellent results. Two series of experiments were made, with from 103 to 250 grammes of lead in each determination. The metal was dissolved in nitric acid, the solution evaporated to dryness with extreme care, and the nitrate weighed. All weighings were reduced to the vacuum standard. In series A the lead nitrate was dried in an air current at a temperature of about 155°. In series B the drying was effected in vacuo. 100 of lead yield of nitrate :

A.

159.973
159.975
159.982
159.975
159.968
159.973

Mean, 159.9743, $\pm$ .0012

* Ann. Chem. Pharm., 113, 35. 1860.
† Aronstein's Translation, 326.

B.

159.970
159.964
159.959
159.965

Mean, 159.9645, ± .0015

Mean from both series, 159.9704, ± .0010

There still remain to be noticed two sets of experiments upon lead nitrate, which were originally intended to establish the atomic weight of nitrogen. Lead nitrate was carefully ignited and the residual oxide weighed. The first series, bearing Svanberg's name,* gives simply the percentage of oxide found, as follows:

67.4030
67.4036
67.4043
67.3956

Mean, 67.4016, ± .0014

The second series is by Anderson,† and gives the weighings upon which the percentages rest. The latter come out thus:

5.19485 grm.	PbN_2O_6 gave	3.5017 grm.	PbO.	67.4071 per cent.
9.7244	"	6.5546	"	67.4037 "
9.2181	"	6.2134	"	67.4044 "
9.6530	"	6.5057	"	67.3957 "

Mean, 67.4027, ± .0016

It will at once be seen that these series are identical; the discordance between the first figures of the two being undoubtedly due to some misprint in the weighings of the Anderson set. How it happens that the same work has been published by two separate authors I will not attempt to explain; neither will I undertake to determine which of the two is really entitled to credit.

* Journ. für Prakt. Chem., 27, 381. 1842.
† Ann. Chim. Phys., (3,) 9, 254. 1843.

We have now seven ratios upon which to base our computations:

(1.) Per cent. of Pb in PbO, 92.8271, $\pm$ .0013
(2.) Per cent. of PbO in PbN_2O_6, 67.4016, $\pm$ .0014
(3.) Pb : $PbSO_4$ :: 100 : 146.4262, $\pm$ .0023
(4.) PbO : $PbSO_4$ :: 100 : 135.804, $\pm$ .018
(5.) $PbSO_4$: PbN_2O_6 :: 100 : 109.307, $\pm$ .002
(6.) Pb : PbN_2O_6 :: 100 : 159.9704, $\pm$ .0010
(7.) Ag : $PbCl_2$ :: 100 : 128.7266, $\pm$ .013

Discussing these separately, we get an equal number of values for the atomic weight of lead:

From (1)_____ _____Pb — 206.587, $\pm$ .059
"   (2)_____ _____ " = 207.046, $\pm$ .041
"   (3)_____ _____ _____ " = 206.435, $\pm$ .041
"   (4)_ __ _____ " = 207.131, $\pm$ .118
"   (5)_____ _____ " = 204.803, $\pm$ .329
"   (6)_____ _____ " = 206.454, $\pm$ .037
"   (7)_____ _____ " = 206.473, $\pm$ .042

General mean_____ " = 206.604, $\pm$ .019

If $O = 16$, this becomes $Pb = 207.079$.

In the above discussion are included several values which diverge widely from this general mean, and which, for other reasons, are probably erroneous. Although but one of these carries much weight, it is as well to exclude them, and to base our computations upon the others. If, now, we reject the second, fourth, and fifth values, we get for the atomic weight of lead, $Pb = 206.471$, $\pm$ .021. If $O = 16$, this becomes $Pb = 206.946$.

From the synthesis of the nitrate Stas found 206.918, and from the sulphate, 206.934. The agreement of these values with our own general mean is certainly very close.

FLUORINE.

The atomic weight of fluorine has been determined only by one general method, namely, by the conversion of fluorides into sulphates. Excluding the early results of Davy,[*] we have only to consider the experiments of Berzelius, Louyet, Dumas, and DeLuca, with reference to the fluorides of calcium, sodium, potassium, barium, and lead.

The ratio between calcium fluoride and sulphate has been determined by the four investigators above named, and by one general process. The fluoride is treated with strong sulphuric acid, the resulting sulphate is ignited, and the product weighed. In order to ensure complete transformation special precautions are necessary; such, for instance, as repeated treatment with sulphuric acid, and so on. For details like these the original papers must be consulted.

The first experiments in chronological order are those of Berzelius,[†] who operated upon an artificial calcium fluoride. He found, in three experiments, for one part of fluoride the following of sulphate:

$$1.749$$
$$1.750$$
$$1.751$$

Mean, 1.750, ± .0004

Louyet's researches[‡] were much more elaborate than the foregoing. He began with a remarkably concordant series of results upon fluor spar, in which one gramme of the fluoride yielded from 1.734 to 1.737 of sulphate. At first he regarded these as accurate, but he soon found that particles of spar had been coated with sulphate, and had therefore escaped action. In the following series this source of error was guarded against.

---

* Phil. Trans., 1814, 64.
† Poggend. Annal., 8, 1. 1826.
‡ Ann. Chim. Phys., (3,) 25, 300. 1849.

Starting with fluor spar, Louyet found of sulphate as follows:

$$1.742$$
$$1.744$$
$$1.745$$
$$1.744$$
$$1.7435$$
$$1.7435$$

Mean, 1.7437, ± .0003

A second series, upon artificial fluoride, gave:

$$1.743$$
$$1.741$$
$$1.741$$

Mean, 1.7417, ± .0004

Dumas[*] published but one result for calcium fluoride. .495 grm. gave .864 grm. sulphate, the ratio being 1 : 1.7455.

De Luca[†] worked with a very pure fluor spar, and published the following results. The ratio between $CaSO_4$ and one gramme of CaF_2 is given in the third column:

.9305 grm. CaF_2 gave 1.630 grm. $CaSO_4$.			1.7518
.836	"	1.459	"	1.7452
.502	"	.8755	"	1.7440
.3985	"	.6945	"	1.7428

If we include Dumas' single result with these, we get a mean of 1.7459, ± .0011.

Upon combining all these series, we get as follows:

Berzelius_____ 1.7500, ± .0004
Louyet, 1st series_____ 1.7437, ± .0003
  "   2d   "   _____ 1.7417, ± .0004
De Luca and Dumas_____ 1.7459, ± .0011

General mean_____ 1.74493, ± .0002

For the ratio between the two sodium salts we have experiments by Dumas and by Louyet.[‡]   According to Louyet one gramme of NaF gives of Na_2SO_4:

[*] Ann. Chem. Pharm., 113, 28.   1860.
[†] Compt. Rend., 51, 299.   1860.
[‡] See the papers already quoted.

$$1.686$$
$$1.683$$
$$1.685$$

Mean, $1.6847, \pm .0006$

The weighings published by Dumas are as follows:

.777 grm. NaF give 1.312 grm. Na_2SO_4.   Ratio, 1.689
1.737   "   2.930   "   "   1.687

Mean, $1.688, \pm .0007$

The general mean of both series is $1.6863, \pm .0004$.

Dumas also gives experiments upon potassium fluoride. The quantity of sulphate formed from one gramme of fluoride is given in the last column:

1.483 grm. KF give 2.225 grm. K_2SO_4.   1.5002
1.309   "   1.961   "   1.4981

Mean, $1.4991, \pm .0007$

The ratios for the fluorides of lead and of barium are due entirely to Louyet. One gramme BaF_2 gave of $BaSO_4$:

$$1.332$$
$$1.331$$
$$1.330$$

Mean, $1.331, \pm .0004$

With the lead fluoride a new method of treatment was adopted. The salt was fused, powdered, dissolved in nitric acid, and precipitated by dilute sulphuric acid. The evaporation of the fluid and the ignition of the sulphate was then effected without transfer. Five grammes of fluoride were taken in each operation, yielding of sulphate:

$$6.179$$
$$6.178$$
$$6.178$$

Mean, $6.1783, \pm .0002$

We now have five ratios to calculate from, as follows:

(1.) $CaF_2 : CaSO_4 : : 1.0 : 1.74493, \pm .0002$
(2.) $NaF : Na_2SO_4 : : 1.0 : 1.6863, \pm .0004$
(3.) $KF : K_2SO_4 : : 1.0 : 1.4991, \pm .0007$
(4.) $BaF_2 : BaSO_4 : : 1.0 : 1.3310, \pm .0004$
(5.) $PbF_2 : PbSO_4 : : 5.0 : 6.1783, \pm .0002$

From these we get five values for F :

From (1)_____$F = 18.926, \pm .009$
  " (2)_____" $= 19.050, \pm .014$
  " (3)_____" $= 18.975, \pm .032$
  " (4)_____" $= 18.993, \pm .033$
  " (5)_____" $= 19.092, \pm .016$

General mean_____" $= 18.984, \pm .0065$

If $O = 16$, this becomes 19.027.

Before leaving the subject of fluorine we must notice two possible sources of error beyond the always to be considered one of impurities in the materials employed. First, an incomplete conversion of a fluoride into a sulphate would lead to results tending to raise the atomic weight of fluorine. On the other hand, the value for fluorine which has most weight is that derived from calcium fluoride. But it was shown under calcium that the atomic weight determined for that metal was probably a trifle too high. This error, introduced into our fluorine calculations, tends to lower our final results. These two errors, then, if they really exist, will, in part at least, compensate each other.

6

PHOSPHORUS.

The material from which we are to calculate the atomic weight of phosphorus is by no means abundant. Berzelius, in his Lehrbuch,* adduces only his own experiments upon the precipitation of gold by phosphorus, and ignores all the earlier work relating to the composition of the phosphates. These experiments we will consider with reference to gold.

Pelouze,† in a single titration of phosphorus trichloride with a standard solution of silver, obtained a wholly erroneous result; and Jacquelain,‡ in his similar experiments, did even worse. Schrötter's criticism upon Jacquelain sufficiently disposes of the latter.‖

There are, in short, but two investigations upon the atomic weight of phosphorus which have any value for present purposes, namely, the researches of Schrötter and of Dumas. These chemists worked with different materials and by different methods, and yet obtained beautifully concordant results.

Schrötter§ burned pure amorphous phosphorus in dry oxygen, and weighed the pentoxide thus formed. One gramme of P yielded P_2O_5 in the following proportions:

$$2.28909$$
$$2.28783$$
$$2.29300$$
$$2.28831$$
$$2.29040$$
$$2.28788$$
$$2.28848$$
$$2.28856$$
$$2.28959$$
$$2.28872$$

Mean, $2.289186, \pm .00033$

Hence $P = 30.9562, \pm .0074$.

* 5th Ed., 1188.
† Compt. Rend., 20, 1047.
‡ Compt. Rend., 33. 693.
‖ Journ. für Prakt. Chem., 57, 315.
§ Journ. für Prakt. Chem., 53, 435.   1851.

Dumas* prepared pure phosphorus trichloride by the action of dry chlorine upon red phosphorus. The portion used in his experiments boiled between 76° and 78°. This was titrated with a standard solution of silver in the usual manner. Dumas publishes weights, from which I calculate the figures given in the third column, representing the quantity of trichloride proportional to 100 parts of silver :

1.787 grm. PCl_3 =	4.208 grm. Ag.		42.4667
1.466 "	3.454 "		42.4435
2.056 "	4.844 "		42.4443
2.925 "	6.890 "		42.4528
3.220 "	7.582 "		42.4690

Mean, 42.4553, ± .0036

Hence P = 31.0314, ± .0467.

Now, combining these two values, we have :

By Schrötter _____ P = 30.9562, ± .0074
By Dumas_____ " = 31.0314, ± .0467

General mean_____ " = 30.9580, ± .0073

If O = 16, this becomes 31.0292.

The fact here noticeable, that Dumas' figures give a value for P slightly higher than that deduced from those of Schrötter, may be accounted for upon the supposition that the phosphorus trichloride contained traces of oxychloride. Such an impurity would tend to raise the apparent atomic weight of phosphorus, and its occurrence is by no means improbable.

---

* Ann. Chem. Pharm., 113, 29. 1860.

BORON.

The atomic weight of this element has been determined by Berzelius and by Laurent, and calculated by Dumas from some experiments by Deville.

Berzelius* based his determination upon three concordant estimations of the percentage of water in borax. Laurent† made use of two similar estimations, and all five may be properly put in one series, thus:

$$
\left.\begin{array}{l}
47.10 \\
47.10 \\
47.10
\end{array}\right\} \text{Berzelius.}
$$

$$
\left.\begin{array}{l}
47.15 \\
47.20
\end{array}\right\} \text{Laurent.}
$$

Mean, 47.13, ± .013

Hence B = 10.943, ± .023.

Dumas'‡ calculations were based on Deville's analyses of the chloride and bromide of boron, which give the ratios between AgCl and BCl$_3$, and between AgBr and BBr$_3$. Reducing the weighings to a common standard, 100 parts of silver chloride correspond to the quantities of boron trichloride given in the third column:

.6763 grm. BCl$_3$ = 2.447 grm. AgCl.		27.303
.923 " 3.395 "		27.187

Mean, 27.245, ± .059

Hence B = 10.808, ± .174.

With the bromide, 2.446 BBr$_3$ gave 5.496 AgBr. If we assign this experiment equal weight with one in the chloride series, and include the probable error of Br, B = 10.964, ± .364.

The three values combine as follows:

---

* Poggend. Annal., 8, 1. 1826.
† Journ. für Prakt. Chem., 47, 415. 1849.
‡ Ann. Chem. Pharm., 113, 31. 1860.

From borax _____ B = 10.943, ± .023
From BCl₃ _____ " = 10.808, ± .174
From BBr₃ _____ " = 10.964, ± .364

General mean _____ " = 10.941, ± .023

If O = 16, B = 10.966.

Further investigation of the atomic weight of boron is evidently desirable.

SILICON.

Although Berzelius* attempted to ascertain the atomic weight of silicon, first by converting pure Si into SiO_2, and later from the analysis of $BaSiF_6$, his results were not satisfactory. We need only consider the estimations of Pelouze, Schiel, and Dumas.

Pelouze,† experimenting upon silicon tetrachloride, employed his usual method of titration with a solution containing a known weight of silver. One hundred parts of Ag gave the following equivalencies of $SiCl_4$:

$$39.4325$$
$$39.4570$$

Mean, 39.4447, ± .0083

Hence Si = 28.408.

Essentially the same method was adopted by Dumas.‡ Pure $SiCl_4$ was weighed in a sealed glass bulb, then decomposed by water, and titrated. The results for 100 Ag are given in the third column:

2.899 grm. $SiCl_4$ = 7.3558 grm. Ag.		39.411
1.242 " 3.154 "		39.379
3.221 " 8.1875 "		39.340

Mean, 39.377, ± .014

Hence Si = 28.117.

---

* Lehrbuch, 5 Aufl., 3, 1200.
† Compt. Rend., 20, 1047. 1845.
‡ Ann. Chem. Pharm., 113, 31. 1860.

Dumas and Pelouze's series combine as follows:

Pelouze_____	39.4447, ± .0083
Dumas _____	39.377, ± .014
General mean_____	39.4265, ± .0071

Hence $SiCl_4 = 169.810, ± .034.$

Schiel,[*] also studying the chloride of silicon, decomposed it by ammonia. After warming and long standing it was filtered, and in the filtrate the chlorine was estimated as AgCl. One hundred parts of AgCl correspond to the quantities of $SiCl_4$ given in the last column:

.6738 grm. $SiCl_4$ gave	2.277 grm. AgCl.	29.592
1.3092 "	4.418 "	29.633
		Mean, 29.6125, ± .0138

Hence $SiCl_4 = 169.437, ± .080$, and $Si = 27.957$.
Combining the values for $SiCl_4$ we have this result:

Pelouze and Dumas_____ $SiCl_4 =$	169.810, ± .034
Schiel_____ " =	169.437, ± .080
General mean _____ " =	169.675, ± .031

Hence $Si = 28.195, ± .066$; or, if $O = 16$, $Si = 28.260$.

It will be observed that all of these determinations rest upon the composition of $SiCl_4$, a compound for which it would not be easy to guarantee absolute purity. All the errors likely to occur in the determination of the atomic weight would be plus errors, so that the value deduced above is almost certainly too high.

---

[*] Ann. Chem. Pharm., 120, 94.

LITHIUM.

The earlier determinations of the atomic weight of lithium by Arfvedson, Stromeyer, C. G. Gmelin, and Kralovanzky were all erroneous, because of the presence of sodium compounds in the material employed. The results of Berzelius, Hagen, and Hermann were also incorrect, and need no further notice here. The only investigations which we need to consider are those of Mallet, Diehl, Troost, and Stas.

Mallet's experiments* were conducted upon lithium chloride, which had been purified as completely as possible. In two trials the chloride was precipitated by nitrate of silver, which was collected upon a filter and estimated in the ordinary way. The figures in the third column represent the LiCl proportional to 100 parts of AgCl:

7.1885 grm. LiCl gave 24.3086 grm. AgCl.		29.606
8.5947 " 29.0621 "		29.574

In a third experiment the LiCl was titrated with a standard solution of silver. 3.9942 grm. LiCl balanced 10.1702 grm. Ag, equivalent to 13.511 grm. AgCl. Hence 100 AgCl = 29.563 LiCl. Mean of all three experiments, 29.581, ± .0087.

Diehl,† whose paper begins with a good resumé of all the earlier determinations, describes experiments made with lithium carbonate. This salt, which was spectroscopically pure, was dried at 130° before weighing. It was then placed in an apparatus from which the carbon dioxide generated by the action of pure sulphuric acid upon it could be expelled, and the loss of weight determined. From this loss the following percentages of CO_2 in Li_2CO_3 were determined:

$$59.422$$
$$59.404$$
$$59.440$$
$$59.401$$

Mean, 59.417, ± .006

---

* Silliman's Amer. Journal, November, 1856. Chem. Gazette, 15, 7.
† Ann. Chem. Pharm., 121, 93.

Diehl's investigation was quickly followed by a confirmation from Troost.* This chemist, in an earlier paper,† had sought to fix the atomic weight of lithium by an analysis of the sulphate, and had found a value not far from 6.5; thus confirming the results of Berzelius and of Hagen, who had employed the same method. But Diehl showed that the $BaSO_4$ precipitated from Li_2SO_4 always retained traces of Li, which were recognizable by spectral analysis, and which accounted for the error. In the later paper Troost made use of the chloride and the carbonate of lithium, both spectroscopically pure. The carbonate was strongly ignited with pure quartz powder, thus losing carbon dioxide, which loss was easily estimated. The subjoined results were obtained:

.970 grm. Li_2CO_3 lost	.577 grm. CO_2.	59.485 per cent.
1.782 "	1.059 "	59.427 "

Mean, 59.456, ± .020

This combined with Diehl's mean, 59.417, ± .006, gives a general mean of 59.420, ± .0057.

The lithium chloride employed by Troost was heated in a stream of dry hydrochloric acid gas; of which the excess, after cooling, was expelled by a current of dry air. The salt was weighed in the same tube in which the foregoing operations had been performed, and the chlorine was then estimated as silver chloride. The usual ratio between LiCl and 100 parts of AgCl is given in the third column:

1.309 grm. LiCl gave	4.420 grm. AgCl.	29.615
2.750 "	9.300 "	29.570

Mean, 29.5925, ± .0145

This combined with Mallet's mean, 29.581, ± .0087, gives a general mean of 59.584, ± .0075.

Finally, we come to the work of Stas,‡ which was exe-

* Zeit. Anal. Chem., 1, 402.

† Annales d. Chim. et d. Phys., 51, 108.

‡ Aronstein's Translation, 279–302.

cuted with his usual wonderful accuracy. In three titrations, in which all the weights were reduced to a vacuum standard, the following quantities of LiCl balanced 100 parts of pure silver:

$$39.356$$
$$39.357$$
$$39.361$$

Mean, 39.358, $\pm$ .001

In a second series of experiments, intended for determining the atomic weight of nitrogen, LiCl was converted into $LiNO_3$. The method was that employed for a similar purpose with the chlorides of sodium and of potassium. One hundred parts of LiCl gave of $LiNO_3$:

$$162.588$$
$$162.600$$
$$162.598$$

Mean, 162.5953, $\pm$ .0025

We have now the following ratios from which to deduce the atomic weight of lithium:

(1.) $AgCl : LiCl :: 100 : 29.584, \pm .0075$
(2.) $Ag : LiCl :: 100 : 39.358, \pm .001$
(3.) $LiCl : LiNO_3 :: 100 : 162.5953, \pm .0025$
(4.) Per cent. of CO_2 in Li_2CO_3, 59.420, $\pm$ .0057

Hence two values for the molecular weight of LiCl:

From (1)_____ LiCl $= 42.3187, \pm .0039$
From (2) _____ " $= 42.3787, \pm .0111$

General mean_____ " $= 42.3720, \pm .0037$

For lithium itself we get three values:

From molecular weight of LiCl___Li $= 7.002, \pm .015$
From ratio (3)_____ " $= 7.0287, \pm .042$
From ratio (4)_____ " $= 7.0085, \pm .008$

General mean_____ " $= 7.0073, \pm .007$

If $O = 16$, then $Li = 7.0235$. Stas himself gives 7.022 as his determination. Difference, .0015.

RUBIDIUM.

The atomic weight of rubidium has been determined by Bunsen, Piccard, and Godeffroy; but only from analyses of the chloride.

Bunsen,[*] employing ordinary gravimetric methods, estimated the ratio between AgCl and RbCl. His rubidium chloride was purified by fractional crystallization of the chloroplatinate. He obtained the following results, to which, in a third column, I add the ratio between RbCl and 100 parts of AgCl:

One grm. RbCl gave	1.1873 grm. AgCl.	84.225
"	1.1873 "	84.225
"	1.1850 "	84.388
"	1.1880 "	84.175

Mean, 84.253, ± .031

The work of Piccard[†] was similar to that of Bunsen. In weighing, the crucible containing the silver chloride was balanced by a precisely similar crucible, in order to avoid the correction for displacement of air. The filter was burned separately from the AgCl, as usual; but the small amount of material adhering to the ash was reckoned as metallic silver. The rubidium chloride was purified by Bunsen's method. The results, expressed according to the foregoing standard, are as follows:

1.1587 grm. RbCl = 1.372 AgCl + .0019 Ag.	84.300
1.4055 " 1.6632 " .0030 "	84.303
1.001 " 1.1850 " .0024 "	84.245
1.5141 " 1.7934 " .0018 "	84.313

Mean, 84.290, ± .0105

Godeffroy,[‡] starting with material containing both rubidium and cæsium, separated the two metals by fractional

---

[*] Zeit. Anal. Chem., 1, 136.   Poggend. Annal., 113, 339.   1861.
[†] Journ. für Prakt. Chem., 86, 454.   1862.   Zeit. Anal. Chem., 1, 518.
[‡] Ann. Chem. Pharm., 181, 185.   1876.

crystallization of their alums, and obtained salts of each spectroscopically pure. The nitric acid employed was tested for chlorine and found to be free from that impurity, and the weights used were especially verified. In two of his analyses of RbCl the AgCl was handled by the ordinary process of filtration. In the other two it was washed by decantation, dried, and weighed in a glass dish. The usual ratio is appended in the third column :

1.4055 grm. RbCl gave	1.6665 grm. AgCl.		84.338
1.8096 "	2.1461	"	84.320
2.2473 "	2.665	"	84.326
2.273 "	2.6946	"	84.354

Mean, 84.3345. ± .0051

Combining the three series, we get the following result :

Bunsen	84.253. ± .031	Rb = 85.150
Piccard	84.290, ± .0105	" = 85.203
Godeffroy	84.3345, ± .0051	" = 85.263

General mean___ 84.324, ± .0045

Hence Rb = 85.251, ± .018. If O = 16, Rb = 85.529.

CÆSIUM.

The atomic weight of cæsium, like that of rubidium, has been determined from the analysis of the chloride. The earliest determination, by Bunsen,* was incorrect, because of impurity in the material employed.

In 1863 Johnson and Allen published their results.† Their material was extracted from the lepidolite of Hebron, Maine, and the cæsium was separated from the rubidium as bitartrate. From the pure cæsium bitartrate cæsium chloride was prepared, and in this the chlorine was estimated as

---

* Zeit. Anal. Chem., 1, 137.
† Amer. Journ. Sci. and Arts, (2,) 35, 94.

silver chloride by the usual gravimetric method. Reducing
their results to the convenient standard adopted in preceding chapters, we have, in a third column, the quantities of
CsCl equivalent to 100 parts of AgCl:

1.8371 grm. CsCl gave	1.5634 grm. AgCl.		117.507
2.1295	"	1.8111	"	117.580
2.7018	"	2.2992	"	117.511
1.56165	"	1.3302	"	117.399

Mean. 117.499, ± .025

Shortly after the results of Johnson and Allen appeared
a new series of estimations was published by Bunsen.[*] His
cæsium chloride was purified by repeated crystallizations of
the chloroplatinate, and the ordinary gravimetric process
was employed. The following results represent, respectively,
material thrice, four times, and five times purified:

1.3835 grm. CsCl gave	1.1781 grm. AgCl.		Ratio, 117.435
1.3682	"	1.1644	"	117.503
1.2478	"	1.0623	"	117.462

Mean, 117.467, ± .013

Godeffroy's work[†] was, in its details of manipulation, sufficiently described under rubidium. In three of the experiments upon cæsium the silver chloride was washed by
decantation, and in one it was collected upon a filter. The
results are subjoined:

1.5825 grm. CsCl gave	1.351 grm. AgCl.		Ratio, 117.135
1.3487	"	1.1501	"	117.265
1.1880	"	1.0141	"	117.148
1.2309	"	1.051	"	117.107

Mean, 117.164, ± .023

We may now combine the three series to form a general
mean:

* Poggend. Annal., 119, 1. 1863.
† Ann. Chem. Pharm., 181, 185. 1876.

Johnson and Allen_____ 117.499, ± .025   Cs = 132.706
Bunsen_____ 117.467, ± .013   " = 132.661
Godeffroy _____ 117.164, ± .023   " = 132.227

General mean _____ 117.413, ± .010

Hence Cs = 132.583, ± .024; or, if O = 16, Cs = 132.918.

THALLIUM.

The atomic weight of this interesting metal has been fixed by the researches of Lamy, Werther, Hebberling, and Crookes. Lamy and Hebberling investigated the chloride and sulphate; Werther studied the iodide; Crooke's experiments involved the synthesis of the nitrate. The last mentioned work was so thorough and admirable that the other researches are included here only for the sake of historical completeness.

Lamy* gives the results of one analysis of thallium sulphate and three of thallium chloride. 3.423 grammes Tl_2SO_4 gave 1.578 grm. $BaSO_4$; whence 100 parts of the latter are equivalent to 216.920 of the former. In the thallium chloride the chlorine was estimated as silver chloride. The following results were obtained. In the third column I give the amount of TlCl proportional to 100 parts of AgCl:

3.912 grm. TlCl gave 2.346 grm. AgCl.   166.752
3.000   "   1.8015   "   166.528
3.912   "   2.336   "   167.466

Mean, 166.915, ± .1905

Hebberling's† work resembles that of Lamy. Reducing his weighings to the standards adopted above, we have from his sulphate series, as equivalent to 100 parts of $BaSO_4$, the amounts of Tl_2SO_4 given in the third column:

---

* Zeit. Anal. Chem., 2, 211. 1863.
† Ann. Chem. Pharm., 134, 11. 1865.

1.4195 grm. Tl$_2$SO$_4$ gave .6534 grm. BaSO$_4$.		217.248
1.1924 " .5507 "		216.524
.8560 " .3957 "		216.325
	Mean,	216.699

Including Lamy's single result, as of equal weight, we get a mean of 216.754. ± .1387.

From the chloride series we have these results, with the ratio stated as usual:

.2984 grm. TlCl gave .1791 grm. AgCl.	166.611
.5452 " .3278 . "	166.321
Mean,	166.465, ± .097

Lamy's mean was 166.915, ± .1905. Both means combined give a general mean of 166.555, ± .0865.

Werther's* determinations of iodine in thallium iodide were made by two methods. In the first series TlI was decomposed by zinc and potassium hydroxide, and in the filtrate the iodine was estimated as AgI. One hundred parts of AgI correspond to the amounts of TlI given in the last column:

.720 grm. TlI gave .51 grm. AgI.	141.176
2.072 " 1.472 "	140.761
.960 " .679 "	141.384
.385 " .273 "	141.026
1.068 " .759 "	140.711
Mean,	141.012, ± .085

In the second series the thallium iodide was decomposed by ammonia in presence of silver nitrate, and the resulting AgI was weighed. Expressed according to the foregoing standard the results are as follows:

1.375 grm. TlI gave .978 grm. AgI.	Ratio, 140.593
1.540 " 1.095 "	140.639
1.380 " .981 "	140.673
	Mean, 140.635, ± .016

General mean of both series, 140.648, ± .016.

---

* Journ. für Prakt. Chem., 92, 128. 1864.

From the foregoing results three values for the atomic weight of thallium are calculable:

From the sulphate_____Tl $=$ 204.169, $\pm$ .166
From the chloride_____ " $=$ 203.879, $\pm$ .126
From the iodide _____ " $=$ 203.886, $\pm$ .054

In 1873 Crookes,[*] the discoverer of thallium, published his final determination of its atomic weight. His method was to effect the synthesis of thallium nitrate from weighed quantities from absolutely pure thallium. No precaution necessary to ensure purity of materials was neglected; the balances were constructed especially for the research; the weights were accurately tested and all their errors ascertained; weighings were made partly in air and partly in vacuo, but all were reduced to *absolute* standards; and unusually large quantities of thallium were employed in each experiment. In short, no effort was spared to attain as nearly as possible absolute precision of results. The details of the investigation are too voluminous, however, to be cited here; the reader who wishes to become familiar with them must consult the original memoir. Suffice it to say that the research is a model which other chemists will do well to copy.

The results of ten experiments by Professor Crookes may be stated as follows. In a final column we may state the quantity of nitrate producible from 100 parts of thallium. The weights given are in grains:

Thallium.	*TlNO₃ + Glass.*	*Glass Vessel.*	*Ratio.*
497.972995	1121.851852	472.557319	130.3875
293.193507	1111.387014	729.082713	130.3930
288.562777	971.214142	594.949719	130.3926
324.963740	1142.569408	718.849078	130.3900
183.790232	1005.779897	766.133831	130.3912
190.842532	997.334615	748.491271	130.3920
195.544324	1022.176679	767.203451	130.3915
201.816345	1013.480135	750.332401	130.3897
295.683523	1153.947672	768.403621	130.3908
299.203036	1159.870052	769.734201	130.3917

Mean, 130.3910, $\pm$ .00034

[*] Philosophical Transactions, 1873, p. 277.

Hence, using the atomic weights and probable errors previously found for N and O, Tl = 203.715, ± .0365. If O = 16, Tl = 204.183.

Crookes himself, using 61.889 as the molecular weight of the group NO_3, gets the value Tl = 203.642; the lowest value in the series being 203.628, and the highest 203.666; an extreme variation of 0.038. This is extraordinary accuracy for so high an atomic weight, at least as far as Crookes' work is concerned. But its value depends in reality upon the accuracy of other chemists in fixing the atomic weights of N and O; a slight variation in either of the latter constants producing a large variation here. What Crookes really has done has been to fix with almost absolute certainty the ratio between Tl and NO_3. If the latter group should have the molecular weight 62, in accordance with Prout's hypothesis, then Tl = 204.008. In other words, the ratio thus fixed by Crookes is almost exactly represented by two whole numbers, and supports Prout's hypothesis in a very decided way. Crookes himself seems to have overlooked this fact, for he regards his results as militating against the hypothesis in question.

GLUCINUM.

The atomic weight of glucinum is at present much in doubt; our knowledge of it depending upon the unsettled question whether the oxide is GlO or Gl_2O_3. The formula GlO agrees with Mendelejeff's law, and is advocated by Reynolds,[*] Lothar Meyer,[†] and Brauner.[‡] The symbol Gl_2O_3, on the other hand, is favored by Nilson and Pettersson,[||] and by Humpidge.[§] Humpidge, Meyer, and Brauner

---

[*] Phil. Mag., (5,) 3, 38. 1877. Chem. News, 42, 273. 1880.

[†] Ber. der Deutsch. Chem. Gesell., 13, 1780. 1880. Also, 11, 576. 1879.

[‡] Phil. Mag., (5,) 11. Jan., 1881.

[||] Berichte, 11, 381 and 906. 1879. Also, 13, 2035. 1880.

[§] Chem. News, 42, 261. 1880.

offer only theoretical discussions of the subject; Reynolds and Nilson and Pettersson have determined the specific heat of the metal, but give opposed results. In the following calculations the simpler formula will be assumed, not as a finality, but because of its accordance with the system of Mendelejeff.

The data from which we are to calculate the atomic weight of glucinum have been determined by Awdejew, Weeren, Klatzo, Debray, and Nilson and Pettersson. Berzelius'[*] single experiment on the sulphate may be left out of account.

Awdejew,[†] whose determination was the earliest of any value, analyzed the sulphate. The sulphuric acid was thrown down as barium sulphate; and in the filtrate, from which the excess of barium had been first removed, the glucina was precipitated by ammonia. The figures which Awdejew publishes represent the ratio between SO_3 and GlO, but not absolute weights. As, however, his calculations were made with $SO_3 = 501.165$, and Ba probably $= 855.29$, we may add a third column showing how much $BaSO_4$ is proportional to 100 parts of GlO:

SO_3.	GlO.	Ratio.
4457	1406	921.242
4531	1420	927.304
7816	2480	915.903
12880	4065	920.814

Mean, 921.316, $\pm$ 1.577

The same method was followed by Weeren and by Klatzo, except that Weeren used ammonium sulphide instead of ammonia for the precipitation of the glucina. Weeren[‡] gives the following weights of GlO and $BaSO_4$. The ratio is given in a third column, just as with the figures by Awdejew:

---

* Poggend. Annal., 8, 1.
†   "   56, 106.   1842.
‡   "   92, 124.   1854.

GlO.	BaSO₄.	Ratio.
.3163 grm.	2.9332 grm.	927.031
.2872 "	2.6377 "	918.419
.2954 "	2.7342 "	925.592
.5284 "	4.8823 "	902.946

Mean, 918.497, ± 3.624

Klatzo's[*] figures are as follows, with the third column added by the writer:

GlO.	BaSO₄.	Ratio.
.2339 grm.	2.1520 grm.	920.052
.1910 "	1.7556 "	919.162
.2673 "	2.4872 "	930.490
.3585 "	3.3115 "	923.710
.2800 "	2.5842 "	922.989

Mean, 923.281, ± 1.346

Combining these series into a general mean, we get the subjoined result:

Awdejew	921.316, ± 1.577
Weeren	918.497, ± 3.624
Klatzo	923.281, ± 1.346
General mean	922.164, ± 0.985

Hence $GlO = 25.224, \pm .269$.

Debray[†] analyzed a double oxalate of glucinum and ammonium, $Gl(NH_4)_2C_4O_8$. In this the glucina was estimated by calcination, after first converting the salt into nitrate. The following percentages were found:

11.5
11.2
11.6

Mean, 11.433, ± .081

The carbon was estimated by an organic combustion. I give the weights, and put in a third column the percentages of CO_2 thus obtained:

---

* Zeitschrift für Anal. Chem., 8, 523. 1869.
† Ann. de Chim. et de Phys., (3,) 44, 37. 1855.

Salt.	CO_2.	Per cent. CO_2.
.600 grm.	.477 grm.	79.500
.603 "	.478 "	79.270
.600 "	.477 "	79.500

Mean, 79.423, ± .052

Calculating the ratio between CO_2 and GlO, we have for the molecular weight of the latter, GlO = 25.220, ± .180. The agreement between this result and the one previously deduced from the sulphate is certainly very striking.

Last of all and best of all we come to the determinations recently published by Nilson and Pettersson.* These chemists sought to use the sublimed chloride of glucinum, but found it to contain traces of lime derived from a glass tube. They finally resorted to the sulphate as the most available salt for their purposes. This, which they write $Gl_2(SO_4)_3$ $12H_2O$, and which we formulate as $GlSO_4.4H_2O$, yields pure glucina upon strong ignition. The subjoined percentages of glucina were thus obtained:

14.171
14.169
14.160
14.176

Mean, 14.169, ± .0023

Hence GlO = 25.048, and Gl = 9.085, ± .0055. If O = 16, Gl = 9.106. If SO_3 = 80, then Gl = 9.096.

If the oxide is Gl_2O_3, then the value Gl = 9.085, ± .0055 becomes Gl = 13.628, ± .0082.

It would be easy enough to combine this value for Gl with those derived from the experiments of the investigators previously cited, but it is hardly worth while. All the other estimations have such high probable errors that they would practically vanish from the general mean. Their influence would hardly extend to the third decimal place, and they may therefore be neglected.

* Compt. Rend., 91, 168. 1880.

MAGNESIUM.

There is perhaps no common metal of which the atomic weight has been subjected to closer scrutiny than that of magnesium. The value is low, and its determination should, therefore, be relatively free from many of the ordinary sources of error; it is extensively applied in chemical analysis, and ought consequently to be accurately ascertained. Strange discrepancies, however, exist between the results obtained by different investigators; so that the generally accepted figure cannot be regarded as absolutely free from doubt.

The determinations of Berzelius* and other early chemists need not be here considered. Nor does the estimation made by Macdonnell† deserve more than a passing mention. He puts the atomic weight of magnesium at 23.9, but gives no details concerning his method of determination. The researches which we have to consider are those of Scheerer, Svanberg and Nordenfeldt, Jacquelain, Bahr, Marchand and Scheerer, and Dumas.

Scheerer's method of investigation was exceedingly simple.‡ He merely estimated the sulphuric acid in anhydrous magnesium sulphate, employing the usual process of precipitation as barium sulphate. He gives no weighings, but reports the percentages of SO_3 thus found. In his calculations, $O = 100$, $SO_3 = 500.75$, and $BaO = 955.29$. It is easy, therefore, to recalculate the figures which he gives, so as to establish what his method really represents, viz., the ratio between the sulphates of barium and magnesium.

Thus revised, his four analyses show that 100 parts of $MgSO_4$ yield the following quantities of $BaSO_4$:

---

* Lehrbuch, 5 Aufl., Bd. 3, s. 1227.
† British Association Report, 1852, part 2, p. 36.
‡ Poggend. Annal., 69, 535. 1846.

	Per cent. SO_3.
193.575	66.573
193.677	66.608
193.767	66.639
193.631	66.592

Mean, 193.6625, $\pm$ .0274

Hence, using the atomic weights deduced in previous chapters for Ba, S, and O, Mg = 24.544, $\pm$ .0311. In a subsequent note* Scheerer shows that the barium sulphate of the foregoing experiments carried down with it magnesium salts in such quantity as to make the atomic weight of magnesium 0.39 too low. Corrected, Mg becomes = 24.545.

The work of Bahr, of Jacquelain, and in part that of Svanberg and Nordenfeldt, also relates to the composition of magnesium sulphate. Jacquelain's experiments were as follows.† Dry magnesium sulphate was prepared by mixing the ordinary hydrous salt to a paste with sulphuric acid, and calcining the mass in a platinum crucible over a spirit lamp to constant weight and complete neutrality of reaction. This dry sulphate was weighed and intensely ignited three successive times. The weight of the residual MgO having been determined, it was moistened with sulphuric acid and recalcined over a spirit lamp, thus reproducing the original weight of $MgSO_4$. Jacquelain's weighings for these two experiments show that 100 parts of MgO correspond to the quantities of $MgSO_4$ given in the last column:

| 1.466 grm. $MgSO_4$ gave .492 grm. MgO. | 297.968 |
| .492 " MgO " 1.466 " $MgSO_4$. | 297.968 |

Jacquelain also made one estimation of sulphuric acid in the foregoing sulphate as $BaSO_4$. His result, (1.464 grm. $MgSO_4$ = 2.838 grm. $BaSO_4$,) reduced to the standard adopted in dealing with Scheerer's experiments, give for 100 parts of $MgSO_4$, 193.852 $BaSO_4$. If this figure be given equal weight with a single experiment in Scheerer's series,

* Poggend. Annal., 70, 407.
† Ann. d. Chim. et Phys., 3 serie, 32, 202.

and combined with the latter, the mean will be 193.700, ±
.0331. Fròm this the atomic weight of magnesium becomes
24.244, ± .033. This again, corrected according to Scheerer
for the magnesium salts carried down by the barium sul-
phate, becomes 0.39 higher, or Mg = 24.283. Of course
this correction, determined by Scheerer for a single experi-
ment, can only be a rough approximation in a mean like
the foregoing. It is better than no correction at all, the
character of the error involved being known.

Bahr's* work resembles in part that of Jacquelain. This
chemist converted pure magnesium oxide into sulphate, and
from the increase in weight determined the composition of
the latter salt. From his weighings 100 parts of MgO equal
the amounts of $MgSO_4$ given in the third column:

1.6938 grm. MgO gave	5.0157 grm. $MgSO_4$.	296.122
2.0459 "	6.0648 "	296.437
1.0784 "	3.1925 "	296.040

Mean, 296.200, ± .0815

About four years previous to the investigations of Bahr
the paper of Svanberg and Nordenfeldt† appeared. These
chemists started with the oxalate of magnesium, which was
dried at a temperature of from 100° to 105° until it no
longer lost weight. The salt then contained two molecules
of water, and upon strong ignition it left a residue of MgO.
The percentage of MgO in the oxalate comes out as follows:

7.2634 grm. oxalate gave	1.9872 grm. oxide.	27.359 per cent.
6.3795 "	1.7464 "	27.375 "
6.3653 "	1.7418 "	27.364 "
6.2216 "	1.7027 "	27.368 "

Mean, 27.3665, ± .0023

In three of these experiments the MgO was treated with
H_2SO_4, and converted, as by Jacquelain and by Bahr in
their later researches, into $MgSO_4$. One hundred parts of
MgO gave of $MgSO_4$ as follows:

---

* Journ. für Prakt. Chem., 56, 310. 1852.
† Journ. für Prakt. Chem., 45, 473. 1848.

1.9872 grm. MgO gave 5.8995 grm. MgSO₄. 296.875
1.7464   "   5.1783   "   296.513
1.7418   "   5.1666   "   296.624

Mean, 296.671, ± .072

We have now for this ratio between MgO and MgSO₄ three series; not at all concordant. We may combine them, assigning to each of Jacquelain's two results a weight corresponding to one of Bahr's:

Jacquelain _____ 297.968, ± .0999
Bahr _____ 296.200, ± .0815
Svanberg and Nordenfeldt_____ 296.671, ± .072

General mean _____ 296.806, ± .0475

In 1850 the elaborate investigations of Marchand and Scheerer* appeared. These chemists undertook to determine the composition of some natural magnesites, and, by applying corrections for impurities, to deduce from their results the sought for atomic weight. The magnesite chosen for the investigation was, first, a yellow, transparent variety from Snarum; second, a white opaque mineral from the same locality; and, third, a very pure quality from Frankenstein. In each case the impurities were carefully determined; but only a part of the details need be cited here. Silica was of course easily corrected for by simple subtraction from the sum of all of the constituents; but iron and calcium, when found, having been present in the mineral as carbonates, required the assignment to them of a portion of the carbonic acid. In the atomic weight determinations the mineral was first dried at 300°. The loss in weight upon ignition was then carbon dioxide. It was found, however, that even here a correction was necessary. Magnesite, upon drying at 300°, loses a trace of CO_2, and still retains a little water; on the other hand, a minute quantity of CO_2 remains even after ignition. The CO_2 expelled at 300° amounted in one experiment to .054 per cent.; that retained after calcination to .055 per cent. Both errors tend in the

* Journ. für Prakt. Chem., 50, 385.

same direction, and increase the apparent percentage of MgO in the magnesite. On the yellow mineral from Snarum the crude results are as follows, giving percentages of MgO, FeO, and CO_2 after eliminating silica:

CO_2.	MgO.	FeO.
51.8958	47.3278	.7764
51.8798	47.3393	.7809
51.8734	47.3154	.8112
51.8875	47.3372	.7753

Mean, 47.3299 ± .0037

After applying corrections for loss and retention of CO_2, as previously indicated, the mean results of the foregoing series become—

CO_2.	MgO.	FeO.
51.9931	47.2743	.7860

The ratio between the MgO and the CO_2, after correcting for the iron, will be considered further on.

Of the white magnesite from Snarum but a single analysis was made, which, for present purposes may be ignored. Concerning the Frankenstein mineral three series of analyses were executed. In the first series the following results were obtained:

8.996 grm. CO_2 = 8.2245 grm. MgO.	47.760 per cent. MgO.
7.960 " 7.2775 "	47.761 "
9.3265 " 8.529 "	47.767 "
7.553 " 6.9095 "	47.775 "

Mean, 47.766, ± .0022

This mean, corrected for loss of CO_2 in drying, becomes 47.681. I give series second with corrections applied:

6.8195 grm. $MgCO_3$ gave 3.2500 grm. MgO.	47.658 per cent.
11.3061 " 5.3849 "	47.628 "
9.7375 " 4.635 "	47.599 "
12.3887 " 5.9033 "	47.650 "
32.4148 " 15.453 "	47.674 "
38.8912 " 18.5366 "	47.663 "
26.5223 " 12.6445 "	47.675 "

Mean, 47.650, ± .0069

The third series was made upon very pure material, so that the corrections, although applied, were less influential. The results were as follows:

4.2913 grm. $MgCO_3$ gave 2.0436 grm. MgO.   47.622 per cent.
27.8286   "   13.2539   "   47.627   "
14.6192   "   6.9692   "   47.672   "
18.3085   "   8.7237   "   47.648   "

Mean, 47.642, $\pm$ .0077

In a supplementary paper[*] by Scheerer, it was shown that an important correction to the foregoing data had been overlooked. Scheerer, re-examining the magnesites in question, discovered in them traces of lime, which had escaped notice in the original analyses. With this correction the two magnesites in question exhibit the following mean composition:

	Snarum.	*Frankenstein.*
CO_2	52.131	52.338
MgO	46.663	47.437
CaO	.430	.225
FeO	.776	----
	100.000	100.000

Correcting for lime and iron, by assigning each its share of CO_2, the Snarum magnesite gives as the true percentage of magnesia in pure magnesium carbonate, the figure 47.624. To this, without serious mistake, we may assign the weight indicated by the probable error, $\pm$ .0037; the quantity previously deduced from the percentages of MgO given in the uncorrected analyses.

From the Frankenstein mineral, similarly corrected, the final mean percentage of MgO in $MgCO_3$ becomes 47.628. This, however, represents three series of analyses, whose combined probable errors may be properly assigned to it. The combination is as follows:

---

[*] Ann. d. Chem. und Pharm., 110, 240.

$$\pm .0022$$
$$\pm .0069$$
$$\pm .0077$$

Result, $\pm$ .0020, probable error of the general mean.

We may now combine the results obtained from both magnesites:

Snarum mineral_____.Per cent. MgO,	47.624,	$\pm$ .0037
Frankenstein mineral __ "	47.628,	$\pm$ .0020
General mean___ "	47.627,	$\pm$ .0018

The last investigation upon the atomic weight of magnesium which we have to consider is that of Dumas.* Pure magnesium chloride was placed in a boat of platinum, and ignited in a stream of dry hydrochloric acid gas. The excess of the latter having been expelled by a current of dry carbon dioxide, the platinum boat, still warm, was placed in a closed vessel and weighed therein. After weighing, the chloride was dissolved and titrated in the usual manner with a solution containing a known quantity of pure silver. The weighings which Dumas reports give, as proportional to 100 parts of silver, the quantities of $MgCl_2$ stated in the third column:

2.203 grm. $MgCl_2$ =	4.964 grm. Ag.		44.380
2.5215 "	5.678	"	44.408
2.363 "	5.325	"	44.376
3.994 "	9.012	"	44.319
2.578 "	5.834	"	44.189
2.872 "	6.502	"	44.171
2.080 "	4.710	"	44.161
2.214 "	5.002	"	44.262
2.086 "	4.722	"	44.176
1.688 "	3.823	"	44.154
1.342 "	3.031	"	44.276

Mean, 44.261, $\pm$ .020

There are now before us the following ratios, from which to deduce the sought-for atomic weight:

* Ann. Chem. Pharm., 113, 33. 1860.

(1.) $MgSO_4 : BaSO_4 :: 100 : 193.700, \pm .0331$
(2.) $MgO : MgSO_4 :: 100 : 296.806, \pm .0475$
(3.) Per cent. of MgO in oxalate, $27.3665, \pm .0023$
(4.) Per cent. of MgO in carbonate, $47.627, \pm .0018$
(5.) $Ag : MgCl_2 :: 100 : 44.261, \pm .020$

From these we find three values for the molecular weight of MgO:

From (2)_____ MgO $= 40.587, \pm .0126$
From (3)_____ " $= 40.603, \pm .0069$
From (4)_____ " $= 39.922, \pm .0030$

General mean_____ " $= 40.054, \pm .0027$

We have also three values for the atomic weight of magnesium:

From molecular weight of MgO_____ Mg $= 24.091, \pm .0044$
From ratio (1,) corrected_____ " $= 24.283, \pm .033$
From ratio (5,) Dumas _____ " $= 24.576, \pm .032$

General mean_____ " $= 24.103, \pm .0043$

Or, if $O = 16$, Mg becomes $= 24.159$.

In this general mean all the determinations are included, good or bad. Dumas' result is unquestionably wrong; the error, probably, being due to the presence of oxychloride in the $MgCl_2$ which was used. It is doubtful whether any precautions could have eliminated that error. If we take only Marchand and Scheerer's work on magnesium carbonate as having positive value, we shall get from their analyses the following result, viz: $Mg = 23.959, \pm .0046$. Or, if $O = 16$, this becomes 24.014. The atomic weight of magnesium, therefore, varies from the whole number 24, only within the ordinary limits of experimental error.

ZINC.

The several determinations of the atomic weight of zinc are by no means closely concordant. The results obtained by Gay-Lussac * and Berzelius † were undoubtedly too low, and may be disregarded here. We need consider only the work done by Jacquelain, Favre, and Axel Erdmann.

In 1842 Jacquelain published the results of his investigations upon this important constant.‡ In two experiments a weighed quantity of zinc was converted into nitrate, and that by ignition in a *platinum* crucible was reduced to oxide. In two other experiments sulphuric acid took the place of nitric. As the zinc contained small quantities of lead and iron, these were estimated, and the necessary corrections applied. From the weights of metal and oxide given by Jacquelain the percentages have been calculated:

<div align="center">Nitric Series.</div>

9.917 grm. Zn gave	12.3138 grm. ZnO.		80.536 per cent. Zn.	
9.809	"	12.1800 "	80.534	"

<div align="center">Sulphuric Series.</div>

2.398	"	2.978 grm. ZnO.	80.524	"
3.197	"	3.968 "	80.570	"

<div align="right">Mean of all four, 80.541, ± .007</div>

Hence $Zn = 66.072, \pm .028$.

The method adopted by Axel Erdmann ‖ is essentially the same as that of Jacquelain, but varies from the latter in certain important details. First, pure zinc oxide was prepared, ignited in a covered crucible with sugar, and then, to complete the reduction, ignited in a porcelain tube in a current of hydrogen. The pure zinc thus obtained was converted into oxide by means of treatment with nitric acid and sub-

* Mémoire d'Arceuil, 2, 174.
† Gilb. Annal., 37, 460.
‡ Compt. Rend., 14, 636.
‖ Poggend. Annal., 62, 611.   Berz. Lehrb., 3, 1219.

sequent ignition in a *porcelain* crucible. Erdmann's figures give us the following percentages of metal in the oxide:

$$80.247$$
$$80.257$$
$$80.263$$
$$80.274$$

Mean, 80.260, $\pm$ .0037

Hence Zn = 64.9045, $\pm$ .019.

If we combine the results of Jacquelain with those of Erdmann, we get a mean percentage of zinc, 80.324, $\pm$ .0032; and an atomic weight of Zn = 65.168, $\pm$ .018. The reason for the discordance between the two experimenters will be considered further along.

Favre* employed two methods of investigation. First, zinc was dissolved in sulphuric acid, the hydrogen evolved was burned, and the weight of water thus formed was determined. To his weighings I append the ratio between metallic zinc and 100 parts of water:

25.389 grm. Zn gave 6.928 grm. H_2O.	366.469
30.369 " 8.297 "	366.024
31.776 " 8.671 "	366.463

Mean, 366.319, $\pm$ .088

Hence Zn = 65.803, $\pm$ .020.

The second method adopted by Favre was to burn pure zinc oxalate, and to weigh the oxide and carbonic acid thus produced. From the ratio between these two sets of weights the atomic weight of zinc is easily deducible. From Favre's weighings, if CO_2 = 100, ZnO will be as given in the third column below:

7.796 grm. ZnO = 8.365 grm. CO_2.	93.198
7.342 " 7.883 "	93.137
5.2065 " 5.588 "	93.173

Mean, 93.169, $\pm$ .012

Hence Zn = 65.8395, $\pm$ .022.

---

* Ann. Chim. Phys., (3,) 10, 163. 1844.

A fourth combustion of the oxalate is omitted from the above series, having been rejected by Favre himself. In this the oxide formed was contaminated by traces of sulphide.

The four values for zinc now before us are so discordant that a combination of them after the usual method can have only a trifling significance. The following is the result thus obtained:

From Jacquelain's figures ___Zn = 66.072, ± .028
From Favre's water series___ " = 65.803, ± .020
From Favre's oxalate series__ " = 65.8395, ± .022
From Erdmann's figures____ " = 64.9045, ± .019

General mean_____ " = 65.557, ± .011

It will be seen that three of these values agree tolerably well, placing the atomic weight of zinc in the neighborhood of 66, while the other is, in round numbers, about a unit lower. This lower figure, however, has the smallest probable error, and it will be found also, upon careful consideration, that it is less likely than the others to be vitiated by experimental inaccuracies. Both chemically and mathematically it is the best.

Upon comparing Erdmann's results with those of Jacquelain two points are worth noticing: first, Erdmann worked with purer material than Jacquelain, although the latter applied corrections for the impurities which he knew were present; secondly, Erdmann calcined his zinc nitrate in a porcelain crucible, while Jacquelain used platinum. In the latter case it has been shown that portions of zinc may become reduced and alloy themselves with the platinum of the crucible. Hence a lower weight of oxide from a given quantity of zinc, a higher percentage of metal, and an increased atomic weight. This source of constant error has undoubtedly affected Jacquelain's experiments, and vitiated his results. In Erdmann's work no such errors seem to be present.

Over Favre's experiments Erdmann's have the important merit of simplicity. In the latter it is difficult to detect sources of error; in the former it is easy. In Favre's water

series it was essential that the hydrogen should first be thoroughly dried before combustion, and then that every trace of water formed should be collected. A trivial loss of hydrogen or of water would tend to increase the apparent atomic weight of zinc.

In the combustion of the zinc oxalate equally great difficulties are encountered. Here a variety of errors are possible, such as are due, for example, to impurity of material, to imperfect drying of the carbon dioxide, and to incomplete collection of the latter. It may not be easy to prove that such errors actually did creep into Favre's work, and yet their possibility hinders us from absolutely accepting his results.

All things considered, then, Erdmann's determination of the atomic weight of zinc is the one most entitled to credit, and must be taken for the present in lieu of the general mean deduced from all four of the values. This determination, $Zn = 64.9045, \pm .019$, becomes, if $O = 16$, 65.054.

CADMIUM.

The earliest determination of the atomic weight of this metal was by Stromeyer, who found that 100 parts of cadmium united with 14.352 of oxygen.* With our value for the atomic weight of oxygen these figures make $Cd = 111.227$. This result has now only a historical interest.

The more modern estimates of the atomic weight of cadmium are four in number, by v. Hauer, Lenssen, Dumas, and Huntington. Of these that by v. Hauer† comes first in chronological order. He heated pure anhydrous cadmium sulphate in a stream of dry hydrogen sulphide, and weighed the cadmium sulphide thus obtained. His results

---

* See Berz. Lehrbuch, 5th Ed., 3, 1219.
† Journ. für Prakt. Chem., 72, 350. 1857.

were as follows, with the percentage of CdS in CdSO₄ therefrom deduced:

7.7650 grm. CdSO₄ gave		5.3741 grm. CdS.		69.209 per cent.	
6.6086	"	4.5746	"	69.222	"
7.3821	"	5.1117	"	69.245	"
6.8377	"	4.7336	"	69.228	"
8.1956	"	5.6736	"	69.227	"
7.6039	"	5.2634	"	69.220	"
7.1415	"	4.9431	"	69.217	"
5.8245	"	4.0335	"	69.251	"
6.8462	"	4.7415	"	69.257	"

Mean, 69.231, ± .0042

Lenssen* worked upon pure cadmium oxalate, handling, however, only small quantities of material. This salt, upon ignition, leaves the following percentages of oxide:

.5128 grm. oxalate gave		.3281 grm. CdO.		63.982 per cent.	
.6552	"	.4193	"	63.996	"
.4017	"	.2573	"	64.053	"

Mean, 64.010, ± .014

Dumas† dissolved pure cadmium in hydrochloric acid, evaporated the solution to dryness, and fused the residue in hydrochloric acid gas. The cadmium chloride thus obtained was dissolved in water and titrated with a solution of silver after the usual manner. From Dumas' weighings I calculate the ratio between CdCl₂ and 100 parts of silver:

2.369 grm. CdCl₂ =		2.791 grm. Ag.		84.880	
4.540	"	5.348	"	84.892	
6.177	"	7.260	"	85.803	
2.404	"	2.841	"	84.618	
3.5325	"	4.166	"	84.794	
4.042	"	4.767	"	84.791	

Mean, 84.843, ± .026

Latest of all comes Huntington's‡ work, done under the direction of Professor J. P. Cooke. Bromide of cadmium

---

* Journ. für Prakt. Chem., 79, 281. 1860.

† Ann. Chem. Pharm., 113, 27. 1860.

‡ Proc. Amer. Acad., 1881.

was prepared by dissolving the carbonate in hydrobromic acid, and the product, dried at 200°, was purified by sublimation in a porcelain tube. Upon the compound thus obtained two series of experiments were made.

In one series the bromide was dissolved in water, and a quantity of silver not quite sufficient for complete precipitation of the bromine was then added in nitric acid solution. After the precipitate had settled, the supernatant liquid was titrated with a standard solution of silver containing one gramme to the litre. The precipitate was washed by decantation, collected by reverse filtration, and weighed. To the weighings I append the ratio between $CdBr_2$ and 100 parts of silver bromide:

1.5592 grm. CdBr₂ gave	2.1529 grm. AgBr.	Ratio,	72.423
* 3.7456	"	5.1724	"		72.415
2.4267	"	3.3511	"		72.415
* 3.6645	"	5.0590	"		72.435
* 3.7679	"	5.2016	"		72.437
2.7938	"	3.8583	"		72.410
* 1.9225	"	2.6552	"		72.405
3.4473	"	4.7593	"		72.433

Mean, 72.4216, ± .0028

The second series was like the first, except that the weight of silver needed to effect precipitation was noted, instead of the weight of silver bromide formed. In the experiments marked with an asterisk, both the amount of silver required and the amount of silver bromide thrown down were determined in one set of weighings. The third column gives the $CdBr_2$ proportional to 100 parts of silver:

* 3.7456 grm. CdBr₂ =	2.9715 grm. Ag.		126.051
5.0270	"	3.9874	"	126.072
* 3.6645	"	2.9073	"	126.045
* 3.7679	"	2.9888	"	126.067
* 1.9225	"	1.5248	"	126.082
2.9101	"	2.3079	"	126.093
3.6510	"	2.8951	"	126.110
3.9782	"	3.1551	"	126.088

Mean, 126.076, ± .0052

8

From the first series _____CdBr$_2$ == 271.49S, ± .032
From the second series___ " == 271.505, ± .027

General mean___ " == 271.502, ± .0215

Hence Cd = 111.966, ± .043.

According to Huntington's own calculations these experiments fix the ratio between silver, bromine, and cadmium as Ag : Br : Cd :: 10S : 80 : 112.31. This result militates strongly against Prout's hypothesis.

Upon combining all the determinations we get the following result:

v. Hauer_____Cd = 111.6S4, ± .040
Lenssen_____ " == 111.S03, ± .062
Dumas_____ " == 111.969, ± .065
Huntington_____ " == 111.966, ± .040

General mean_____ " == 111.S35, ± .024

Or, if O = 16, then Cd = 112.092.

It will be seen that Dumas and Huntington's determinations, both made with haloid salts of cadmium, agree with wonderful closeness, and so confirm each other. On the other hand, v. Hauer's data give a value for the atomic weight of cadmium which is much lower. Apparently, v. Hauer's method was good, and the reason for the discrepancy remains to be discovered. Until it is ascertained I prefer to use the above mean value for Cd, rather than to adopt one investigation and reject the others.

MERCURY.

In dealing with the atomic weight of mercury we may reject the early determinations by Sefström* and a large part of the work done by Turner.† The latter chemist, in addition to the data which will be cited below, gives figures

---

* Sefström. Berz. Lehrb., 5th Ed., 3, 1215. Work done in 1812.
† Phil. Trans., 1833, 531–535.

to represent the percentage composition of both the chlorides of mercury; but these results are neither reliable nor in proper shape to be used.

First in order we may consider the percentage composition of mercuric oxide, as established by Turner and by Erdmann and Marchand. In both investigations the oxide was decomposed by heat, and the mercury was accurately weighed. Gold leaf served to collect the last traces of mercurial vapor.

Turner gives four estimations.* Two represent oxide obtained by the ignition of the nitrate, and two are from commercial oxide. In the first two the oxide still contained traces of nitrate, but hardly in weighable proportions. A comparison of the figures from this source with the others is sufficiently conclusive on this point. The third column represents the percentage of mercury in HgO:

144.805 grains Hg	= 11.54 grains O.	92.619 per cent.
125.980 "	10.08 "	92.592 "
173.561 "	13.82 "	92.625 "
114.294 "	9.101 "	92.620 "

Mean, 92.614, ± .0050

In the experiments of Erdmann and Marchand† every precaution was taken to ensure accuracy. Their weighings, reduced to a vacuum standard, give the subjoined percentages:

82.0079 grm. HgO	gave 75.9347 grm. Hg.	92.594 per cent.
51.0320 "	47.2538 "	92.597 "
84.4996 "	78.2501 "	92.604 "
44.6283 "	41.3285 "	92.606 "
118.4066 "	109.6408 "	92.597 "

Mean, 92.5996, ± .0015

Combining, we have:

Turner	92.614,	± .0050
Erdmann and Marchand	92.5996,	± .0015
General mean	92.601,	± .0014

---

* Phil. Trans., 1833, 531–535.
† Journ. für Prakt. Chem., 31, 395. 1844.

With a view to establishing the atomic weight of sulphur Erdmann and Marchand also made a series of analyses of pure mercuric sulphide. These data are now best available for discussion under mercury. The sulphide was mixed with pure copper and ignited; mercury distilling over and copper sulphide remaining behind. Gold leaf was used to retain traces of mercurial vapor, and the weighings were reduced to vacuum :

34.3568 grm.	HgS gave	29.6207 grm. Hg.		86.215 per cent. Hg.	
24.8278	"	21.40295	"	86.206	"
37.2177	"	32.08416	"	86.207	"
80.7641	"	69.6372	"	86.223	"

Mean, 86.2127, $\pm$ .0027

For the percentage of mercury in mercuric chloride we have data by Turner, Millon, and Svanberg. Turner,[*] in addition to some precipitations of mercuric chloride by silver nitrate, gives two experiments in which the compound was decomposed by pure stannous chloride, and the mercury thus set free was collected and weighed. The results were as follows :

44.782 grains Hg =	15.90 grains Cl.		73.798 per cent.	
73.09	"	25.97	"	73.784

Mean, 73.791, $\pm$ .005

Millon[†] purified mercuric chloride by solution in ether and sublimation, and then subjected it to distillation with lime. The mercury was collected as in Erdmann and Marchand's experiments. Percentages of metal as follows :

73.87
73.81
73.83
73.87

Mean, 73.845, $\pm$ .010

Svanberg,[‡] following the general method of Erdmann

* Phil. Trans., 1833, 531-535.
† Ann. Chim. Phys., (3,) 18, 345 1846.
‡ Journ. für Prakt. Chem., 45, 472. 1848.

and Marchand, made three distillations of mercuric chloride with lime, and got the following results:

12.048 grm.	HgCl₂ gave	8.889	grm. Hg.	73.780 per cent.
12.529	"	9.2456	"	73.794	"
12.6491	"	9.3363	"	73.810	"

Mean, 73.795, ± .006

Combining these series we have:

Turner _____ 73.791, ± .005
Millon_____ 73.845, ± .010
Svanberg _____ 73.795, ± .006

General mean _____ 73.798, ± .0034

In this mean Turner's figures undoubtedly receive undue weight, for, on experimental grounds, they are probably inferior to both of the other series. It is better, however, that the general mean should remain as it is, than that I should deal arbitrarily with any of the data.

We now have three figures to calculate from:

Per cent. of Hg in HgO_____ 92.601, ± .0014
" HgS_____ 86.2127, ± .0027
" HgCl₂ _____ 73.798, ± .0034

These give us three values for the atomic weight of mercury and a general mean as follows:

From HgO_____Hg = 199.786, ± .059
From HgS_____ " = 200.016, ± .088
From HgCl₂ _____ " = 199.239, ± .086

General mean _____ " = 199.712, ± .042

If $O = 16$, then this becomes 200.171.

CHROMIUM.

Concerning the atomic weight of chromium there has been much discussion, and many experimenters have sought to establish the true value. The earliest work upon it hav-

ing any importance was that of Berzelius,* in 1818 and
1826, which led to results much in excess of the correct
figure. His method consisted in precipitating a known
weight of lead nitrate with an alkaline chromate and weigh-
ing the lead chromate thus produced. The error in his de-
termination arose from the fact that lead chromate, except
when thrown down from very dilute solutions, carries with
it minute quantities of alkaline salts, and so has its apparent
weight notably increased. When dilute solutions are used,
a trace of the precipitate remains dissolved, and the weight
obtained is too low. In neither case is the method trust-
worthy.

In 1844 Berzelius' results were first seriously called in
question. The figure for chromium deduced from his ex-
periments was somewhat over 56; but Peligot† now showed,
by his analyses of chromous acetate and of the chlorides of
chromium, that the true number was near 52.5. Unfortu-
nately, Peligot's work, although good, was published with
insufficient details to be useful here. For chromous acetate
he gives the percentages of carbon and hydrogen, but not
the actual weights of salt, carbon dioxide, and water from
which they were calculated. His figures vary considerably
moreover; enough to show that their mean would carry but
little weight when combined with the more explicit data
furnished by other chemists.

Jacquelain's‡ work we may omit entirely. He gives an
atomic weight for chromium which is notoriously too low,
and prints none of the numerical details upon which his
result rests. The researches which particularly command
our attention are those of Berlin, Moberg, Lefort, Wilden-
stein, Kessler, and Siewert.

Among the papers upon the atomic weight under consid-
eration that by Berlin is one of the most important.‖ His
starting point was normal silver chromate; but in one ex-

---

* Schweigg. Journ., 22, 53, and Poggend. Annal., 8, 22.
† Compt. Rend., 19, 609 and 734; 20, 1187; 21, 74.
‡ Compt. Rend., 24, 679.   1847.
‖ Journ. für Prakt. Chem., 37, 509, and 38, 149.   1846.

periment the anhydrochromate $Ag_2Cr_2O_7$ was used. These salts, which are easily obtained in a perfectly pure condition, were reduced in a large flask by means of hydrochloric acid and alcohol. The chloride of silver thus formed was washed by decantation, dried, fused, and weighed without transfer. The united washings were supersaturated with ammonia, evaporated to dryness, and the residue treated with hot water. The resulting chromic oxide was then collected upon a filter, dried, ignited, and weighed. The results were as follows:

4.6680 grm. Ag_2CrO_4 gave	4.027 grm. AgCl and	1.0754 grm. Cr_2O_3.	
3.4568 "	2.983 "	.7960 "	
2.5060 "	2.1605 "	.5770 "	
2.1530 "	1.8555 "	.4945 "	
4.3335 grm. $Ag_2Cr_2O_7$ gave	2.8692 "	1.5300 "	

From these weighings three values are calculable for the atomic weight of chromium. The three ratios upon which these values depend we will consider separately; taking first that between the chromic oxide and the original silver salt. In the four analyses of the normal chromate the percentages of Cr_2O_3 deducible from Berlin's weighings are as follows:

23.037
23.027
23.025
22.968
———
Mean, 23.014, ± .011

And from the single experiment with $Ag_2Cr_2O_7$ the percentage of Cr_2O_3 was 35.306.

For the ratio between Ag_2CrO_4 and AgCl, putting the latter at 100, we have for the former:

115.917
115.883
115.992
116.033
———
Mean, 115.956, ± .023

In the single experiment with anhydrochromate 100 AgCl is formed from 151.035 $Ag_2Cr_2O_7$.

Finally, for the ratio between AgCl and Cr_2O_3, the five experiments of Berlin give, for 100 parts of the former, the following quantities of the latter:

$$26.705$$
$$26.685$$
$$26.707$$
$$26.650$$
$$26.662$$

Mean, 26.682, $\pm$ .0076

These results will be discussed in connection with the work of other investigators at the end of this chapter.

In 1848 the researches of Moberg[*] appeared. His method simply consisted in the ignition of anhydrous chromic sulphate and of ammoniacal chrome alum, and the determination of the amount of chromic oxide thus left as residue. In the sulphate, $Cr_2(SO_4)_3$, the subjoined percentages of Cr_2O_3 were found. The brackets indicate two different samples of material, to which, however, we are justified in ascribing equal value:

.542 grm. sulphate gave	.212 grm. Cr_2O_3.	39.114 per cent.	⎱
1.337 "	.523 "	39.117 "	⎰
.5287 "	.207 "	39.153 "	
1.033 "	.406 "	39.303 "	⎱
.868 "	.341 "	39.286 "	⎰

Mean, 39.1946, $\pm$ .0280

From the alum, $(NH_4)_2Cr_2(SO_4)_2.24H_2O$, we have these percentages of Cr_2O_3. The first series represents a salt long dried under a bell jar at a temperature of 18°. The crystals taken were clear and transparent, but may possibly have lost traces of water,[†] which would tend to increase the atomic weight found for chromium. In the second series the salt was carefully dried between folds of filter paper, and

---

[*] Journ. für Prakt. Chem., 43, 114.

[†] This objection is suggested by Berlin in a short note upon Lefort's paper. Journ. für Prakt. Chem., 71, 191.

results were obtained quite near those of Berlin. Both of these series are discussed together, neither having a remarkable value:

1.3185 grm. alum gave	.213	grm. Cr_2O_3.	16.155 per cent.	⎫
.7987 "	.129	"	16.151 "	⎟
1.0185 "	.1645	"	16.151 "	⎟
1.0206 "	.1650	"	16.167 "	⎟
.8765 "	.1420	"	16.201 "	⎟
.7680 "	.1242	"	16.172 "	⎬
1.6720 "	.2707	"	16.190 "	⎟
.5410 "	.0875	"	16.174 "	⎟
1.2010 "	.1940	"	16.153 "	⎟
1.0010 "	.1620	"	16.184 "	⎭
.7715 "	.1235	"	16.007 "	⎫
1.374 "	.2200	"	16.012 "	⎬

Mean, 16.143, $\pm$ .0125

The determinations made by Lefort* are even less valuable than those by Moberg. This chemist started out from pure barium chromate, which, to thoroughly free it from moisture, had been dried for several hours at 250°. The chromate was dissolved in pure nitric acid, the barium thrown down by sulphuric acid, and the precipitate collected upon a filter, dried, ignited, and weighed in the usual manner. The natural objection to the process is that traces of chromium may be carried down with the sulphate, thus increasing its weight. In fact, Lefort's results are somewhat too high. Calculated from his weighings, 100 parts of $BaSO_4$ correspond to the amounts of $BaCrO_4$ given in the third column:

1.2615 grm. $BaCrO_4$ gave	1.1555 grm. $BaSO_4$.	109.174
1.5895 "	1.4580 "	109.019
2.3255 "	2.1340 "	108.974
3.0390 "	2.7855 "	109.101
2.3480 "	2.1590 "	108.754
1.4230 "	1.3060 "	108.708
1.1975 "	1.1005 "	108.814
3.4580 "	3.1690 "	109.119
2.0130 "	1.8430 "	109.224

---

* Journ. für Prakt. Chem., 51, 261. 1850.

3.5570 grm. BaCrO$_4$ gave	3.2710 grm. BaSO$_4$.	108.744
1.6470 "	1.5060 "	109.363
1.8240 "	1.6725 "	109.058
1.6950 "	1.5560 "	108.933
2.5960 "	2.3870 "	108.756

Mean, 108.9815, $\pm$ .0369

Wildenstein,* in 1853, also made barium chromate the basis of his researches. A known weight of pure barium chloride was precipitated by a neutral alkaline chromate, and the precipitate allowed to settle until the supernatant liquid was perfectly clear. The barium chromate was then collected on a filter, washed with hot water, dried, gently ignited, and weighed. Here again arises the objection that the precipitate may have retained traces of alkaline salts, and again we find deduced an atomic weight which is too high. One hundred parts BaCrO$_4$ correspond to BaCl$_2$ as follows:

81.87	81.57
81.80	81.75
81.61	81.66
81.78	81.83
81.52	81.66
81.84	81.80
81.85	81.66
81.70	81.85
81.68	81.57
81.54	81.83
81.66	81.71
81.55	81.63
81.81	81.56
81.86	81.58
81.54	81.67
81.68	81.84

Mean, 81.702, $\pm$ .014

Next in order we have to consider two papers by Kessler, who employed a peculiar volumetric method entirely his own. In brief, he compared the oxidizing power of potassium anhydrochromate with that of the chlorate, and from

---

* Journ. für Prakt. Chem., 59, 27.

his observations deduced the ratio between the molecular weights of the two salts.

In his earlier paper* the mode of procedure was about as follows: The two salts, weighed out in quantities having approximate chemical equivalency, were placed in two small flasks, and to each was added 100 cc. of a ferrous chloride solution and 30 cc. hydrochloric acid. The ferrous chloride was added in trifling excess, and, when action ceased, the amount unoxidized was determined by titration with a standard solution of anhydrochromate. As in each case the quantity of ferrous chloride was the same, it became easy to deduce from the data thus obtained the ratio in question. I have reduced all of his somewhat complicated figures to a simple common standard, and give below the amount of chromate equivalent to 100 of chlorate:

$$120.118$$
$$120.371$$
$$120.138$$
$$120.096$$
$$120.241$$
$$120.181$$

Mean, 120.191, $\pm$ .028

In his later paper† Kessler substituted arsenic trioxide for the iron solution. In one series of experiments the quantity of anhydrochromate needed to oxidize 100 parts of the arsenic trioxide was determined, and in another the latter substance was similarly compared with the chlorate. The subjoined columns give the quantity of each salt proportional to 100 of As_2O_3:

$K_2Cr_2O_7$.	$KClO_3$.
98.95	41.156
98.94	41.116
99.17	41.200
98.98	41.255
99.08	41.201
99.15	41.086
	41.199
Mean, 99.045, $\pm$ .028	41.224

---

* Poggend. Annal., 95, 208. 1855.
† Poggend. Annal., 113, 137. 1861.

$$KClO_3.$$

41.161
41.193
41.149
41.126

Mean, 41.172, $\pm$ .009

From the data given in the earlier paper, if we use our recent values for chlorine, potassium, and oxygen,

$$K_2Cr_2O_7 = 293.937, \pm .086$$

And from the later,   " $= 294.159, \pm .119$

General mean,   " $= 294.013, \pm .0697$

Finally, we come to the determinations published by Siewert,[*] whose work does not seem to have attracted general attention. He, reviewing Berlin's work, found that upon reducing silver chromate with hydrochloric acid and alcohol, the chromic chloride solution always retained traces of silver chloride dissolved in it. These could be precipitated by dilution with water; but, in Berlin's process, they naturally came down with the chromium hydroxide, making the weight of the latter too high. Hence too large a value for the atomic weight of chromium. In order to find a more correct value Siewert resorted to the analysis of sublimed, violet, chromic chloride. This salt he fused with sodium carbonate and a little nitre, treated the fused mass with water, and precipitated from the resulting solution the chlorine by silver nitrate in presence of nitric acid. The weight of the silver chloride thus obtained, estimated after the usual manner, gave means for calculating the atomic weight of chromium. His figures, reduced to a common standard, give, as proportional to 100 parts of chloride of silver, the quantities of chromic chloride stated in the third of the subjoined columns:

---

[*] Zeitschrift Gesammt. Wissenschaften, 17, 530.   1861.

.2367 grm. Cr_2Cl_6 gave	.6396 grm. AgCl.		37.007
.2946	"	.7994	"	36.853
.2593	"	.7039	"	36.838
.4935	"	1.3395	"	36.842
.5850	"	1.5884	"	36.830
.6511	"	1.76681	"	36.852
.5503	"	1.49391	"	36.836

Mean, 36.865, ± .0158

The first of these figures varies so widely from the others that we are justified in rejecting it; in which case the mean becomes 36.842, ± .0031.

Siewert also made two analyses of silver anhydrochromate by the following process. The salt, dried at 120°, was dissolved in nitric acid. The silver was then thrown down by hydrochloric acid, and, in the filtrate, chromium hydroxide was precipitated by ammonia. Reduced to a uniform standard, we find from his results, corresponding to 100 parts of AgCl, $Ag_2Cr_2O_7$, as in the last column:

.7866 grm. $Ag_2Cr_2O_7$ gave .52202 AgCl and .2764 Cr_2O_3.　150.684
1.089　　　　　"　　　　　.72249　　"　　.3840　"　　150.729

Mean, 150.706, ± .015

Giving Berlin's single estimation equal weight with one of these, and combining, we get a general mean of 150.816, ± .074.

Siewert's percentages of Cr_2O_3 obtained from $Ag_2Cr_2O_7$, are as follows, calculated from the above weighings.

35.139
35.262

Mean, 35.2005, ± .0415

Combining, as before, with Berlin's single result, giving the latter equal weight with one of these, we have a general mean of 35.236, ± .0335.

For the ratio between silver chloride and chromic oxide, Siewert's two analyses of the anhydrochromate come out as follows. For 100 parts of AgCl we have of Cr_2O_3:

$$52.948$$
$$53.150$$

Mean, 53.049, ± .068

This figure, reduced to the standard of Berlin's work on the monochromate, becomes 26.525, ± .034. Berlin's mean was 26.682, ± .0076. The two means, combined, give a general mean of 26.676, ± .074.

We may now consider the ratios before us, which are as follows:

(1.) Percentage Cr_2O_3 from Ag_2CrO_4, 23.014, ± .011
(2.) Percentage Cr_2O_3 from $Ag_2Cr_2O_7$, 35.236, ± .0335
(3.) $AgCl : Ag_2CrO_4 :: 100 : 115.956$, ± .023
(4.) $AgCl : Ag_2Cr_2O_7 :: 100 : 150.816$, ± .074
(5.) $AgCl : Cr_2O_3 :: 100 : 26.676$, ± .0074
(6.) Percentage Cr_2O_3 in chromic sulphate, 39.1946, ± .0280
(7.) Percentage Cr_2O_3 in ammonia chrome alum, 16.143, ± .0125
(8.) $BaSO_4 : BaCrO_4 :: 100 : 108.9815$, ± .0369
(9.) $BaCrO_4 : BaCl_2 :: 100 : 81.702$, ± .014
(10.) Molecular weight of $K_2Cr_2O_7$, 294.013, ± .0697
(11.) $AgCl : CrCl_3 :: 100 : 36.842$, ± .0031

From these ratios we can at once deduce five values for the molecular weight of Cr_2O_3, as follows:

From (1)---------------$Cr_2O_3 = 152.612$, ± .074
"   (2)--------------- "   = 151.905, ± .165
"   (5)--------------- "   = 152.634, ± .044
"   (6)--------------- "   = 154.464, ± .135
"   (7)--------------- "   = 154.512, ± .125

General mean____ "   = 152.855, ± .034

For barium chromate we get two values:

From (8)-------------$BaCrO_4 = 253.494$, ± .094
"   (9)-------------- "   = 253.976, ± .067

General mean___ "   = 253.816, ± .054

From (3) we get $Ag_2CrO_4 = 331.739$, ± .070
"   (4)   " $Ag_2Cr_2O_7 = 431.470$, ± .215
"   (11)   " $CrCl_3 = 158.102$, ± .018

Finally, from these intermediate data we derive six values for the atomic weight of chromium:

From	$BaCrO_4$	$Cr = 53.200, \pm .064$	
"	Cr_2O_3	" $= 52.482, \pm .018$	
"	Ag_2CrO_4	" $= 52.536, \pm .074$	
"	$Ag_2Cr_2O_7$	" $= 52.188, \pm .109$	
"	$K_2Cr_2O_7$	" $= 52.116, \pm .078$	
"	$CrCl_3$	" $= 51.992, \pm .047$	
	General mean	" $= 52.453, \pm .015$	
	Or, if $O = 16$	" $= 52.574$	

On account of the wide discrepancies between different data, and of the known constant errors vitiating some of the series of experiments, the foregoing general mean can have but little real value. In fact, a careful consideration of all the work represented in it will show that the most accurate estimate of the atomic weight of chromium must be deduced from the experiments of either Berlin, Kessler, or Siewert. Berlin's figures, taken by themselves, and combined, give, if the single analysis of silver anhydrochromate be assigned equal weight with a single analysis in the monochromate series, $Cr = 52.389, \pm .019$; or, if $O = 16$, $Cr = 52.511$.

Siewert's results, both for chromic chloride and the silver anhydrochromate, properly combined, give $Cr = 52.009$, $\pm .025$. If $O = 16$, this value becomes $Cr = 52.129$. In brief, the atomic weight of chromium may be nearly 52.5, or it may be 52. Only a revision of all the experiments could enable us to decide positively between these values. But as Siewert has pointed out probable sources of error in Berlin's work, I am inclined to give preference to the lower value.

MANGANESE.

Rejecting the early experiments of J. Davy and of Arf- vedson, the first determinations of the atomic weight of manganese which we encounter are those of Turner[*] and of Berzelius.[†] Both of these chemists used the same method.

---

[*] Trans. Roy. Soc. Edin., 11, 143. 1831.

[†] Lehrbuch, 5th Ed., 3, 1224.

The chloride of manganese was fused in a current of dry hydrochloric acid, and subsequently precipitated with a solution of silver. From the subjoined weighings I calculate the ratio given in the third column between $MnCl_2$ and 100 parts of AgCl:

4.20775 grm. $MnCl_2$	=	9.575 grm. AgCl.	43.945	Berzelius.
3.063 "	=	6.96912 "	43.950	
12.47 grains $MnCl_2$	=	28.42 grains AgCl.	43.878—Turner.	

Mean, 43.924, $\pm$ .015

Hence the molecular weight of $MnCl_2$ is 125.662, $\pm$ .045.

Many years later Dumas * also made the chloride of manganese the starting point of some atomic weight determinations. The salt was fused in a current of hydrochloric acid, and afterwards titrated with a standard solution of silver in the usual way. 100 parts of Ag are equivalent to the quantities of $MnCl_2$ given in the third column:

3.3672 grm. $MnCl_2$	=	5.774 grm. Ag.	58.317
3.0872 "		5.293 "	58.326
2.9671 "		5.0875 "	58.321
1.1244 "		1.928 "	58.320
1.3134 "		2.251 "	58.321

Mean, 58.321, $\pm$ .001

Hence $MnCl_2$ = 125.594, $\pm$ .011. This, combined with Berzelius and Turner's figures, gives $MnCl_2$ = 125.598, $\pm$ .011. And Mn = 54.858, $\pm$ .031.

An entirely different method of investigation was followed by v. Hauer,† who, as in the case of cadmium, ignited the sulphate in a stream of sulphuretted hydrogen, and determined the quantity of sulphide thus formed. I subjoin his weighings, and also the percentage of MnS in $MnSO_4$ as calculated from them:

---

* Ann. Chem. Pharm., 113, 25. 1860.
† Journ. für Prakt. Chem., 72, 360. 1857.

4.0626 grm. MnSO$_4$ gave 2.3425 grm. MnS.			57.660 per cent.
4.9367	"	2.8442 "	57.613 "
5.2372	"	3.0192 "	57.649 "
7.0047	"	4.0347 "	57.600 "
4.9175	"	2.8297 "	57.543 "
4.8546	"	2.7955 "	57.585 "
4.9978	"	2.8799 "	57.625 "
4.6737	"	2.6934 "	57.629 "
4.7240	"	2.7197 "	57.572 "

Mean, 57.608, ± .008

Hence Mn = 54.785, ± .031.

This method of v. Hauer's, which seemed to give good results with cadmium, is, according to Schneider,[*] inapplicable to manganese; for the reason that the sulphide of the latter metal is liable to be contaminated with traces of oxysulphide. Such an impurity would bring the atomic weight out too high. The results of two different processes, one carried out by himself and the other in his laboratory by Rawack, are given by Schneider in this paper.

Rawack reduced manganoso-manganic oxide to manganous oxide by ignition in a stream of hydrogen, and weighed the water thus formed. From his weighings I get the values in the third column, which represent the Mn$_3$O$_4$ equivalent to one gramme of water:

4.149 grm. Mn$_3$O$_4$ gave 0.330 grm. H$_2$O.			12.5727
4.649	"	.370 "	12.5643
6.8865	"	.5485 "	12.5552
7.356	"	.5855 "	12.5636
8.9445	"	.7135 "	12.5361
11.584	"	.9225 "	12.5572

Mean, 12.5582, ± .0034

Hence Mn = 53.911, ± .026.

Here the most obvious source of error lies in the possible loss of water. Such a loss, however, would increase the apparent atomic weight of manganese; but we see that the value found is much lower than that obtained either by Dumas or v. Hauer.

---

* Poggend. Annal., 107, 605.

9

Schneider himself effected the combustion of manganous oxalate with oxide of copper. The salt was not absolutely dry, so that it was necessary to collect both water and carbon dioxide. Then, upon deducting the weight of water from that of the original material, the weight of anhydrous oxalate was easily ascertained. Subtracting from this the CO_2, we get the weight of Mn. If we put $CO_2 = 100$, the quantities of manganese equivalent to it will be found in the last column:

1.5075 grm. oxalate gave	.306 grm. H_2O and	.7445 grm. CO_2.		61.3835
2.253 "	.4555 "	1.1135 "		61.4291
3.1935 "	.652 "	1.5745 "		61.4163
5.073 "	1.028 "	2.507 "		61.3482

Mean, 61.3943, $\pm$ .0122

Hence Mn = 53.904, $\pm$ .014.

This result agrees beautifully with the value calculated from Rawack's experiments.

Now to combine the four independent values which we have thus far obtained:

From $MnCl_2$ ----------------Mn = 54.858, $\pm$ .031
   " $MnSO_4$-------------- " = 54.785, $\pm$ .031
   " Mn_3O_4 -------------- " = 53.911, $\pm$ .026
   " MnC_2O_4-------------- " = 53.904, $\pm$ .014
        General mean_____ " = 54.128, $\pm$ .011
        If O = 16 _____ " = 54.251

The considerations already cited, however, go to show that this general mean must be slightly affected by some plus constant error. It is probable, therefore, that a more correct figure will result from rejecting the first and second values in the above combination, and taking the data furnished by Rawack and Schneider alone. Combining their figures, we get as follows. Mn = 53.906, $\pm$ .012. Or, if O = 16, Mn = 54.029.

Since the foregoing calculations were made Dewar and Scott* have reported the following experiments. From the

---

* Nature, Sept. 15, 1881, p. 470.

complete analysis of silver permanganate, putting $Ag = 108$ and $O = 16$, they find in three estimations $Mn = 55.51$, 54.04, and 54.45. From the analysis of pure MnO_2, made from the nitrate, $Mn = 53.3$ to 53.6. Up to the date of writing a detailed account of the methods employed has not been published.

IRON.

The atomic weight of iron has been determined almost exclusively from the composition of ferric oxide. Beyond this there are only a few comparatively unimportant experiments by Dumas relative to ferrous and ferric chlorides.

Most of the earlier data relative to the percentage of metal and oxygen in ferric oxide we may reject at once, as set aside by later investigations. Among this no longer valuable material there is a series of experiments by Berzelius, another by Döbereiner, and a third by Capitaine. The work done by Stromeyer and by Wackenroder was probably good, but I am unable to find its details. The former found 30.15 per cent. of oxygen in the oxide under consideration, while Wackenroder obtained figures ranging from a minimum of 30.01 to a maximum of 30.38 per cent.*

In 1844 Berzelius† published two determinations of the ratio in question. He oxidized iron by means of nitric acid, and weighed the oxide thus formed. He thus found that when $O = 100$ $Fe = 350.27$ and 350.369.

Hence the following percentages of Fe in Fe_2O_3.

$$70.018$$
$$70.022$$

Mean, $70.020, \pm .0013$

About the same time Svanberg and Norlin‡ published

---

* For additional details concerning these earlier papers I must refer to Oudemans' monograph, pp. 140, 141.

† Ann. Chem. Pharm., 50, 432. Berz. Jahresb., 25, 43.

‡ Berzelius' Jahresbericht, 25, 42.

two elaborate series of experiments; one relating to the synthesis of ferric oxide, the other to its reduction. In the first set pure piano-forte wire was oxidized by nitric acid, and the amount of oxide thus formed was determined. The results were as follows:

1.5257 grm. Fe gave	2.1803 grm. Fe$_2$O$_3$.	69.977 per cent. Fe.
2.4051 "	3.4390 "	69.936 "
2.3212 "	3.3194 "	69.928 "
2.32175 "	3.3183 "	69.968 "
2.2772 "	3.2550 "	69.960 "
2.4782 "	3.5418 "	69.970 "
2.3582 "	3.3720 "	69.935 "

Mean, 69.9534, ± .0050

In the second series ferric oxide was reduced by ignition in a current of hydrogen, yielding the subjoined percentages of metal:

2.98353 grm. Fe$_2$O$_3$ gave	2.08915 grm. Fe.	70.025 per cent.
2.41515 "	1.6910 "	70.015 "
2.99175 "	2.09455 "	70.014 "
3.5783 "	2.505925 "	70.030 "
4.1922 "	2.9375 "	70.072 "
3.1015 "	2.17275 "	70.056 "
2.6886 "	1.88305 "	70.036 "

Mean, 70.0354, ± .0055

It is evident that one or both of these series must be vitiated by constant errors, and that these probably arise from impurities in the materials employed. Impurities in the wire taken for the oxidation series could hardly have been altogether avoided, and in the reduction series it is possible that weighable traces of hydrogen may have been retained by the iron. At all events it is probable that the errors of both series are in contrary directions, and, therefore, in some measure compensatory.

In 1844 there was also published an important paper by Erdmann and Marchand.* These chemists prepared ferric oxide by the ignition of pure ferrous oxalate, and submitted

---

* Journ. für Prakt. Chem., 33, 1.

it to reduction in a stream of hydrogen. Two sets of results were obtained with two different samples of ferrous oxalate, prepared by two different methods. For present purposes, however, it is not necessary to discuss these sets separately. The percentages of iron in Fe_2O_3 come out as follows:

$$
\left.\begin{array}{l}
70.013 \\
69.962 \\
69.979 \\
70.030 \\
69.977
\end{array}\right\} \text{A.}
$$

$$
\left.\begin{array}{l}
70.044 \\
70.015 \\
70.055
\end{array}\right\} \text{B.}
$$

Mean, 70.0094, ± .0080

In 1850 Maumené's[*] results appeared. He dissolved pure iron wire in aqua regia, precipitated with ammonia, filtered off the precipitate, washed thoroughly, ignited, and weighed, after the usual methods of quantitative analysis. The percentages of Fe in Fe_2O_3 are given in the third column:

1.482 grm. Fe gave	2.117 grm. Fe_2O_3.		70.005 per cent.	
1.452 "	2.074	"	70.010	"
1.3585 "	1.941	"	69.990	"
1.420 "	2.0285	"	70.002	"
1.492 "	2.1315	"	69.998	"
1.554 "	2.220	"	70.000	"

Mean, 70.0008, ± .0019

Two more results, obtained by Rivot[†] through the reduction of ferric oxide in hydrogen, remain to be noticed. The percentages are:

$$
\begin{array}{l}
69.31 \\
69.35
\end{array}
$$

Mean, 69.33, ± .013

We have thus before us six series of results, which we may now combine.

---

[*] Compt. Rend., Oct. 17, 1850.
[†] Ann. Chem. Pharm., 78, 214. 1851.

Berzelius-------------------------	70.020, ± .0013
Erdmann and Marchand----------	70.0094, ± .0080
Svanberg and Norlin, Oxyd. -----	69.9534, ± .0050
" Reduc. ---	70.0354, ± .0055
Maumené ---------------------------	70.0008, ± .0019
Rivot------- ------ -------------	69.33, ± .013
General mean-------------	70.0075, ± .0010

From this we get $Fe = 55.891, \pm .012$; or, if $O = 16$, this becomes 56.0195.

Dumas'[*] results, obtained from the chlorides of iron, are of so little weight that they might safely be omitted from our present discussion. For the sake of completeness, however, we will include them.

Pure ferrous chloride, ignited in a stream of hydrochloric acid gas, was dissolved in water and titrated with a silver solution in the usual way. One hundred parts of silver are equivalent to the amounts of $FeCl_2$ given in the third column:

3.677 grm. $FeCl_2$ = 6.238 grm. Ag.		58.945
3.924 " = 6.675 "		58.787
		Mean, 58.866, ± .053

Ferric chloride, titrated in the same way, gave these results:

1.179 grm. Fe_2Cl_6 = 2.3475 grm. Ag.		50.224
1.242 " 2.471 "		50.263
		Mean, 50.2435, ± .0132

These give us two additional values for Fe, as follows:

From $FeCl_2$------ ----------- Fe = 56.028. ± .119
" Fe_2Cl_6 ------------ --- " = 56.189, ± .062

Combining these with the value deduced from the composition of Fe_2O_3, $Fe = 55.891, \pm .012$, we get this general mean, $Fe = 55.913, \pm .012$. If $O = 16$, this becomes $Fe = 56.042$.

---

[*] Ann. Chem. Pharm.. 113. 26. 1860.

COPPER.

The atomic weight of copper has been chiefly determined from the composition of the black oxide and the anhydrous sulphate. In dealing with the first named compound all experimenters have agreed in reducing it with a current of hydrogen, and weighing the metal thus set free.

The earliest experiments of any value were those of Berzelius,[*] whose results were as follows:

7.68075 grm. CuO lost 1.55 grm. O.	79.820 per cent. Cu in CuO.	
9.6115 " 1.939 "	79.826 " "	

Mean, 79.823, $\pm$ .002

Erdmann and Marchand,[†] who come next in chronological order, corrected their results for weighing in air. Their weighings, thus corrected, give us the subjoined percentages of metal in CuO:

63.8962 grm. CuO gave 51.0391 grm. Cu.	79.878 per cent.	
65.1590 " 52.0363 "	79.860 "	
60.2878 " 48.1540 "	79.874 "	
46.2700 " 36.9449 "	79.846 "	

Mean, 79.8645, $\pm$ .0038

Still later we find a few analyses by Millon and Commaille.[‡] These chemists not only reduced the oxide by hydrogen, but they also weighed, in addition to the metallic copper, the water formed in the experiments. In three determinations the results were as follows:

6.7145 grm. CuO gave 5.3565 grm. Cu and 1.5325 grm. H_2O.	79.775 per cent.	
3.3945 " 2.7085 " .7680 "	79.791 "	
2.7880 " 2.2240 grm. Cu.	79.770 "	

Mean, 79.7787, $\pm$ .0043

For the third of these analyses the water estimation was not made, but for the other two it yielded results which, in

---

[*] Poggend. Annal., 8, 177.

[†] Journ. für Prakt. Chem., 31, 389. 1844.

[‡] Fresenius' Zeitschrift, 2, 475. 1863.

the mean, would make the atomic weight of copper 63.087, ± .222. This figure has so high a probable error that we need not consider it further.

The results obtained by Dumas[*] are wholly unavailable. Indeed, he does not even publish them in detail. He merely says that he reduced copper oxide, and also effected the synthesis of the subsulphide, but without getting figures which were wholly concordant. He puts Cu = 63.5.

Latest of all, and probably the best also, we have the determinations by Hampe.[†] First, he attempted to estimate the atomic weight of copper by the quantity of silver which the pure metal could precipitate from its solutions. This attempt failed to give satisfactory results, and he fell back upon the old method of reducing the oxide. From ten to twenty grammes of material were taken in each experiment, and the weights were reduced to a vacuum standard:

20.3260 grm. CuO gave	16.2279 grm. Cu.	79.838 per cent.
20.68851 "	16.51669 "	79.835 "
10.10793 "	8.06926 "	79.831 "

Mean, 79.8347, ± .0013

Hampe also determined the quantity of copper in the anhydrous sulphate, $CuSO_4$. From 40 to 45 grammes of the salt were taken at a time, the metal was thrown down by electrolysis, and the weights were all corrected. I subjoin the results:

40.40300 grm. $CuSO_4$ gave	16.04958 grm. Cu.	39.724 per cent.
44.64280 "	17.73466 "	39.726 "

Mean, 39.725, ± .0007

We now have four series of experiments upon copper oxide, as follows:

Berzelius	79.823,	± .0020
Erdmann and Marchand	79.8645,	± .0038
Millon and Commaille	79.7787,	± .0043
Hampe	79.8347,	± .0013
General mean	79.830,	± .0010

---

[*] Ann. d. Chim. et Phys., (3.) 55, 129.

[†] Fresenius' Zeitschrift, 13, 352.

For copper we have—

$$
\begin{array}{ll}
\text{From composition of } CuO \dots\dots Cu = 63.181, \pm .036 \\
\text{``} \quad CuSO_4, \text{ (Hampe)} \dots\dots \text{``} = 63.171, \pm .012 \\
\text{General mean} \dots\dots \text{``} = 63.173, \pm .011
\end{array}
$$

If $O = 16$, then Cu becomes $= 63.318$.

The close agreement between the two independent values for Cu is certainly very striking. It will be seen that Hampe's two estimates upon the sulphate carry (perhaps accidentally) much greater weight than all the experiments upon the oxide. This might seem like giving them undue credit, were it not for the fact of the remarkable concordance of the results above referred to. Either estimate for Cu would be valid without the other.

MOLYBDENUM.

If we leave out of account the inaccurate determination made by Berzelius,[*] we shall find that the data for the atomic weight of molybdenum lead to two independent estimates of its value; one near 92, the other near 96. The earlier results found by Berlin and by Svanberg and Struve lead to the lower number; the more recent work of Debray, Dumas, and Lothar Meyer sustains the higher. The latter value is the more probable, although both may be vitiated by constant errors in opposite directions.

The earliest investigation which we need especially to consider is that of Svanberg and Struve.[†] These chemists tried a variety of different methods, but finally based their conclusions upon the two following: first, molybdenum trioxide was fused with potassium carbonate, and the carbon dioxide which was expelled was estimated; secondly, molybdenum disulphide was converted into the trioxide by

---

[*] Poggend. Annal., 8, 1. 1826.
[†] Journ. für Prakt. Chem., 44, 301. 1848.

roasting, and the ratio between the weights of the two substances was determined.

By the first method it was found that 100 parts of MoO_3 will expel the following quantities of CO_2:

$$31.4954$$
$$31.3749$$
$$31.4705$$

Mean, 31.4469, $\pm$ .0248

The carbon dioxide was determined simply from the loss of weight when the weighed quantities of trioxide and carbonate were fused together. It is plain that if, under these circumstances, a little of the trioxide should be volatilized, the total loss of weight would be slightly increased. A constant error of this kind would tend to bring out the atomic weight of molybdenum too low.

By the second method, the conversion by roasting of MoS_2 into MoO_3, Svanberg and Struve obtained these results. Two samples of artificial disulphide were taken, A and B, and yielded for each hundred parts the following of trioxide:

$$89.7919 \left.\right\} A.$$
$$89.7291$$

$$89.6436 \left.\right.$$
$$89.7082$$
$$89.7660 \left.\right\} B.$$
$$89.7640$$
$$89.8635$$

Mean, 89.7523, $\pm$ .0176

Three other experiments in series B gave divergent results, and, although published, are rejected by the authors themselves. Hence it is not necessary to cite them in this discussion. We again encounter in these figures the same source of constant error which apparently vitiates the preceding series, namely, the possible volatilization of the trioxide. Here, also, such an error would tend to reduce the atomic weight of molybdenum.

Upon discussing the data given in the foregoing para-

graphs we get somewhat noticeable results. From the carbon dioxide series, $Mo = 91.711$, $\pm .113$, a figure having no unusual interest. From the other series, if $S = 31.987$ and $O = 15.9633$, we get $Mo = 92.979$, $\pm .354$; but if we take $S = 32$ and $O = 16$, then Mo becomes $= 92.133$. In this case the higher values for oxygen and sulphur lead to a lower number for molybdenum. In the carbonate series the assumption of 12 and 16 for C and O, respectively, makes $Mo = 92.033$. In other words, if we assume the ordinary even numbers for C, O, and S, Svanberg and Struve's two methods yield more nearly concordant results than when the revised values for these elements are taken.

Berlin,[*] a little later than Svanberg and Struve, determined the atomic weight of molybdenum by igniting a molybdate of ammonium and weighing the residual MoO_3. Here, again, a loss of the latter by volatilization may (and probably does) lead to too low a result. The salt used was $(NH_4)_4Mo_5O_{17}.3\,H_2O$, and in it these percentages of MoO_3 were found:

$$81.598$$
$$81.612$$
$$81.558$$
$$81.555$$

Mean, 81.581, $\pm .0095$

Hence $Mo = 91.9817$, $\pm .0776$; a result agreeing quite well with those of Svanberg and Struve.

Until 1859 the value 92 was generally accepted on the basis of the foregoing researches, but in this year Dumas[†] published some figures tending to sustain a higher number. He prepared molybdenum trioxide by roasting the disulphide, and then reduced it to metal by ignition in hydrogen. At the beginning the hydrogen was allowed to act at a comparatively low temperature, in order to avoid volatilization of trioxide; but at the end of the operation the heat

* Journ. für Prakt. Chem., 49, 444. 1850.
† Ann. Chem. Pharm.. 105, 84, and 113, 23.

was raised sufficiently to insure a complete reduction. From the weighings I calculate the percentages of metal in MoO_3:

.448 grm. MoO_3 gave	.299 grm. Mo.	66.741 per cent.
.484 "	.323 "	66.736 "
.484 "	.322 "	66.529 "
.498 "	.332 "	66.667 "
.559 "	.373 "	66.726 "
.388 "	.258 "	66.495 "

Mean, 66.649, $\pm$ .030

In 1868 the same method was employed by Debray.* His trioxide was purified by sublimation in a platinum tube. His percentages are as follows:

5.514 grm. MoO_3 gave	3.667 grm. Mo.	66.503 per cent.
7.910 "	5.265 "	66.561 "
9.031 "	6.015 "	66.604 "

Mean, 66.556, $\pm$ .020

This mean, combined with that of Dumas', gives a general mean of 66.585, $\pm$ .017.

Hence Mo = 95.429, $\pm$ .057.

Debray also made two experiments upon the precipitation of molybdenum trioxide in ammoniacal solution by nitrate of silver. In his results, as published, there is curious discrepancy, which, I have no doubt, is due to typographical error. These results I am, therefore, compelled to leave out of consideration. They could not, however, exert a very profound influence upon the final discussion.

The most recent investigation upon the atomic weight of molybdenum is the discussion by Lothar Meyer† of the experimental results obtained by Liechti and Kemp‡ in their analyses of the chlorides. Of these compounds there are four: $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$. The chlorine in each was estimated as silver chloride, and the molybdenum as disulphide. From these analyses Meyer deduces three

---

* Compt. Rend., 66, 734.

† Ann. Chem. Pharm., 169, 365. 1873.

‡ Ann. Chem. Pharm., 169, 344.

sets of ratios, namely: between $MoCl_n$ and n $AgCl$; between $MoCl_n$ and MoS_2, and between MoS_2 and n $AgCl$. We will use only the first and last of these; the probable error of the atomic weight deduced from the second being relatively so high as to make the value connected with it comparatively unimportant. The analyses of the trichloride, being discordant, are here rejected.

By reducing the weighings published by Liechti and Kemp[*] to a common standard we get the following percentage results. In $MoCl_2$ the subjoined quantities of the original substance and of MoS_2 correspond to 100 parts of $AgCl$:

$MoCl_2$.	MoS_2.
58.299	55.762
58.194	55.591
58.524	56.065
Mean, 58.339, $\pm$ .066	Mean, 55.806, $\pm$ .093

Hence $MoCl_2 = 166.902$, $\pm$ .188, and $MoS_2 = 159.652$, $\pm$ .268.

With the tetrachloride similarly calculated we get these figures, corresponding to 100 parts $AgCl$:

$MoCl_4$.	MoS_2.
41.492	27.957
41.319	
Mean, 41.4055, $\pm$ .0583	

Hence $MoCl_4 = 236.914$, $\pm$ .358, and MoS_2, if given the weight of a single experiment in the dichloride series, $= 159.964$, $\pm$ .627.

---

[*] These are as follows :

.2666 grm. $MoCl_2$ gave .2550 grm. MoS_2 and .4573 grm. $AgCl$.
.1811   "   .1730   "   .3112   "
.2530   "   .2422   "   .4320   "
.4126 grm. $MoCl_4$ gave .2780   "   .9944   "
.1923   "   ———   "   .4654   "
.5810 grm. $MoCl_5$ gave .3414   "   1.5222   "
.2466   "   .1441   "   .6465   "

For the pentachloride the following quantities balance 100 of AgCl:

$MoCl_5$.	MoS_2.
38.168	22.428
38.057	22.289
Mean, 38.112, $\pm$ .038	Mean, 22.3585, $\pm$ .040

Hence $MoCl_5 = 272.587, \pm .271$, and $MoS_2 = 159.914, \pm .287$.

We have now the molecular weight of each chloride, and three values for that of the disulphide. Combining the latter we get a general mean, as follows:

From $MoCl_2$ series_____ $MoS_2 = 159.652, \pm .268$
" $MoCl_4$ " _____ " $= 159.964, \pm .627$
" $MoCl_5$ " _____ " $= 159.914, \pm .287$

General mean_____ " $= 159.790, \pm .187$

With these data, in addition to those given by Dumas and by Debray, we get five estimates of the atomic weight of molybdenum:

Dumas and Debray's data _____ $Mo = 95.429, \pm .057$
From molecular weight of $MoCl_2$_____ " $= 96.262, \pm .190$
"   " $MoCl_4$_____ " $= 95.434, \pm .363$
"   " $MoCl_5$_____ " $= 95.737, \pm .280$
"   " MoS_2 _____ " $= 95.816, \pm .188$

General mean_____ " $= 95.527, \pm .051$

Or, if $O = 16$, $Mo = 95.747$.

It will at once be seen that the most reliable results are those obtained by the reduction of molybdenum trioxide. Traces of oxychlorides may possibly have contaminated the chlorides and augmented their atomic weight. Our final figure, therefore, may be a trifle too high, but the early value, 92, is unquestionably very far too low.

Since the foregoing discussion was written a single experiment by Rammelsberg * has been brought to my notice.

---

* Berlin Monatsbericht, 1877, 574.

Closely following Dumas' method, he reduced molybdenum trioxide to metal, finding in it 66.708 per cent. of the latter. This figure comes within the limits of variation of Dumas' experiments, and therefore gives them additional confirmation. Its introduction into the general mean, however, would exert too little influence upon the latter to justify the labor of recalculation.

TUNGSTEN.

The atomic weight of tungsten has been determined from analyses of the trioxide, the hexchloride, and the tungstates of iron, silver, and barium.

The composition of the trioxide has been the subject of many investigations. Malaguti [*] reduced this substance to the blue oxide, and from the difference between the weights of the two compounds obtained a result now known to be considerably too high. In general, however, the method of investigation has been to reduce WO_3 to W in a stream of hydrogen at a white heat, and afterwards to reoxidize the metal, thus getting from one sample of material two results for the percentage of tungsten. This method is unquestionably accurate, provided that the trioxide used be pure.

The first experiments which we need consider are, as usual, those of Berzelius.[†] 899 parts WO_3 gave, on reduction, 716 of metal. 676 of metal, reoxidized, gave 846 WO_3. Hence these percentages of W in WO_3 :

> 79.644, by reduction.
> 79.905, by oxidation.
> _____
> Mean, 79.7745, ± .0880

These figures are far too high, the error being undoubtedly due to the presence of alkaline impurity in the trioxide employed.

---

* Journ. für Prakt. Chem., 8, 179.   1836.
† Poggend. Annal., 8, 1.   1826.

Next in order of time comes the work of Schneider,* who, with characteristic carefulness, took every precaution to get pure material. His percentages of tungsten are as follows:

Reduction Series.

79.336
79.254
79.312
79.326
79.350
———
Mean, 79.3156, ± .0112

Oxidation Series.

79.329
79.324
79.328
———
Mean, 79.327, ± .0010

Closely agreeing with these figures are those of Marchand,[†] published in the following year:

Reduction Series.

79.307
79.302
———
Mean, 79.3045, .0017

Oxidation Series.

79.321
79.352
———
Mean, 79.3365, ± .0105

The figures obtained by v. Borch[‡] agree in mean tolerably well with the foregoing. They are as follows:

Reduction Series.

79.310
79.212
79.289
79.313
79.225
79.290
79.302
———
Mean, 79.277, ± .0106

---

* Journ. für Prakt. Chem., 50, 152. 1850.
† Ann. Chem. Pharm., 77, 261. 1851.
‡ Journ. für Prakt. Chem., 54, 254. 1851.

Oxidation Series.
79.359
79.339

Mean, 79.349, $\pm$ .0067

Dumas[*] gives only a reduction series, based upon trioxide obtained by the ignition of a pure ammonium tungsten. The reduction was effected in a porcelain boat, platinum being objectionable on account of the tendency of tungstate to alloy with it. Dumas publishes only weighings, from which I have calculated the percentages:

2.784 grm. WO_3 gave	2.208 grm. W.	79.310 per cent.	
2.994 "	2.373 "	79.259 "	
4.600 "	3.649 "	79.326 "	
.985 "	.781 "	79.289 "	
.917 "	.727 "	79.280 "	
.917 "	.728 "	79.389 "	
1.717 "	1.362 "	79.324 "	
2.988 "	2.370 "	79.317 "	

Mean, 79.312, $\pm$ .009

The data furnished by Bernoulli[†] differ widely from those just given. This chemist undoubtedly worked with impure material, the trioxide having a greenish tinge. Hence the results are too high. These are the percentages of W:

Reduction Series.
79.556
79.526
79.553
79.558
79.549
78.736

Mean, 79.413, $\pm$ .091

Oxidation Series.
79.558
79.656
79.555
79.554

Mean, 79.581, $\pm$ .017

---

[*] Ann. Chem. Pharm., 113, 23. 1860.
[†] Poggend. Annal., 111, 573. 1860.

Two reduction experiments by Persoz [*] give the following results:

1.7999 grm. WO_3 gave	1.4274 grm. W.	79.304 per cent.
2.249 "	1.784 "	79.324 "

Mean, 79.314, $\pm$ .007

Finally, we have the work done by Roscoe.[†]   This chemist used a porcelain boat and tube, and made six weighings, after successive reductions and oxidations, with the same sample of 7.884 grammes of trioxide.   These weighings give me the following five percentages, which, for the sake of uniformity with foregoing series, I have classified under the usual, separate headings:

Reduction Series.

79.196
79.285
79.308

Mean, 79.263, $\pm$ .023

Oxidation Series.

79.230
79.299

Mean, 79.2645, $\pm$ .0233

There are still other experiments by Riche,[‡] which I have not been able to get in detail.   They cannot be of any value, however, for they give to tungsten an atomic weight of about ten units too low.   We may therefore neglect this series, and go on to combine the others:

Berzelius	79.7745, $\pm$ .088
Schneider, Reduction	79.3156, $\pm$ .0112
" Oxidation	79.327, $\pm$ .0010
Marchand, Reduction	79.3045, $\pm$ .0017
" Oxidation	79.3365, $\pm$ .0105
v. Borch, Reduction	79.277, $\pm$ .0106
" Oxidation	79.349, $\pm$ .0067

[*] Zeit. Anal. Chem., 3, 260.   1864.
[†] Ann. Chem. Pharm., 162, 368.   1872.
[‡] Journ. für Prakt. Chem., 69, 10.   1857.

Dumas	79.312,	± .009
Bernouilli, Reduction	79.413,	± .091
" Oxidation	79.581,	± .017
Persoz	79.314,	± .007
Roscoe, Reduction	79.263,	± .023
" Oxidation	79.2645,	± .0233
General mean	79.3215,	± .00085

The rejection of the figures given by Berzelius and by Bernoulli exerts an unimportant influence upon the final result. There is, therefore, no practical objection to retaining them in the discussion.

In 1861 Scheibler[*] deduced the atomic weight of tungsten from analyses of barium metatungstate, $BaO.4\,WO_3.9\,H_2O$. In four experiments he estimated the barium as sulphate, getting closely concordant results, which were, however, very far too low. These, therefore, are rejected. But from the percentage of water in the salt a very good result was attained. The percentages of water are as follows:

$$13.053$$
$$13.054$$
$$13.045$$
$$13.010$$
$$13.022$$

Mean, 13.0368, ± .0060

The work of Zettnow,[†] published in 1867, was somewhat more complicated than any of the foregoing researches. He prepared the pure tungstates of silver and of iron, and from their composition determined the atomic weight of tungsten.

In the case of the iron salt the method of working was this: The pure, artificial $FeWO_4$ was fused with sodium carbonate, the resulting sodium tungstate was extracted by water, and the thoroughly washed, residual ferric oxide was dissolved in hydrochloric acid. This solution was then reduced by zinc, and titrated for iron with potassium permanganate. Corrections were applied for the drop in excess of

[*] Journ. für Prakt. Chem., 83, 324.
[†] Poggend. Annal.. 130, 30.

permanganate needed to produce distinct reddening, and for the iron contained in the zinc. 11.956 grammes of the latter metal contained iron corresponding to 0.6 cc. of the standard solution. The permanganate was standardized by comparison with pure ammonium-ferrous sulphate, $Am_2Fe(SO_4)_2 . 6 H_2O$, so that, in point of fact, Zettnow establishes directly only the ratio between that salt and the ferrous tungstate. From Zettnow's four experiments in standardizing I find that 1 cc. of his solution corresponds to 0.0365457 grammes of the double sulphate, with a probable error of $\pm$ .0000012.

Three sets of titrations were made. In the first a quantity of ferrous tungstate was treated according to the process given above; the iron solution was diluted to 500 cc., and four titrations made upon 100 cc. at a time. The second set was like the first, except that three titrations were made with 100 cc. each, and a fourth upon 150 cc. In the third set the iron solution was diluted to 300 cc., and only two titrations upon 100 cc. each were made. In sets one and two thirty grammes of zinc were used for the reduction of each, while in number three but twenty grammes were taken. Zettnow's figures, as given by him, are quite complicated; therefore I have reduced them to a common standard. After applying all corrections the following quantities of tungstate, in grammes, correspond to 1 cc. of permanganate solution:

.028301	
.028291	First set.
.028311	
.028301	
.028367	
.028368	
.028367	Second set.
.028367	
.028438	Third set.
.028438	

Mean, .0283549, $\pm$ .0000115

With the silver tungstate, Ag_2WO_4, Zettnow employed two methods. In two experiments the substance was de-

composed by nitric acid, and the silver thus taken into solution was titrated with standard sodium chloride. In three others the tungstate was treated directly with common salt, and the residual silver chloride collected and weighed. Here again, on account of some complexity in Zettnow's figures, I am compelled to reduce his data to a common standard. To 100 parts of AgCl the following quantities of Ag_2WO_4 correspond:

By First Method.

161.665
161.603
———
Mean, 161.634, ± .021

By Second Method.

161.687
161.651
161.613
———
Mean, 161.650, ± .014

General mean from both series, 161.645, ± .012

Finally, we have two analyses by Roscoe of tungsten hexchloride, published in the same paper with his results upon the trioxide. In one experiment the chlorine was determined as AgCl; in the other the chloride was reduced by hydrogen, and the residual tungsten estimated. By bringing both results into one form of expression we have for the percentage of chlorine in WCl_6 : *

53.588
53.632
———
Mean, 53.610, ± .015

We have now five ratios from which to calculate the atomic weight of tungsten :

(1.) Percentage of W in WO_3, 79.3215, ± .00085
(2.) Percentage of H_2O in $BaO.4WO_3.9H_2O$, 13.0368, ± .0060

———

* The actual figures are as follows :

19.5700 grm. WCl_6 gave 42.4127 grm. AgCl.
10.4326   "   4.8374 " tungsten.

(3.) $Am_2Fe(SO_4)_2.6H_2O$: $FeWO_4$: : .0365457, $\pm$ .0000012 : .0283549, $\pm$ .0000115

(4.) $AgCl$: Ag_2WO_4 : : 100 : 161.645, $\pm$ .012

(5.) Percentage of Cl in WCl_6, 53.610, $\pm$ .015

From these we get five values for tungsten, as follows:

From	(1)	W = 183.703,	$\pm$ .041
"	(2)	" = 183.532,	$\pm$ .156
"	(3)	" = 183.923,	$\pm$ .120
"	(4)	" = 183.248,	$\pm$ .069
"	(5)	" = 183.639,	$\pm$ .109

General mean _____ " = 183.610, $\pm$ .032

Or, if O = 16, then " = 184.032

URANIUM.

It is not the purpose of the present investigation to examine at all systematically such questions as are involved in the discussion whether the atomic weight of uranium is 120 or 240. For convenience we may use the formulæ based upon the smaller number, and, if eventually the larger value proves to be correct, it will be easy to double the figures which we obtain. Suffice it to say here, that the specific heat of the green oxide, according to Donath,* agrees best with the formula U_3O_4 and the lower atomic weight. On the other hand, the value 240 fits best into such schemes as that given by Mendelejeff in his paper on the periodic law. An accurate determination of the specific heat of the metal itself is much needed, for the material with which Regnault worked was of uncertain quality; furthermore, the vapor density of some volatile uranium compounds ought to be ascertained.† Until some such data have been rigidly

---

* Ber. d. Deutsch. Chem. Gesell., 12, 742. 1879.

† The value of 240 for uranium is strongly sustained by the recent experiments of Zimmermann upon the vapor density of the tetrachlorid and tetrabromid. For UBr_4 the vapor density is 19.46, while theory (U = 240) requires 19.36. For UCl_4 the v. d. 13.33 was found. Theory, 13.21. (Ber. der Deutsch. Chem. Gesell., 14, s. 1934. 1881.)

established the controversy over the two rival values can hardly be satisfactorily settled.

The earlier attempts to determine the atomic weight of uranium were all vitiated by the erroneous supposition that the uranous oxide was really the metal. The supposition, of course, does not affect the weighings and analytical data which were obtained, although these, from their discordance with each other and with later and better results, have now only a historical value.

For present purposes the determinations made by Berzelius,* by Arfvedson,† and by Marchand,‡ may be left quite out of account. Berzelius employed various methods, while the others relied upon estimating the percentage of oxygen lost upon the reduction of U_3O_4 to UO. Rammelsberg's‖ results also, although very suggestive, need no full discussion. He analyzed the green chloride, UCl_2; effected the synthesis of uranyl sulphate from uranous oxide; determined the amount of residue left upon the ignition of the sodio and bario-uranic acetates; estimated the quantity of magnesium uranate formed from a known weight of UO, and attempted also to fix the ratio between the green and the black oxides. His figures vary so widely that they could count for little in the establishing of any general mean; and, moreover, they lead to estimates of the atomic weight which are mostly below the true value. For instance, twelve lots of U_3O_4 from several different sources were reduced to UO by heating in hydrogen. The percentages of loss varied from 3.83 to 4.67, the mean being 4.121. These figures give values for the atomic weight of uranium ranging from 92.66 to 117.65, or, in mean, 107.50. Such discordance is due partly to impurity in some of the material studied, and illustrates the difficulties inherent in the problem to be solved. Some of the uranoso-uranic oxide was prepared by

* Schweigg. Journ., 22, 336. 1818. Poggend. Annal., 1, 359. 1825.

† Poggend. Annal., 1, 245. Berz. Jahr., 3, 120. 1822.

‡ Journ. für Prakt. Chem., 23, 497. 1841.

‖ Poggend. Annal., 55, 318, 1842; 56, 125, 1842; 59, 9, 1843; 66, 91, 1845. Journ. für Prakt. Chem., 29, 324.

calcining the oxalate, and retained an admixture of carbon. Many such points were worked up by Rammelsberg with much care, so that his papers should be scrupulously studied by any chemist who contemplates a redetermination of the atomic weight of uranium.

In 1841 and 1842 Peligot published certain papers[*] showing that the atomic weight of uranium must be somewhere near 120. A few years later the same chemist published fuller data concerning the constant in question, but in the time intervening between his earlier and his final researches other determinations were made by Ebelmen and by Wertheim. These investigations we may properly discuss in chronological order. For present purposes the early work of Peligot may be dismissed as only preliminary in character. It showed that what had been previously regarded as metallic uranium was in reality an oxide, but gave figures for the atomic weight of the metal which were merely approximations.

Ebelmen's[†] determinations of the atomic weight of uranium were based upon analyses of uranic oxalate. This salt was dried at 100°, and then, in weighed amount, ignited in hydrogen. The residual uranous oxide was weighed, and in some cases converted into U_3O_4 by heating in oxygen. The following weights are reduced to a vacuum standard:

10.1644 grm. oxalate gave	7.2939 grm. UO.			
12.9985	"	9.3312	"	Gain on oxidation, .3685
11.8007	"	8.4690	"	" .3275
9.9923	"	7.1731	"	" .2812
11.0887	"	7.9610	"	" .3105
10.0830	"	7.2389	"	
6.7940	"	4.8766	"	
16.0594	"	11.5290	"	" .4531

Reducing these figures to percentages, we may present the results in two columns. Column A gives the percentages of UO in the oxalate, while B represents the amount of U_3O_4 formed from 100 parts of UO:

* Compt. Rend., 12. 735. 1841. Ann. Chim. Phys., (3,) 55. 1842.
† Journ. für Prakt. Chem., 27, 385. 1842.

A.	B.
71.924	------
71.787	103.949
71.767	103.867
71.621	103.920
71.794	103.900
71.793	------
71.778	------
71.790	103.930

Mean, 71.782, $\pm$ .019   Mean, 103.913, $\pm$ .009

From column A, the molecular weight of $UO = 134.523, \pm .102$
"   B,   "   " $= 135.985, \pm .326$

General mean _____ ____ ____ $UO = 134.652, \pm .097$

From column A _____ _____ _____ $U = 118.560$
"   B_____ _____ " $= 120.022$
From general mean of both columns __ " $= 118.689, \pm .097$

Wertheim's [*] experiments were even simpler in character than those of Ebelmen. Sodio-uranic acetate, carefully dried at 200°, was ignited, leaving the following percentages of sodium uranate:

67.51508
67.54558
67.50927

Mean, 67.52331, $\pm$ .0076

Hence the molecular weight of $Na_2U_4O_7 = 634.865$, $\pm$ .191. And $U = 119.282, \pm .048$.

The final results of Peligot's [†] investigations appeared in 1846. Both the oxalate and the acetate of uranium were studied and subjected to combustion analysis. The oxalate was scrupulously purified by repeated crystallizations, and thirteen analyses, representing different fractions, were made. Seven of these gave imperfect results, due to incomplete purification of the material; six only, from the later crystallizations, need to be considered. In these the uranium

---

[*] Journ. für Prakt. Chem., 29, 209. 1843.
[†] Compt. Rend., 22, 487.

was weighed as U_3O_4, and the carbon as CO_2. From the ratio between the CO_2 and U_3O_4 the atomic weight of uranium may be calculated without involving any error due to traces of moisture possibly present in the oxalate. I subjoin Peligot's weighings, and give, in the third column, the U_3O_4 proportional to 100 parts of CO_2:

CO_2.	U_3O_4.	Ratio.
1.456 grm.	4.649 grm.	319.299
1.369 "	4.412 "	322.279
2.209 "	7.084 "	320.688
.1019 "	3.279 "	321.786
1.069 "	3.447 "	322.461
1.052 "	3.389 "	322.148

Mean, 321.443, ± .338

Hence $U_3O_4 = 423.342, \pm .451$.

From the acetate, $C_2H_3(UO)O_2.H_2O$, the following percentages of U_3O_4 were obtained:

		U_3O_4.	per cent.
5.061 grm. acetate gave	3.354 grm.	66.2715	
4.601 "	3.057 "	66.4421 "	
1.869 "	1.238 "	66.2386 "	
3.817 "	2.541 "	66.5706 "	
10.182 "	6.757 "	66.3622 "	
4.393 "	2.920 "	66.4694 "	
2.868 "	1.897 "	66.1437 "	

Mean, 66.3569, ± .038

The acetate also yielded the subjoined percentages of carbon and of water. Assuming that the figures for carbon were calculated from known weights of dioxide, with $C = 12$ and $O = 16$, I have added a third column, in which the carbon percentages are converted into percentages of CO_2:

H_2O.	C.	CO_2.
21.60	11.27	41.323
21.16	11.30	41.433
21.10	11.30	41.433
21.20	11.10	40.700

Mean, 21.265, ± .187   11.24   41.222, ± .092

From all of these figures we may calculate the molecular weight of the uranic acetate as follows:

From percentage of U_3O_4 ----- $C_2H_3(UO)O_2.H_2O$ = 212.629, $\pm$ .242
" CO_2 -----   " = 212.999, $\pm$ .476
" H_2O -----   " = 211.184, $\pm$ 1.863

General mean ----------   " = 212.685, $\pm$ .214

We have now before us the molecular weights of four uranium compounds, giving us four values for U:

(1.) $UO = 134.652, \pm .097$ -------------- Ebelmen.
(2.) $Na_2U_4O_7 = 634.865, \pm .191$ ---------- Wertheim.
(3.) $U_3O_4 = 423.342, \pm .451$ ------ -------- Peligot.
(4.) $C_2H_3(UO)O_2.H_2O = 212.685, \pm .214$ -   "

The four values for uranium combine as follows:

From (1) ---------------- $U = 118.689, \pm .097$ Ebelmen.
"   (2) ---------------- " $= 119.282, \pm .048$ Wertheim.
"   (3) ---------------- " $= 119.830, \pm .150$ Peligot.
"   (4) ---------------- " $= 119.885, \pm .215$ "

General mean ------- " $= 119.241, \pm .041$

Or, if $O = 16$, $U = 119.515$, or 239.030.

Considering Peligot's figures by themselves, and combining values 3 and 4, we have $U = 119.849, \pm .123$; or, if $O = 16$, $U = 120.125$, or 240.250.

It is plain that the atomic weight of uranium needs to be scrupulously revised. The foregoing figures are by no means satisfactory. Chemically considered, it is probable that Peligot's work is the best, and that his results should be given preference. His figures from the oxalate and the acetate tally well with each other, whereas Ebelmen's two sets of results vary widely. From the percentage of UO yielded by the oxalate, Ebelmen's figures give a low value for U. From his oxidation of UO to U_3O_4 we get a value nearly two units higher. Peligot, in his work with the oxalate, found it, even after three or four crystallizations, to be contaminated with oxalic acid, and rejected the figures obtained from impure material. Probably Ebelmen's low values are due to the same impurity.

ALUMINUM.

The atomic weight of aluminum has been determined by Berzelius, Mather, Tissier, Dumas, Isnard, Terreil, and Mallet. The early calculations of Davy and of Thomson we may properly disregard.

Berzelius'[*] determination rests upon a single experiment. He ignited 10 grammes of dry aluminum sulphate, $Al_2(SO_4)_3$, and obtained 2.9934 grammes of Al_2O_3 as residue. Hence, if $S = 31.987$ and $O = 15.9633$, $Al = 27.243$.

In 1835[†] Mather published a single analysis of aluminum chloride, from which he sought to fix the atomic weight of the metal. 0.646 grm. of Al_2Cl_6 gave him 2.056 of AgCl and 0.2975 of Al_2O_3. These figures give worthless values for Al, and are included here only for the sake of completeness. From the ratio between AgCl and Al_2Cl_6, $Al = 28.925$.

Tissier's[‡] determination, also resting on a single experiment, appeared in 1858. Metallic aluminum, containing .135 per cent. of sodium, was dissolved in hydrochloric acid. The solution was evaporated with nitric acid to expel all chlorine, and the residue was strongly ignited until only alumina remained. 1.935 grm. of Al gave 3.645 grm of Al_2O_3. If we correct for the trace of sodium in the aluminum, we have $Al = 27.073$.

Essentially the same method of determination was adopted by Isnard,[||] who, although not next in chronological order, may fittingly be mentioned here. He found that 9 grm. of aluminum gave 27 grm. of Al_2O_3. Hence $Al = 26.938$.

In 1858 Dumas,[§] in connection with his celebrated revision of the atomic weights, made seven experiments with aluminum chloride. The material was prepared in quantity,

---

[*] Poggend. Annal., 8, 177.

[†] Silliman's Amer. Journ., 27, 241.

[‡] Compt. Rend., 46, 1105.

[||] Compt. Rend., 66, 508.   1868.

[§] Ann. Chim. Phys., (3,) 55, 151.   Ann. Chem. Pharm., 113, 26.

sublimed over iron filings, and finally resublimed from metallic aluminum. Each sample used was collected in a small glass tube, after sublimation from aluminum in a a stream of dry hydrogen, and hermetically enclosed. Having been weighed in the tube, it was dissolved in water, and the quantity of silver necessary for precipitating the chlorine was determined. Reducing to a common standard, his weighings give the quantities of Al_2Cl_6 stated in the third column, as proportional to 100 parts of silver:

1.8786 grm.	Al_2Cl_6 =	4.543 grm. Ag.		41.352	
3.021	"	7.292	"	41.459—Bad.	
2.399	"	5.802	"	41.348	
1.922	"	4.6525	"	41.311	
1.697	"	4.1015	"	41.375	
4.3165	"	10.448	"	41.314	
6.728	"	16.265	"	41.365	

In the second experiment the Al_2Cl_6 contained traces of iron. Rejecting this experiment the remaining six give a mean of 41.344, ± .007. Hence Al = 27.441, ± .082.

In consequence of these figures of Dumas, the atomic weight of aluminum has generally of late years been put at 27.5, and the lower results deduced from the work of other investigators have been disregarded.

In 1879 Terreil* published a new determination of the atomic weight under consideration, based upon a direct comparison of the metal with hydrogen. Metallic aluminum, contained in a tube of hard glass, was heated strongly in a current of dry hydrochloric acid. Hydrogen was set free, and was collected over a strong solution of caustic potash. 0.410 grm. of aluminum thus were found equivalent to 508.2 cc., or .0455 grm. of hydrogen. Hence Al = 27.033.

About a year after Terreil's determination appeared the lower value for aluminum was thoroughly confirmed by J. W. Mallet.† After giving a full resumé of the work done by others, exclusive of Isnard, the author describes his own experiments, which may be summarized as follows:

---

* Bulletin de la Soc. Chimique, 31, 153.
† Phil. Trans., 1880, p. 1003.

Four methods of determination were employed, each one simple and direct, and at the same time independent of the others. First, pure ammonia alum was calcined, and the residue of aluminum oxide was estimated. Second, aluminum bromide was titrated with a standard solution of silver. Third, metallic aluminum was attacked by caustic soda, and the hydrogen evolved was measured. Fourth, hydrogen was set free by aluminum, and weighed as water. Every weight was carefully verified, the verification being based upon the direct comparison, by J. E. Hilgard, of a kilogramme weight with the standard kilogramme at Washington. The specific gravity of each piece was determined, and also of all materials and vessels used in the weighings. During each weighing both barometer and thermometer were observed, so that every result represents a real weight *in vacuo*.

The ammonium alum used in the first series of experiments was specially prepared, and was absolutely free from ascertainable impurities. The salt was found, however, to lose traces of water at ordinary temperatures; a circumstance which tended towards a slight elevation of the apparent atomic weight of aluminum as calculated from the weighings. Two sets of experiments were made with the alum; one upon a sample air-dried for two hours at 21°–25°, the other upon material ·dried for twenty-four hours at 19°–26°. These sets, marked A and B respectively, differ slightly; B being the less trustworthy of the two, judged from a chemical standpoint. Mathematically it is the better of the two. Calcination was effected with a great variety of precautions, concerning which the original memoir must be consulted. To Mallet's weighings I append the percentages of Al_2O_3 deduced from them:

Series A.

8.2144 grm. of the alum gave	.9258 grm. Al_2O_3.	11.270 per cent.
14.0378 "	1.5825 "	11.273 "
5.6201 "	.6337 "	11.275 "
11.2227 "	1.2657 "	11.278 "
10.8435 "	1.2216 "	11.266 "

Mean, 11.2724, ± .0014

12.1023 grm. of the alum gave 1.3660 grm. Al_2O_3. 11.287 per cent.
10.4544   "   1.1796   "   11.283   "
6.7962   "   .7670   "   11.286   "
8.5601   "   .9654   "   11.278   "
4.8992   "   .5528   "   11.283   "

Mean, 11.2834, $\pm$ .0011

Combined, these series give a general mean of 11.2793, $\pm$ .0008. Hence Al = 27.075, $\pm$ .011.

The aluminum bromide used in the second series of experiments was prepared by the direct action of bromine upon the metal. The product was repeatedly distilled, the earlier portions of each distillate being rejected, until a constant boiling point of 263.°3 at 747 mm. pressure was noted. The last distillation was effected in an atmosphere of pure nitrogen, in order to avoid the possible formation of oxide or oxy-bromide of aluminum; and the distillate was collected in three portions, which proved to be sensibly identical. The individual samples of bromide were collected in thin glass tubes, which were hermetically sealed after nearly filling. For the titration pure silver was prepared, and after fusion upon charcoal it was heated in a Sprengel vacuum in order to eliminate occluded gases. This silver was dissolved in specially purified nitric acid, the latter but very slightly in excess. The aluminum bromide, weighed in the sealed tube, was dissolved in water, precautions being taken to avoid any loss by splashing or fuming which might result from the violence of the action. To the solution thus obtained the silver solution was added, the silver being something less than a decigramme in deficiency. The remaining amount of silver needed to complete the precipitation of the bromine was added from a burette, in the form of a standard solution containing one milligramme of metal to each cubic centimetre. The final results were as follows, the figures in the third column representing the quantities of bromide proportional to 100 parts of silver. Series A is from the first portion of the last distillate of Al_2Br_6; series

B from the second portion, and series C from the third portion :

Series A.

6.0024 grm. Al_2Br_6 =		7.2793 grm. Ag.	82.458
8.6492	"	10.4897 "	82.454
3.1808	"	3.8573 "	82.462

Series B.

6.9617	"	8.4429 "	82.456
11.2041	"	13.5897 "	82.445
3.7621	"	4.5624 "	82.459
5.2842	"	6.4085 "	82.456
9.7338	"	11.8047 "	82.457

Series C.

9.3515	"	11.3424 "	82.447
4.4426	"	5.3877 "	82.458
5.2750	"	6.3975 "	82.454

Mean, 82.455, ± .001

Hence Al = 27.046, ± .061.

The high probable error of this result is due to the high probable error of the atomic weight of bromine.

The experiments to determine the amount of hydrogen evolved by the action of caustic soda upon metallic aluminum were conducted with pure metal, specially prepared, and with caustic soda made from sodium. The soda solution was so strong as to scarcely lose a perceptible amount of water by the passage through it of a dry gas at ordinary temperature. As the details of the experiments are somewhat complex, the original memoir must be consulted for them. The following results were obtained, the weight of the hydrogen being calculated from the volume, by Regnault's data corrected for the latitude and elevation of the University of Virginia :

Weight of Al.	*Vol. of H.*	*Wt. of H.*	*At. Wt.*
.3697 grm.	458.8 c. c.	.04106 grm.	27.012
.3769 "	467.9 "	.04187 "	27.005
.3620 "	449.1 "	.04019 "	27.022
.7579 "	941.5 "	.08425 "	26.998
.7314 "	907.9 "	.08125 "	27.006
.7541 "	936.4 "	.08380 "	26.996

Mean, 27.005, ± .0032

The closing series of experiments was made with larger quantities of aluminum than were used in the foregoing set. The hydrogen, evolved by the action of the caustic alkali, was dried by passing it through two drying tubes containing pumice stone and sulphuric acid, and two others containing asbestos and phosphorus pentoxide. Thence it passed through a combustion tube containing copper oxide heated to redness. A stream of dry nitrogen was employed to sweep the last traces of hydrogen into the combustion tube, and dry air was afterwards passed through the entire apparatus to reoxidize the surface of reduced copper, and to prevent the retention of occluded hydrogen. The water formed by the oxidation of the hydrogen was collected in three drying tubes. The results obtained were as follows. The third column gives the amount of water formed from 10 grammes of aluminum:

2.1704 grm. Al gave	2.1661 grm. H_2O.	9.9802
2.9355 "	2.9292 "	9.9785
5.2632 "	5.2562 "	9.9867

Mean, 9.9818, $\pm$ .0017

Hence Al = 26.998, $\pm$ .007.

In combining the various determinations of the atomic weight of aluminum into one general mean, we must arbitrarily assign weight to the single experiments of Berzelius, Isnard, Tissier, and Terreil. This may fairly be done by giving to each the probable error, and therefore the weight, of a single observation in Dumas' series. Mather's work may be ignored altogether:

From Berzelius	Al = 27.243,	$\pm$ .201
" Tissier	" = 27.096,	$\pm$ .201
" Isnard	" = 26.938,	$\pm$ .201
" Dumas	" = 27.441,	$\pm$ .082
" Terreil	" = 27.033,	$\pm$ .201
" Mallet's alum experiments.	" = 27.075,	$\pm$ .011
" " Al_2Br_6 "	" = 27.046,	$\pm$ .061
" " H "	" = 27.005,	$\pm$ .003
" " H_2O "	" = 26.998,	$\pm$ .007

General mean " = 27.0092, $\pm$ .0028

11

If O = 16, Al = 27.075. Taking Mallet's work alone, Al = 27.0089, ± .0028.

Evidently all the data except Mallet's might be rejected without affecting sensibly the final result. Dumas' work is clearly vitiated by constant errors, but the determinations by Isnard, Tissier, and Terreil may be regarded as having some confirmative value.

GOLD.

The only determinations of the atomic weight of gold which are worthy of consideration are those of Berzelius and of Levol.

The earliest method adopted by Berzelius[*] was that of precipitating a solution of gold chloride by means of a weighed quantity of metallic mercury. The weight of gold thus thrown down gave the ratio between the atomic weights of the two metals. In the single experiment which Berzelius publishes, 142.9 parts of Hg precipitated 93.55 of Au. Hence, using the value for mercury given in a preceding chapter, 199.712, Au = 196.113.

In a later investigation[†] Berzelius resorted to the analysis of potassio-auric chloride, $2KCl.AuCl_3$. Weighed quantities of this salt were ignited in hydrogen; the resulting gold and potassium chloride were separated by means of water, and both were collected and estimated. The loss of weight upon ignition was, of course, chlorine. As the salt could not be perfectly dried without loss of chlorine, the atomic weight under investigation must be determined by the ratio between the KCl and the Au. If we reduce to a common standard, and compare with 100 parts of KCl, the equivalent amounts of gold will be those which I give in the last of the subjoined columns:

---

[*] Poggend. Annal., 8, 177.
[†] Lehrbuch, 5 Aufl., 3, 1212.

4.1445 grm. K_2AuCl_5 gave	.8185 grm. KCl and	2.159 grm. Au.	263.775
2.2495 "	.44425 "	1.172 "	263.815
5.1300 "	1.01375 "	2.67225 "	263.600
3.4130 "	.674 "	1.77725 "	263.687
4.19975 "	.8295 "	2.188 "	263.773

Mean, 263.730, ± .026

Hence Au = 196.186, ± .101.

Still a third series of experiments by Berzelius* may be included here. In order to establish the atomic weight of phosphorus he employed that substance to precipitate gold from a solution of gold chloride in excess. Between the weight of phosphorus taken and the weight of gold obtained it was easy to fix a ratio. Since the atomic weight of phosphorus has been better established by other methods, we may properly reverse this ratio and apply it to our discussion of gold. 100 parts of P precipitate the quantities of Au given in the third column:

.829 grm. P precipitated	8.714 grm. Au.	1051.15
.754 "	7.930 "	1051.73

Mean, 1051.44, ± .196

Hence Au = 195.303, ± .589.

Levol's† estimation of the atomic weight under consideration can hardly have much value. A weighed quantity of gold was converted in a flask into $AuCl_3$. This was reduced by a stream of sulphur dioxide, and the resulting sulphuric acid was determined as $BaSO_4$. One gramme of gold gave 1.782 grm. $BaSO_4$. Hence Au = 195.794.

If we give this single experiment and Berzelius' single result with mercury each equal weight with one analysis in the potassio-auric chloride series, and include respectively the probable errors appertaining to Hg and to $BaSO_4$, we may combine all the data as follows:

* Lehrbuch, 5 Aufl., 3, 1188.
† Ann. d. Chim. et d. Phys., (3,) 30, 355. 1850.

From KCl : Au ratio _____ Au = 196.186, ± .101
From Hg : Au ratio _____ " = 196.113, ± .335
From P : Au ratio _____ " = 195.303, ± .589
From BaSO$_4$: Au ratio ____ " = 195.794, ± 1.234

General mean _____ " = 196.155, ± .095

Or, if O = 16, Au = 196.606.

As gold is a metal which can be readily applied to the determination of the atomic weights of other elements, an experimental revision of its atomic weight is very desirable.

NICKEL AND COBALT.

On account of the close similarity of these metals to each other, their atomic weights, approximately if not actually identical, have received of late years much attention.

The first determinations, and the only ones up to 1852, were made by Rothhoff;[*] each with but a single experiment. For nickel 188 parts of the monoxide were dissolved in hydrochloric acid; the solution was evaporated to dryness, the residue was dissolved in water, and precipitated by silver nitrate. 718.2 parts of silver chloride were thus formed; whence Ni = 58.925. The same process was applied also to cobalt, 269.2 parts of the oxide being found equivalent to 1029.9 of AgCl. Hence Co = 58.817. These values are so nearly equal that their differences were naturally ascribable to experimental errors. They are, however, entitled to no special weight at present, since it cannot be certain from any evidence recorded that the oxide of either metal was absolutely free from traces of·the other.

In 1852 Erdmann and Marchand[†] published some results, but without details, concerning the atomic weight of nickel. They reduced the oxide by heating in a current of

---

[*] Cited by Berzelius. Poggend. Annal., 8, 184. 1826.
[†] Journ. für Prakt. Chem., 55, 202. 1852.

hydrogen, and obtained values ranging from 58.2 to 58.6, when $O = 16$. Their results were not very concordant, and the lowest was probably the best.

In 1856, incidentally to other work, Deville* found that 100 parts of pure metallic nickel yielded 262 of sulphate; whence $Ni = 59.15$.

To none of the foregoing estimations can any importance now be attached. The modern discussion of the atomic weights under consideration began with the researches of Schneider† in 1857. This chemist examined the oxalates of both metals, determining carbon by the combustion of the salts with copper oxide in a stream of dry air. The carbon dioxide thus formed was collected as usual in a potash bulb, which, in weighing, was counterpoised by a similar bulb, so as to eliminate errors due to the hygroscopic character of the glass. The metal in each oxalate was esti- mated, first by ignition in a stream of dry air, followed by intense heating in hydrogen. Pure nickel or cobalt was left behind in good condition for weighing. Four analyses of each oxalate were made, with the results given below. The nickel salt contained three molecules of water, and the cobalt salt two molecules:

$$NiC_2O_4.3H_2O.$$

1.1945 grm. gave	.528	grm. CO_2.	44.203 per cent.
2.5555	"	1.12625	"	44.072	"
3.199	"	1.408	"	44.014	"
5.020	"	2.214	"	44.104	"

Mean, 44.098, $\pm$ .027

The following percentages of nickel were found in this salt:

29.107
29.082
29.066
29.082

Mean, 29.084, $\pm$ .006

---

* Ann. Chim. Phys., (3,) 46, 182. 1856.
† Poggend. Annal., 101, 387. 1857.

$$CoC_2O_4.2H_2O.$$

1.6355 grm. gave	.781	grm. CO_2.	47.753 per cent.
1.107	"	.5295	"	47.832 "
2.309	"	1.101	"	47.683 "
3.007	"	1.435	"	47.722 "

Mean, 47.7475, $\pm$ .0213

The following were the percentages found for cobalt:

32.552
32.619
32.528
32.523

Mean, 32.5555, $\pm$ .0149

In a later paper* Schneider also gives some results obtained with a nickel oxalate containing but two molecules of water. This gave him 47.605 per cent. of CO_2, and the following percentages of nickel:

31.4115
31.4038

Mean, 31.4076, $\pm$ .0026

The conclusion at which Schneider arrived was, that the atomic weights of cobalt and nickel are not identical, being about 60 and 58 respectively. The percentages given above will be discussed at the end of this chapter in connection with all the other data relative to the constants in question.

The next chemist to take up the discussion of these atomic weights was Marignac, in 1857.† His original paper is not accessible to me, and I am therefore obliged to give only such features of it as I can get from abstracts and reviews. He worked with the chlorides and sulphates of nickel and cobalt, using apparently common gravimetric methods. The sulphates, taken as anhydrous, were first ignited to expel $SO_2 + O$, after which the residues were heated with weighed amounts of lead silicate. The increase in weight

---

* Poggend. Annal., 107, 616.

† Jahresbericht, 1857, 225. Bibl. Univ. de Genève, (nouv. s.,) 1, 373.

was CoO or NiO respectively. The anhydrous chlorides were prepared from the hydrated salts by ignition in dry chlorine or hydrochloric acid. With cobalt, the monohydrated chloride, dried at 100°, was also employed. For nickel he gives the following values, referred probably to $O = 16$, $S = 32$, $Ag = 108$, $Cl = 35.5$:

From $NiSO_4$ _____ Ni = 58.4 to 59.0
" $NiCl_2$ _____ " = 58.4 " 59.28

To cobalt these values are assigned:

From $CoSO_4$ _____ Co = 58.64 to 58.76
" $CoCl_2 \cdot H_2O$ _____ " = 58.84 " 59.02
" $CoCl_2$ _____ " = 58.72 " 59.02

That is, contrary to Schneider's view, the two atomic weights are approximately the same. The values for nickel, however, run a little lower than those for cobalt; a fact which is probably not without significance. Marignac criticizes Schneider's earlier paper, holding that the nickel oxalate may have contained some free oxalic acid, and that the cobalt salt was possibly contaminated with carbonate or with basic compounds. In his later papers Schneider rejects these suggestions as unfounded, and in turn criticizes Marignac. The purity of anhydrous $NiSO_4$ is not easy to guarantee, and, according to Schneider, the anhydrous chlorides of cobalt and nickel are liable to be contaminated with oxides. This is the case even when the chlorides are heated in chlorine, unless the gas is carefully freed from all traces of air and moisture.

Dumas'[*] determinations of the two atomic weights were made with the chlorides of nickel and cobalt. The pure metals were dissolved in aqua regia, the solutions were repeatedly evaporated to dryness, and the residual chlorides were ignited in dry hydrochloric acid gas. The last two estimations in the nickel series were made upon $NiCl_2$ formed by heating the spongy metal in pure chlorine. In the third column I give the $NiCl_2$ or $CoCl_2$, equivalent to 100 parts of silver:

---

[*] Ann. Chem. Pharm., 113, 25. 1860.

.9123 grm. $NiCl_2$ =	1.515	grm. Ag.		60.218
2.295	"	3.8115	"	60.212
3.290	"	5.464	"	60.212
1.830	"	3.041	"	60.178
3.001	"	4.987	"	60.176

Mean, 60.1992, $\pm$ .0062

2.352 grm. $CoCl_2$ =	3.9035	grm. Ag.		60.254
4.210	"	6.990	"	60.229
3.592	"	5.960	"	60.268
2.492	"	4.1405	"	60.186
4.2295	"	7.0255	"	60.202

Mean, 60.2278, $\pm$ .011

These results give values for Co and Ni differing by less than a tenth of a unit; here, as elsewhere, the figure for Ni being a trifle the lower.

In 1863 * the idea that nickel and cobalt have equal atomic weights was strengthened by the researches of Russell. He found that the black oxide of cobalt, by intense heating in an atmosphere of carbon dioxide, became converted into a brown monoxide of constant composition. The ordinary oxide of nickel, on the other hand, was shown to be convertible into a definite monoxide by simple heating over the blast lamp. The pure oxides of the two metals, thus obtained, were reduced by ignition in hydrogen, and their exact composition thus ascertained. Several samples of each oxide were taken, yielding the following percentages of metal:

NiO.

78.597	
78.584	1st sample.
78.608	
78.581	
78.589	2d sample.
78.583	
78.616	
78.590	3d sample.
78.588	
78.590	
78.594	4th sample.
78.597	
78.588	

Mean of all, 78.593, $\pm$ .0018

* Journ. Chem. Soc., (2,) 1, 51.

Co O.

$\left.\begin{array}{l}78.591 \\ 78.588 \\ 78.550 \\ 78.598 \\ 78.614\end{array}\right\}$ 1st sample.

$\left.\begin{array}{l}78.603 \\ 78.591 \\ 78.591\end{array}\right\}$ 2d sample.

$\left.\begin{array}{l}78.588 \\ 78.592\end{array}\right\}$ 3d sample.

$\left.\begin{array}{l}78.597 \\ 78.598\end{array}\right\}$ 4th sample.

$\left.\begin{array}{l}78.595 \\ 78.589 \\ 78.596\end{array}\right\}$ 5th sample.

Mean of all, 78.592, ± .0023

These percentages are practically identical, and lead to essentially the same mean value for each atomic weight.

In a later paper Russell* confirmed the foregoing results by a different process. He dissolved metallic nickel and cobalt in hydrochloric acid and measured the hydrogen evolved. Thus the ratio between the metal and the ultimate standard was fixed without the intervention of any other element. About two-tenths of a gramme of metal, or less, was taken in each experiment. 100 parts by weight of Co or Ni give the following weights of H, calculated from the volume of the latter:

Ni.		Co.	
3.420		3.395	
3.418		3.398	
3.416		3.397	
3.417	} 1st sample.	3.398	} 1st sample.
3.412		3.403	
3.415		3.401	
3.416		3.401	} 2d sample.

* Journ. Chem. Soc., (2,) 7, 494. 1869.

Ni.		*Co.*	
3.398		3.404	
3.409 } 2d sample.		3.405 } 3d sample.	
3.404		3.410	
3.401 —3d sample.		3.407 } 4th sample.	
3.412			
3.408 } 4th sample.		Mean of all, 3.4017, $\pm$ .0009	
3.410			

Mean of all, 3.411, $\pm$ .001

A glance at the tabulated discussion which closes this chapter will show that these figures agree well with each other, and well with those found from the analyses of the oxides. The probable errors assigned in the hydrogen series may be a little too low, since they ought to be modified by the probable error of the weight of a unit volume of hydrogen. So insignificant a correction may, however, be neglected.

Some time after the publication of Russell's first paper, but before the appearance of his second, some other investigations were made known. Of these the first was by Sommaruga,[*] whose results, obtained by novel methods, closely confirmed those of Schneider and antagonized those of Dumas, Marignac, and Russell. The atomic weight of nickel Sommaruga deduced from analyses of the nickel potassium sulphate, $K_2Ni(SO_4)_2.6H_2O$, which, dried at 100°, has a perfectly definite composition. In this salt the sulphuric acid was determined in the usual way as barium sulphate, a process to which there are obvious objections. In the third column are given the quantities of the nickel salt proportional to 100 parts of $BaSO_4$:

0.9798 grm. gave 1.0462 grm. $BaSO_4$.		93.653
1.0537 "	1.1251 "	93.654
1.0802 "	1.1535 "	93.645
1.1865 "	1.2669 "	93.654
3.2100 "	3.4277 "	93.649
3.2124 "	3.4303 "	93.648

Mean, 93.6505, $\pm$ .001

* Sitzungsb. Wien Akad., 54, 2 Abth., 50. 1866.

For cobalt Sommaruga used the purpureo cobalt chloride of Gibbs and Genth. This salt, dried at 110°, is anhydrous and stable. Heated hotter, $CoCl_2$ remains. The latter, ignited in hydrogen, yields metallic cobalt. In every experiment the preliminary heating must be carried on cautiously until ammoniacal fumes no longer appear:

.6656	grm. gave	.1588	grm. Co.		23.858	per cent.
1.0918	"	.2600	"		23.814	"
.9058	"	.2160	"		23.846	"
1.5895	"	.3785	"		23.813	"
2.9167	"	.6957	"		23.847	"
1.8390	"	.4378	"		23.806	"
2.5010	"	.5968	"		23.808	"

Mean, 23.827, ± .006

Further along this series will be combined with a similar one by Lee. It may here be said that Sommaruga's paper was quickly followed by a critical essay from Schneider,* endorsing the former's work, and objecting to the results of Russell.

In 1867 still another new process for the estimation of these atomic weights was put forward by Winkler,† who determined the amount of gold which pure metallic nickel and cobalt could precipitate from a neutral solution of sodio-auric chloride. Experimentally, the method seems to be quite accurate; practically, it involves a knowledge of the defectively ascertained atomic weight of gold. In order to obtain pure cobalt Winkler prepared purpureo-cobalt chloride, which, having been four or five times recrystallized, was ignited in hydrogen. His nickel was repeatedly purified by precipitation with sodium hypochlorite. From material thus obtained pure nickel chloride was prepared, which, after sublimation in dry chlorine, was also reduced by hydrogen. 100 parts of gold are precipitated by the quantities of nickel and cobalt given in the third columns respectively. In the cobalt series I include one experiment

* Poggend. Annal., 130, 310.
† Zeit. Anal. Chem., 6, 18. 1867.

by Weselsky which was published by him in a paper presently to be cited:

.4360 grm. nickel precipitated	.9648 grm. gold.	45.191
.4367 "	.9666 "	45.179
.5189 "	1.1457 "	45.291
.6002 "	1.3286 "	45.175

Mean, 45.209, $\pm$ .019

.5890 grm. cobalt precipitated	1.3045 grm. gold.	45.151
.3147 "	.6981 "	45.080
.5829 "	1.2913 "	45.141
.5111 "	1.1312 "	45.182
.5821 "	1.2848 "	45.307
.559 "	1.241 "	45.044—Weselsky.

Mean, 45.151, $\pm$ .025

Weselsky's paper,[*] already cited, relates only to cobalt. He ignited the cobalticyanides of ammonium and of phenylammonium in hydrogen, and from the determinations of cobalt thus made deduced its atomic weight. His results are as follows:

.7575 grm. $(NH_4)_6Co_2Cy_{12}$ gave	.166 grm. Co.	21.914 per cent.
.5143 "	.113 "	21.972 "

Mean, 21.943, $\pm$ .029

.8529 grm. $(C_6H_8N)_6Co_2Cy_{12}$ gave	.1010 grm. Co.	11.842 per cent.
.6112 "	.0723 "	11.829 "
.7140 "	.0850 "	11.905 "
.9420 "	.1120 "	11.890 "

Mean, 11.8665, $\pm$ .0124

Finally, we come to the work done by Lee[†] in the laboratory of Wolcott Gibbs. Like Weselsky, Lee ignited certain cobalticyanides and nickelocyanides in hydrogen and determined the residual metal. The double cyanides chosen were those of strychnia and brucia; salts of very high molecular weight, in which the percentages of metal are relatively low. A series of experiments with purpureo-cobalt

---

[*] Ber. d. Deutsch. Chem. Gesell., 2, 592. 1868.

[†] Am. Journ. Sci. and Arts, (3,) 2, 44. 1871.

chloride was also carried out. In order to avoid admixture of carbon in the metallic residues, the salts were first ignited in air, and then in oxygen. Reduction by hydrogen followed. The salts were in each case covered by a porous septum of earthenware, through which the hydrogen diffused, and which served to prevent the mechanical carrying away of solid particles; furthermore, heat was applied from above. The results attained were very satisfactory, and assign to nickel and cobalt atomic weights varying from each other by about a unit; Ni being nearly 58, and Co about 59. The exact figures will appear later. The cobalt results agree remarkably well with those of Weselsky. The following are the percentages of metal found:

In *brucia nickelocyanide*, $Ni_3Cy_{12}(C_{23}H_{26}N_2O_4)_6H_6.10H_2O$.

$$5.724$$
$$5.729$$
$$5.750$$
$$5.733$$
$$5.712$$
$$5.729$$

Mean, 5.7295, $\pm$ .0034

In *strychnia nickelocyanide*, $Ni_3Cy_{12}(C_{21}H_{22}N_2O_2)_6.H_6.8H_2O$.

$$6.607$$
$$6.613$$
$$6.589$$
$$6.607$$
$$6.561$$
$$6.595$$

Mean, 6.595, $\pm$ .005

In *brucia cobalticyanide*, $Co_2Cy_{12}(C_{23}H_{26}N_2O_4)_6.H_6.20H_2O$.

$$3.759$$
$$3.720$$
$$3.739$$
$$3.748$$
$$3.747$$
$$3.749$$

Mean, 3.7437, $\pm$ .0036

In strychnia cobalticyanide, $Co_2Cy_{12}(C_{21}H_{22}N_2O_2)_6.H_6.8H_2O.$

$$4.583$$
$$4.596$$
$$4.554$$
$$4.564$$
$$4.577$$
$$4.549$$

Mean. 4.5705, $\pm$ .005

In purpureo-cobalt chloride, $Co_2(NH_3)_{10}Cl_6.$

$$23.575$$
$$23.587$$
$$23.586$$
$$23.579$$
$$23.569$$
$$23.581$$

Mean, 23.5795, $\pm$ .0019

The last series may be combined with Sommaruga's, thus :

Sommaruga _____ _____ 23.827, $\pm$ .006
Lee _____ 23.5795, $\pm$ .0019

General mean____ _____ 23.6045, $\pm$ .0018

In discussing the atomic weights of nickel and cobalt, we may ignore the work of Rothhoff, Erdmann and Marchand and Deville. That of Marignac must also be omitted, for want of sufficient data. For nickel we have the following ratios. The probable error assigned in No. 4, is that of a single experiment in No. 2 :

(1.) Per cent. of Ni in $NiC_2O_4.3H_2O$, 29.084, $\pm$ .006
(2.)   " CO_2 from   "   44.098, $\pm$ .027
(3.)   "   Ni in $NiC_2O_4.2H_2O$, 31.4076, $\pm$ .0026
(4.)   " CO_2 from   "   47.605, $\pm$ .053
(5.)   "   Ni in NiO, 78.593, $\pm$ .0018
(6.)   "   "   brucia nickelocyanide, 5.7295, $\pm$ .0034
(7.)   "   "   strychnia   "   6.595, $\pm$ .005
(8.) Ag : $NiCl_2$: : 100 : 60.1992, $\pm$ .0062
(9.) Ni : H : : 100 : 3.411, $\pm$ .001
(10.) Au : Ni : : 100 : 45.209, $\pm$ .019
(11.) $BaSO_4$: $K_2Ni(SO_4)_2.6H_2O$: : 100 : 93.6505, $\pm$ .001

Since the proportion of water in the oxalates is not an absolutely certain quantity, the data concerning such salts

are best handled by employing the ratios between the carbon dioxide and the metal. Accordingly ratios (1) and (2) give a single value for Ni, and ratios (3) and (4) another. In all, we have nine values for the atomic weight in question:

From (1) and (2)_____Ni $=$ 57.907, $\pm$ .0379
" (3) " (4)_____ " $=$ 57.926, $\pm$ .0654
" (6)_____ " $=$ 57.884, $\pm$ .0396
" (7)_____ " $=$ 57.947, $\pm$ .0467
" (11)_____ " $=$ 58.170, $\pm$ .0829
" (5)_____ " $=$ 58.607, $\pm$ .0139
" (9)_____ " $=$ 58.634, $\pm$ .0165
" (8)_____ " $=$ 58.899, $\pm$ .0339
" (10)_____ " $=$ 59.120, $\pm$ .0376

General mean_____ " $=$ 58.547, $\pm$ .0089

If O $=$ 16, Ni $=$ 58.682.

In the foregoing result it will be seen that the two sets of figures due to Russell receive very great weight. This is because the one set is referred directly to hydrogen, without the intervention of the probable error of any other element; while the second set involves only the atomic weight of oxygen, of which the probable error is small. As regards accuracy of methods, however, and certainty concerning the purity of material, Russell's work is no better than Schneider's, and probably inferior to Lee's. Now values one to five in the above table represent the tolerably concordant results of Schneider, Lee, and Sommaruga. They, combined by themselves, give a general mean of Ni $=$ 57.928, $\pm$ .0215; or, if O $=$ 16, of Ni $=$ 58.062. This value, taking everything into account, I cannot but regard as more likely to prove correct than the larger mean deduced from all the ratios. At all events, the atomic weight of nickel needs further careful investigation.

For cobalt these ratios are available:

(1.) Per cent. of Co in $CoC_2O_4.2H_2O$, 32.5555, $\pm$ .0149
(2.) " CO_2 from " 47.7475, $\pm$ .0213
(3.) " Co in CoO, 78.592, $\pm$ .0023
(4.) " " purpureo-cobalt chloride, 23.6045, $\pm$ .0018
(5.) " " phenylammonium cobalticyanide, 11.8665, $\pm$ .0124
(6.) " " ammonium " 21.943, $\pm$ .029

(7.) Per cent. of Co in brucia cobalticyanide, 3.7437, ± .0036
(8.)   "   "   strychnia   "   4.5705, ± .005
(9.) Ag : CoCl$_2$ :: 100 : 60.2278, ± .011
(10.) Co : H :: 100 : 3.4017, ± .0009
(11.) Au : Co :: 100 : 45.151, ± .025

Hence we have ten values for Co, as follows:

From (1) and (2)_____ Co = 59.865, ± .0394
"   (4)_____ " = 59.080, ± .0152
"   (5)_____ " = 58.913, ± .0628
"   (6)_____ " = 59.177, ± .0816
"   (7)_____ " = 59.057, ± .0581
"   (8)_____ " = 58.960, ± .0708
"   (11)_____ " = 59.044, ± .0436
"   (9)_____ " = 58.961, ± .0392
"   (3)_____ " = 58.604, ± .0145
"   (10)_____ " = 58.794, ± .0162

General mean_____ " = 58.887, ± .008

If O = 16, Co = 59.023.

SELENIUM.

The atomic weight of this element was first determined by Berzelius,[*] who, saturating 100 parts of selenium with chlorine, found that 179 of chloride were produced. Further on these figures will be combined with similar results by Dumas.

We may omit, as unimportant for present purposes, the analyses of alkaline selenates made by Mitscherlich and Nitzsch,[†] and pass on to the experiments published by Sacc[‡] in 1847. This chemist resorted to a variety of methods, some of which gave good results, while others were unsatisfactory. First, he sought to establish the exact composition of SeO$_2$, both by synthesis and by analysis. The former plan, according to which he oxidized pure selenium by

---

[*] Poggend. Annal., 8, 1. 1826.
[†] Poggend. Annal., 9, 623. 1827.
[‡] Ann. d. Chim. et d. Phys.. (3,) 21, 119.

nitric acid, gave poor results; better figures were obtained upon reducing SeO_2 with ammonium bisulphite and hydrochloric acid, and determining the percentage of selenium set free:

.6800 grm. SeO_2 gave .4828 grm. Se.			71.000 per cent.
3.5227	"	2.5047 "	71.102 "
4.4870	"	3.1930 "	71.161 "

Mean, 71.088, $\pm$ .032

In a similar manner Sacc also reduced barium selenite, and weighed the resulting mixture of barium sulphate and free selenium. This process gave discordant results, and a better method was found in calcining $BaSeO_3$ with sulphuric acid, and estimating the resulting quantity of $BaSO_4$. In the third column I give the amounts of $BaSO_4$ equivalent to 100 of $BaSeO_3$:

.5573 grm. $BaSeO_3$ gave .4929 grm. $BaSO_4$.			88.444
.9942	"	.8797 "	88.383
.2351	"	.2080 "	88.473
.9747	"	.8621 "	88.448

Mean, 88.437, $\pm$ .013

Still other experiments were made with the selenites of silver and lead; but the figures were subject to such errors that they need no further discussion here.

A few years after Sacc's work was published, Erdmann and Marchand made with their usual care a series of experiments upon the atomic weight under consideration.* They alalyzed pure mercuric selenide, which had been repeatedly sublimed and was well crystallized. Their method of manipulation has already been described in the chapter upon mercury. These percentages of Hg in HgSe were found:

71.726
71.731
71.741

Mean, 71.7327, $\pm$ .003

* Journ. für Prakt. Chem., 55, 202. 1852.

The next determinations were made by Dumas,* who returned to the original method of Berzelius. Pure selenium was converted by dry chlorine into $SeCl_4$, and from the gain in weight the ratio between Se and Cl was easily deducible. I include Berzelius' single experiment, which I have already cited, and give in a third column the quantity of chlorine absorbed by 100 parts of selenium:

1.709 grm. Se absorb	3.049 grm. Cl.		178.409
1.810 "	3.219 "		177.845
1.679 "	3.003 "		178.856
1.498 "	2.688 "		179.439
1.944 "	3.468 "		178.395
1.887 "	3.382 "		179.226
1.935 "	3.452 "		178.398
			179.000—Berzelius.

Mean, 178.696, $\pm$ .125

The question may here be properly asked, whether it would be possible thus to form $SeCl_4$ and be certain of its absolute purity? A trace of oxychloride, if simultaneously formed, would increase the apparent atomic weight of selenium. In point of fact, this method gives a higher value for Se than any of the other processes which have been adopted, and that value has the largest probable error of any one in the entire series. A glance at the table which summarizes the discussion at the end of this chapter will render this point sufficiently clear.

Latest of all, we come to the determinations made by Ekman and Pettersson.* They tried various methods of investigation, and finally decided upon the two following:

First. Pure silver selenite, Ag_2SeO_3 was ignited, leaving behind metallic silver in the subjoined percentages:

---

* Ann. Chem. Pharm., 113, 32. 1860.
† Ber. d. Deutsch. Chem. Gesell., 9, 1210. 1876. Published in detail by the society at Upsala.

$$62.93$$
$$62.95$$
$$62.97$$
$$62.94$$
$$62.98$$
$$62.98$$
$$62.95$$

Mean, $62.957, \pm .005$

Second. A warm aqueous solution of selenious acid was mixed with HCl, and reduced by a current of SO_2. The reduced Se was collected upon a glass filter, dried, and weighed. Percentages of Se in SeO_2:

$$71.199$$
$$71.185$$
$$71.193$$
$$71.187$$
$$71.191$$

Mean, $71.191, \pm .0016$

This series, combined with that of Sacc, $71.088, \pm .032$, gives a general mean of $71.1907, \pm .0016$.

There are now five series of figures from which to deduce the atomic weight of selenium:

(1.) Per cent. of Se in SeO_2, $71.1907, \pm .0016$
(2.) $BaSeO_3 : BaSO_4 :: 100 : 88.437, \pm .013$
(3.) Per cent. of Hg in HgSe, $71.7327, \pm .003$
(4.) $Se : SeCl_4 :: 100 : 178.696, \pm .125$
(5.) Per cent. of Ag in Ag_2SeO_3, $62.957, \pm .005$

From these we get the following values for selenium:

From (1) _____ Se $= 78.894, \pm .018$
" (2) _____ " $= 78.362, \pm .053$
" (3) _____ " $= 78.700, \pm .019$
" (4) _____ " $= 79.174, \pm .064$
" (5) _____ " $= 78.819, \pm .025$

General mean _____ " $= 78.797, \pm .011$

If $O = 16$, $Se = 78.978$.

TELLURIUM.

Particular interest attaches to the atomic weight of tellurium, on account of the speculations of Mendelejeff. According to the "periodic law" of that chemist, tellurium should lie between antimony and iodine, having an atomic weight greater than 120, and less than 127. Theoretically, Mendelejeff assigns it a value of $Te = 125$; but all the published determinations lead to a mean number higher than would be admissible under the aforesaid "periodic law." Whether theory or experiment is at fault remains to be discovered.

The first, and for many years the only, determinations of the constant in question, were made by Berzelius.[*] By means of nitric acid he oxidized tellurium to the dioxide, and from the increase in weight deduced a value for the metal. He published only his final results; from which, if $O = 100$, $Te = 802.121$. The three separate experiments give $Te = 801.74, 801.786$, and 802.838; whence we can calculate the following percentages of metal in the dioxide :

<div align="center">

80.057
80.036
80.034
_____

Mean, 80.042, $\pm$ .005

</div>

The next determinations were made by von Hauer,[†] who resorted to the analysis of the well crystallized double salt $TeBr_4.2KBr$. In this compound the bromine was estimated as silver bromide, the values assumed for Ag and Br being respectively 108.1 and 80. Recalculating, with our newer atomic weights for the above named elements, we get from v. Hauer's analyses, for 100 parts of the salt, the quantities of AgBr which are put in the third column :

---

* Poggend. Annal., 28, 395.   1833.
† Sitzungsb. Wien Akad., 25, 142.

2.000 grm. K$_2$TeBr$_6$ gave	69.946 per cent. Br.	164.460
6.668	"	69.8443	"	164.221
2.934	"	69.9113	"	164.379
3.697	"	70.0163	"	164.626
1.000	"	69.901	"	164.355

Mean, 164.408, ± .045

From Berzelius' series we may calculate Te = 128.045, and from v. Hauer's Te = 127.419. Dumas,* by a method for which he gives absolutely no particulars, found Te = 129.

In 1879, with direct reference to Mendelejeff's speculations, the subject of the atomic weight of tellurium was taken up by Wills.† The methods of both Berzelius and von Hauer were employed, with various rigid precautions in the way of testing balance and weights, and to ensure purity of material. In the first series of experiments tellurium was oxidized by nitric acid to form TeO_2. The results gave figures ranging from Te = 126.31 to 129.34 :

2.21613 grm. Te gave	2.77612 grm. TeO$_2$.	79.828 per cent. Te.
1.45313	"	1.81542	"	80.044	"
2.67093	"	3.33838	"	80.007	"
4.77828	"	5.95748	"	80.207	"
2.65029	"	3.31331	"	79.989	"

Mean, 80.015, ± .041

In the second series tellurium was oxidized by aqua regia to TeO_2 ; with results varying from Te = 127.77 to 128.00 :

2.85011 grm. Te gave	3.56158 grm. TeO$_2$.	80.024 per cent. Te.
3.09673	"	3.86897	"	80.040	"
5.09365	"	6.36612	"	80.012	"
3.26604	"	4.08064	"	80.037	"

Mean, 80.028, ± .004

Combining these series with that due to Berzelius, we have the following general mean :

---

* Ann. d. Chim. et d. Phys., (3,) 55, 129. 1859.
† Journ. Chem. Society, Oct., 1879, p. 704.

Berzelius_____ So.042, ± .005
Will,, 1st series_____ So.015, ± .041
  "   2d   "   _____ So.028, ± .004
                                    _____
        General mean_____ So.035, ± .003

Hence Te = 127.986, ± .035.

By von Hauer's process, the analysis of $TeBr_4.2KBr$, Will's figures give results ranging from Te = 126.07 to 127.61. Reduced to a common standard, 100 parts of the salt yield the quantities of AgBr given in the third column:

1.70673 grm. K_2TeBr_6 gave	2.80499 grm. AgBr.	164.349
1.75225 "	2.88072 "	164.398
2.06938 "	3.40739 "	164.657
3.29794 "	5.43228 "	164.717
2.46545 "	4.05742 "	164.571

Mean, 164.538, ± .048

Combined with von Hauer's mean, 164.408, ± .045, this gives a general mean of 164.468, ± .033. Hence Te = 127.170, ± .173.

The two independent values for Te combine thus:

From TeO_2_____Te = 127.986, ± .035
  " TeK_2Br_6_____ " = 127.170, ± .173
                                    _____
        General mean_____ " = 127.960, ± .034

If O = 16, Te = 128.254.

A careful consideration of the foregoing figures, and of the experimental methods by which they were obtained, will show that they are not absolutely conclusive with regard to the place of tellurium under the periodic law. The atomic weight of iodine, calculated in a previous chapter, is 126.557. Wills' values for Te, rejecting his first series as relatively unimportant, range from 126.07 to 128.00; that is, some of them fall below the atomic weight of iodine, although none descend quite to the 125 assumed by Mendelejeff.

In considering the experimental methods, reference may properly be made to the controversy regarding the atomic weight of antimony. It will be seen that Dexter, estimating the latter constant by the conversion of the metal

into Sb_2O_4, obtained a value approximately of Sb = 122. Dumas, working with $SbCl_3$, obtained a similar value. Schneider and Cooke, on the other hand, have established an atomic weight for antimony near 120, and Cooke in particular has traced out the constant errors which lurked unsuspected in the work of Dumas and Dexter. Now in some physical respects tellurium and antimony are quite similar. As constant errors vitiated the recently accepted values for Sb, so they may also effect our estimates for Te. The oxidation of Te by nitric acid resembles in minor particulars that of Sb. The analysis of K_2TeBr_6, gives a low value for Te, and yet the material may have contained traces of oxybromides, the presence of which would render even that lower value too high. A careful revision of the atomic weight of tellurium is still necessary.

VANADIUM.

Roscoe's determination of the atomic weight of vanadium is the only one having any present value. The results obtained by Berzelius [*] and by Czudnowicz [†] are unquestionably too high; the error being probably due to the presence of phosphoric acid in the vanadic acid employed. This particular impurity, as Roscoe has shown, prevents the complete reduction of V_2O_5 to V_2O_3 by means of hydrogen. All vanadium ores contain small quantities of phosphorus, which can only be detected with ammonium molybdate; a reaction unknown in Berzelius' time. Furthermore, the complete purification of vanadic acid from all traces of phosphoric acid is a matter of great difficulty, and probably never was accomplished until Roscoe undertook his researches.

In his determination of the atomic weight, Roscoe [‡]

---

[*] Poggend. Annal., 22, 14. 1831.

[†] Poggend. Annal., 120, 17. 1863.

[‡] Journ. Chem. Soc., 6, pp. 330 and 344. 1868.

studied two compounds of vanadium; namely, the pent-oxide, V_2O_5 and the oxychloride, $VOCl_3$. The pentoxide, absolutely pure, was reduced to V_2O_3 by heating in hydrogen, with the following results:

7.7397 grm. V_2O_5 gave 6.3827 grm. V_2O_3.	17.533 per cent. of loss.
6.5819 " 5.4296 "	17.507 "
5.1895 " 4.2819. "	17.489 "
5.0450 " 4.1614 "	17.515 "
5.4296 grm. V_2O_3, reoxidized, gave 6.5814 grm. V_2O_5.	17.501 per cent. difference.

Mean, 17.509, ± .005

Hence $V = 51.264, \pm .025$.

Upon the oxychloride, $VOCl_3$, two series of experiments were made, one volumetric, the other gravimetric. In the volumetric series the compound was titrated with solutions containing known weights of silver, which had been purified according to the methods recommended by Stas. Roscoe publishes his weighings, and gives percentages deduced from them; his figures, reduced to a common standard, make the quantities of $VOCl_3$ given in the third column proportional to 100 parts of silver. He was assisted by two analysts:

Analyst A.

2.4322 grm. $VOCl_3$ =	4.5525 grm. Ag.	53.425
4.6840 "	8.7505 "	53.528
4.2188 "	7.8807 "	53.533
3.9490 "	7.3799 "	53.510
.9243 "	1.7267 "	53.530
1.4330 "	2.6769 "	53.532

Analyst B.

2.8530 "	5.2853 "	53.980
2.1252 "	3.9535 "	53.755
1.4248 "	2.6642 "	53.479

Mean, 53.586, ± .039

The gravimetric series, of course, fixes the ratio between $VOCl_3$ and $AgCl$. If we put the latter at 100 parts, the proportion of $VOCl_3$ comes out as given in the third column:

Analyst A.

1.8521 grm. VOCl$_3$ gave	4.5932 grm. AgCl.		40.323
.7013	"	1.7303	"	40.531
.7486	"	1.8467	"	40.537
1.4408	"	3.5719	"	40.337
.9453	"	2.3399	"	40.399
1.6183	"	4.0282	"	40.174

Analyst B.

2.1936	"	5.4039	"	40.391
2.5054	"	6.2118	"	40.333

Mean, 40.378, $\pm$ .028

These two series give us two values for the molecular weight of VOCl$_3$:

From the volumetric series ___ VOCl$_3$ = 173.096, $\pm$ .126
" gravimetric " ___ " = 173.276, $\pm$ .141
General mean_____ " = 173.177, $\pm$ .094

Hence V = 51.104, $\pm$ .104.

Combining the two values for V we get the following result :

From V$_2$O$_5$_____ V = 51.264, $\pm$ .025
" VOCl$_3$ _____ " = 51.104, $\pm$ .104
General mean_____ " = 51.256, $\pm$ .024

Or, if O = 16, V = 51.373.

ARSENIC.

For the determination of the atomic weight of arsenic two compounds have been studied; the chloride and the trioxide. The bromide may also be considered, since it was analyzed by Wallace in order to establish the atomic weight of bromine. His series, in the light of more recent knowledge, may properly be inverted, and applied to the determination of arsenic.

In 1826, Berzelius * heated arsenic trioxide with sulphur

---

* Poggend. Annal., 8, 1.

in such a way that only SO_2 could escape.   2.203 grammes of As_2O_3, thus treated, gave a loss of 1.069 of SO_2.   Hence As = 74.840.   This is a close estimation; but, being drawn from a single experiment, has so little weight that it need not be included in our final general mean.

In 1845 Pelouze[*] applied his method of titration with known quantities of pure silver to the analysis of the trichloride of arsenic, $AsCl_3$.   Using the old Berzelian atomic weights, and putting Ag = 1349.01, and Cl = 443.2, he found in three experiments for As the values 937.9, 937.1, and 937.4.   Hence 100 parts of silver balance the following quantities of $AsCl_3$:

$$56.029$$
$$56.009$$
$$56.016$$
$$\overline{}$$

Mean, 56.018, $\pm$ .004

Later, the same method was employed by Dumas,[†] whose weighings, reduced to the foregoing standard, give the following results:

4.298 grm. $AsCl_3$ =	7.673 grm. Ag.	Ratio,	56.015
5.535 "	9.880 "		56.022
7.660 "	13.686 "		55.970
4.680 "	8.358 "		55.993

Mean, 56.000, $\pm$ .008

The two series of Pelouze and Dumas, combined, give a general mean of 56.014, $\pm$ .0035, as the amount of $AsCl_3$ equivalent to 100 parts of silver.   Hence As = 74.829, $\pm$ .048, a value closely agreeing with that deduced from the single experiment of Berzelius.

The same process of titration with silver was applied by Wallace[‡] to the analysis of arsenic tribromide, $AsBr_3$.   This compound was repeatedly distilled to ensure purity, and was well crystallized.   His weighings show that the quanti-

---

* Compt. Rend., 20, 1047.

† Ann. Chim. Phys., (3,) 55, 174.   1859.

‡ Philosophical Magazine, (4,) 18, 279.

ties of bromide given in the third column are proportional to 100 parts of silver:

8.3246 grm. $AsBr_3$ =	8.58 grm. Ag.		97.023
4.4368 "	4.573 "		97.022
5.098 "	5.257 "		96.970

Mean, 97.005, ± .012

Hence As = 74.046, ± .058. Why this value should be so much lower than that from the chloride is unexplained.

The volumetric work done by Kessler,[*] for the purpose of establishing the atomic weights of chromium and of arsenic, has already been described in the chromium chapter. In that investigation the amount of potassium dichromate required to oxidize 100 parts of As_2O_3 to As_2O_5 was determined, and compared with the quantity of potassium chlorate necessary to produce the same effect. From the molecular weight of $KClO_3$, that of $K_2Cr_2O_7$ was then calculable.

From the same figures, the molecular weights of $KClO_3$ and of $K_2Cr_2O_7$ being both known, that of As_2O_3 may be easily determined. The quantities of the other compounds proportional to 100 parts of As_2O_3 are as follows:

$K_2Cr_2O_7$.	$KClO_3$.
98.95	41.156
98.94	41.116
99.17	41.200
98.98	41.255
99.08	41.201
99.15	41.086
	41.199
Mean, 99.045, ± .028	41.224
	41.161
	41.193
	41.149
	41.126

Mean, 41.172, ± .009

---

[*] Poggend. Annal., 95, 204. 1855. Also 113, 134. 1861.

Another series with the bichromate gave the following figures:

$$99.08$$
$$99.06$$
$$99.10$$
$$98.97$$
$$98.97$$

Mean, 99.036, $\pm$ .019
Mean of previous series, 99.045, $\pm$ .028

General mean, 99.039, $\pm$ .016

Other defective series are given to illustrate the partial oxidation of the As_2O_3 by action of air. The foregoing figures give us two distinct values for the molecular weight of As_2O_3. In calculating from the bichromate results the value for chromium deduced from Siewert's determinations will be used, viz., $Cr = 52.009$, $\pm$ .025.

From $KClO_3$ series_____ $As_2O_3 = 197.996$, $\pm$ .049
" $K_2Cr_2O_7$ " _____   " $= 197.777$, $\pm$ .051

General mean____   " $= 197.894$, $\pm$ .035

Hence As $= 75.002$, $\pm$ .018.

The general mean for As comes out as follows:

From $AsCl_3$_____As $= 74.829$, $\pm$ .048
" $AsBr_3$_____ " $= 74.046$, $\pm$ .058
" As_2O_3_____ " $= 75.002$, $\pm$ .018

General mean_____ " $= 74.918$, $\pm$ .016

If $O = 16$, then As becomes $= 75.090$.

ANTIMONY.

After some earlier, unsatisfactory determinations, Berzelius,[*] in 1826, published his final estimation of the atomic weight of antimony. He oxidized the metal by means of nitric acid, and found that 100 parts of antimony gave 124.8 of Sb_2O_4. Hence, if $O = 16$, $Sb = 129.03$. The

---

[*] Poggend. Annal., 8, 1

value 129 remained in general acceptance until 1855, when Kessler,* by special volumetric methods, showed that it was certainly much too high. Kessler's results will be considered more fully further along, in connection with a later paper; for present purposes a brief statement of his earlier conclusions will suffice. Antimony, and various compounds of antimony, were oxidized partly by potassium anhydrochromate and partly by potassium chlorate; and from the amounts of oxidizing agent required, the atomic weight in question was deduced:

By oxidation of Sb_2O_3 from 100 parts of Sb .... Sb = 123.84

   "   Sb with $K_2Cr_2O_7$ .... " = 123.61

   "   " $KClO_3 + K_2Cr_2O_7$ .... " = 123.72

   " Sb_2O_3 with   "   .... " = 123.80

   " Sb_2S_3 with $K_2Cr_2O_7$ .... " = 123.58

   "   tartar emetic .... " = 119.80

The figures given are those calculated by Kessler himself. A recalculation with our newer atomic weights for O, K, Cl, Cr, S, and C, would yield slightly lower values. It will be seen that five of the estimates agree closely, while one diverges widely from the others. It will be shown hereafter that the concordant values are all vitiated by constant errors, and that the exceptional figure is after all the best.

Shortly after the appearance of Kessler's first paper, Schneider† published some results obtained by the reduction of antimony sulphide in hydrogen. The material chosen was a very pure stibnite from Arnsberg, of which the gangue was only quartz. This was corrected for, and corrections were also applied for traces of undecomposed sulphide carried off mechanically by the gas stream, and for traces of sulphur retained by the reduced antimony. The latter sulphur was estimated as barium sulphate. From 3.2 to 10.6 grammes of material were taken in each experiment. The final corrected percentages of S in Sb_2S_3 were as follows:

---

* Poggend. Annal., 95, 215.

† Poggend. Annal., 98, 293. 1856. Preliminary note in Bd. 97.

$$28.559$$
$$28.557$$
$$28.501$$
$$28.554$$
$$28.532$$
$$28.485$$
$$28.492$$
$$28.481$$

Mean, 28.520, ± .008

Hence, if S = 32, Sb = 120.3.

Immediately after the appearance of Schneider's memoir, Rose * published the result of a single analysis of antimony trichloride, previously made under his supervision by Weber. This analysis, if Cl = 35.5, makes Sb = 120.7, a value of no great weight, but in a measure confirmatory of that obtained by Schneider.

The next research upon the atomic weight of antimony was that of Dexter,† published in 1857. This chemist, having tried to determine the amount of gold precipitable by a known weight of antimony, and having obtained discordant results, finally resorted to the original method of Berzelius. Antimony, purified with extreme care, was oxidized by nitric acid, and the gain in weight was determined. From 1.5 to 3.3 grammes of metal were used in each experiment. The reduction of the weights to a vacuum standard was neglected as being superfluous. From the data obtained, we get the following percentages of Sb in Sb_2O_4 :

$$79.268$$
$$79.272$$
$$79.255$$
$$79.266$$
$$79.253$$
$$79.271$$
$$79.264$$
$$79.260$$
$$79.286$$

* Poggend. Annal., 98, 455.   1856.
† Poggend. Annal., 100, 563.

$$79.274$$
$$79.232$$
$$79.395$$
$$79.379$$

Mean, 79.283, $\pm$ .009

Hence, if O = 16, Sb = 122.46.

The determinations of Dumas [*] were published in 1859. This chemist sought to fix the ratio between silver and antimonicus chloride, and obtained results for the atomic weight of antimony quite near to those of Dexter. The $SbCl_3$ was prepared by the action of dry chlorine upon pure antimony ; it was distilled several times over antimony powder, and it seemed to be perfectly pure. Known weights of this preparation were added to solutions of tartaric acid in water, and the silver chloride was precipitated without previous removal of the antimony. Here, as Cooke has since shown, is a possible source of error, for under such circumstances the crystalline argento-antimonious tartrate may also be thrown down and contaminate the chloride of silver. But be that as it may ; Dumas' weighings, reduced to a common standard, give as proportional to 100 parts of silver, the quantities of $SbCl_3$ which are stated in the third of the subjoined columns:

1.876 grm. $SbCl_3$ =	2.660 grm. Ag.		70.526
4.336	"	6.148 "	70.527
5.065	"	7.175 "	70.592
3.475	"	4.930 "	70.487
3.767	"	5.350 "	70.411
5.910	"	8.393 "	70.416
4.828	"	6.836 "	70.626

Mean, 70.512, $\pm$ .021

Hence, if Ag = 108, and Cl = 355, Sb = 122.

In 1861 Kessler's second paper [†] relative to the atomic weight of antimony appeared. Kessler's methods were somewhat complicated, and for full details the original memoirs must be consulted. A standard solution of potassium anhydrochromate was prepared, containing 6.1466

---

[*] Ann. Chim. Phys., (3,) 55, 175.

[†] Poggend. Annal., 113, 145.

grammes to the litre.   With this, solutions containing
known quantities of antimony or of antimony compounds
were titrated, the end reaction being adjusted with a stand-
ard solution of ferrous chloride.   In some cases the titration
was preceded by the addition of a definite weight of potas-
sium chlorate, insufficient for complete oxidation; the an-
hydrochromate then served to finish the reaction.   The
object in view was to determine the amount of oxidizing
agent, and therefore of oxygen, necessary for the conver-
sion of known quantities of antimonious into antimonic
compounds.

In the later paper Kessler refers to his earlier work, and
shows that the values then found for antimony were all too
high, except in the case of the series made with tartar
emetic.   That series he merely states, and subsequently
ignores, evidently believing it to be unworthy of further
consideration.   For the remaining series he points out the
sources of error.   These need not be rediscussed here, as the
discussion would have no value for present purposes; suffice
it to say that in the series representing the oxidation of
Sb_2O_3 with anhydrochromate and chlorate, the material
used was found to be impure.   Upon estimating the im-
purity and correcting for it, the earlier value of $Sb = 123.80$
becomes $Sb = 122.36$, according to Kessler's calculations.

In the paper now under consideration four series of results
are given.   The first represents experiments made upon a
pure antimony trioxide which had been sublimed, and which
consisted of shining colorless needles.   This was dissolved,
together with some potassium chlorate, in hydrochloric acid,
and titrated with anhydrochromate solution.   Six experi-
ments were made, but Kessler rejects the first and second as
untrustworthy.   The data for the others are as follows:

Sb_2O_3.	$KClO_3$.	$K_2Cr_2O_7$ sol. in cc.
1.7888 grm.	.4527 grm.	19.2 cc.
1.6523 "	.4506 "	3.9 "
3.2998 "	.8806 "	16.5 "
1.3438 "	.3492 "	10.2 "

From these figures Kessler deduces $Sb = 122.16$.

These data, reduced to a common standard, give the following quantities of oxygen needed to oxidize 100 parts of Sb_2O_3 to Sb_2O_5. Each cubic centimetre of the $K_2Cr_2O_7$ solution corresponds to one milligramme of O :

<div align="center">

10.985
10.939
10.951
10.936

Mean, 10.953, ± .0075

</div>

In the second series of experiments pure antimony was dissolved in hydrochloric acid with the aid of an unweighed quantity of potassium chlorate. The solution, containing both antimonious and antimonic compounds, was then reduced entirely to the antimonious condition by means of stannous chloride. The excess of the latter was corrected with a strong hydrochloric acid solution of mercuric chloride, then, after diluting and filtering, a weighed quantity of potassium chlorate was added, and the titration with anhydrochromate was performed as usual. Calculated as above, the percentages of oxygen given in the last column correspond to 100 parts of antimony :

Sb.	$KClO_3$.	$K_2Cr_2O_7$ sol. cc.	Per cent. O.
1.636 grm.	0.5000 grm.	18.3	13.088
3.0825 "	0.9500 "	30.2	13.050
4.5652 "	1.4106 "	45.5	13.098

<div align="right">Mean, 13.079, ± .0096</div>

This series gave Kessler Sb = 122.34.

The third and fourth series of experiments were made with pure antimony trichloride, $SbCl_3$, prepared by the action of mercuric chloride upon metallic antimony. This preparation, in the third series, was dissolved in hydrochloric acid, and titrated. In one experiment solid $K_2Cr_2O_7$ in weighed amount was added before titration: in the other two estimations $KClO_3$ was taken as usual. If, according to Siewert's work, we take Cr = 52.009, the percentages of oxygen in the last column correspond to 100 parts of $SbCl_3$:

13

1.8576 grm. SbCl$_3$ needed .5967 grm. K$_2$Cr$_2$O$_7$ and 33.4 cc. sol.	7.0338
1.9118 " .3019 " KClO$_3$ " 16.2 "	7.0321
4.1235 " .6801 " " " 23.2 "	7.0222

Mean, 7.0294, ± .0024

The fourth set of experiments was gravimetric. The solution of SbCl$_3$, mixed with tartaric acid, was first precipitated by hydrogen sulphide, in order to remove the antimony. The excess of H$_2$S was corrected by copper sulphate, and then the chlorine was estimated as silver chloride in the ordinary manner. 100 parts of AgCl correspond to the amounts of SbCl$_3$ given in the third column.

1.8662 grm. SbCl$_3$ gave 3.483 grm. AgCl.	53.580
1.6832 " 3.141 "	53.588
2.7437 " 5.1115 "	53.677
2.6798 " 5.0025 "	53.569
5.047 " 9.411 "	53.629
3.8975 " 7.2585 "	53.696

Mean, 53.623, ± .015

The volumetric series with SbCl$_3$ gave Kessler values for Sb ranging from 121.16 to 121.47. The gravimetric series, on the other hand, yielded results from Sb = 124.12 to 124.67. This discrepancy Kessler rightly attributes to the presence of oxygen in the chloride; and, ingeniously correcting for this error, he deduces from both sets combined, the value of Sb = 122.37.

The several mean results for antimony agree so fairly with each other, and with the estimates obtained by Dexter and Dumas, that we cannot wonder that Kessler felt satisfied of their general correctness, and of the inaccuracy of the figures published by Schneider. Still, the old series of data obtained by the titration of tartar emetic with anhydrochromate contained no evident errors, and was not accounted for. This series,* if we reduce all of Kessler's figures to a single common standard, give a ratio between K$_2$Cr$_2$O$_7$ and C$_4$H$_4$KSbO$_7$.$\frac{1}{2}$H$_2$O. 100 parts of the former will oxidize of the latter:

---

* Poggend. Annal., 95, 217.

$$336.64$$
$$338.01$$
$$336.83$$
$$337.93$$
$$338.59$$
$$335.79$$

Mean, 337.30, $\pm$ .29

From this, if $K_2Cr_2O_7 = 294.64$, $Sb = 119.8$.

The newer atomic weights found in the previous chapters of this work will be applied to the discussion of all these series further along. It may, however, be properly noted at this point, that the probable errors assigned to the percentages of oxygen in three of Kessler's series are too low. These percentages are calculated from the quantities of $KClO_3$ involved in the several reactions, and their probable errors should be increased with reference to the probable error of the molecular weight of that salt. The necessary calculations would be more laborious than the importance of the figures would warrant, and, accordingly, in computing the final general mean for antimony, Kessler's figures will receive somewhat higher weight than they are legitimately entitled to.

Naturally, the concordant results of Dexter, Kessler, and Dumas led to the general acceptance of the value of 122 for antimony as against the lower figure 120 of Schneider. Still, in 1871, Unger* published the results of a single analysis of Schlippe's salt, $Na_3SbS_4.9H_2O$. This analysis gave $Sb = 119.76$, if $S = 32$ and $Na = 23$, but no great weight could be attached to the determination. It served, nevertheless, to show that the controversy over the atomic weight of antimony was not finally settled.

More than ten years after the appearance of Kessler's second paper the subject of the atomic weight of antimony was again taken up, this time by Professor Cooke. His results appeared in the autumn of 1877,† and were conclusive in favor of the lower value, approximately 120. For full

* Archiv. der Pharmacie, 197, 194. Quoted by Cooke.
† Proceedings American Academy, v. 13.

details the original memoir must be consulted; only a few
of the leading points can be cited here.

Schneider analyzed a sulphide of antimony which was
already formed. Cooke, reversing the method, effected the
synthesis of this compound. Known weights of pure anti-
mony were dissolved in hydrochloric acid containing a little
nitric acid. In this solution weighed balls of antimony
were boiled until the liquid became colorless; subsequently
the weight of metal lost by the balls was ascertained. To
the solution, which now contained only antimonious com-
pounds, tartaric acid was added, and then, with a supersat-
urated aqueous sulphhydric acid, antimony trisulphide was
precipitated. The precipitate was collected by an ingenious
process of reverse filtration, converted into the black modi-
fication by drying at 210°, and weighed. After weighing,
the Sb_2S_3 was dissolved in hydrochloric acid, leaving a car-
bonaceous residue unacted upon. This was carefully esti-
mated and corrected for. About two grammes of antimony
were taken in each experiment and thirteen syntheses were
performed. In two of these, however, the antimony tri-
sulphide was weighed only in the red modification, and the
results were uncorrected by conversion into the black va-
riety and estimation of the carbonaceous residue. In fact,
every such conversion and correction was preceded by a
weighing of the red modification of the Sb_2S_3. The mean
result of these weighings, if S = 32, gave Sb = 119.994.
The mean result of the corrected syntheses gave Sb =
120.295. In these eleven experiments the following per-
centages of S in Sb_2S_3 were established:

$$28.57$$
$$28.60$$
$$28.57$$
$$28.43$$
$$28.42$$
$$28.53$$
$$28.50$$
$$28.49$$
$$28.58$$
$$28.50$$
$$28.51$$

Mean, 28.5182, ± .0120

These results, confirmatory of the work of Schneider, were presented to the American Academy in 1876. Still, before publication, Cooke thought it best to repeat the work of Dumas, in order to detect the cause of the old discrepancy between the values $Sb = 120$ and $Sb = 122$. Accordingly, various samples of antimony trichloride were taken, and purified by repeated distillations. The final distillate was further subjected to several recrystallizations from the fused state; or, in one case, from a saturated solution in bisulphide of carbon. The portions analyzed were dissolved in concentrated aqueous tartaric acid, and precipitated by silver nitrate, many precautions being observed. The silver chloride was collected by reverse filtration, and dried at temperatures from $110°$ to $120°$. In one experiment the antimony was first removed by H_2S. Seventeen experiments were made, giving, if $Ag = 108$ and $Cl = 35.5$, a mean value of $Sb = 121.94$. If we reduce to a common standard, Cooke's analyses give, as proportional to 100 parts of AgCl, the quantities of $SbCl_3$ stated in the third column:

1.5974 grm. $SbCl_3$ gave	3.0124 grm. AgCl.		53.028
1.2533	"	2.3620	"	53.061
.8876	"	1.6754	"	52.978
.8336	"	1.5674	"	53.184
.5326	"	1.0021	"	53.148
.7270	"	1.3691	"	53.101
1.2679	"	2.3883	"	53.088
1.9422	"	3.6646	"	52.999
1.7702	"	3.3384	"	53.025
2.5030	"	4.7184	"	53.048
2.1450	"	4.0410	"	53.081
1.7697	"	3.3281	"	53.175
2.3435	"	4.4157	"	53.072
1.3686	"	2.5813	"	53.020
1.8638	"	3.5146	"	53.030
2.0300	"	3.8282	"	53.028
2.4450	"	4.6086	"	53.053

Mean, 53.066, $\pm$ .0096

This mean may be combined with that of Kessler's series, as follows:

Kessler _____ _____ 53.623, ± .015
Cooke _____ _____ _____ 53.066, ± .0096
                                  ─────────────
      General mean ___ _____ 53.2311, ± .008

The results thus obtained with $SbCl_3$ confirmed Dumas' determination of the atomic weight of antimony as remarkably as the syntheses of Sb_2S_3 had sustained the work of Schneider.   Evidently, in one or the other series a constant error must be hidden, and much time was spent by Cooke in searching for it.   It was eventually found that the chloride of antimony invariably contained traces of oxychloride, an impurity which tended to increase the apparent atomic weight of the metal under consideration.   If was also found, in the course of the investigation, that hydrochloric acid solutions of antimonious compounds oxidize in the air during boiling as rapidly as ferrous compounds; a fact which explains the high values for antimony found by Kessler.

In order to render "assurance doubly sure," Professor Cooke also undertook the analysis of the bromide and the iodide of antimony.   The bromide, $SbBr_3$, was prepared by adding the finely powdered metal to a solution of bromine in carbon disulphide.   It was purified by repeated distillation over pulverized antimony, and by several recrystallizations from bisulphide of carbon.   The bromine determinations resembled those of chlorine, and gave, if $Ag = 108$ and $Br = 80$, a mean value for antimony of $Sb = 120$. Reduced to a common standard, the fifteen analyses give the subjoined quantities of $SbBr_3$ proportional to 100 parts of silver bromide:

1.8621 grm. $SbBr_3$ gave	2.9216 grm. AgBr.	63.736
.9856 "	1.5422 "	63.909
1.8650 "	2.9268 "	63.721
1.5330 "	2.4030 "	63.795
1.3689 "	2.1445 "	63.833
1.2124 "	1.8991 "	63.841
.9417 "	1.4749 "	63.848
2.5404 "	3.9755 "	63.901
1.5269 "	2.3905 "	63.874
1.8604 "	2.9180 "	63.756
1.7298 "	2.7083 "	63.870

3.2838 grm. SbBr₃ gave	5.1398 grm. AgBr.		63.890
2.3589 "	3.6959 "		63.825
1.3323 "	2.0863 "		63.859
2.6974 "	4.2285 "		63.791

Mean, 63.830, ± .008

The iodide of antimony was prepared like the bromide, and analyzed in the same way. At first, discordant results were obtained, due to the presence of oxyiodide in the iodide studied. The impurity, however, was removed by subliming the iodide in an atmosphere of dry carbon dioxide. With this purer material, seven estimations of iodine were made, giving, if $Ag = 108$ and $I = 127$, a value for antimony of $Sb = 120$. Reduced to a uniform standard, Cooke's weighings give the following quantities of SbI_3 proportional to 100 parts of silver iodide:

1.1877 grm. SbI₃ gave	1.6727 grm. AgI.		71.005
.4610 "	.6497 "		70.956
3.2527 "	4.5716 "		71.150
1.8068 "	2.5389 "		71.165
1.5970 "	2.2456 "		71.117
2.3201 "	3.2645 "		71.071
.3496 "	.4927 "		70.956

Mean, 71.060, ± .023

Although Cooke's work was practically conclusive, as between the rival values for antimony, his results were severely criticized by Kessler,* who, evidently, had read Cooke's paper in a very careless way. On the other hand, Schneider published in Poggendorff's Annalen a friendly review of the new determinations, which so splendidly vindicated his own accuracy. In reply to Kessler, Cooke undertook still another series of experiments with antimony bromide,† and obtained absolute confirmation of his previous results. To a solution of antimony bromide was added a solution containing a known weight of silver not quite sufficient to precipitate all the bromine. The excess

---

* Berichte d. Deutsch. Chem. Gesell., 12, 1044. 1879.
† Amer. Journ. Sci. and Arts, May, 1880. Berichte, 13, 951.

of the latter was estimated by titration with a normal silver solution. Five analyses gave values for antimony ranging from 119.98 to 120.02, when Ag = 108 and Br = 80. Reduced to a common standard, the weights obtained gave the amounts of $SbBr_3$ stated in the third column as proportional to 100 parts of silver:

2.5032 grm. $SbBr_3$ =	2.2528 grm. Ag.	111.115
2.0567 "	1.8509 "	111.119
2.6512 "	2.3860 "	111.115
3.3053 "	2.9749 "	111.106
2.7495 "	2.4745 "	111.113

Mean, 111.114, ± .0014

Schneider,[*] also, in order to more fully answer Kessler's objections, repeated his work upon the Arnsberg stibnite. This he reduced in hydrogen as before, correcting scrupulously for impurities. The following percentages of sulphur were found:

28.546
28.534
28.542

Mean, 28.541, ± .0024

These figures confirm his old results, and may be fairly combined with them and with the percentages found by Cooke, as follows:

Schneider, early series _____ 28.520, ± .008
       "   late   "   _____ 28.541, ± .0024
Cooke _____ 28.5182, ± .0120

General mean _____ 28.5385, ± .0023

We have now before us the following ratios, good and bad, from which to calculate the atomic weight of antimony. The single results obtained by Weber and by Unger, being unimportant, are not included:

(1.) Percentage of S in Sb_2S_3, 28.5385, ± .0023
(2.)   "   Sb in Sb_2O_4, 79.283, ± .009
(3.) O needed to oxidize 100 parts $SbCl_3$, 7.0294, ± .0024
(4.) O   "   " Sb_2O_3, 10.953, ± .0075
(5.) O   "   "   Sb, 13.079, ± .0096

* Journ. für Prakt. Chem., (2,) 22, 131.

(6.) $K_2Cr_2O_7$: tartar emetic :: 100 : 337.30, $\pm$ .29

(7.) Ag : $SbCl_3$ :: 100 : 70.512, $\pm$ .021

(8.) AgCl : $SbCl_3$ ·: 100 : 53.2311, $\pm$ .008

(9.) Ag : $SbBr_3$ :: 100 : 111.114, $\pm$ .0014

(10.) AgBr : $SbBr_3$ :: 100 : 63.830, $\pm$ .008

(11.) AgI : SbI_3 :: 100 : 71.060, $\pm$ .023

Three of these ratios give estimates for the molecular weight of antimony trichloride, and two give corresponding values for the bromide. These values may be combined, as follows: First, for the chloride we have—

From (3) — — — — — — — — $SbCl_3$ = 227.094, $\pm$ .115

" (7) — — — — — — — — " = 227.771, $\pm$ .091

" (8) — — — — — — — — " = 228.433, $\pm$ .039

General mean — — — — " = 228.225, $\pm$ .034

Hence Sb = 122.115, $\pm$ .055.

For the bromide we get:

From (9). — — — — — — — $SbBr_3$ = 358.926, $\pm$ .032

" (10) — — — — — — — — " = 358.935, $\pm$ .060

General mean — — — " = 358.929, $\pm$ .029

Hence Sb = 119.625, $\pm$ .063.

From all the data eight values for Sb may be deduced. These fall into two groups; the one near the number 120, the other not far from 122. In making the calculation the atomic weights found in previous chapters are applied; the value selected for chromium being that deduced from Siewert's experiments:

1. From Sb_2S_3, ratio (1) — — — — — — Sb = 120.145, $\pm$ .045 ⎱
2. " $SbBr_3$ — — — — — — — — " = 119.625, $\pm$ .063 ⎰ Low.
3. " SbI_3, ratio (11) — — — — — — " = 119.665, $\pm$ .179
4. " tartar emetic, ratio (6) — — — " = 118.690, $\pm$ .278 ⎰
5. " Sb_2O_4, ratio (2) — — — — — — " = 122.181, $\pm$ .061 ⎱
6. " $SbCl_3$ — — — — — — — — — " = 122.115, $\pm$ .055 ⎰ High.
7. " ratio (4) — — — — — — — — " = 121.798, $\pm$ .105
8. " " (5) — — — — — — — — " = 122.053, $\pm$ .094 ⎰

General mean — — — — — — — " = 121.027, $\pm$ .025

General mean of values 1 to 4 — " = 119.935, $\pm$ .036

" " 5 " 8 — " = 122.092, $\pm$ .035

Although the means of the four lower values and of the four higher values are thus shown to be approximately

equal in weight, we know from Cooke's experiments that the larger mean is vitiated by serious constant errors. Only in value 5, the result calculated from Dexter's experiments, has the constant error not been pointed out. Cooke considers it probable, however, that the Sb_2O_4 involved in this work contained traces of some lower oxide, which, if present, would render the atomic weight of antimony apparently too high. Chemically considered, the preponderance of evidence is strongly in favor of values 1 to 3, deduced from the experiments of Schneider and of Cooke. These give a general mean of $Sb = 119.955, \pm .036$; or, if $O = 16$, this becomes $Sb = 120.231$.

This we may accept as most nearly the true result, and reject the data of Dexter, Dumas, and Kessler altogether.

Since this chapter was written, Pfeifer has compared the amount of antimony thrown down electrolytically, with the quantity of silver deposited by the same current in the same time. From rather meagre data he concludes that the atomic weight of antimony, thus determined, may be 121. Additional investigation is promised. The figures thus far published would weigh little as against Cooke's experiments. (Ann. Chem. Pharm., 209, 161. 1881.)

BISMUTH.

Early in the century the combining weight of bismuth was approximately fixed through the experiments of Lagerhjelm.* Effecting the direct union of bismuth and sulphur, he found that ten parts of the metal yield the following quantities of trisulphide:

$$12.2520$$
$$12.2065$$
$$12.2230$$
$$12.2465$$

Mean, 12.2320

* Annals of Philosophy, 4, 358. 1814. Results adopted by Berzelius.

Hence B = 215 in round numbers, a value now known to be much too high. Lagerhjelm also oxidized bismuth with nitric acid, and, after ignition, weighed the trioxide thus formed. Ten parts of metal gave the following quantities of Bi_2O_3 :

11.1382
11.1275

Mean, 11.13285

Hence, if O = 16, Bi = 211.85, a figure still too high.

In 1851 the subject of the atomic weight of bismuth was taken up by Schneider,* who, like Lagerhjelm, studied the oxidation of the metal with nitric acid. The work was executed with a variety of experimental refinements, by means of which every error due to possible loss of material was carefully avoided. For full details the original paper must be consulted; there is only room in these pages for the actual results, as follows. The figures represent the percentages of Bi in Bi_2O_3 :

89.652
89.682
89.644
89.634
89.656
89.666
89.655
89.653

Mean, 89.6552, ± .0034

Hence Bi = 207.523, ± .082 ; or, if O = 16, Bi = 208.001.

Finally, we come to the results obtained by Dumas.† Bismuth trichloride was prepared by the action of dry chlorine upon bismuth, and repeatedly rectified by distillation over bismuth powder. The product was weighed in a closed tube, dissolved in water, and precipitated with sodium carbonate. In the filtrate, after strongly acidulating

* Poggend. Annal., 82, 303. 1851.
† Ann. de Chim. et de Phys., (3,) 55, 176. 1859.

with nitric acid, the chlorine was precipitated by a known amount of silver. The figures in the third column show the quantities of $BiCl_3$ proportional to 100 parts of silver :

3.506 grm. $BiCl_3$ =	3.545 grm. Ag.			98.900
1.149	"	1.168	"	98.373
1.5965	"	1.629	"	98.005
2.1767	"	2.225	"	97.829
3.081	"	3.144	"	97.996
2.4158	"	2.470	"	97.806
1.7107	"	1.752	"	97.643
3.523	"	3.6055	"	97.712
5.241	"	. 5.361	"	97.762

Mean, 98.003, $\pm$ .090

Hence Bi = 210.464, $\pm$ .294.

The first three of the foregoing series of experiments were made with slightly discolored material, and may therefore be rejected. The remaining six percentages give a mean of 97.791; whence Bi = 209.78; or, if O = 16, Bi = 210.26.

As between the unaccordant results of Schneider and of Dumas, those of the former chemist are probably nearest correct. His method of determination was the more reliable, and the details which he gives concerning his manipulations afford strong presumptions of accuracy. Doubtless the bismuth trichloride used by Dumas, contained, like the corresponding antimony compounds, traces of oxychloride. We may fairly assume, for all practical purposes, that the atomic weight of bismuth cannot be far from 208.

TIN.

Stannic oxide and stannic chloride are the compounds which have been studied in estimating the atomic weight of tin.

The composition of stannic oxide has been fixed in two ways; by synthesis from the metal, and by reduction in hydrogen. For the first method we may consider the work of Berzelius, Mulder and Vlaanderen, and Dumas.

Berzelius[*] oxidized 100 parts of tin by nitric acid, and found that 127.2 parts of SnO_2 were formed.

The work done by Mulder and Vlaanderen[†] was done in connection with a long investigation into the composition of Banca tin, which was found to be almost absolutely pure. For the atomic weight determinations, however, really pure tin was taken, prepared from pure tin oxide. This metal was oxidized by nitric acid, with the following results. 100 parts of tin gave of SnO_2 :

> 127.56—Mulder.
> 127.56—Vlaanderen.
> 127.43—   "

> Mean, 127.517, $\pm$ .029

Dumas[‡] oxidized pure tin by nitric acid in a flask of glass. The resulting SnO_2 was strongly ignited, first in the flask, and afterwards in platinum. His weighings, reduced to the foregoing standard, give for dioxide from 100 parts of tin the amounts stated in the third column :

| 12.443 grm. Sn gave 15.820 grm. SnO_2. | 127.14 |
| 15.976   "   20.301   " | 127.07 |

> Mean, 127.105, $\pm$ .024

In an investigation later than that previously cited, Vlaanderen[||] found that when tin was oxidized in glass or porcelain vessels, and the resulting oxide ignited in them, traces of nitric acid were retained. When, on the other hand, the oxide was strongly heated in platinum, the latter was perceptibly attacked, so much so as to render the results uncertain. He therefore, in order to fix the atomic weight of tin, reduced the oxide by heating it in a porcelain boat in a stream of hydrogen. Two experiments gave Sn = 118.08, and Sn = 118.24. These, when O = 16, become, if reduced to the above common standard,

---

[*] Poggend. Annal., 8, 177.
[†] Journ. für Prakt. Chem., 49, 35.   1849.
[‡] Ann. Chem. Pharm., 113, 26.
[||] Jahresbericht, 1858, 183.

$$127.100$$
$$127.064$$

Mean, 127.082, $\pm$ .012

We have now four series of results showing the quantity of SnO_2 formed from 100 parts of tin. To Berzelius' single value may be assigned the probable error of a single experiment in Mulder and Vlaanderen's series:

Berzelius_____ 127.200, $\pm$ .041—Oxidation.
Mulder and Vlaanderen_____ 127.517, $\pm$ .029—   "
Dumas _____ 127.105, $\pm$ .024—   "
Vlaanderen_____ 127.082, $\pm$ .012—Reduction.

General mean_____ _____ 127.143, $\pm$ .0098

Dumas, in the paper previously quoted, also gives the results of some experiments with stannic chloride, $SnCl_4$. This was titrated with a solution containing a known weight of silver. From the weighings given, 100 parts of silver correspond to the quantities of $SnCl_4$ named in the third column:

1.839 grm. $SnCl_4$ = 3.054 grm. Ag.   60.216
2.665   "   4.427   "   60.199

Mean, 60.207, $\pm$ .006

All these data properly combined give us the following values for the atomic weight of tin:

From SnO_2 _____ _____Sn = 117.624, $\pm$ .050
  " $SnCl_4$_____ " = 117.832, $\pm$ .067

General mean_____ " = 117.698, $\pm$ .040

If O = 16, this becomes Sn = 117.968.

TITANIUM.

The earliest determinations of the atomic weight of titanium are due to Heinrich Rose.[*] In his first investigation he studied the conversion of titanium sulphide into titanic acid, and obtained erroneous results; later, in 1829, he published his analyses of the chloride.[†] This compound was purified by repeated rectifications over mercury and over potassium, and was weighed in bulbs of thin glass. These were broken under water in tightly stoppered flasks; the titanic acid was precipitated by ammonia, and the chlorine was estimated as silver chloride. The following results were obtained. In a fourth column I give the TiO_2 in percentages referred to $TiCl_4$ as 100; and in a fifth column the quantity of $TiCl_4$ proportional to 100 parts of AgCl:

$TiCl_4$.	TiO_2.	AgCl.	Per cent. TiO_2.	AgCl Ratio.
.885 grm.	.379 grm.	2.661 grm.	42.825	33.258
2.6365 "	1.120 "	7.954 "	42.481	33.147
1.7157 "	.732 "	5.172 "	42.665	33.173
3.0455 "	1.322 "	9.198 "	43.423	33.100
2.4403 "	1.056 "	7.372 "	43.273	33.102

Mean, 42.933, ± .121   33.156, ± .019

If we directly compare the AgCl with the TiO_2 we shall find 100 parts of the former proportional to the following quantities of the latter:

14.243
14.081
14.153
14.373
14.324

Mean, 14.235, ± .036

From all these figures we can get three values for Ti, thus:

* Gilbert's Annalen, 1823, 67 and 129.
† Poggend. Annal., 15, 145. Berz. Lehrbuch, 3, 1210.

$$\text{From per cent. } TiO_2 \text{---------} Ti = 50.493, \pm .410$$
$$\text{`` } AgCl : TiCl_4 \text{---------} \text{`` } = 48.232, \pm .127$$
$$\text{`` } AgCl : TiO_2 \text{---------} \text{`` } = 49.523, \pm .206$$

$$\text{General mean} \text{---------} \text{`` } = 48.710, \pm .105$$

These results will be discussed further along in connection with others.

Shortly after the appearance of Rose's paper, Mosander [*] published some figures giving the percentages of oxygen in titanium dioxide, from which a value for the atomic weight of titanium was deduced. Although no details are furnished as to experimental methods, and no actual weighings are given, I cite his percentages for whatever they may be worth :

$$40.814$$
$$40.825$$
$$40.610$$
$$40.180$$
$$40.107$$
$$40.050$$
$$40.780$$
$$40.660$$
$$39.830$$

Mean, 40.428

These figures give values for Ti ranging from 46.277 to 48.231; or, in mean, Ti = 47.045. They are not, however, sufficiently explicit to deserve any further consideration. It will be noticed that the highest value nearly coincides with Rose's lowest.

In 1847 Isidor Pierre made public a series of important determinations.[†] Titanium chloride, free from silicon and from iron, was prepared by the action of chlorine upon a mixture of carbon with pure, artificial, titanic acid. This chloride was weighed in sealed tubes, these were broken under water, and the resulting hydrochloric acid was titrated with a standard solution of silver after the method

---

[*] Berz. Jahresbericht, 10, 108. 1831.
[†] Ann. de Chim. et Phys., (3.) 20, 257.

of Pelouze. I subjoin Pierre's weighings, and add, in a third column, the ratio of $TiCl_4$ to 100 parts of silver:

$TiCl_4$.	$Ag.$	Ratio.
.8215 grm.	1.84523 grm.	44.520
.7740 "	1.73909 "	44.506
.7775 "	1.74613 "	44.527
.7160 "	1.61219 "	44.412
.8085 "	1.82344 "	44.339
.6325 "	1.42230 "	44.470
.8155 "	1.83705 "	44.392
.8165 "	1.83899 "	44.399
.8065 "	1.81965 "	44.322

Mean, 44.432, $\pm$ .0173

It will be seen that the first three of these results agree well with each other and are much higher than the remaining six. The last four experiments were made purposely with tubes which had been previously opened, in order to determine the cause of the discrepancy. According to Pierre, the opening of a tube of titanium chloride admits a trace of atmospheric moisture. This causes a deposit of titanic acid near the mouth of the tube, and liberates hydrochloric acid. The latter gas being heavy, a part of it falls back into the tube, so that the remaining chloride is richer in chlorine and poorer in titanium than it should be. Hence, upon titration, too low figures for the atomic weight of titanium are obtained. Pierre accordingly rejects all but the first three of the above estimations:

From all of Pierre's_____Ti $= 49.889, \pm$ .096
" the first three_____ " $= 50.259, \pm$ .063

The memoir of Pierre upon the atomic weight of titanium was soon followed by a paper from Demoly,[*] who obtained much higher results. He also started out from titanic chloride, which was prepared from rutile. The latter substance was found to contain 1.8 per cent. of silica; whence Demoly inferred that the $TiCl_4$ investigated by Rose and by Pierre

---

14

might have been contaminated with $SiCl_4$, an impurity
which would lower the value deduced for the atomic weight
under consideration.   Accordingly, in order to eliminate all
such possible impurities, this process was resorted to : the
chloride, after rectification over mercury and potassium, was
acted upon by dry ammonia, whereupon the compound
$TiCl_4.4NH_3$ was deposited as a white powder.   This was
ignited in dry ammonia gas, and the residue, by means of
chlorine, was reconverted into titanic chloride, which was
again repeatedly rectified over mercury, potassium, and
potassium amalgam.   The product boiled steadily at 135°.
This chloride, after weighing in a glass bulb, was decomposed
by water, the titanic acid was precipitated by ammonia, and
the chlorine was estimated in the filtrate as silver chloride.
Three analyses were performed, yielding the following re-
sults.   I give the actual weighings:

> 1.470 grm. $TiCl_4$ gave 4.241 grm. AgCl and .565 grm. TiO_2.
> 2.330   "   6.752   "   .801   "
> 2.880   "   8.330   "   1.088   "

The ".801" in the last column is certainly a misprint for
.901.   Assuming this correction, the results may be given
in three ratios, thus:

Per cent. TiO_2 from $TiCl_4$.	$TiCl_4$: 100 AgCl.	TiO_2 : 100 AgCl.
38.435	34.662	13.322
38.669	34.508	13.344
37.778	34.574	13.061
Mean, 38.294, ± .180	34.581, ± .030	13.242, ± .061

These three ratios give three widely divergent values for
the atomic weight of titanium;

> From per cent. TiO_2 _ _ _ _ _ _ _ _ Ti $= 36.063$, ± .519
> "   AgCl : TiO_2 _ _ _ _ _ _ _ _ _ _ " $= 43.841$, ± .350
> "   AgCl : $TiCl_4$ _ _ _ _ _ _ _ _ _ _ " $= 56.386$, ± .181
>
> General mean_ _ _ _ _ _ _ _ " $= 52.191$, ± .153

The value assumed by Demoly is 56; who employs but
one ratio and ignores practically the others.

Upon comparing Demoly's figures with those obtained by Rose, certain points of similarity are plainly to be noted. Both sets of results were reached by essentially the same method; and in both the discordance between the percentages of titanic acid and of silver chloride is glaring. This discordance can rationally be accounted for by assuming that the titanic chloride was in neither case absolutely what it purported to be; that, in brief, it must have contained impurities; such for example as hydrochloric acid, as shown in the experiments of Pierre, or possibly traces of oxychlorides. Considerations of this kind also throw doubt upon the results attained by Pierre, for he neglected the direct estimation of the titanic acid altogether, thus leaving us without means for correctly judging as to the character of his material. In fact, not one of the determinations of the atomic weight of titanium can be regarded as trustworthy. All depend upon the chloride, and the volatile chlorides of metals are as a class especially liable to contaminations of a kind most difficult to recognize. Possibly a series of good determinations might be based upon analyses of some of the titanofluorides. I subjoin a combination of the foregoing mean values, feeling that such a general average is a little better than any one set of determinations taken singly:

$$
\begin{array}{llll}
\text{From Rose's analyses} & \text{Ti} & = 48.710, & \pm\ .105 \\
\text{``} \quad \text{Pierre's} \quad \text{``} & \text{``} & = 49.889, & \pm\ .096 \\
\text{``} \quad \text{Demoly's} \ \text{``} & \text{``} & = 52.191, & \pm\ .153 \\
\hline
\text{General mean} & \text{``} & = 49.846, & \pm\ .064
\end{array}
$$

Or, if $O = 16$, $Ti = 49.961$.

This mean agrees with the average of all of Pierre's experiments.

ZIRCONIUM.

The atomic weight of zirconium has been determined by Berzelius, by Hermann, and by Marignac.   Berzelius[*] ignited the neutral sulphate, and thus ascertained the ratio in it between the ZrO_2 and the SO_3.   Putting SO_3 at 100, he gives the following proportional quantities of ZrO_2 :

<div align="center">

75.84
75.92
75.80
75.74
75.97
75.85

</div>

<div align="center">

Mean, 75.853, ± .023

</div>

Hence $Zr = 89.255, \pm .039$; or, if $O = 16$, then $Zr = 89.461$.

Hermann's[†] estimate of the atomic weight of zirconium was based upon analyses of the chloride, concerning which he gives no details or weighings.   From sublimed zirconium chloride he finds $Zr = 831.8$, when $O = 100$; and from two lots of the basic chloride $2ZrOCl_2.9H_2O$, $Zr = 835.65$ and 851.40 respectively.   The mean of all three is 839.62; whence, with modern formulæ and $O = 15.9633$, Zr becomes $= 89.351$.

Marignac's results[‡] were obtained by analyzing the double fluoride of zirconium and potassium.   His weights are as follows :

<div align="center">

1.000 grm. gave .431 grm. ZrO_2 and .613 grm. K_2SO_4.
2.000   "   .864   "   1.232   "
 .654   "   .282   "   .399   "
5.000   "   2.169   "   3.078   "

</div>

These figures give us three ratios.   A, the ZrO_2 from 100

[*] Poggend. Annal., 4, 126.   1825.

[†] Journ. für Prakt. Chem., 31, 77.   Berz. Jahresb., 25, 147.

[‡] Ann. Chim. Phys., (3,) 60, 270.   1860.

parts of salt; B, the K_2SO_4 from 100 parts of salt; and C, the ZrO_2 proportional to 100 parts of K_2SO_4 :

A.	B.	C.
43.100	61.300	70.310
43.200	61.600	70.130
43.119	61.000	70.677
43.380	61.560	70.468
Mean, 43.200, $\pm$ .043	61.365, $\pm$ .094	70.396, $\pm$ .079

From A $Zr = 89.775, \pm .216$
" B " $= 91.408, \pm .437$
" C " $= 90.476, \pm .138$

General mean " $= 90.328, \pm .113$

Or, if $O = 16$, $Zr = 90.536$.

Combining with Berzelius' work we get this result:

Berzelius $Zr = 89.255, \pm .039$
Marignac " $= 90.328, \pm .113$

General mean " $= 89.367, \pm .037$

Or, if $O = 16$, $Zr = 89.573$.

These figures need little criticism. They show conclusively that the atomic weight of zirconium ought to be redetermined. Probably the method employed by Berzelius was the best with respect to manipulation, while on the other hand it is likely that Marignac worked with purer material. Hermann's experiments could hardly have yielded certain results, since the zirconium chloride might so easily become contaminated with traces of moisture and thence of oxygen.

THORIUM.

The atomic weight of thorium has been determined from analyses of the sulphate, oxalate, formate, and acetate, with widely varying results. The earliest figures are due to Berzelius,[*] who worked with the sulphate, and with the double sulphate of potassium and thorium. The thoria was precipitated by ammonia, and the sulphuric acid was estimated as $BaSO_4$. The sulphate gave the following ratios in two experiments. The third column represents the weight of ThO_2 proportional to 100 parts of $BaSO_4$:

.6754 grm. ThO_2 = 1.159 grm. $BaSO_4$.   Ratio, 58.274
1.0515   "   1.832   "   "   57.396

The double potassium sulphate gave .265 grm. ThO_2, .156 grm. SO_3, and .3435 K_2SO_4. The SO_3, with the Berzelian atomic weights, represents .4537 grm. $BaSO_4$. Hence 100 $BaSO_4$ is equivalent to 58.408 ThO_2. This figure, combined with the two previous values for the same ratio, give a mean of 58.026, ± .214. Hence ThO_2 = 269.940, ± .997.

From the ratio between the K_2SO_4 and the ThO_2 in the double sulphate, ThO_2 = 268.284.

In 1861 new determinations were published by Chydenius,[†] whose memoir is accessible to me only in an abstract[‡] which gives results without details. Thoria is regarded as a monoxide, ThO, and the old equivalents (O = 8) are used. The following values are assigned for the molecular weight of ThO, as found from analyses of several salts:

From Sulphate.	From K. Th. Sulphate.
66.33	67.02
67.13	
67.75	
68.03	
Mean, 67.252, ± .201	

---

* Poggend. Annal., 16, 398. 1829. Lehrbuch, 3, 1224.

† Kemisk undersökning af Thorjord och Thorsalter. Helsingfors, 1861. An academic dissertation.

‡ Poggend. Annal., 119, 55. 1863.

From Acetate.	*From Formate.*	*From Oxalate.*	
67.31	68.06	65.87	} Two results
66.59	67.89	65.95	} by Berlin.
67.27	68.94	65.75	
67.06	———	65.13	
68.40	Mean, 68.297, $\pm$ .219	66.54	
———		65.85	
Mean, 67.326, $\pm$ .201		———	
		Mean, 65.85, $\pm$ .123	

We may fairly assume that these figures were calculated with $O = 8$, $C = 6$, and $S = 16$. Correcting by the values for these elements which have been found in previous chapters, ThO_2 becomes as follows:

From sulphate _____$ThO_2 =$ 268.584, $\pm$ .803
  " acetate _____ " $=$ 268.735, $\pm$ .805
  " formate _____ " $=$ 272.586, $\pm$ .877
  " oxalate_____ " $=$ 262.804, $\pm$ .493

The single result from the double potassium sulphate is included with the column from the ordinary sulphate, and the influence of the atomic weight of potassium is ignored.

Chydenius was soon followed by Marc Delafontaine, whose researches appeared in 1863.[*] This chemist especially studied thorium sulphate; partly in its most hydrous form, partly as thrown down by boiling. In $Th(SO_4)_2.9H_2O$, the following percentages of ThO_2 were found:

45.08
44.90
45.06
45.21
45.06
———
Mean, 45.062, $\pm$ .0332

Hence $ThO_2 =$ 263.637, $\pm$ .256.

The lower hydrate, $2Th(SO_4)_2.9H_2O$, was more thoroughly investigated. The thoria was estimated in two ways; first, (A,) by precipitation as oxalate and subsequent ignition; second, (B,) by direct calcination. These percentages of ThO_2 were found:

———

[*] Arch. des Sci. Phys. et Nat., (2,) 18, 343.

$$
\left.\begin{array}{l}
52.83 \\
52.52 \\
52.72 \\
52.13
\end{array}\right\} \text{A.}
$$

$$
\left.\begin{array}{l}
52.47 \\
52.49 \\
52.53 \\
52.13 \\
52.13 \\
52.43 \\
52.60 \\
52.40 \\
52.96 \\
52.82
\end{array}\right\} \text{B.}
$$

Mean, 52.511, $\pm$ .047

Hence $ThO_2 = 266.025, \pm .363.$

In three experiments with this lower hydrate the sulphuric acid was also estimated, being thrown down as barium sulphate after removal of the thoria:

1.2425 grm. gave	.400 SO_3.	(1.1656 grm. $BaSO_4$.)
1.138 "	.366 "	(1.0665 ")
.734 "	.2306 "	(.6720 ")

The figures in parenthesis are reproduced by myself from Delafontaine's results, he having calculated his analyses with $O = 100$, $S = 200$, and $Ba = 857$. These data may be reduced to a common standard, so as to represent the quantity of $2Th(SO_4)_2.9H_2O$ equivalent to 100 parts of $BaSO_4$. We then have the following results:

$$
\begin{array}{l}
106.597 \\
106.704 \\
109.226
\end{array}
$$

Mean, 107.509, $\pm$ .585

Hence $ThO_2 = 259.555, \pm 2.725.$

Delafontaine seems himself to have calculated from the ratio between the percentages of SO_3 and ThO_2; whence, with our revised values for S, Ba, and O, $ThO_2 = 262.643$.

Delafontaine's work was soon confirmed by Hermann,*

---

* Journ. für Prakt. Chem., 93, 114.

who published a single analysis of the lower hydrated sulphate, as follows:

$$ThO_2 \text{ ---------- } 52.87$$
$$SO_3 \text{ ----- ------ } 32.11$$
$$H_2O \text{ ----------- } 15.02$$

_____

$$100.00$$

Hence, from the ratio between SO_3 and ThO_2, $ThO_2 = 263.030$. Probably the SO_3 percentage was loss upon calcination.

The latest, and probably also the best determinations, are those of Cleve,[*] whose results, obtained from both the sulphate and the oxalate of thorium, agree admirably. The anhydrous sulphate, calcined, gave the subjoined percentages of thoria:

$$62.442$$
$$62.477$$
$$62.430$$
$$62.470$$
$$62.357$$
$$62.366$$

_____

Mean, $62.423, \pm .014$

Hence $ThO_2 = 265.380, \pm .123$.

The oxalate was subjected to a combustion analysis, whereby both thoria and carbonic acid could be estimated. From the direct percentages of these constituents no accurate value can be deduced, there having undoubtedly been moisture in the material studied. From the ratio between CO_2 and ThO_2, however, good results are attainable. This ratio I put in a fourth column, making the thoria proportional to 100 parts of carbon dioxide:

Oxalate.	ThO_2.	CO_2.	Ratio.
1.7135 grm.	1.0189 grm.	.6736 grm.	151.262
1.3800 "	.8210 "	.5433 "	151.114
1.1850 "	.7030 "	.4650 "	151.183
1.0755 "	.6398 "	.4240 "	150.896

Mean, $151.114, \pm .053$

Hence $ThO_2 = 265.357, \pm .104$.

_____

* K. Svenska Vet. Akad. Handlinger. Bd. 2, No. 6. 1874.

There are now before us twelve estimates for the molecular weight of thoria. Two of these represent single experiments, and have no probable error attached to them; namely, the one due to Hermann, and the one deduced from Berzelius' K_2SO_4 : ThO_2 ratio. A third value, from Delafontaine's sulphuric acid estimations, has so high a probable error that it could be rejected without influencing the general mean. These three values might all be excluded without serious objection; but it is perhaps better to arbitrarily assign them equal weight, average them together, and give their mean the same probable error as that which attaches to Berzelius' $BaSO_4$: ThO_2 series. This mean is indicated as "A" in the following combination:

Value "A"	ThO_2 =	263.623, ± .997
Berzelius	" =	269.940, ± .997
Chydenius—Sulphate	" =	268.584, ± .803
" Acetate	" =	268.735, ± .805
" Formate	" =	272.586, ± .877
" Oxalate	" =	262.804, ± .493
Delafontaine—Higher hydrate	" =	263.637, ± .256
" Lower "	" =	266.025, ± .363
Cleve—Sulphate	" =	265.380, ± .123
" Oxalate	" =	265.357, ± .104
General mean	" =	265.341, ± .072

Hence Th = 233.414, ± .0725; or, if O = 16, Th = 233.951.

These values vary from those derived from Cleve's experiments alone only in the second decimal.

GALLIUM.

Gallium has been so recently discovered, and obtained in such small quantities, that its atomic weight has not as yet been determined with much precision. The following data were fixed by the discoverer, Lecoq de Boisbaudran:[*]

---

[*] Journ. Chem. Soc., 1878, p. 646.

3.1044 grammes gallium ammonium alum, upon ignition, left .5885 grm. Ga_2O_3.

Hence Ga = 68.071. If O = 16, Ga = 68.233.

.4481 grammes gallium, converted into nitrate and ignited, gave .6024 grm. Ga_2O_3.

Hence Ga = 69.538. If O = 16, Ga = 69.693.

These values, assigned equal weight, give these means:

If O = 15.9633, Ga = 68.854. If O = 16, Ga = 68.963.

In brief, for all practical purposes, 69 may be assumed as the atomic weight of gallium.

INDIUM.

Reich and Richter, the discoverers of indium, were also the first to determine its atomic weight.[*] They dissolved weighed quantities of the metal in nitric acid, precipitated the solution with ammonia, ignited the precipitate, and ascertained its weight. Two experiments were made, as follows:

.5135 grm. indium gave .6243 grm. In_2O_3.
.699   "   .8515   "

Hence, in mean, In = 110.61, if O = 16; a value known now to be too low.

An unweighed quantity of fresh, moist indium sulphide was also dissolved in nitric acid, yielding, on precipitation,

.2105 grm. In_2O_3 and .542 grm. $BaSO_4$.

Hence, with $BaSO_4$ = 233, In = 111.544; also too low.

Soon after the publication of Reich and Richter's paper the subject was taken up by Winkler.[†] He dissolved indium in nitric acid, evaporated to dryness, ignited the residue, and weighed the oxide thus obtained.

---

[*] Journ. für Prakt. Chem., 92, 484.
[†] Journ. für Prakt. Chem., 94, 8.

.5574 grm. In gave .6817 grm. In$_2$O$_3$.
  .6661   "   .8144   "
  .5011   "   .6126   "

Hence, in mean, if O = 16, In = 107.76; a result even lower than the values already cited.

In a later paper by Winkler[*] better results were obtained. Two methods were employed. First, metallic indium was placed in a solution of pure, neutral, sodio-auric chloride, and the amount of gold precipitated was weighed. I give the weighings and, in a third column, the amount of indium proportional to 100 parts of gold:

In.	Au.	Ratio.
.4471 grm.	.8205 grm.	57.782
.8445 "	1.4596 "	57.858
		Mean, 57.820, ± .026

Hence, if Au = 196.155, ± .095, In = 113.417, ± .074.

Winkler also repeated his earlier process, converting indium into oxide by solution in nitric acid and ignition of the residue. An additional experiment, the third as given below, was made after the method of Reich and Richter. The third column gives the percentage of In in In$_2$O$_3$:

1.124 grm. In gave 1.3616 grm. In$_2$O$_3$.   Per cent., 82.550
1.015   "   1.2291   "   "   82.581
 .6376   "   .7725   "   "   82.537

These figures were confirmed by a single experiment of Bunsen's,[†] published simultaneously with the specific heat determinations which showed that the oxide of indium was In$_2$O$_3$, and not InO as had been previously supposed :

1.0592 grm. In gave 1.2825 grm. In$_2$O$_3$.   Per cent. In, 82.589

For convenience we may add this figure in with Winkler's series, which gives us a mean percentage of In in In$_2$O$_3$ of 82.564, ± .0082. Hence, if O = 15.9633, ± .0035, In = 113.385, ± .060.

---

* Journ. für Prakt. Chem., 102, 282.
† Poggend. Annal., 141, 28.

Combining results, we have the following general mean:

From gold series _____ In $= 113.417, \pm .074$
" oxide " _____ " $= 113.385, \pm .060$

General mean _____ " $= 113.398, \pm .047$

Or, if $O = 16$, In $= 113.659$.

CERIUM.

Although cerium was discovered almost at the beginning of the present century, its atomic weight was not properly determined until after the discovery of lanthanum and didymium by Mosander. In 1842 the investigation was undertaken by Beringer,[*] who employed several methods. His cerium salts, however, were all rose-colored, and therefore were not wholly free from didymium; and his results are further affected by a negligence on his part to fully describe his analytical processes.

First, a neutral solution of cerium chloride was prepared by dissolving the carbonate in hydrochloric acid. This gave weights of ceroso-ceric oxide and silver chloride as follows. The third column shows the amount of CeO_2 proportional to 100 parts of AgCl:

CeO_2.	$AgCl$.	Ratio.
.5755 grm.	1.419 grm.	40.557
.6715 "	1.6595 "	40.464
1.1300 "	2.786 "	40.560
.5366 "	1.3316 "	40.297

Mean, 40.469, $\pm$ .0415

The analysis of the dry cerium sulphate gave results as follows. In a fourth column I show the amount of CeO_2 proportional to 100 parts of $BaSO_4$:

* Ann. Chem. Pharm., 42, 134.

Sulphate.	CeO_2.	$BaSO_4$.	Ratio.
1.379 grm.	.8495 grm.	1.711 grm.	49.649
1.276 "	.7875 "	1.580 "	49.836
1.246 "	.7690 "	1.543 "	49.838
1.553 "	.9595 "	1.921 "	49.948

Mean, 49.819, ± .042

Beringer also gives a single analysis of the formate and the results of one conversion of the sulphide into oxide. The figures are, however, not valuable enough to cite.

The foregoing data involve one variation from Beringer's paper. Where I put CeO_2 as found he puts Ce_2O_3. The latter is plainly inadmissible, although the atomic weights calculated from it agree curiously well with some other determinations. For instance, in the chloride series, the assumption of Ce_2O_3 as the formula of the oxide obtained, gives Ce = 137.749, while CeO_2 makes Ce = 141.636. The former agrees with the results of Wolf, Wing, and others quite fairly; the latter is near the value obtained by Bührig. Obviously, the presence of didymium in the salts analyzed should tend to raise rather than to lower the apparent atomic weight of cerium.

Shortly after Beringer, Hermann * published the results of one experiment. 23.532 grm. of anhydrous cerium sulphate gave 29.160 grm. of $BaSO_4$. Hence 100 parts of the sulphate correspond to 123.926 of $BaSO_4$.

In 1848 similar figures were published by Marignac,† who found the following amounts of $BaSO_4$ proportional to 100 of dry cerium sulphate:

122.68
122.00
122.51

Mean, 122.40, ± .138

If we give Hermann's single result the weight of one experiment in this series, and combine, we get a mean value of 123.019, ± .113.

---

* Journ. für Prakt. Chem., 30, 185. 1843.
† Arch. des Sciences Phys. et Nat., (1,) 8, 273. 1848.

Still another method was employed by Marignac. A definite mixture was made of solutions of cerium sulphate and barium chloride. To this were added, volumetrically, solutions of each salt successively, until equilibrium was attained. The figures published give maxima and minima for the $BaCl_2$ proportional to each lot of $Ce_2(SO_4)_3$. In another column, using the mean value for $BaCl_2$ in each case, I put the ratio between 100 parts of this salt and the equivalent quantity of sulphate. The latter compound was several times recrystallized:

		$Ce_2(SO_4)_3$.		$BaCl_2$.		Ratio.
First crystallization		11.011 grm.	11.990 — 12.050 grm.			91.606
"	"	13.194 "	14.365 — 14.425	"		91.657
Second	"	13.961 "	15.225 — 15.285	"		91.518
"	"	12.627 "	13.761 — 13.821	"		91.559
"	"	11.915 "	12.970 — 13.030	"		91.654
Third	"	14.888 "	16.223 — 16.283	"		91.602
"	"	14.113 "	15.383 — 15.423	"		91.755
Fourth	"	13.111 "	14.270 — 14.330	"		91.685
"	"	13.970 "	15.223 — 15.283	"		91.588

Mean, 91.625, $\pm$ .016

Omitting the valueless experiments of Kjerulf,[*] we come next to the figures published by Bunsen and Jegel[†] in 1858. From the air dried sulphate of cerium the metal was precipitated as oxalate, which, ignited, gave CeO_2. In the filtrate from the oxalate the sulphuric acid was estimated as $BaSO_4$:

1.5726 grm. sulphate gave .7899 grm. CeO_2 and 1.6185 grm. $BaSO_4$.
1.6967   "   .8504   "   1.7500   "

Hence, for 100 parts $BaSO_4$, the CeO_2 is as follows:

48.804
48.575

Mean, 48.689, $\pm$ .077

One experiment was also made upon the oxalate:

.3530 grm. oxalate gave .1913 CeO_2 and .0506 H_2O.

Hence, in the dry salt, we have 63.261 per cent. of CeO_2.

---

[*] Ann. Chem. Pharm., 87, 12.
[†] Ann. Chem. Pharm., 105, 45.

In each sample of CeO_2 the excess of oxygen over true Ce_2O_3 was estimated by an iodometric titration; but the data thus obtained need not be further considered.

In two papers by Rammelsberg[*] data are given for the atomic weight of cerium, as follows. In the earlier paper cerium sulphate is analyzed, the cerium being thrown down by caustic potash, and the acid precipitated from the filtrate as barium sulphate:

.413 grm. $Ce_2(SO_4)_3$ gave .244 grm. CeO_2 and .513 grm $BaSO_4$.

Hence 100 $BaSO_4$ = 47.563 CeO_2, a value which may be combined with others, thus; this figure being assigned a weight equal to one experiment in Bunsen's series:

Beringer _____ 49.819, ± .042
Bunsen and Jegel_____ 48.689, ± .077
Rammelsberg_____ 47.563, ± .108

General mean_____ 49.360, ± .035

It should be noted here that this mean is somewhat arbitrary, since Bunsen and Rammelsberg's cerium salts were undoubtedly freer from didymium than the material studied by Beringer.

In his later paper Rammelsberg gives these figures concerning cerium oxalate. 100 parts gave 10.43 of carbon and 21.73 of water. Hence the dry salt should yield 48.862 per cent. of CO_2, whence Ce = 137.83.

In all of the foregoing experiments the ceroso-ceric oxide was somewhat colored, the tint ranging from one shade to another of light brown according to the amount of didymium present. Still, at the best, a faint color remained, which was supposed to be characteristic of the oxide itself. In 1868, however, some experiments of Dr. C. Wolf[†] were posthumously made public, which went to show that pure ceroso-ceric oxide is white, and that all samples previously studied were contaminated with some other earth, not necessarily didymium but possibly a new substance, the removal of

---

[*] Poggend. Annal., 55, 65; 108, 44.
[†] Amer. Journ. Science and Arts, (2,) 46, 53.

which tended to lower the apparent atomic weight of cerium very perceptibly.

Cerium sulphate was recrystallized at least ten times. Even after twenty recrystallizations it still showed spectroscopic traces of didymium. The water contained in each sample of the salt was cautiously estimated, and the cerium was thrown down by boiling concentrated solutions of oxalic acid. The resulting oxalate was ignited with great care. I deduce from the weighings the percentage of CeO_2 given by the *anhydrous* sulphate:

Sulphate.	Water.	CeO₂.	Per cent. CeO₂.
1.4542 grm.	.19419 grm.	.76305 grm.	60.559
1.4104 "	.1898 "	.7377 "	60.437
1.35027 "	.1820 "	.70665 "	60.487

Mean, 60.494, $\pm$ .024

After the foregoing experiments the sulphate was further purified by solution in nitric acid and pouring into a large quantity of boiling water. The precipitate was converted into sulphate and analyzed as before:

Sulphate.	Water.	CeO₂.	Per cent. CeO₂.
1.4327 grm.	.2733 grm.	.69925 grm.	60.311
1.5056 "	.2775 "	.7405 "	60.296
1.44045 "	.2710 "	.7052 "	60.300

Mean, 60.302, $\pm$ .004

From another purification the following weights were obtained:

1.4684 grm.   .1880 grm.   .7717 grm.   60.270 per cent.

A last purification gave a still lower percentage:

1.3756 grm.   .1832 grm.   .7186 grm.   60.265 per cent.

The last oxide was perfectly white, and was spectroscopically free from didymium. In each case the CeO_2 was titrated iodometrically for its excess of oxygen. It will be noticed that in the successive series of determinations the percentage of CeO_2 steadily and strikingly diminishes, to an extent for which no ordinary impurity of didymium can

15

account. The death of Dr. Wolf interrupted the investiga-
tion, the results of which were edited and published by Pro-
fessor F. A. Genth.

The experiments of Wolf seem to have hitherto escaped
general notice, except from Wing, who has partially verified
them.* This chemist, incidentally to other researches, puri-
fied some cerium sulphate after the method of Wolf, and
made two similar analyses of it, as follows:

Sulphate.	Water.	CeO_2.	Per cent. CeO_2.
1.2885 grm.	.1707 grm.	.6732 grm.	60.225
1.4090 "	.1857 "	.7372 "	60.263

Mean, 60.244, $\pm$ .012

The ceroso-ceric oxide in this case was perfectly white.
The cerium oxalate which yielded it was precipitated boil-
ing by a boiling concentrated solution of oxalic acid. The
precipitate stood twenty-four hours before filtering.

We may now combine the results of Wolf and of Wing,
as follows. The two concordant experiments of Wolf's
series three and four may be united, giving a mean of
60.267, $\pm$ .001 :

Wolf, 1st series	60.494, $\pm$ .024
" 2d "	60.302, $\pm$ .004
" 3d and 4th series	60.267, $\pm$ .001
Wing	60.244, $\pm$ .012
General mean	60.271, $\pm$ .001

This mean, the percentage of CeO_2 in the anhydrous sul-
phate, gives Ce = 137.724; or, if O = 16, Ce = 138.039.
This varies widely from the ordinarily accepted value as
determined by Buehrig.

In 1875 Buehrig's† paper upon the atomic weight of
cerium was issued. He first studied the sulphate, which,
after eight crystallizations, still retained traces of free sul-
phuric acid. He found furthermore that the salt obstinately
retained traces of water, which could not be wholly expelled
by heat without partial decomposition of the material.

---

* Amer. Journ. Sci. and Arts, (2,) 49, 358. 1870.
† Journ. für Prakt. Chem., 120, 222.

These sources of error probably affect all the previously cited series of experiments; although, in the case of Wolf's work, it is doubtful whether they could have influenced the atomic weight of cerium by more than one or two tenths of a unit. Buehrig also found, as Marignac had earlier shown, that upon precipitation of cerium sulphate with barium chloride the barium sulphate invariably carried down traces of cerium. Furthermore, the ceroso-ceric oxide from the filtrate always contained barium. For these reasons the sulphate was abandoned, and the atomic weight determinations of Buehrig were made with air-dried oxalate. This salt was placed in a series of platinum boats in a combustion tube behind copper oxide. It was then burned in a stream of pure, dry oxygen, and the carbonic acid and water were collected after the usual method. Ten experiments were made; in all of them the above named products were estimated, and in five analyses the resulting ceroso-ceric oxide was also weighed. By deducting the water found from the weight of the air-dried oxalate, the weight of the anhydrous oxalate is obtained, and the percentages of its constituents are easily determined. In weighing, the articles weighed were always counterpoised with similar materials. The following weights were found:

Oxalate.	Water.	CO_2.	CeO_2.
9.8541 grm.	2.1987 grm.	3.6942 grm.	------
9.5368 "	2.1269 "	3.5752 "	------
9.2956 "	2.0735 "	3.4845 "	------
10.0495 "	2.2364 "	3.7704 "	------
10.8249 "	2.4145 "	4.0586 "	------
9.3679 "	2.0907 "	3.5118 "	4.6150 grm.
9.7646 "	2.1769 "	3.6616 "	4.8133 "
9.9026 "	2.2073 "	3.7139 "	4.8824 "
9.9376 "	2.2170 "	3.7251 "	4.8971 "
9.5324 "	2.1267 "	3.5735 "	4.6974 "

These figures give us the following percentages for CO_2 and CeO_2 in the anhydrous oxalate:

CO_2.	CeO_2.
48.256	------
48.249	------
48.248	------

CeO_2.	CO_2.
48.257	------
48.257	------
48.258	63.417
48.257	63.436
48.262	63.446
48.249	63.429
48.253	63.430

Mean, 48.2546, $\pm$ .001   63.4316, $\pm$ .0032

From percentage CO_2 _____ Ce $=$ 141.228, $\pm$ .025
       " CeO_2 _____ " $=$ 141.141, $\pm$ .020

Obviously the single oxalate experiments of Jegel and of Rammelsberg would exert no appreciable influence upon these mean results. They may therefore be ignored.

In combining all of these data in one general mean, we may begin as usual by tabulating our ratios :

(1.) $BaSO_4 : Ce_2(SO_4)_3 : : 100 : 123.019$, $\pm$ .113
(2.) $BaSO_4 : CeO_2 : : 100 : 49.360$, $\pm$ .035
(3.) $BaCl_2 : Ce_2(SO_4)_3 : : 100 : 91.625$, $\pm$ .016
(4.) $AgCl : CeO_2 : : 100 : 40.469$, $\pm$ .0415
(5.) Percentage CeO_2 from anhydrous sulphate, 60.271, $\pm$ .001
(6.)   "   "   "   oxalate, 63.4316, $\pm$ .0032
(7.)   " CO_2 "   "   48.2546, $\pm$ .001

These ratios give us four values for the molecular weight of CeO_2 and two values for $Ce_2(SO_4)_3$:

From (2) _____ $CeO_2 =$ 172.218, $\pm$ .124
   "   (4) _____ " $=$ 173.663, $\pm$ .179
   "   (5) _____ " $=$ 169.651, $\pm$ .034
   "   (6) _____ " $=$ 173.068, $\pm$ .033

General mean_____ " $=$ 171.490, $\pm$ .023

From (1) _____ $Ce_2(SO_4)_3 =$ 567.234, $\pm$ .522
   "   (3) _____ " $=$ 570.375, $\pm$ .165

General mean_ " $=$ 570.093, $\pm$ .156

Hence we have three independent values for the atomic weight of cerium, as follows :

From molecular weight of CeO_2 ---------- Ce = 139.563, ± .024
"   " $Ce_2(SO_4)_3$ ----- " = 141.281, ± .083
From ratio (7,) CO_2 in oxalate --------- ---- " = 141.228, ± .025

General mean------------- ---- ---- " = 140.424, ± .017

Or, if O = 16, Ce = 140.747.

Buehrig's results alone, both sets combined, give Ce = 141.198, ± .020; or, if O = 16, Ce = 141.523.

Wolf and Wing's figures alone make Ce = 137.724; or, if O = 16, Ce = 138.039.

The latter result is subject to the errors pointed out by Buehrig as involved in the use of cerium sulphate; but the ceroso-ceric oxide obtained in the analyses was pure white. Buehrig's ceroso-ceric oxide, on the other hand, was yellow. In neither case was didymium present. All things considered, therefore, it is probable that the lower result is too low and the higher result too high. How near the general mean of all may be to the truth we have no evidence to show. It is clear that new determinations are needed, made with material yielding *white* ceroso-ceric oxide, and with avoidance of the sources of error which Buehrig pointed out.

LANTHANUM.

Leaving out of account the work of Mosander, and the valueless experiments of Choubine, we may consider the estimates of the atomic weight of lanthanum which are due to Hermann, Rammelsberg, Marignac, Czudnowicz, Holzmann, Zschiesche, Erk, and Cleve.

From Rammelsberg* we have but one analysis. .700 grm. of lanthanum sulphate gave .883 grm. of barium sulphate. Hence 100 parts of $BaSO_4$ are equivalent to 79.276 of $La_2(SO_4)_3$.

---

* Poggend. Annal., 55, 65.

Marignac,[*] working also with the sulphate of lanthanum, employed two methods. First, the salt in solution was mixed with a slight excess of barium chloride. The resulting barium sulphate was filtered off and weighed; but, as it contained some occluded lanthanum compounds, its weight was too high. In the filtrate the excess of barium was estimated, also as sulphate. This last weight of sulphate, deducted from the total sulphate which the whole amount of barium chloride could form, gave the sulphate actually proportional to the lanthanum compound. The following weights are given:

$La_2(SO_4)_3$.	$BaCl_2$.	$1st\ BaSO_4$.	$2d\ BaSO_4$.
4.346 grm.	4.758 grm.	5.364 grm.	.115 grm.
4.733 "	5.178 "	5.848 "	.147 "

Hence we have the following quantities of $La_2(SO_4)_3$ proportional to 100 parts of $BaSO_4$. Column A is deduced from the first $BaSO_4$ and column B from the second, after the manner above described:

A.	B.
81.022	83.281
80.934	83.662
Mean, 80.978, $\pm$ .030	Mean, 83.471. $\pm$ .128

From A_____La = 138.776
"   B_____ " = 147.474

A agrees best with other determinations, although, theoretically, it is not so good as B.

Marignac's second method, described in the same paper with the foregoing experiments, consisted in mixing solutions of $La_2(SO_4)_3$ with solutions of $BaCl_2$, titrating one with the other until equilibrium was established. The method has already been described under cerium. The weighings give maxima and minima for $BaCl_2$. In another column I give $La_2(SO_4)_3$ proportional to 100 parts of $BaCl_2$, mean weights being taken for the latter:

---

[*] Archives des Sci Phys. et Naturelles, (1,) 11, 29. 1849.

$La_2(SO_4)_3$.	$BaCl_2$.	Ratio.
11.644 grm.	12.765 — 12.825 grm.	91.004
12.035 "	13.195 — 13.265 "	90.968
10.690 "	11.669 — 11.749 "	91.297
12.750 "	13.920 — 14.000 "	91.332
10.757 "	11.734 — 11.814 "	91.362
12.672 "	13.813 — 13.893 "	91.475
9.246 "	10.080 — 10.160 "	91.364
10.292 "	11.204 — 11.264 "	91.615
10.192 "	11.111 — 11.171 "	91.482

Mean, 91.322, $\pm$ .048

Hence La = 140.484.

Although not next in chronological order, some still more recent work of Marignac's [*] may properly be considered here. The salt studied was the sulphate of lanthanum, purified by repeated crystallizations. In two experiments the salt was calcined, and the residual oxide weighed; in two others the lanthanum was precipitated as oxalate, and converted into oxide by ignition. The following percentages are given for La_2O_3 :

$$\left.\begin{matrix} 57.56 \\ 57.58 \end{matrix}\right\} \text{By calcination.}$$

$$\left.\begin{matrix} 57.50 \\ 57.55 \end{matrix}\right\} \text{Ppt. as oxalate.}$$

Mean, 57.5475, $\pm$ .0115

The atomic weight determinations of Holzmann [†] were made by analyses of the sulphate and iodate of lanthanum, and the double nitrate of magnesium and lanthanum. In the sulphate experiments the lanthanum was first thrown down as oxalate, which, on ignition, yielded oxide. The sulphuric acid was precipitated as $BaSO_4$ in the filtrate.

$La_2(SO_4)_3$.	La_2O_3.	$BaSO_4$.
.9663 grm.	.5157 grm.	1.1093 grm.
.6226 "	.3323 "	.7123 "
.8669 "	.4626 "	.9869 "

---

[*] Ann. de Chim. et de Phys., (4,) 30, 68. 1873.
[†] Journ. für Prakt. Chem., 75, 321. 1858.

These results are best used by taking the ratio between the $BaSO_4$, put at 100, and the La_2O_3. The figures are then as follows:

$$46.489$$
$$46.652$$
$$46.873$$

Mean, 46.671, $\pm$ .075

In the analyses of the iodate the lanthanum was thrown down as oxalate, as before. The iodic acid was also esti- mated volumetrically, but the figures are hardly available for present discussion. The following percentages of La_2O_3 were found:

$$23.454$$
$$23.419$$
$$23.468$$

Mean, 23.447, $\pm$ .0216

The formula of this salt is $La_2(IO_3)_6.3H_2O$.

The double nitrate, $La_2(NO_3)_6.3Mg(NO_3)_2.24H_2O$, gave the following analytical data:

Salt.	H_2O.	MgO.	La_2O_3.
.5327 grm.	.1569 grm.	.0417 grm.	.1131 grm.
.5931 "	.1734 "	.0467 "	.1262 "
.5662 "	.1647 "	.0442 "	.1197 "
.3757 "	------	.0297 "	.0813 "
.3263 "	------	.0256 "	.0693 "

These weighings give the subjoined percentages of La_2O_3:

$$21.231$$
$$21.278$$
$$21.141$$
$$21.640$$
$$21.238$$

Mean, 21.3056, $\pm$ .058

These data of Holzmann give values for the molecular weight of La_2O_3 as follows:

From sulphate _____ $La_2O_3 = 325.674, \pm .522$
" iodate _____ " $= 322.419, \pm .113$
" magnesian nitrate __ " $= 324.355, \pm .923$

Czudnowicz[*] based his determination of the atomic weight of lanthanum upon one analysis of the air-dried sulphate. The salt contained 22.741 per cent. of water.

.598 grm. gave .272 grm. La_2O_3 and .586 grm. $BaSO_4$.

The La_2O_3 was found by precipitation as oxalate and ignition. The $BaSO_4$ was thrown down from the filtrate. Reduced to the standards already adopted these data give for the percentage of La_2O_3 in the anhydrous sulphate the figure 58.668. 79.117 parts of the salt are proportional to 100 parts of $BaSO_4$.

Hermann[†] studied both the sulphate and the carbonate of lanthanum. From the anhydrous sulphate, by precipitation as oxalate and ignition, the following percentages of La_2O_3 were obtained:

$$57.690$$
$$57.663$$
$$57.610$$

Mean, $57.654, \pm .016$

The carbonate, dried at 100°, gave the following percentages:

$$68.47 \ La_2O_3.$$
$$27.67 \ CO_2.$$
$$3.86 \ H_2O.$$

Reckoning from the ratio between CO_2 and La_2O_3 the molecular weight of the latter becomes 325.896.

Zschiesche's[‡] experiments consist of six analyses of lanthanum sulphate, which salt was dehydrated at 230°, and afterwards calcined. I subjoin his percentages, and in a fourth column deduce from them the percentage of La_2O_3 in the *anhydrous* salt:

$H_2O.$	$SO_3.$	$La_2O_3.$	La_2O_3 *in anhydrous salt.*
22.629	33.470	43.909	56.745
22.562	33.306	44.132	56.964
22.730	33.200	44.070	57.034

* Journ. für Prakt. Chem., 80, 33. 1860.
† Journ. für Prakt. Chem., 82, 396. 1861.
‡ Journ. für Prakt. Chem., 104, 174.

H_2O.	SO_3.	La_2O_3.	La_2O_3 *in anhydrous salt.*
22.570	33.333	44.090	56.947
22.610	33.160	44.240	57.150
22.630	33.051	44.310	57.277

Mean, 57.021, ± .051

Erk * found that .474 grm. of $La_2(SO_4)_3$, by precipitation as oxalate and ignition, gave .2705 grm. of La_2O_3, or 57.068 per cent. .7045 grm. of the sulphate also gave .8815 grm. of $BaSO_4$. Hence 100 parts of $BaSO_4$ are equivalent to 79.921 of $La_2(SO_4)_3$.

Last of all, and probably best of all, we come to the determinations of Cleve.† Strongly calcined La_2O_3, spectroscopically pure, was dissolved in nitric acid, and then, by evaporation with sulphuric acid, converted into sulphate:

1.9215 grm. La_2O_3 gave	3.3365 grm. sulphate.	57.590 per cent.
2.0570	"	3.5705	"	57.611	"
1.6980	"	2.9445	"	57.667	"
2.0840	"	3.6170	"	57.617	"
1.9565	"	3.3960	"	57.612	"

Mean, 57.619, ± .0085

From the last column, which indicates the percentage of La_2O_3 in $La(SO_4)_3$, we get, if $SO_3 = 80$, $La = 139.15$.

We may now combine the similar means into general means, and deduce a value for the atomic weight of lanthanum. For the percentage of oxide in sulphate we have six estimates, as follows. The single experiments of Czudnowicz and of Erk are assigned the probable error and weight of a single experiment in Hermann's series :

Czudnowicz	58.668,	± .027
Erk	57.068,	± .027
Hermann	57.654,	± .016
Zschiesche	57.021,	± .051
Marignac	57.5475,	± .0115
Cleve	57.619,	± .0085
General mean	57.620,	± .0059

* Jenaisches' Zeitschrift, 6, 306. 1871.
† K. Svenska Vet. Akad. Handlingar, Bd. 2, No. 7. 1874.

For the quantity of $La_2(SO_4)_3$ proportional to 100 parts of $BaSO_4$, we have five experiments, which may be given equal weight and averaged together:

Marignac _____ 81.022
      "   _____ 80.934
Rammelsberg _____ 79.276
Czudnowicz _____ 79.117
Erk _____ 79.921

Mean, 80.054, ± .270

In all, there are seven ratios from which to calculate:

(1.) Percentage of La_2O_3 in $La_2(SO_4)_3$, 57.620, ± .0059
(2.) $BaCl_2 : La_2(SO_4)_3 :: 100 : 91.322$, ± .048—Marignac.
(3.) $BaSO_4 : La_2(SO_4)_3 :: 100 : 80.054$, ± .270
(4.) $BaSO_4 : La_2O_3 :: 100 : 46.671$, ± .075—Holzmann.
(5.) Percentage of La_2O_3 in iodate, 23.447, ± .0216—Holzmann.
(6.)   "   "   magnesian nitrate, 21.3056, ± .058—Holzmann.
(7.)   "   "   carbonate, 68.47—Hermann.

These ratios give five values for the molecular weight of lanthanum oxide, and two for that of the sulphate:

From (2)_____$La_2(SO_4)_3$ = 568.488, ±   .320
  "   (3)_____   "   = 558.624, ± 1.888
  General mean,   "   = 568.212, ± .316

Hence La = 140.346, ± .160.

From (1)_____La_2O_3 = 325.791, ± .074
  "   (4)_____   "   = 325.674, ± .522
  "   (5)_____   "   = 322.419, ± .113
  "   (6)_____   "   = 324.355, ± .923
  "   (7)_____   "   = 325.896, ± .488
  General mean ____   "   = 324.810, ± .061

Here the value derived from ratio (7) is given the weight of a single experiment in ratio (1.)   Hence La = 138.460, ± .031.

Combining the two values for La, we get this final result:

From La_2O_3 _____La = 138.460, ± .031
  " $La_2(SO_4)_3$ _____ " = 140.346, ± .160
  General mean_____ " = 138.526, ± .030

Or, if O = 16, La = 138.844.

Since this value is a little under and Cleve's a little over 139, the latter figure may fairly be used in all calculations involving a knowledge of the atomic weight of lanthanum.

DIDYMIUM.

The atomic weight of didymium has been determined by Marignac, Hermann, Zschiesche, Erk, and Cleve. Mosander's early experiments we may leave out of account.

Marignac[*] mixed a solution of the sulphate with a slight excess of barium chloride, filtered, weighed the precipitate, and estimated the excess of barium in the filtrate by the ordinary method. The first precipitate always contained didymium, and therefore weighed too much. By deducting the weight of the second precipitate, representing the excess of the barium chloride, from the weight of barium sulphate theoretically formable, the weight of the latter proportional to the quantity of didymium salt taken was found:

$Di_2(SO_4)_3$.	$BaCl_2$.	1st $BaSO_4$.	2d $BaSO_4$.
3.633 grm.	3.902 grm.	4.412 grm.	.084 grm.
3.862 "	4.227 "	4.679 "	.075 "
3.330 "	3.552 "	4.027 "	.088 "
1.386 "	1.477 "	1.681 "	.014 "

These figures give us a ratio between the sulphates of didymium and barium which we may express as follows. Column A gives the $Di_2(SO_4)_3$ proportional to 100 parts of $BaSO_4$, as calculated from the first precipitate of the latter. Column B gives a similar ratio calculated with the second $BaSO_4$ precipitate, this being deduced from the total $BaSO_4$ which the chloride used could form:

A.	B.
82.344	84.685
82.539	82.626
82.692	85.545
82.451	84.425
82.247 — Erk.	
	Mean, 84.320, ± .414
Mean, 82.455, ± .052	

[*] Arch. des Sci. Phys. et Naturelles, (1,) 11, 29. 1849.

To A I have added a single result of Erk's, to be described further along. It will be seen that although A is theoretically defective, its figures are much more concordant than those in B. In fact, the latter would almost vanish for the final general mean for the atomic weight of didymium:

From A _____ Di = 143.929
" B_____ " = 150.436

In a later paper* Marignac adopts two other methods for establishing the atomic weight of didymium. The carefully dehydrated sulphate was taken, the didymium was precipitated as oxalate, and the latter, ignited, yielded oxide. The following percentages of oxide were found:

58.22
58.24
58.29
58.31
58.29
—————
Mean, 58.27, ± .0115

The chloride of didymium was also studied. As the anhydrous salt could not be obtained in an absolutely definite state, Marignac prepared neutral solutions of it and determined the ratio between didymium oxide and silver chloride. The latter compound was first precipitated in the usual way, and filtered off; the excess of silver in the filtrate was removed by hydrochloric acid, and after that the didymium was thrown down as oxalate and weighed as oxide. The subjoined weights of AgCl and Di_2O_3 were found. In a third column I give the ratio between the two compounds, putting AgCl at 100:

$AgCl$.	Di_2O_3.	$Ratio$.
10.058 grm.	3.946 grm.	39.232
5.029 "	1.960 "	38.974
5.844 "	2.276 "	38.946
		—————
	Mean, 39.051,	± .061

Hence Di = 143.637, ± .263.

* Ann. d. Chim. et d. Phys., (3,) 38, 148. 1853.

Hermann's* determination of the atomic weight of didymium rests on a single experiment with the sulphate. By precipitation as oxalate and subsequent ignition, he found that this salt yielded 58.14 per cent. of Di_2O_3.

Zschiesche† also analyzed didymium sulphate, which he dehydrated at 230°, and afterwards converted into oxide by calcination. I give his percentages, and also, in a fourth column, the percentage of oxide from the *anhydrous* sulphate as deduced from his figures:

H_2O.	SO_3.	Di_2O_3.	Di_2O_3 *in anhyd. salt.*
23.19	32.97	43.83	57.070
23.03	32.39	44.58	57.919
23.00	32.56	44.95	58.006
23.547	31.938	44.515	58.225
22.550	32.870	44.570	57.554

The salt used in the first experiment probably contained lanthanum. Rejecting this, the mean of the figures remaining in the fourth column is 57.926, $\pm$ .094. Hence Di = 141.007.

Erk,‡ to whom reference has already been made, estimated didymium in the sulphate by precipitation as oxalate and calcination to oxide:

$Di_2(SO_4)_3$	Di_2O_3.	*Per cent.* Di_2O_3.
.556 grm.	.323 grm.	58.094
.674 "	.3915 "	58.087

Hermann's single result for this percentage, 58.14, agrees more nearly with Erk's series than with any other. It may therefore be averaged in with Erk's two experiments, giving a mean of 58.107, $\pm$ .0112. Erk also obtained from .7065 grm. of sulphate .859 grm. $BaSO_4$. This experiment has already been averaged with Marignac's earlier results.

The latest determinations of the atomic weight of didymium were published by Cleve‖ in 1874. Strongly calcined

* Journ. für Prakt. Chem., 82. 367.   1861.

† Journ. für Prakt. Chem., 107, 74.

‡ Jenaisches' Zeitschrift, 6, 306.   1871.

‖ K. Svenska Vet. Akad. Handlingar, Bd. 2, No. 8.   These figures were kindly transcribed for me by Professor Delafontaine of Chicago, as I had not access to a copy of the original memoir.

didymium oxide was dissolved in nitric acid, the solution was evaporated with sulphuric acid, and the weight of the resulting sulphate was ascertained. I subjoin the weighings and the percentage of Di_2O_3 in $Di_2(SO_4)_3$:

Di_2O_3.	$Di_2(SO_4)_3$.	Per cent. Di_2O_3.
2.257 grm.	3.844 grm.	58.715
1.086 "	1.8485 "	58.750
1.1525 "	1.9615 "	58.756
1.3635 "	2.319 "	58.797
1.9655 "	3.3435 "	58.786
1.528 "	2.599 "	58.792

Mean, 58.766, ± .0087

Hence Di = 146.804. If SO_3 = 80, Di = 147.021.

This determination is undoubtedly the best of all, and might properly be accepted to the exclusion of the others. Still, it is worth while to combine all the figures into one general mean. For the percentage of Di_2O_3 in $Di_2(SO_4)_3$ we have the following data:

Marignac	58.270, ± .0115
Erk and Hermann	58.107, ± .0112
Zschiesche	57.926, ± .094
Cleve	58.766, ± .0087
General mean	58.451, ± .0059

For the atomic weight of didymium we have now three independent values:

From per cent. Di_2O_3 in $Di_2(SO_4)_3$	Di = 144.604, ± .031
" Marignac's chloride analyses	" = 143.637, ± .263
" Marignac's and Erk's $BaSO_4$ ratio	" = 143.929, ± .189
General mean	" = 144.573, ± .0306

If O = 16, Di = 144.906.

THE YTTRIUM GROUP.

The atomic weights of the metals in this group can only be said to have been determined approximately. Not only do great difficulties attend the purification of the material used for study and the separation of the earths from each other, but there have been and still are grave doubts as to the actual nature of some of the latter. The figures for scandium, yttrium, and ytterbium seem to be tolerably good; those for decipium, philippium, thulium, erbium, and terbium are little more than estimates; for samarium we have no data whatever. All the atomic weights in this group are based upon analyses or syntheses of sulphates; and from analogy to the cerium metals all of these elements are regarded as forming sesquioxides.

SCANDIUM.

Cleve,* who was the first to make accurate experiments on the atomic weight of this metal, obtained the following data. 1.451 grm. of sulphate, ignited, gave .5293 grm. of Sc_2O_3. .4479 grm. of Sc_2O_3, converted into sulphate, yielded 1.2255 grm. of the latter, which, upon ignition, gave .4479 grm. of Sc_2O_3. Hence, for the percentage of Sc_2O_3 in $Sc_2(SO_4)_3$ we have:

$$36.478$$
$$36.556$$
$$36.556$$

Mean, 36.530

Hence, if $SO_3 = 80$, $Sc = 45.044$.

Later and better results are those of Nilson,† who converted scandium oxide into the sulphate. I give in a third column the percentage of oxide in sulphate:

---

* Compt. Rend., 89, 419.
† Compt. Rend., 91, 118.

.3379 grm. Sc_2O_3 gave .9343 grm. $Sc_2(SO_4)_3$.   36.166 per cent.

.3015   "   .8330   "   36.194   "

.2998   "   .8257   "   36.187   "

.3192   "   .8823   "   36.178   "

Mean, 36.181, $\pm$ .004

Hence $Sc = 43.980$, $\pm$ .015; or, if $O = 16$, then $Sc = 44.081$. If $SO_3 = 80$, then $Sc = 44.032$. These values are doubtless very nearly correct.

YTTRIUM.

For yttrium we need consider only the determinations of Popp, Delafontaine, Bahr and Bunsen, and Cleve.

Popp[*] evidently worked with material not wholly free from earths of higher molecular weight than yttria. The yttrium sulphate was dehydrated at 200°; the sulphuric acid was then estimated as barium sulphate; and after the excess of barium in the filtrate had been removed, the yttrium was thrown down as oxalate, and ignited to yield oxide. The following are the weights given by Popp:

Sulphate.	$BaSO_4$.	Yt_2O_3.	H_2O.
1.1805 grm.	1.3145 grm.	.4742 grm.	.255 grm.
1.4295 "	1.593 "	.5745 "	.308 "
.8455 "	.9407 "	.3392 "	.1825 "
1.045 "	1.1635 "	.4195 "	.2258 "

Eliminating water, these figures give us for the percentages of Yt_2O_3 in $Yt_2(SO_4)_3$ the values in column A. In column B I put the quantities of Yt_2O_3 proportional to 100 parts of $BaSO_4$:

A.	B.
51.237	36.075
51.226	36.064
51.161	36.058
51.209	36.055
Mean, 51.208, $\pm$ .011	Mean, 36.063, $\pm$ .003

From B, $Yt = 101.880$. The values in A will be combined with similar data from other experimenters.

---

[*] Ann. Chem. Pharm., 131, 179.

In 1865 Delafontaine* published some results obtained from yttrium sulphate, the yttrium being thrown down as oxalate and weighed as oxide. In the fourth column I give the percentages of Yt_2O_3 reckoned from the anhydrous sulphate:

Sulphate.	Yt_2O_3.	H_2O.	Per cent. Yt_2O_3.
.9545 grm.	.371 grm.	.216 grm.	50.237
2.485 "	.9585 "	.565 "	49.922
2.153 "	.827 "	.4935 "	49.834

Mean, 49.998, $\pm$ .081

In another paper† Delafontaine gives the following percentages of Yt_2O_3 in dry sulphate. The mode of estimation was the same as before:

48.23
48.09
48.37

Mean, 48.23, $\pm$ .055

Bahr and Bunsen,‡ and likewise Cleve, adopted the method of converting dry yttrium oxide into anhydrous sulphate, and noting the gain in weight. Bahr and Bunsen give us the two following results. I add the usual percentage column:

Yt_2O_3.	$Yt_2(SO_4)_3$.	Per cent. Yt_2O_3.
.7266 grm.	1.4737 grm.	49.304
.7856 "	1.5956 "	49.235

Mean, 49.2695, $\pm$ .0233

Cleve's‖ results are published in a joint memoir by Cleve and Hoeglund, and are as follows:

* Ann. Chem. Pharm., 134, 108.
† Arch. des Sci. Phys. et Nat., (2,) 25, 119. 1866.
‡ Ann. Chem. Pharm., 137, 21. 1866.
‖ K. Svenska Vet. Akad. Handlingar, Bd. 1, No. 8.

Yt_2O_3.	$Yt_2(SO_4)_3$.	Per cent. Yt_2O_3.
1.4060 grm.	2.8925 grm.	48.608
1.0930 "	2.2515 "	48.545
1.4540 "	2.9895 "	48.637
1.3285 "	2.7320 "	48.627
2.3500 "	4.8330 "	48.624
2.5780 "	5.3055 "	48.591

Mean, 48.605, ± .0096

This series is unquestionably the best of all. From it, if $SO_3 = 80$, $Yt = 89.485$.

Combining all these data we have the subjoined general mean for the percentage of Yt_2O_3:

Popp ----------------------------	51.208, ± .011
Delafontaine, 1st ---------------	49.998, ± .081
" 2d ----------------	48.230, ± .055
Bahr and Bunsen-----------------	49.2695, ± .0233
Cleve---------------------------	48.605, ± .0096
General mean-----------	49.637, ± .0069
Rejecting Popp ---------	48.705, ± .0087

From the general mean of all, $Yt = 97.616$. From the mean after excluding Popp's work, $Yt = 89.816$, ± .067; or, if $O = 16$, $Yt = 90.023$.

YTTERBIUM.

For ytterbium we have one very good set of determinations by Nilson.* The oxide was converted into the sulphate after the usual manner:

Yb_2O_3.	$Yb_2(SO_4)_3$.	Per cent. Yb_2O_3.
1.0063 grm.	1.6186 grm.	62.171
1.0139 "	1.6314 "	62.149
.8509 "	1.3690 "	62.155
.7371 "	1.1861 "	62.145
1.0005 "	1.6099 "	62.147
.8090 "	1.3022 "	62.126
1.0059 "	1.6189 "	62.134

Mean, 62.147, ± .0036

* Compt. Rend., 91, 56. 1880.

Hence $Yb = 172.761$, $\pm$ .038. If $O = 16$, then $Yb = 173.158$. If $SO_3 = 80$, $Yb = 173.016$. The true number cannot be far from 173.

<div align="center">ERBIUM.</div>

Since the earth which was formerly regarded as the oxide of this metal is now known to be a mixture of two or three different oxides, the older determinations of its molecular weight have little more than historical interest. Nevertheless the work done by several investigators may properly be cited, since it sheds some light upon certain important problems.

First, Delafontaine's[*] early investigations may be considered. A sulphate, regarded as erbium sulphate, gave the following data. An oxalate was thrown down from it, which, upon ignition, gave oxide. The percentages in the fourth column refer to the anhydrous sulphate. In the last experiment water was not estimated, and I assume for its water the mean percentage of the four preceding experiments:

Sulphate.	Er_2O_3.	H_2O.	Per cent. Er_2O_3.
.827 grm.	.353 grm.	.177 grm.	54.308
1.0485 "	.4475 "	.226 "	54.407
.803 "	.3415 "	.171 "	54.035
1.232 "	.523 "	.264 "	54.028
1.1505 "	.495 "	------	54.760
		Mean,	54.308, $\pm$ .0915

Bahr and Bunsen[†] give a series of results, representing successive purifications of the earth which was studied. The final result, obtained by the conversion of oxide into sulphate, was as follows:

.7870 grm. oxide gave 1.2765 grm. sulphate. 61.653 per cent. oxide.

Hoeglund,[‡] following the method of Bahr and Bunsen, secured these results:

---

[*] Ann. Chem. Pharm., 134, 108. 1865.
[†] Ann. Chem. Pharm., 137, 21. 1866.
[‡] K. Svenska Vet. Akad. Handlingar, Bd. 1, No. 6.

Er_2O_3.	$Er_2(SO_4)_3$.	Per cent. Er_2O_3.
1.8760 grm.	3.0360 grm.	61.792
1.7990 "	2.9100 "	61.821
2.8410 "	4.5935 "	61.848
1.2850 "	2.0775 "	61.853
1.1300 "	1.827 "	61.850
.8475 "	1.370 "	61.861

Mean, 61.8375, $\pm$ .0063

Humpidge and Burney[*] give data as follows:

1.9596 grm. $Er_2(SO_4)_3$ gave 1.2147 grm. Er_2O_3. 61.987 per cent.
. 1.9011   "   1.1781   "   61.965   "

Mean, 61.976, $\pm$ .0074

Combining all four series we get the subjoined general mean for the percentage of oxide in sulphate. Bahr and Bunsen's single experiment is given the probable error of one experiment in Hoeglund's series:

Delafontaine	54.308,	$\pm$ .0915
Bahr and Bunsen	61.653,	$\pm$ .0178
Hoeglund	61.8375,	$\pm$ .0063
Humpidge and Burney	61.976,	$\pm$ .0074
General mean	61.860,	$\pm$ .0046
Rejecting the first	61.880,	$\pm$ .0046

From the mean of all, Er = 170.379, $\pm$ .082; or, if O = 16, Er = 170.770. From Bahr and Bunsen's determination, Er = 168.683; and from Humpidge and Burney's highest, Er = 171.428.

The foregoing data were all published before the composite nature of the supposed erbia was fully recognized. It will be seen, however, that three sets of results were fairly comparable, while Delafontaine evidently studied an earth widely different from that investigated by the others. Since the discovery of ytterbium, some light has been thrown on the matter. The old erbia is a mixture of at least three earths, to one of which, a rose-colored body, the name erbia is now restricted. For the atomic weight of the true erbium

[*] Journ. Chem. Society, Feb., 1879, p. 116.

Cleve* gives three values, but without data concerning weighings or methods. Doubtless the oxide was converted into sulphate, and the calculations were made with $SO_3 = 80$:

$$166.00$$
$$166.21$$
$$166.25$$
$$\overline{}$$

Mean, 166.153

With $SO_3 = 79.874$, this becomes 165.891, and if only O $= 16$, 166.273. These figures are undoubtedly the nearest yet reached to the true value. According to Thalén,[†] who reasons from spectroscopic evidence, the erbium of Hoeglund was largely ytterbium.

TERBIUM, SAMARIUM, PHILIPPIUM, DECIPIUM, THULIUM, HOLMIUM, AND SORET'S EARTH X.

Concerning these substances, real or alleged, the data are exceedingly vague. For phillippium Delafontaine[‡] gives an atomic weight approximating to 123 or 125, and in the same memoir decipium is put at 171. It seems probable that philippium may be identical with Cleve's holmium and the metal of Soret's earth X, while decipium comes near Cleve's thulium, for which the discoverer gives a value of about 170.7.[||] If decipium and thulium are identical, or if either proves to be erbium or ytterbium contaminated with the other, then we shall have a triad of metals with atomic weights ranging from $Er = 166$ to $Yb = 173$, strikingly parallel with lanthanum, cerium, and didymium. If we take the natural arrangement of the elements as tabulated after Mendelejeff's plan, somewhat modified in Roscoe and Schorlemmer's "Treatise on Chemistry,[§] we find that such a triad should exist, and, furthermore, that another similar

---

* Compt. Rend., 91, 382.
† Poggend. Beiblätter, 5, 122.   1881.
‡ Arch. des Sci. Phys. et Nat., Mars, 1880.
|| Compt. Rend., 91, 329.   1880.
§ Vol. 2, Part 2, p. 507.

group ought to lie between indium and tin. The latter triad should have atomic weights ranging from 114 to 117; and here possibly, or else forming a triad with yttrium, the other metals of this group may lie.

COLUMBIUM.[*]

The atomic weight of this metal has been determined by Rose, Hermann, Blomstrand, and Marignac. Rose[†] analyzed a compound which he supposed to be chloride, but which, according to Rammelsberg,[‡] must have been nearly pure oxychloride. If it was chloride, then the widely varying results give approximately Cb = 122; if it was oxychloride, the value becomes nearly 94. If it was chloride, it was doubtless contaminated with tantalum compounds.

Hermann's[||] results seem to have no present value, and as for Blomstrand's,[§] I am not able to get at a copy of his original memoir. The results of the latter chemist are thus summed up in Becker's "Digest." Three chlorine estimations in the pentachloride give, in mean, Cb = 96.67. Eleven weighings of columbic acid from the same compound make Cb = 96.16. Other experiments on sodium columbate lead Blomstrand to regard 95 as the most probable value.

Marignac[¶] made about twenty analyses of the potassium fluoxycolumbate, $CbOF_3.2KF.H_2O$. 100 parts of this salt give the following percentages:

Cb_2O_5	Extremes	44.15	to 44.60	Mean, 44.36
K_2SO_4	"	57.60	" 58.05	
H_2O	"	5.75	" 5.98	
F	"	30.62	" 32.22	

---

* This name has priority over the more generally accepted "niobium," and therefore deserves preference.

† Poggend. Annal., 104, 439. 1858.

‡ Poggend. Annal., 136, 353. 1869.

|| Journ. für Prakt. Chem., 68, 73. 1856.

§ Acta Univ. Lund, 1864.

¶ Archives des Sci. Phys. et Nat., (2,) 23, 258. 1865.

From the mean percentage of Cb_2O_5, $Cb = 93.217$. If $O = 16$, this becomes 93.431.

From the mean between the extremes given for K_2SO_4, $Cb = 93.812$. If $O = 16$, this becomes 94.027.

As Deville and Troost's[*] results for the vapor density of the chloride and oxychloride agree fairly well with $Cb = 94$, we may adopt this value as approximately correct.

TANTALUM.

The results obtained for the atomic weight of this metal by Berzelius,[†] Rose,[‡] and Hermann[||] may be fairly left out of account as valueless. These chemists could not have worked with pure preparations, and their data are sufficiently summed up in Becker's "Digest."

Marignac[§] made four analyses of a pure potassium fluotantalate, and four more experiments upon the ammonium salt. The potassium compound, K_2TaF_7 was treated with sulphuric acid, and the mixture was then evaporated to dryness. The potassium sulphate was then dissolved out by water, while the residue was ignited and weighed as Ta_2O_5. 100 parts of the salt gave the following quantities of Ta_2O_5 and K_2SO_4 :

Ta_2O_5.	K_2SO_4.
56.50	44.37
56.75	44.35
56.55	44.22
56.56	44.24
Mean, 56.59, = .037	Mean, 44.295, ± .026

[*] Comptes Rend., 56, 891. 1863.
[†] Poggend. Annal., 4, 14. 1825. Lehrbuch, 3, 1209.
[‡] Poggend. Annal., 99, 80. 1856.
[||] Journ. für Prakt. Chem., 70, 193. 1857.
[§] Archives des Sci. Phys. et Nat., 26, 89, serie 2. 1866.

From these figures, 100 parts of K_2SO_4 correspond to the subjoined quantities of Ta_2O_5:

$$127.338$$
$$127.960$$
$$128.178$$
$$127.848$$

Mean, $127.831, \pm .120$

The ammonium salt, $(NH_4)_2TaF_7$, ignited with sulphuric acid, gave these percentages of Ta_2O_5. The figures are corrected for a trace of K_2SO_4 which was always present:

$$63.08$$
$$63.24$$
$$63.27$$
$$63.42$$

Mean, $63.25, \pm .047$

Hence we have four values for Ta :

From potassium salt, per cent. Ta_2O_5 ----- Ta =	$183.033, \pm .343$
" " " K_2SO_4----- " =	$181.619, \pm .242$
" " $K_2SO_4 : Ta_2O_5$ ------ " =	$182.361, \pm .411$
" ammonium salt, per cent. Ta_2O_5 ---- " =	$182.149, \pm .456$
General mean_____ _____ _____ " =	$182.144, \pm .166$

Or, if $O = 16$, $Ta = 182.562$.

If we assume $K = 39$, $O = 16$, $F = 19$, $S = 32$, and $N = 14$; the percentage of K_2SO_4 from K_2TaF_7 gives $Ta = 181.912$; and the analyses of the ammonium salt make $Ta = 182.020$. Evidently, 182 is not far from the true value.

PLATINUM.

For this metal we have to consider only experiments by Berzelius, by Andrews, and by Scubert. In an early paper Berzelius* reduced platinous chloride, and found it to contain 73.3 per cent. of platinum. Hence, $Pt = 194.204$, a

---

* Poggend. Annal., 8, 177. 1826.

value very near that obtained most recently by Seubert. In his later investigations, Berzelius * studied the potassium chloroplatinate, K_2PtCl_6. 6.981 parts of this salt, ignited in hydrogen, lost 2.024 of chlorine. The residue consisted of 2.822 platinum, and 2.135 potassium chloride. From these data we may calculate the atomic weight of platinum in four ways:

1st. From loss of Cl upon ignition _____Pt = 197.722
2d.   "   weight of Pt in residue_____ _____ " = 196.942
3d.   "   "   KCl   "   _____ " = 196.215
4th.   "   ratio between KCl and Pt _____ " = 196.652

The last of these values is undoubtedly the most reliable, since it involves no errors due to the possible presence of moisture in the salt analyzed. If O = 16, the value becomes Pt = 197.104.

The work done by Andrews† is even less satisfactory than the foregoing, for the reason that its full details seem never to have been published. Andrews dried potassium chloroplatinate at 105°, and then decomposed it by means of zinc and water. The excess of zinc having been dissolved by treatment with acetic and nitric acids, the platinum was collected upon a filter and weighed, while the chlorine in the filtrate was estimated by Pelouze's method. Three determinations gave as follows for the atomic weight of platinum:

197.86
197.68
198.12
_____
Mean, 197.887

If we assume that these values were calculated with K = 39 and Cl = 35.5, the mean, corrected by our later figures for these elements, becomes Pt = 197.382. If O = 16, this becomes Pt = 197.836. Unfortunately, Andrews does not, in his brief note upon the subject, indicate the manner by which his calculations were made.

_____

* Poggend. Annal., 13, 468. 1828.
† British Association Report, 1852. Chem. Gazette, 10, 380.

Latest of all we have to consider the experiments of Seubert.* This chemist prepared very pure chloroplatinates of ammonium and potassium, and from their composition deduced the atomic weight of the metal under consideration. The ammonium salt, $(NH_4)_2PtCl_6$ was analyzed by heating in a stream of hydrogen, expelling the excess of that gas by a current of carbon dioxide, and weighing the residual metal. In three experiments the hydrochloric acid formed during such a reduction was collected in an absorption apparatus, and estimated by precipitation as silver chloride. Three series of results are given for the percentage of platinum in this salt, together with another single result which may be considered alone. Here are the figures :

Series I.	Series II.	Series III.
43.957	43.871	43.990
43.948	43.876	43.986
43.960	43.872	44.001
43.946	43.881	44.020
43.963	43.875	43.994
43.961	43.879	43.996
		44.004
Mean, 43.956, $\pm$ .002	Mean, 43.876, $\pm$ .001	44.026
		43.998
		Mean, 44.001, $\pm$ .003

These series represent three preparations. The additional single experiment above referred to was made with material belonging to series II, but recrystallized from water. This salt gave 43.955 per cent. of platinum, a figure to which we may assign the probable error of one experiment in the first series. Combining, we get the subjoined general mean percentage of Pt in $(NH_4)_2PtCl_6$:

Series I _____ 43.956, $\pm$ .002
  "   II _____ 43.876, $\pm$ .001
  "   III _____ 44.001, $\pm$ .003
Extra experiment _____ 43.955, $\pm$ .004

      General mean _____ 43.907, $\pm$ .0009

* Ber. der Deutsch. Chem. Gesell., 14, 865. 1881.

Hence Pt = 194.314, ± .078. If N = 14, and Cl = 35.5, then Pt = 194.906. Calculating with Stas' values for N and Cl, Seubert gets from the four results combined above, the following figures for Pt, respectively: 194.685, 194.039, 195.034, 194.665.

For the chlorine estimations in the ammonium salt the subjoined weighings are given:

Salt.	*Pt.*	*AgCl.*
2.7054 grm.	1.1871 grm.	5.2226 grm.
2.2748 "	.9958 "	4.3758 "
3.0822 "	1.3561 "	5.9496 "

Hence 100 parts of AgCl correspond to the following quantities of salt:

$$51.802$$
$$51.986$$
$$51.805$$

Mean, 51.864, ± .041

Hence, calculating directly from the ratio between $6AgCl$ and $(NH_4)_2PtCl_6$, Pt = 196.871, ± .363.

Seubert himself reckons the percentage of chlorine from the weight of silver chloride, and then calculates the ratio between Cl_6 and Pt. He thus finds, with Stas' value for Cl, Pt = 195.330.

The potassium salt, K_2PtCl_6, was also analyzed by ignition in hydrogen, treatment with water, and weighing both the platinum and the potassium chloride. These percentages were found:

Pt.	*KCl.*
40.119	30.706
40.120	30.728
40.076	30.698
40.070	30.666
40.107	30.700
40.120	30.627
40.114	30.710
40.130	30.621

Mean 40.107, ± .005   Mean, 30.682, ± .009

From the first column _____ Pt = 194.370, ± .068
  "   second "   _____ " = 194.645, ± .213

If K = 39, and Cl = 35.5, the first column gives Pt = 194.933. Seubert, from the percentage of platinum, gets Pt = 194.392; and from the ratio 2KCl : Pt he finds Pt = 194.494.

As with the ammonium salt, three experiments were made upon the potassium compound to determine the amount of chlorine lost upon reduction in hydrogen. I cite the weighings, and add in a fourth column the quantity of K_2PtCl_6 proportional to 100 parts of AgCl. This AgCl represents but *four* atoms of the chlorine:

Salt.	Pt.	AgCl.	Ratio.
6.7771 grm.	2.7158 grm.	7.9725 grm.	85.006
3.5834 "	1.4372 "	4.2270 "	84.774
4.4139 "	1.7713 "	5.2144 "	84.648

Mean, 84.809, ± .071

Hence Pt = 195.002, ± .415. If K = 39, Ag = 108, and Cl = 35.5, then Pt = 194.955. Seubert, calculating the percentage of chlorine and thence the ratio Cl_4 : Pt, gets Pt = 194.631.

Combining all the values we have the following result for the atomic weight of platinum :

1.   From per cent. Pt in $(NH_4)_2PtCl_6$ _____Pt = 194.314, ± .078
2.   "   6AgCl : $(NH_4)_2PtCl_6$ ratio_____ " = 196.871, ± .363
3.   "   per cent. Pt in K_2PtCl_6 _____ " = 194.370, ± .068
4.   "   "   KCl   "   _____ " = 194.645, ± .213
5.   "   4AgCl : K_2PtCl_6 ratio_____ " = 195.002, ± .415

General mean _____ " = 194.415, ± .049

Or, if O = 16, Pt = 194.867.

Seubert, taking the arithmetical mean of his eight values, gets Pt = 194.620. He regards, however, those results as best which are dependent upon the percentage of platinum in the ammonium salt, and upon the complete analysis of the potassium compound. These give him a mean of Pt = 194.461, which, if corrected by reduction to a vacuum standard, becomes Pt = 194.34.

In will be noticed that three of the ratios, calculated with

K = 39, N = 14, Ag = 108, and Cl = 35.5, give nearly
Pt = 195, namely:

$$194.906$$
$$194.933$$
$$194.955$$

The general mean of all, if O = 16, gives Pt = 194.867.
Hence, for all practical calculations, the value 195 may be
safely employed.

OSMIUM.

The atomic weight of this metal has been determined by
Berzelius and by Fremy.

Berzelius[*] analyzed potassium osmichloride, igniting it
in hydrogen like the corresponding platinum salt. 1.3165
grammes lost .3805 of chlorine, and the residue consisted of
.401 grm. of potassium chloride, with .535 grm. of osmium.
Calculating only from the ratio between the Os and the KCl,
we have, Os = 198.494; or, if O = 16, Os = 198.951.

Fremy's determination[†] is based upon the composition of
osmium tetroxide. No details as to weighings or methods
are given; barely the final result is stated. This, if O =
15.9633, is Os = 199.190. If O = 16, Os = 199.648.

Berzelius' work is evidently entitled to preference, although
neither determination is in any sense equal to the present
requirements of chemical science. The values given are
doubtless several units too high.

IRIDIUM.

The only early determination of the atomic weight of
iridium was made by Berzelius,[‡] who analyzed potassium
iridichloride by the same method employed with the plati-
num and the osmium salts. The result found from a single

---

[*] Poggend. Annal., 13, 530. 1828.
[†] Compt. Rend., 19, 468. Journ. für Prakt. Chem., 33, 410. 1844.
[‡] Poggend. Annal., 13, 435. 1828.

analysis was not far from Ir = 196.7. This is now known to be too high. I have not, therefore, thought it worth while to recalculate Berzelius' figures, but give his estimation as it is stated in Roscoe and Schorlemmer's "Treatise on Chemistry."

In 1878 the matter was taken up by Seubert,[*] who had at his disposal 150 grammes of pure iridium. From this he prepared the iridichlorides of ammonium and potassium, $(NH_4)_2IrCl_6$ and K_2IrCl_6, which salts were made the basis of his determinations. The potassium salt was dried by gentle heating in a stream of dry chlorine.

Upon ignition of the ammonium salt in hydrogen, metallic iridium was left behind in white coherent laminæ. The percentages of metal found in seven estimations were as follows:

$$43.742$$
$$43.725$$
$$43.745$$
$$43.739$$
$$43.726$$
$$43.739$$
$$43.705$$

Mean, 43.732, ± .0035

The potassium salt was also analyzed by decomposition in hydrogen with special precautions. In the residue the iridium and the potassium chloride were separated after the usual method, and both were estimated. Eight analyses gave the following results, expressed in percentages:

Ir.	$2KCl$.	Cl_4.
39.881	30.829	29.290
39.890	30.842	29.277
39.868	30.813	29.300
39.876	30.835	29.289
39.877	30.825	29.287
39.879	30.811	29.310
39.882	30.814	29.285
39.883	30.792	29.288
Mean, 39.880, ± .0015	30.820, ± .0037	29.291, ± .0024

* Ber. d. Deutsch. Chem. Gesell., 11, 1767.

From these data several values for the atomic weight of iridium may be calculated:

From per cent. Ir in $(NH_4)_2IrCl_6$ _____ Ir $=$ 192.951, $\pm$ .064

"   " K_2IrCl_6 _____ " $=$ 192.536, $\pm$ .060

"   KCl in "   _____ " $=$ 192.474, $\pm$ .111

" Cl_4 in   "   _____ " $=$ 192.757, $\pm$ .148

General mean _____ " $=$ 192.702, $\pm$ .039

If $O = 16$, this becomes Ir $= 193.145$.

In the potassium salt, instead of calculating from the percentages directly, we may reckon upon the ratios between Ir and Cl_4, and between Ir and 2KCl:

From Ir : Cl_4 ratio _____ ____ ___ Ir $=$ 192.626, $\pm$ .081

"   Ir : 2KCl ratio _____ _____ _____ " $=$ 192.514, $\pm$ .044

General mean _____ _____ " $=$ 192.539, $\pm$ .039

Or, if $O = 16$, Ir $= 192.982$.

Again, we may combine this mean with the value derived from the ammonium iridichloride, and so estimate the relative importance of the latter:

From K_2IrCl_6 _____ _____ Ir $=$ 192.539, $\pm$ .039

" $(NH_4)_2IrCl_6$ ___ _____ _____ " $=$ 192.951, $\pm$ .064

General mean ____ _____ ____ _____ " $=$ 192.651, $\pm$ .033

If $O = 16$, this becomes Ir $= 193.094$.

We may assume, then, from all the facts before us, that if $O = 16$, the atomic weight of iridium varies from the even number 193 only within the limits of experimental error.

PALLADIUM.

The atomic weight of palladium has been studied by Berzelius and by Quintus Icilius. In an early paper Berzelius[*] found that 100 parts of the metal united with 28.15 of sulphur. Hence Pd $= 113.63$, a result which is unquestionably far too high.

---

* Poggend. Annal., 8, 177. 1826.

In a later paper* Berzelius published two analyses of potassium palladiochloride, K_2PdCl_4. The salt was decomposed by ignition in hydrogen, as was the case with the double chlorides of potassium with platinum, osmium, and iridium. Reducing his results to percentages, we get the following composition for the substance in question:

Pd.	*2KCl.*	*Cl$_2$.*
32.726	46.044	21.229
32.655	45.741	21.604
Mean, 32.690	45.892	21.416

From these percentages, calculating directly, very discordant results are obtained:

From percentage of metal _____Pd = 106.612
"   "   KCl _____ _____ " = 104.674
"   "   Cl$_2$, (loss) _____ " = 110.796

Obviously, the only way to get satisfactory figures is to calculate from the ratio between the Pd and 2KCl. Doing this, we get, Pd = 105.737; or, if O = 16, Pd = 105.981.

This last value varies so slightly from the even number 106 that the latter may be safely used for all purposes of chemical calculation.

The determination made by Quintus Icilius* need be given only for the sake of completeness. He ignited potassium palladichloride in hydrogen, and found the following amounts of residue. His weights are here recalculated into percentages:

64.708
64.965
64.781
Mean, 64.818

From this mean, Pd = 111.879. Upon looking at the values deduced from Berzelius' figures, it will be seen that

---

* Poggend. Annal., 13, 454. 1828.

† " Die Atomgewichte vom Pd, K, Cl, Ag, C, und H, nach der Methode der kleinsten Quadrate berechnet." Inaug. Diss. Göttingen, 1847. Contains no other original analyses.

the highest, 110.796, is calculated from the chlorine lost upon igniting the palladiochloride. The same kind of error which vitiates that result probably affects also these data drawn from the palladiochloride.

RHODIUM.

Berzelius[*] determined the atomic weight of this metal by the analysis of sodium and potassium rhodiochlorides, Na_3RhCl_6, and K_2RhCl_5. The latter salt was dried by heating in chlorine. The compounds were analyzed by reduction in hydrogen, after the usual manner. Reduced to percentages the analyses come out as follows:

<center>In Na_3RhCl_6.</center>

Rh.	3 NaCl.	Cl_3.
26.959	45.853	27.189
27.229	45.301	27.470
		27.616
Mean, 27.094	45.577	
		27.425

<center>In K_2RhCl_5.</center>

Rh.	2 KCl.	Cl_3.
28.989	41.450	29.561

From the analyses of the sodium salt we get the following values for Rh:

From per cent. of metal _____ Rh = 104.507
  "   "   NaCl _____ " = 102.980
  "   " Cl_3 ____ _____ " = 105.696
  "   ratio between Cl_3 and Rh _____ " = 104.829
  "   "   NaCl   "   _____ " = 104.093

These are discordant figures, and indicate some doubt as to purity of material. The last value is fairly good, however, and is confirmed by results from the potassium compound:

---

* Poggend. Annal., 13, 435.   1828.

From per cent. of metal _____Rh = 104.054
    "   "   KCl _____ " = 104.046
    "   "   Cl₃ _____ " = 104.065
    "   Rh : Cl₃ ratio _____ " = 104.057
    "   Rh : KCl ratio _____ " = 104.051 .

        Mean_____ " = 104.055

If O = 16, this becomes Rh = 104.285.

RUTHENIUM.

The atomic weight of this metal has been determined only by Claus.* Although he employed several methods, the only results worthy of present notice come from the analysis of potassium rutheniochloride, K_2RuCl_5. The salt was dried by heating to 200° in chlorine gas, but even then retained a trace of water. The percentage results of analysis are as follows:

Ru.	*2KCl.*	*Cl₃.*
28.96	40.80	30.24
28.48	41.39	· 30.22
28.91	41.08	30.04
Mean, 28.78	41.09	30.17

Reckoning directly from the percentages we get the following discordant values for Ru:

From percentage of metal_____Ru = 103.016
    "   "   KCl_____ " = 107.190
    "   "   Cl₃_____ " = 96.854

Obviously, the best result is to be obtained from the ratio between Ru and 2KCl. This gives Ru = 104.217; or, if O = 16, Ru = 104.457. But little weight can be attached to this determination.

---

* Journ. für Prakt. Chem., 34, 435. 1845.

APPENDIX.

In the year 1815 Prout put forth his famous hypothesis that the atomic weights of all the elements were multiples of that of hydrogen. His views were adopted by many chemists, but opposed by others; among them Berzelius and Turner; and down to the present day "Prout's Law" has been the subject of earnest controversy. Of course the fact was early recognized that in its original form the hypothesis could not stand, and accordingly it was modified by Dumas in such manner that half and quarter multiples of the atomic weight of hydrogen were considered as well as the whole numbers.

But of late years Prout's hypothesis, even with its elastic modification, has been in disfavor. Only a few chemists still clung to it as the representative of a veritable law. The researches of Stas were especially directed towards ascertaining its truth or falsity; and his results, as well as those obtained by Marignac, were such as to lead most chemists to the belief that it had been forever overthrown. The atomic weights determined by Stas agreed neither with whole, half, nor quarter multiples of that of hydrogen, and the variations seemed to be wholly outside the range of recognizable experimental errors.

In 1878, however, a probable source of error in some of Stas' researches was pointed out by Dumas.* Many of Stas' ratios had involved the use of pure metallic silver, which had been fused under a cover of borax containing a little

---

* Ann. Chim. Phys., (5s.,) 14, 289.

nitre. Such silver Dumas heated to redness in a Sprengel vacuum, and found that it gave up weighable quantities of oxygen, which had been absorbed by the metal when in the melted state. In one experiment a kilogramme of silver gave 82 milligrammes of occluded gas, and in three other cases 226, 140, and 249 milligrammes respectively were found. In other words, the silver which had been considered pure by Stas and others, was really not pure, and a correction became necessary in nearly all series of atomic weight determinations.

The amount of this correction, which I think may hereafter be appropriately designated as " Dumas' correction," will naturally vary in different cases, and in no particular case can we tell, without actual examination of the silver employed, exactly how great it should be. We may, however, assume that all the metallic silver heretofore used in establishing atomic weight ratios was subject to it; and, reckoning from the largest error indicated in the experiments of Dumas, namely, 249 milligrammes of oxygen in the kilogramme of metal, we may ascertain its tendency with reference to Prout's law.

In the chapter upon the atomic weights of silver, chlorine, bromine, iodine, potassium, sodium, and sulphur, twenty ratios are given, of which nine are subject to Dumas' correction. Applying it as suggested above, we get the following results. The values previously found and given in the chapter just quoted, we may designate as uncorrected. For convenience in future reference I assume that $O = 16$:

	Uncorrected.	Corrected.	Difference.
Silver	107.923	107.896	— .027
Chlorine	35.451	35.478	+ .027
Bromine	79.951	79.978	+ .027
Iodine	126.848	126.875	+ .027
Potassium	39.109	39.083	— .026
Sodium	23.051	23.024	— .027
Sulphur	32.058	32.058	------

The result of the correction, it will be seen, is generally favorable to Prout's hypothesis. Of the seven elements

under consideration, one has its atomic weight unaffected, one is rendered less in accord with the hypothesis, and five approximate more closely than before to even multiples or multiples half of hydrogen.

In the later chapters of this work the effect of Dumas' correction is generally less striking. One general statement, however, may be made concerning it. Whenever the atomic weight of a metal is calculated from the ratio between its haloid salts and metallic silver, the total effect of Dumas' correction, including the above corrections for the halogens themselves, will be to *lower* the final result. This point will be further considered presently. Only chlorine, bromine, and iodine have their atomic weights raised by the correction.

In view of Dumas' correction the question naturally arises as to how far other metals, used in atomic weight researches, may occlude gaseous impurities. For example, when the atomic weight of oxygen is fixed by the synthesis of water over copper oxide, may not the copper occlude appreciable quantities of the hydrogen in which it cools? If it does, then the apparent weight of metallic copper would be too high, and the atomic weight of oxygen would come out too low. Such an error might possibly account for the difference between 16 and 15.9633 in the atomic weight of oxygen, and it would also increase the atomic weight of copper as determined by the same process. At all events, every metal of which the atomic weight has been determined by the reduction of its compounds in hydrogen, ought to be scrupulously investigated with reference to the possible occlusion of gaseous impurities. With all of these metals the effect of such impurities would be to render the apparent atomic weights decidedly too high.

Although every series of atomic weight determinations must be considered by itself, and weighed on its own merits, it may not be out of place for me just here to point out two general sources of error in addition to the one we have been considering. First, every value after oxygen, with one or two partial exceptions, involves whatever error may attach

to the atomic weight of oxygen. If the latter be 16, instead of 15.9633, this error in some instances becomes multiplied to a large fraction of a unit, as the subjoined example will show.

If O = 16, the atomic weight of uranium = 239.030
If O = 15.9633,   "   "   = 238.482
                                                    ———
        Difference _____ ____ ___ _____ __ __   0.548

Other similar errors are repeated continually. The value assigned to any element is necessarily affected by whatever errors may attach to the atomic weights of those other elements through whose medium it is compared with the standard, hydrogen. Thus, the atomic weight of carbon depends upon that of oxygen; calcium depends upon both carbon and oxygen; and fluorine, as determined from calcium fluoride, involves the foregoing elements, together with sulphur, silver, and chlorine. Since, however, some atomic weights are affected by plus errors and others by minus errors, there is a fortunate tendency to compensation of errors in cases like that of fluorine, and, in reality, better results are obtained than considerations such as these would lead us to look for.

Another general source of error is to be found in the fact that some of the weighings involved in our discussions had been reduced to absolute standards, while others were merely uncorrected weighings in air. The errors thus introduced into the work are doubtless small, but still they ought not to be absolutely ignored.

Now, having considered the larger classes of errors, we may properly pass on to a comparison of our atomic weights with reference to Prout's hypothesis. In order to facilitate work, I have tabulated the figures in two columns, one giving atomic weights referred to hydrogen as unity, the other based upon the standard of oxygen as exactly sixteen. Such imperfectly known elements as decipium, philippium, samarium, terbium, and thulium are not included.

TABLE OF ATOMIC WEIGHTS.

	H = 1.	O = 16.	Remarks.
Aluminum	27.009, ± .003	27.075	
Antimony	119.955, ± .036	120.231	Cooke's and Schneider's data.
Arsenic	74.918, ± .016	75.090	
Barium	136.763, ± .031	137.007	
Bismuth	207.523, ± .082	208.001	From Schneider's data.
Boron	10.941, ± .023	10.966	
Bromine	79.768, ± .019	79.951	
Cadmium	111.835, ± .024	112.092	
Cæsium	132.583, ± .024	132.918	
Calcium	39.990, ± .010	40.082	
Carbon	11.9736, ± .0028	12.0011	
Cerium	140.424, ± .017	140.747	Buehrig's data give 141.523. (O = 16.)
Chlorine	35.370, ± .014	35.451	
Chromium	52.009, ± .025	52.129	From Siewert's data.
Cobalt	58.887, ± .008	59.023	
Columbium	93.812 ●	94.027	From one ratio only.
Copper	63.173, ± .011	63.318	
Didymium	144.573, ± .031	144.906	Cleve's data give 147.021. (SO_3 = 80.)
Erbium	165.891	166.273	From Cleve's data only.
Fluorine	18.984, ± .0065	19.027	
Gallium	68.854	68.963	Imperfectly determined.
Glucinum	9.085, ± .0055	9.106	Nilson and Pettersson's data.
Gold	196.155, ± .095	196.606	
Hydrogen	1.0000	1.0023	
Indium	113.398, ± .047	113.659	
Iodine	126.557, ± .022	126.848	
Iridium	192.651, ± .033	193.094	Seubert's data.
Iron	55.913, ± .012	56.042	
Lanthanum	138.526, ± .030	138.844	
Lead	206.471, ± .021	206.946	
Lithium	7.0073, ± .007	7.0235	
Magnesium	23.959, ± .005	24.014	Marchand and Scheerer's data.
Manganese	53.906, ± .012	54.029	Schneider and Rawack's data.
Mercury	199.712, ± .042	200.171	
Molybdenum	95.527, ± .051	95.747	
Nickel	57.928, ± .022	58.062	Schneider, Sommaruga, and Lee.
Nitrogen	14.0210, ± .0035	14.029	
Osmium	198.494	198.951	Very doubtful.
Oxygen	15.9633, ± .0035	16.000	
Palladium	105.737	105.981	Badly determined.
Phosphorus	30.958, ± .007	31.029	
Platinum	194.415, ± .049	194.867	Seubert's data.
Potassium	39.019, ± .012	39.109	
Rhodium	104.055	104.285	Badly determined.
Rubidium	85.251, ± .018	85.529	
Ruthenium	104.217	104.457	Badly determined.
Scandium	43.980, ± .015	44.081	
Selenium	78.797, ± .011	78.978	

TABLE OF ATOMIC WEIGHTS—Continued.

	H = 1.		O = 16.	Remarks.
Silicon	28.195,	± .066	28.260	Very badly determined.
Silver	107.675,	± .0096	107.923	
Sodium	22.998,	± .011	23.051	
Strontium	87.374,	± .032	87.575	
Sulphur	31.984,	± .012	32.058	
Tantalum	182.144,	± .166	182.562	
Tellurium	127.960,	± .034	128.254	Imperfectly determined.
Thallium	203.715,	± .0365	204.183	Crookes' data.
Thorium	233.414,	± .073	233.951	
Tin	117.698,	± .040	117.968	
Titanium	49.846,	± .064	49.961	Imperfectly determined.
Tungsten	183.610,	± .032	184.032	
Uranium	238.482,	± .082	239.030	
Vanadium	51.256,	± .024	51.373	
Ytterbium	172.761,	± .038	173.158	If $SO_3 = 80$, Yb = 173.016.
Yttrium	89.816,	± .067	90.023	Doubtful.
Zinc	64.9045,	± .019	65.054	Axel Erdmann's data.
Zirconium	89.367,	± .037	89.573	Doubtful.

At the close of his admirable paper on the atomic weight of aluminum Mallet makes substantially the following argument in favor of Prout's hypothesis. Citing the atomic weights of eighteen elements which he considers well determined, he shows that ten of them have values falling within one-tenth of a unit of whole numbers. Now, what is the mathematical probability that this close approximation to conformity, with Prout's law, in ten cases out of eighteen, is purely accidental, as those chemists who reject the hypothesis seem to hold? Working this problem out, Mallet finds the probability in favor of mere coincidence to be in the ratio of 1 : 1097.8, and hence he concludes that Prout's views are still worthy of respectful consideration.

Applying Mallet's reasoning to the table of atomic weights now before us, we find that in the first column, when H = 1, twenty-five elements out of sixty-six have values falling within the limits of one-tenth of a unit variation from whole numbers. But many of the figures which fall without this limit involve the variation of oxygen multiplied many times over. We must therefore study the second column, which assumes that the atomic weight of oxygen is exactly six-

teen. Here we have forty elements falling within the limit of variation assigned by Mallet, and twenty-six falling without. The variations we may properly study in some detail.

Taking first the elements whose atomic weights vary from even multiples of unity by less than a tenth of a unit, we have to consider the following: aluminum, arsenic, barium, bismuth, boron, bromine, cadmium, cæsium, calcium, carbon, cobalt, columbium, didymium, fluorine, gallium, hydrogen, iridium, iron, lead, lithium, magnesium, manganese, nickel, nitrogen, osmium, oxygen, palladium, phosphorus, scandium, selenium, silver, sodium, sulphur, thorium, tin, titanium, tungsten, uranium, yttrium, and zinc. Of these, aluminum, arsenic, barium, bismuth, cadmium, calcium, carbon, cobalt, columbium, fluorine, hydrogen, iridium, iron, lithium, magnesium, manganese, nickel, nitrogen, phosphorus, scandium, sodium, sulphur, tungsten, uranium, yttrium, and zinc have plus variations, while boron, bromine, cæsium, didymium, gallium, lead, osmium, palladium, selenium, silver, thorium, tin, and titanium fall slightly under the units to which they approximate. Oxygen, as the standard of comparison, of course shows here no variation, its possible error having been transferred to hydrogen.

Of the foregoing elements it will be seen that twenty-six have plus variations from whole numbers, while thirteen are minus. Among the latter, boron, gallium, osmium, palladium, thorium, and titanium have been but roughly determined. Bromine, by Dumas' correction, has its variation diminished. In the cases of lead, cæsium, selenium, and tin, the cause of variation, supposing one to exist, remains to be determined. The value for osmium is undoubtedly several units too high, so that its agreement with Prout's law may be considered purely accidental. As for didymium, the figure assigned is the mean of all determinations; whereas Cléve's data, calculated with $SO_3 = 80$, make $Di = 147.021$, a variation which, like most of the others, is far within the limits of ordinary experimental error. In the

case of silver it has already been shown that Dumas' correction is unfavorable to it considered in its bearings upon Prout's law. Silver is the only element among those having minus variations which could carry very much weight against the hypothesis.

Among the elements whose variations are plus, columbium, uranium, and yttrium have been poorly determined. Yttrium especially may be considered doubtful. The atomic weights of aluminum, arsenic, barium, cadmium, lithium, phosphorus, and sodium involve Dumas' correction to a greater or less extent, and will be lowered by its application, that is, brought nearer to whole numbers. For aluminum, certain other causes for variation were pointed out in the chapter upon that metal; and it may be noted that the direct ratio between it and hydrogen gives $Al = 27.998$, $\pm .007$. Here the variation is less than the probable error. For calcium, and consequently for fluorine also, sources of plus error were indicated in the discussion of their respective atomic weights, and reiteration here is unnecessary. Cobalt, iridium, iron, nickel, and tungsten all involve such errors as may arise from the possible occlusion of hydrogen by the metals after reduction from their compounds. For scandium, the atomic weight, calculated with $SO_3 = 80$, becomes 44.032, a variation much within the limits of experimental error. For carbon and bismuth the variations are insignificant. In short, in the majority of instances the errors may be diminished by corrections which are in all probability needed, and which can be easily pointed out. The more carefully we scrutinize the data the more probable Prout's hypothesis appears.

Among the twenty-six elements whose atomic weights are removed by more than a tenth of a unit from whole numbers, chlorine, rubidium, and strontium have values nearly half multiples of that of hydrogen, and in each case Dumas' correction will make the approximation still closer. Erbium, gold, indium, lanthanum, rhodium, ruthenium, silicon, and zirconium may be dismissed from consideration as too imperfectly determined to carry much weight in the present

discussion. For chromium, copper, molybdenum, and vana-
dium I have no criticisms to offer ; but the remaining ele-
ments may be considered individually.

The value assigned to antimony, 120.231, is the general
mean of Cooke's and Schneider's work upon the bromide,
iodide, and sulphide. If $Ag = 108$, $Br = 80$, and $I = 127$,
Cooke's data for the bromide and iodide give the following
values for Sb, all of which fall within a tenth of a unit of
the whole number 120:

Early bromide series_____ _____Sb $=$ 119.901
Late   "   _____ _____ " $=$ 120.009
Iodide series _____ _____ _____ " $=$ 119.973

In the case of cerium, the value assigned in the table is
the general mean of all reputable determinations. But it is
subject to doubt on account of the facts observed by Wolf
and by Wing, whose ceroso-ceric oxide was white, while
that of all other observers was yellowish. Wolf's and
Wing's data, calculated with $O = 16$, give $Ce = 138.039$.
Cerium, then, is not an *established* exception to Prout's law.

Glucinum and ytterbium have their atomic weights cal-
culated from analyses of the sulphates. But if Prout's law
is true, $SO_3 = 80$. Calculated with this figure, we have
$Gl = 9.096$ and $Yb = 173.016$. Both elements thus fall
within reasonable limits of variation from the hypothetical
values.

Iodine is one of the most important seeming exceptions.
If we assume $Ag = 108$, and calculate the atomic weight of
iodine only from the direct ratio between iodine and silver,
we have, with Dumas' correction applied, $I = 126.966$;
that is, it comes within one-tenth of a unit of the whole
number 127.

The atomic weight of mercury depends upon analyses of
the chloride, oxide, and sulphide. Of these three com-
pounds the purity of the chloride is most easily assured.
Calculated from its composition, with $Cl = 35.5$, $Hg =$
199.971. With so high an atomic weight small errors are
easily multiplied.

For the atomic weight of platinum Seubert's data give five values, ranging both above and below the round number 195. Calculated with integer values for the other elements, three of these figures fall very close to 195, as follows:

$$
\begin{aligned}
\text{From per cent. Pt in } (NH_4)_2PtCl_6 \text{----} Pt &= 194.906 \\
\text{``} \qquad \text{``} \qquad K_2PtCl_6 \text{--------} \text{``} &= 194.933 \\
\text{From chlorine estimation in } K_2PtCl_6 \text{--} \text{``} &= 194.955
\end{aligned}
$$

Potassium is the most serious exception of all. But if $O = 16$ and Dumas' correction be applied, the general mean from all the available data becomes $K = 39.083$. That is, potassium falls within the limit of 0.1 variation.

The atomic weight assigned to tantalum is the mean of four values. Two of these, recalculated with integers, come out as follows:

$$
\begin{aligned}
\text{From per cent. } K_2SO_4 \text{ in } K_2TaF_7 \text{------------} Ta &= 181.912 \\
\text{``} \qquad Ta_2O_5 \text{ from } (NH_4)_2TaF_7 \text{------} \text{``} &= 182.020
\end{aligned}
$$

For tellurium I need only call attention to the discrepancies between the several sets of determinations made by Wills. A reference to the chapter on tellurium will show that his figures give results ranging from $Te = 126.07$ to $Te = 129.34$. The mean value is therefore too much subject to doubt to carry weight as an exception.

As for thallium, the last case to be considered, I have already shown that Crookes' data, recalculated with integer values for N and O, give $Tl = 204.008$. That is, instead of an exception, we have here an admirable instance in support of Prout's hypothesis.

Enough has been said in this brief resumé to show that none of the seeming exceptions to Prout's law are inexplicable. Some of them, indeed, carefully investigated, support it strongly. In short, admitting half multiples as legitimate, it is more probable that the few apparent exceptions are due to undetected constant errors, than that the great number of close agreements should be merely accidental. I began this recalculation of the atomic weights

with a strong prejudice against Prout's hypothesis, but the facts as they came before me have forced me to give it a very respectful consideration. All chemists must at least admit that the strife over it is not yet ended, and that its opponents cannot thus far claim a perfect victory.

INDEX.